



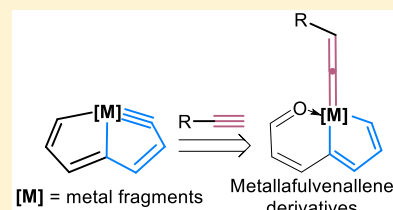
Reactions of Metallacyclopentadiene with Terminal Alkynes: Isolation and Characterization of Metallafulvenallene Complexes

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Supporting Information

ABSTRACT: Metallacyclopentadienes play an important role in transition-metal-catalyzed cyclotrimerization of alkynes. Isolation and characterization of these unique five-membered metallacycles could promote further understanding of related catalytic reactions. In this work, the first metallafulvenallene complexes were synthesized by the reaction of fused metallacyclopentadiene with terminal alkynes. Single-crystal X-ray diffraction and NMR spectroscopic studies on the metallafulvenallene complexes demonstrate that the bicyclic framework consists of a metallacyclopentadiene fused with a six-membered metallacycle, featuring an η^1 -vinylidene ligand. Deuterium labeling experiments were carried out to investigate the mechanism for the transformation of fused metallacyclopentadiene to fused metallafulvenallene. The UV–vis absorption spectra of these unique structures were measured.



INTRODUCTION

The origin of fulvenes can be traced back more than one century to their discovery in 1900.¹ Fulvenes and their derivatives have been recognized as versatile building blocks and have broad applications in pharmaceutical research and materials science.² Metal-mediated and/or metal-catalyzed reactions involving metallafulvene intermediates have been reported by O'Connor and Rheingold in 1987,³ in which the C_{sp} atoms of fulvenes have been replaced by metal fragments, providing a series of attractive organometallic molecules (Figure 1). Although fulvenallenes have been isolated successfully in 1986,⁴ their organometallic analogues, metallafulvenallene derivatives have never been observed.⁵

Metallacyclopentadiene complexes have attracted considerable interest and are regarded as versatile intermediates for

the discovery of new reactions.⁶ In many cases, metallacyclopentadienes can react with alkynes, followed by reductive elimination to produce the corresponding benzene derivatives.⁷ Besides, the reactions of metallacyclopentadienes with alkynes can lead to the formation of metallapentadiene–carbene complexes^{3,8} or new metallacycles through ring expansion.⁹ The reactions of preformed iridacyclopentadiene complexes with terminal alkynes have also been shown to produce fulvene complexes.⁵ Even though the reaction appears to involve the formation of metallafulvenallene intermediates, which have been trapped by nucleophiles^{7,9a–d} or undergo a reductive coupling with the butadiendiyl ligand,⁵ isolation of the metallafulvenallene has not been reported, probably due to the high reactivity of vinylidene ligands.¹⁰

Drawing inspiration from metallacyclic chemistry, we recently investigated the reactions of metallapentynes, which are derived from the reactions of multiyne chains with metal complexes.¹¹ The bicyclic framework of metallapentynes can be viewed as fused metallacyclopentadiene derivatives, which exhibit unique reactivities and provide access to interesting and attractive molecules, particularly concerning the isolation of some important intermediates.¹² Intrigued by the possibility that the fused metallacyclic system could facilitate the isolation of metallafulvenallene complexes, we employed the metallapentynyl as a fused metallacyclopentadiene to react with terminal alkyne substrates. Herein, we report the first examples of the desired transformation of metallacyclopentadiene to metallafulvenallene. The resulting metallafulvenallene complexes have been fully characterized, and the detailed mechanisms of the reactions have been

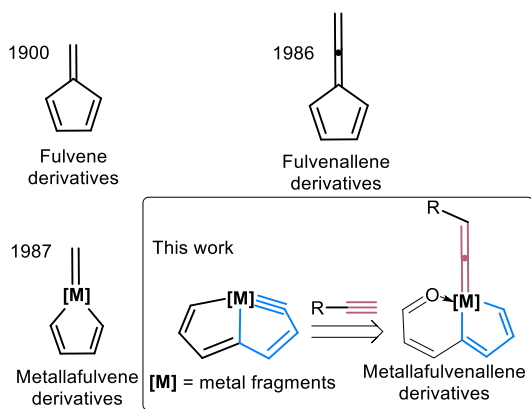


Figure 1. History of fulvene, fulvenallene, metallafulvene, and metallafulvenallene derivatives.

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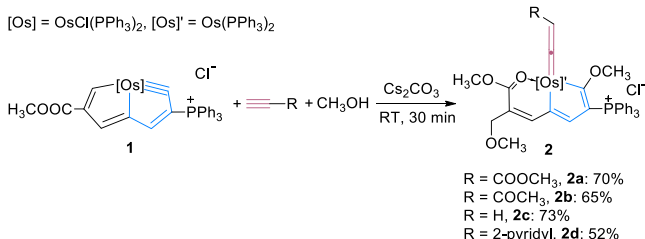


investigated with the aid of deuterium labeling experiments and a computational study.

RESULTS AND DISCUSSION

Our previous work showed that the reactions of osmapentalene (1) with CO in methanol solution led to the formation of osmapentalene, which contains two fused osmacyclopentadiene rings.¹³ Thus, we envisage the reaction of osmapentalene 1 with terminal alkynes in the presence of methanol may lead to the transformation of osmacyclopentadiene to osmafulvenallene. Treatment of the osmapentalene 1 with methyl propiolate in methanol solution at room temperature (RT) for 30 min led to the formation of a complex (2a), which could be isolated as a blue solid in 70% yield (Scheme 1). The structure of 2a has been characterized by NMR spectroscopy, HRMS data, elemental analysis, and single-crystal X-ray diffraction.

Scheme 1. Synthesis of Osmafulvenallene Complexes



As depicted in Figure 2, complex 2a contains an essentially planar bicyclic metallacycle framework, as indicated by the

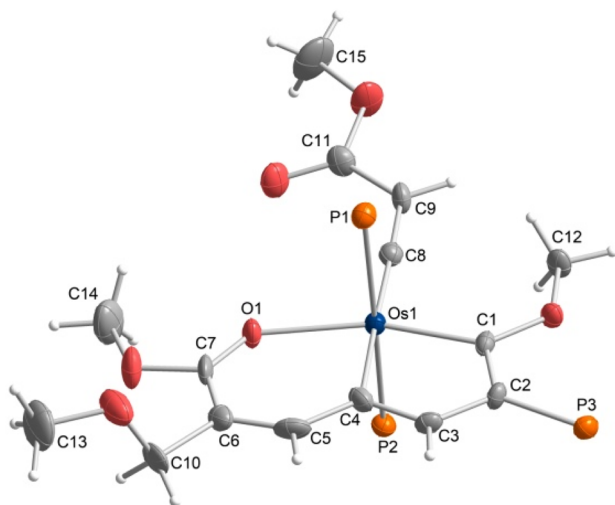


Figure 2. X-ray molecular structure for the cation of 2a. Thermal ellipsoids are set at the 50% probability level. Phenyl groups in the triphenylphosphine (PPh₃) ligands are omitted for clarity. Selected bond lengths (Å) and angles: Os(1)–C(1) 2.039(7), Os(1)–C(4) 2.127(7), Os(1)–C(8) 1.864(7), Os(1)–O(1) 2.166(5), C(1)–C(2) 1.413(9), C(2)–C(3) 1.427(9), C(3)–C(4) 1.347(9), C(4)–C(5) 1.429(9), C(5)–C(6) 1.336(10), C(6)–C(7) 1.478(10), C(7)–O(1) 1.228(8), C(8)–C(9) 1.339(9); Os(1)–C(1)–C(2) 117.1(5)°, C(1)–C(2)–C(3) 114.0(6)°, C(2)–C(3)–C(4) 116.1(6)°, C(3)–C(4)–Os(1) 115.6(5)°, C(4)–Os(1)–C(1) 77.1(3)°, Os(1)–C(4)–C(5) 126.5(5)°, C(4)–C(5)–C(6) 130.4(7)°, C(5)–C(6)–C(7) 119.8(6)°, C(6)–C(7)–O(1) 126.8(7)°, C(7)–O(1)–Os(1) 133.5(5)°, O(1)–Os(1)–C(4) 82.8(2)°, Os(1)–C(8)–C(9) 177.4(5)°.

mean deviation of 0.024 Å from the least-squares plane through Os1, O1, and C1–C7. The bond lengths of Os1–C1 and Os1–C4 are 2.039 and 2.127 Å, respectively, which are close to those found in other osmacyclopentadienes.¹⁴ The Os1–O1 bond (2.166(5) Å) is much longer than the reported Os–O σ bond,¹⁵ suggesting a dative O → Os bond character. The C–C bond distances of the bicyclic ring in 2a are in the range 1.336–1.478 Å and show considerable bond distance alternation in comparison to other metallaromatic systems.¹⁶ The η¹-vinylidene ligand in 2a has bond lengths of Os1–C8 (1.864 Å) and C8–C9 (1.339 Å) and an angle of Os1–C8–C9 (177.4°), which is within the range of typical metal vinylidene structures.¹⁷ The 11 atoms (Os1, O1, C1–C9) of the two rings and the vinylidene ligand are approximately coplanar, which is reflected by the mean deviation (0.037 Å) from the least-squares plane. In the ¹H NMR spectrum, signals for the metallafulvenallene unit were observed at δ = 6.41 ppm (C3H) and δ = 1.76 ppm (C9H). The ¹³C{¹H} NMR spectrum displayed the signals of the three metal-bonded carbon atoms of the metallafulvenallene unit at δ = 232.5 (C1), 165.3 (C4), and 302.5 (C8) ppm. The ¹³C chemical shifts of the remaining carbon atoms of the metallacycles were located at δ = 97.6 (C2), 161.4 (C3), and 111.8 (C9) ppm.

In a search for more complexes with a metallafulvenallene unit, the reactions of complex 1 with other terminal alkynes, such as 3-butyne-2-one, acetylene, and 2-ethynylpyridine, were investigated. As shown in Scheme 1, similar reactions took place and the desired metallafulvenallene complexes (2b, 2c, and 2d) were isolated in good yield. These complexes were identified by NMR and elemental analysis, and the structure of 2b was also characterized by X-ray diffraction analysis (details in section 2 of the Supporting Information). The X-ray diffraction study confirmed that the complex 2b also contains a six-membered metallacycle fused osmacyclopentadiene, as well as a linear vinylidene ligand (Figure 3). The Os–C bond lengths of the metallafulvenallene unit in 2b (Os1–C1 (2.043 Å), Os1–C4 (2.144 Å), and Os1–C8 (1.858 Å)) are close to those in 2a and the C–C bond distances of the osmacyclopentadiene ring are 1.404, 1.434, and 1.360 Å, indicating the π-electron delocalization within the fused metallacycle. The structural parameters of the linear vinylidene ligand are all similar to those of 2a.

The crystal data indicate that resonance structure 2' contributes to the structure of 2 (Scheme 2). In contrast to high reactivities of metallafulvene,¹⁸ these fused metallafulvenallene complexes are thermally stable. For example, complex 2a in the solid state can be kept under air for at least 3 h at 60 °C. As suggested by *in situ* NMR spectroscopy, complex 2a slowly decomposes when heated in solution at 80 °C, to generate a mixture of compounds with triphenylphosphine oxide as the dominant product. Coupling of the vinylidene ligand and the metallacyclopentadiene ring has been demonstrated in the metal-mediated [2 + 2 + 1] cyclo-trimerizations of alkynes, which leads to the reductive cyclization giving the fulvene products.⁵ We reasoned that the exceptional thermal stability of fused metallafulvenallene (2) can be attributed to the rigid chelating properties of fused bicyclic frameworks.

DFT calculations were conducted to examine the effect of the newly generated six-membered metallacycle on the relative stability of the metallafulvenallene structure. For the fused metallafulvenallene complex (2a), in which the carbonyl is coordinated to the metal center, the fused metallafulvenallene

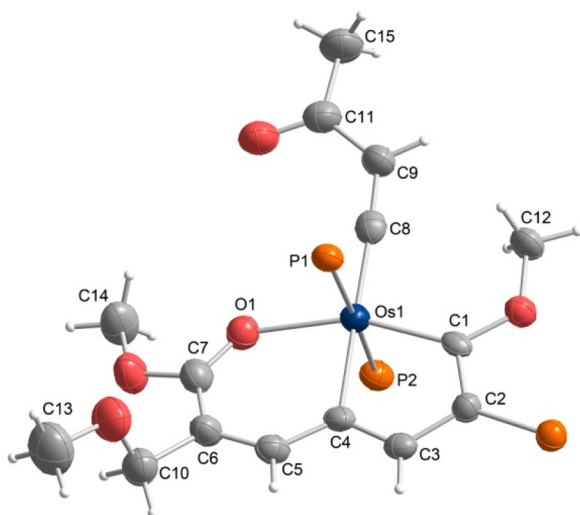
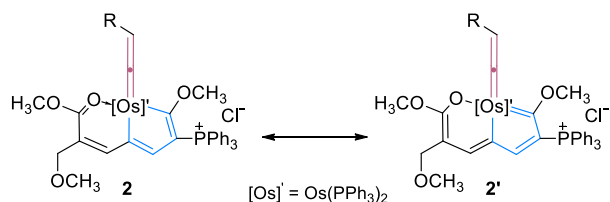


Figure 3. X-ray molecular structure for the cation of complex **2b**. Phenyl groups in the PPh_3 groups have been omitted. Thermal ellipsoids of the remaining non-hydrogen atoms are drawn with 50% probability. Selected bond distances (Å) and angles: Os(1)–C(1) 2.043(6), Os(1)–C(4) 2.144(6), Os(1)–C(8) 1.858(6), Os(1)–O(1) 2.162(4), C(1)–C(2) 1.404(8), C(2)–C(3) 1.434(8), C(3)–C(4) 1.360(8), C(4)–C(5) 1.405(8), C(5)–C(6) 1.357(8), C(6)–C(7) 1.412(8), C(7)–O(1) 1.255(7), C(8)–C(9) 1.339(8); Os(1)–C(1)–C(2) 118.6(4)°, C(1)–C(2)–C(3) 112.5(5)°, C(2)–C(3)–C(4) 117.8(5)°, C(3)–C(4)–Os(1) 114.0(4)°, C(4)–Os(1)–C(1) 77.0(2)°, Os(1)–C(4)–C(5) 125.6(5)°, C(4)–C(5)–C(6) 128.7(6)°, C(5)–C(6)–C(7) 121.5(6)°, C(6)–C(7)–O(1) 127.7(6)°, C(7)–O(1)–Os(1) 131.3(4)°, O(1)–Os(1)–C(4) 82.6(2)°, Os(1)–C(8)–C(9) 176.9(5)°.

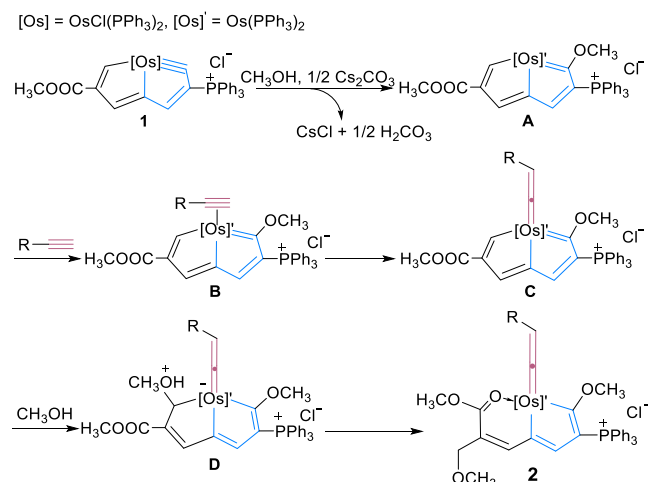
Scheme 2. Resonance Structures of Complexes **2**



structure is calculated to be more stable than its isomeric monocyclic structure by 23.4 kcal/mol (section 3 of the Supporting Information).

To shed light on the mechanism of the metallacyclopentadiene \rightarrow metallafulvenallene transformation, a number of substituted alkynes were tested under the same reaction conditions. NMR experiments *in situ* suggest that compound **1** is unreactive toward internal alkynes, such as dimethyl acetylenedicarboxylate and diphenylacetylene. On the basis of experimental observations and computational results, we propose the following putative mechanism for the reactions of **1** with alkynes (Scheme 3). Initial nucleophilic addition of a methanol molecule to a carbyne carbon leads to the formation of the metallapentalene (**A**), i.e., the fused metallacyclopentadiene complex. Similar nucleophilic addition reactions of carbyne carbon in a metallapentalene complex have been shown by a number of nucleophiles.¹⁹ Subsequent reaction of **A** with a terminal alkyne may generate the π -alkyne complex (**B**), which could undergo isomerization to form the vinylidene η^1 -complex (**C**). At this point, another molecule of methanol attacks the α -carbon within the five-membered metallacycle to

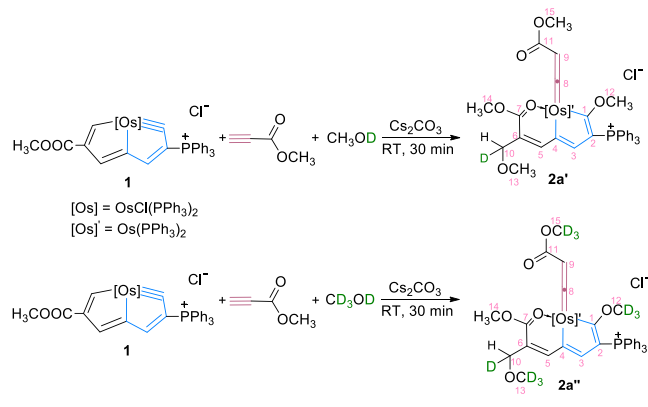
Scheme 3. Proposed Reaction Mechanism for the Formation of **2**



give **D**, and this is followed by the ring opening and coordination of the ester group to afford the final fused metallafulvenallene complex (**2**).

To understand the mechanistic aspects of the reactions of complex **1** with methanol, we performed the same experiments starting from deuterium-labeled MeOH. As shown in Scheme 4, these experiments suggest that the hydrogen atom at the

Scheme 4. Reactions of Osmapentalene **1** with Methyl Propiolate in CH_3OD or CD_3OD Solutions



C10 position in the final metallafulvenallene product comes from the OH proton of MeOH. When the reaction was performed with $\text{CD}_3\text{OD}/\text{Cs}_2\text{CO}_3$, CD_3O groups (instead of CH_3O) were found at the C12, C13, and C15 positions. The isotopic-labeling experiments suggest that three molecules of methanol are involved in this reaction (for more details on the isotope-labeling experiments, see section 1 of the Supporting Information). We inferred that the nucleophilic substitution of the methoxyl group at C7 does not occur, probably due to the coordination of the ester group with the metal center. In accordance with isotope labeling experiments, the high-resolution mass spectrometry shows molecular ion peaks (m/z) at 1271.3380 (**2a**), 1272.3446 (**2a'**), and 1281.4008 (**2a''**) respectively.

The UV–vis absorption spectra of these interesting osmafulvenallenes **2a–2d** are summarized in Figure 4. The absorption maxima of **2a–2d** in the visible region are 597 nm (complex **2a**, $\log \epsilon = 4.00$, ϵ : molar extinction coefficient in L

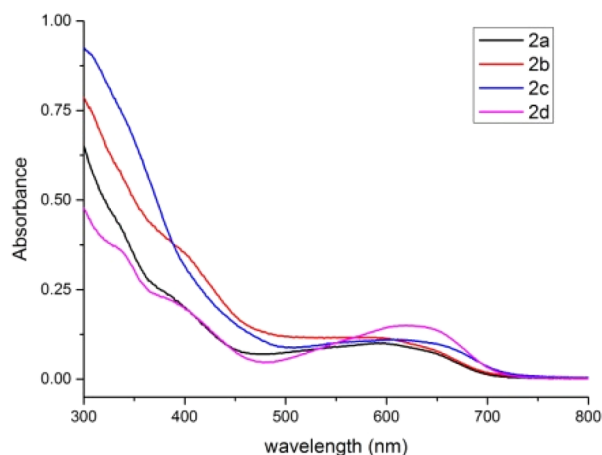


Figure 4. UV-vis absorption spectra of **2a–2d** measured in CH_2Cl_2 at room temperature.

$\text{mol}^{-1}\cdot\text{cm}^{-1}$), 598 nm (complex **2b**, $\log \epsilon = 4.06$), 618 nm (complex **2c**, $\log \epsilon = 4.03$), and 627 nm (complex **2d**, $\log \epsilon = 4.17$), respectively. Compared with the absorption spectra of **2c** and **2d**, those of complex **2a** and **2b** show a slight blue shift, which might be attributed to the electron withdrawing groups of vinylidene ligands.

CONCLUSIONS

In conclusion, the first metallafulvenallenes have been identified by the use of osmapentalyne as fused metallacyclopentadiene to react with terminal alkynes. To account for the formation of metallafulvenallenes, we propose a mechanism with the aid of DFT calculations and suggest that the incorporation of metallacyclopentadiene and η^1 -vinylidene ligand might be stabilized by the newly formed six-membered metallacycle fused system.

EXPERIMENTAL SECTION

General Procedures. All syntheses were carried out under an inert atmosphere (N_2) employing standard Schlenk techniques unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane) or calcium hydride (dichloromethane and chloroform) under N_2 prior to use. The metallapentalyne was synthesized according to the previously published procedure.^{19a} Other reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were performed on a Bruker AVII-400 (^1H 400.1 MHz; ^{31}P 162.0 MHz; ^{13}C 100.6 MHz) or a Bruker AVII-600 (^1H 600.1 MHz; ^{31}P 242.9 MHz; ^{13}C 150.9 MHz) spectrometer at room temperature. ^1H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 . Two-dimensional and one-dimensional NMR are abbreviated as heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and distortionless enhancement by polarization transfer (DEPT). The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), and broad (br). Elemental analyses were performed on a Vario EL III elemental analyzer. The high-resolution mass spectra (HRMS) experiments were recorded on a Bruker En Apex Ultra 7.0T FT-MS.

General Procedure for Synthesis of Complex 2. A solution of 1.5 equiv of alkynes was added to a solution of complex **1** (286 mg, 0.24 mmol) and Cs_2CO_3 (235 mg, 0.72 mmol) in MeOH (10 mL). The reaction mixture was stirred for 30 min at RT to give a blue solution. The solution was evaporated under a vacuum and then purified by column chromatography (neutral alumina, eluent: DCM:MeOH = 20:1) to give a dark blue solution. Compound **2**

was collected as a blue solid after the solvent was evaporated to dryness under a vacuum.

2a, ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.76 (s, 1H, H5), 6.41 (s, 1H, H3), 3.56 (s, 2H, C^{10}H_2), 3.63 (s, 3H, C^{15}H_3), 3.45 (s, 3H, C^{14}H_3), 3.10 (s, 3H, C^{13}H_3), 1.76 (s, 1H, C^9H), 1.67 (s, 3H, C^{12}H_3), 7.66–7.05 ppm (m, 45H, other aromatic protons). ^{31}P NMR (162.0 MHz, CDCl_3): δ = 7.80 (s, $\text{C}^{\text{P}}\text{PPh}_3$), 1.63 ppm (s, OsPPh_3). ^{13}C NMR, DEPT-135, $^1\text{H}-^{13}\text{C}$ HMBC (100.6 MHz, CDCl_3) and $^1\text{H}-^{13}\text{C}$ HSQC (100.6 MHz, CDCl_3): δ = 302.5 (br, C8), 232.5 (s, C1), 169.8 (s, C7, confirmed by $^1\text{H}-^{13}\text{C}$ HMBC), 165.3 (br, C4), 164.5 (s, C5), 161.7 (s, C11, confirmed by $^1\text{H}-^{13}\text{C}$ HMBC), 161.4 (d, $J_{\text{P-C}}$ = 17.3 Hz, C3), 111.8 (s, C9), 110.7 (s, C6), 97.6 (d, $J_{\text{P-C}}$ = 87.1 Hz, C2), 71.7 (s, C10), 60.3, 57.8, 54.3, 51.1 (s, CH_3), 135.2–127.0 ppm (m, other aromatic carbon atoms). Elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{62}\text{ClO}_6\text{OsP}_3$: C, 63.47; H, 4.79. Found: C, 63.54; H, 5.05. HRMS (ESI): m/z calcd for $[\text{C}_{69}\text{H}_{62}\text{O}_6\text{OsP}_3]^+$, 1271.3376; found, 1271.3380.

2a', ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.76 (s, 1H, H5), 6.41 (s, 1H, H3), 3.54 (s, 1H, C^{10}H), 1.71 (s, 1H, C^9H), 3.63, 3.45, 3.10, 1.63 (s, 3H, CH_3), 7.66–7.06 ppm (m, 45H, other aromatic protons). ^2H NMR (400.1 MHz, CDCl_3): δ = 3.56 ppm (s, 1D, C^{10}D). Elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{61}\text{DClO}_6\text{OsP}_3$: C, 63.42; H, 4.86; Found: C, 63.69; H, 4.75. HRMS (ESI): m/z calcd for $[\text{C}_{69}\text{H}_{61}\text{DO}_6\text{OsP}_3]^+$, 1272.3438; found, 1272.3446.

2a'', ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.77 (s, 1H, H5), 6.41 (s, 1H, H3), 3.55 (s, 1H, C^{10}H), 3.45 (s, 3H, C^{14}H_3), 1.74 (s, 1H, C^9H), 7.7–7.0 ppm (m, 45H, other aromatic protons). ^2H NMR (400.1 MHz, CDCl_3): δ = 3.51 (br, 4D, C^{15}D_3 and C^{10}D), 2.93 (s, 3D, C^{13}D_3), 1.67 ppm (s, 3D, C^{12}D_3). Elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{61}\text{DClO}_6\text{OsP}_3$: C, 62.98; H, 5.51. Found: C, 62.87; H, 5.66. HRMS (ESI): m/z calcd for $[\text{C}_{69}\text{H}_{52}\text{D}_{10}\text{O}_6\text{OsP}_3]^+$, 1281.4003; found, 1281.4008.

2b, ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.85 (s, 1H, H5), 6.47 (s, 1H, H3), 3.62 (s, 2H, C^{10}H_2), 2.50 (s, 1H, C^9H), 3.48, 3.14, 1.92, 1.76 (s, 3H, CH_3), 7.66–7.00 ppm (m, 45H, other aromatic protons). ^{31}P NMR (162.0 MHz, CDCl_3): δ = 7.04 (s, $\text{C}^{\text{P}}\text{PPh}_3$), 2.21 ppm (s, OsPPh_3). ^{13}C NMR plus DEPT-135 and $^1\text{H}-^{13}\text{C}$ HSQC (100.6 MHz, CDCl_3): δ = 303.9 (br, C8), 232.2 (s, C1), 190.5 (s, C7), 169.7 (s, C11, confirmed by $^1\text{H}-^{13}\text{C}$ HMBC), 164.8 (br, C4), 164.3 (s, C5), 161.2 (d, $J_{\text{P-C}}$ = 15.4 Hz, C3), 119.9 (s, C9), 112.0 (s, C6), 97.9 (d, $J_{\text{P-C}}$ = 88.4 Hz, C2), 72.9 (s, C10), 60.7, 57.6, 54.3, 30.3 (s, CH_3), 135.0–127.2 ppm (m, other aromatic carbon atoms). Elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{62}\text{ClO}_5\text{OsP}_3$: C, 64.25; H, 4.84. Found: C, 64.17; H, 4.98.

2c, ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.75 (s, 1H, H5), 6.45 (s, 1H, H3), 3.52 (s, 2H, C^{10}H_2), 1.36 (s, 1H, C^9H), 3.17, 3.11, 1.83 (s, 3H, CH_3), 7.69–6.91 ppm (m, 45H, other aromatic protons). ^{31}P NMR (162.0 MHz, CDCl_3): δ = 7.43 (s, $\text{C}^{\text{P}}\text{PPh}_3$), 1.01 ppm (s, OsPPh_3). ^{13}C NMR plus DEPT-135 and $^1\text{H}-^{13}\text{C}$ HSQC (100.6 MHz, CDCl_3): δ = 307.0 (br, C8), 235.8 (s, C1), 169.7 (s, C7), 165.8 (br, C4), 164.8 (s, C5), 161.5 (d, $J_{\text{P-C}}$ = 15.7 Hz, C3), 110.4 (s, C6), 100.6 (s, C9), 95.7 (d, $J_{\text{P-C}}$ = 89.9 Hz, C2), 72.1 (s, C10), 59.4, 57.5, 53.2 (s, CH_3), 135.4–118.6 ppm (m, other aromatic carbon atoms). Elemental analysis calcd (%) for $\text{C}_{67}\text{H}_{60}\text{ClO}_4\text{OsP}_3$: C, 64.49; H, 4.85. Found: C, 64.42; H, 4.64.

2d, ^1H NMR plus $^1\text{H}-^{13}\text{C}$ HSQC (400.1 MHz, CDCl_3): δ = 6.54 (s, 1H, H5), 6.39 (s, 1H, H3), 3.79 (s, 2H, C^{10}H_2), 2.20 (s, 1H, C^9H), 3.59, 3.22, 1.91 (s, 3H, CH_3), 8.92–6.90 ppm (m, 49H, other aromatic protons). ^{31}P NMR (162.0 MHz, CDCl_3): δ = 7.41 (s, $\text{C}^{\text{P}}\text{PPh}_3$), 0.96 ppm (s, OsPPh_3). ^{13}C NMR plus DEPT-135 and $^1\text{H}-^{13}\text{C}$ HSQC (100.6 MHz, CDCl_3): δ = 310.0 (br, C8), 234.5 (s, C1), 169.5 (s, C7), 165.3 (br, C4), 164.5 (s, C5), 161.1 (d, $J_{\text{P-C}}$ = 14.7 Hz, C3), 119.8 (s, C9), 118.7 (s, C6), 96.5 (d, $J_{\text{P-C}}$ = 86.9 Hz, C2), 71.7 (s, C10), 60.2, 57.3, 53.6 (s, CH_3), 135.4–118.6 ppm (m, other aromatic carbon atoms). Elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{63}\text{ClNO}_4\text{OsP}_3$: C, 65.27; H, 4.79; N, 1.06. Found: C, 65.01; H, 4.92; N, 1.21.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from chloroform solutions layered with hexane. Single-crystal X-ray diffraction data were collected on a Rigaku R-Axis

SPIDER IP CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Semiempirical or multiscan absorption corrections (SADABS) were applied.²⁰ All structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 using the SHELXTL program package.²¹ All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model.

Computational Details. All of the structures evaluated were optimized at the B3LYP/6-31G* level of DFT²² with a double- ζ valence basis set (LanL2DZ) being used to describe P and Os atoms. Single-point energy calculations were then performed on the mechanism using the B3LYP/6-311++G** method with the PCM solvation method in dichloromethane.²³ Frequency calculations were performed to confirm all stationary points as minima. In all of the calculations, we employed the effective core potentials (ECPs) of Hay and Wadt with polarization functions being added for P ($\zeta(d) = 0.34$) and Os ($\zeta(f) = 0.886$).²⁴ All of the calculations were performed using the Gaussian 09 software package.²⁵

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00371.

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

Computed structures (XYZ)

Accession Codes

CCDC 1888403–1888404 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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■ REFERENCES

- (1) Thiele, J. Ueber Ketonreactionen bei dem Cyclopentadien. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 666–673.
- (2) For a recent review, see: Preethalayam, P.; Krishnan, K. S.; Thulasi, S.; Chand, S. S.; Joseph, J.; Nair, V.; Jaroschik, F.; Radhakrishnan, K. V. Recent Advances in the Chemistry of Pentafulvenes. *Chem. Rev.* **2017**, *117*, 3930–3989.
- (3) O'Connor, J. M.; Pu, L.; Rheingold, A. L. The First Stable Metallacycle-Carbene Complexes: structural characterization of $\text{Ir}(\text{CR} = \text{C}(\text{R})\text{CR} = \text{CR})(\text{PPh}_3)_2(\text{CO})(=\text{C}(\text{CH}_2)_3\text{O})^+\text{BF}_4^-$, $\text{R} = \text{CO}_2\text{CH}_3$. *J. Am. Chem. Soc.* **1987**, *109*, 7578–7579.

(4) Stowasser, B.; Hafner, K. Synthesis of a Dicyclopenta[a,e]-pentalene by [6 + 2]-Cycloaddition of 1,3-Di-tert-butyl-5-vinylidenecyclopentadiene and Consecutive 8π -Electrocyclic Reaction. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 466–468.

(5) (a) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S.; Adams, M.; Rheingold, A. L. [2 + 2+1] Alkyne Cyclotrimerizations: A Metallacyclopentadiene Route to Fulvenes. *J. Am. Chem. Soc.* **1997**, *119*, 3631–3632. (b) O'Connor, J. M.; Closson, A.; Hiibner, K.; Merwin, R.; Gantzel, P.; Roddick, D. M. Iridacyclopentadiene Reactions with Terminal Alkynes: Tandem Cycloaromatization and Orthometalation. *Organometallics* **2001**, *20*, 3710–3717. (c) O'Connor, J. M.; Closson, A. P.; Holland, R. L.; Cope, S. K.; Velez, C. L.; Moore, C. E.; Rheingold, A. L. Synthesis and Solid-State Structures of (Triphos)iridacyclopentadiene Complexes as Models for Vinylidene Intermediates in the [2 + 2+1] Cyclo-trimerization of Alkynes. *Inorg. Chim. Acta* **2010**, *364*, 220–225.

(6) (a) Xu, L.; Wang, Y.-C.; Wei, J.; Wang, Y.; Wang, Z.; Zhang, W.-X.; Xi, Z. The First Lutetacyclopentadienes: Synthesis, Structure, and Diversified Insertion/C-H Activation Reactivity. *Chem. - Eur. J.* **2015**, *21*, 6686–6689. (b) Xu, L.; Wei, J.; Zhang, W.-X.; Xi, Z. Insertion/Rearrangement Reactivity of a Lutetacyclopentadiene towards N,N' -Diphenylcarbodiimide: Cooperative Effect of the Metal Center, Concentration of LiCl, and Solvent. *Chem. - Eur. J.* **2015**, *21*, 15860–15866. (c) Ma, W.; Yu, C.; Chen, T.; Xu, L.; Zhang, W.-X.; Xi, Z. Metallacyclopentadienes: Synthesis, Structure and Reactivity. *Chem. Soc. Rev.* **2017**, *46*, 1160–1192. (d) Zhang, Y.; Liu, L.; Chen, T.; Huang, Z.; Zhang, W.-X.; Xi, Z. Dilithio Spiro Zincacyclopentadienes and Dizinca[10]cycles: Synthesis and Structural Characterization. *Organometallics* **2019**, *38*, 2174–2178.

(7) (a) Domínguez, G.; Pérez-Castells, J. Recent Advances in [2 + 2] Cycloaddition Reactions. *Chem. Soc. Rev.* **2011**, *40*, 3430–3444. (b) Bottari, G.; Santos, L. L.; Posadas, C. M.; Campos, J.; Mereiter, K.; Paneque, M. Reaction of $[\text{TpRh}(\text{C}_2\text{H}_4)_2]$ with Dimethyl Acetylenedicarboxylate: Identification of Intermediates of the [2 + 2+2] Alkyne and Alkyne-Ethylene Cyclo(trimerizations). *Chem. - Eur. J.* **2016**, *22*, 13715–13723. (c) Orsino, A. F.; Gutiérrez del Campo, M.; Lutz, M.; Moret, M.-E. Enhanced Catalytic Activity of Nickel Complexes of an Adaptive Diphosphine-Benzophenone Ligand in Alkyne Cyclotrimerization. *ACS Catal.* **2019**, *9*, 2458–2481.

(8) (a) O'Connor, J. M.; Pu, L.; Rheingold, A. L. Oxidative Coupling of Cis-carbene Ligands: Synthesis, Structure, and Reactivity of an Iridium(III) Bis(oxacyclopentylidene) Complex. *J. Am. Chem. Soc.* **1989**, *111*, 4129–4130. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. Synthesis, Structure, and Reactivity of Metallacycle-Carbene and Bis(carbene) Complexes. A New Intramolecular Carbene-Carbene Coupling Process. *J. Am. Chem. Soc.* **1990**, *112*, 6232–6247. (c) O'Connor, J. M.; Hiibner, K.; Closson, A.; Gantzel, P. Synthesis and Solid State Characterization of a Meridional Triphos Iridium Metallacycle-Carbene Complex: $[\{\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}\text{Ir}(\text{CR} = \text{C}(\text{R})\text{CR} = \text{CR})\{\text{C}(\text{CH}_2)_3\text{O}\}][\text{BF}_4^-]$ ($\text{R} = \text{CO}_2\text{Me}$). *Organometallics* **2001**, *20*, 1482–1485.

(9) (a) O'Connor, J. M.; Pu, L.; Chadha, R. Synthesis and Structure of Annelated Carbon Rings Containing a Bridgehead Transition Metal. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 543–546. (b) O'Connor, J. M.; Pu, L.; Chadha, R. K. Metallacycle Annelation: Reaction of a Metallacycle-Substituent and a Vinylidene Ligand to Give a Bicyclic Metallalactone Complex. *J. Am. Chem. Soc.* **1990**, *112*, 9627–9628. (c) O'Connor, J. M.; Pu, L.; Rheingold, A. L. On the Mechanism of a New Metallacycle Annelation Reaction: Evidence for an Intramolecular Methoxy Group Transfer. *J. Am. Chem. Soc.* **1990**, *112*, 9663–9665. (d) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Pu, L.; Rheingold, A. L. Formal Vinylidene Ligand Insertion into a Metal Halide Bond. *J. Am. Chem. Soc.* **1995**, *117*, 8861–8862. (e) Chin, C. S.; Lee, H. New Iridacyclohexadienes and Iridabenzenes by [2 + 2+1] Cyclotrimerization of Alkynes and Facile Interconversion between Iridacyclohexadienes and Iridabenzenes. *Chem. - Eur. J.* **2004**, *10*, 4518–4522. (f) Chin, C. S.; Lee, H.; Eum, M.-S. Iridabenzenes from Iridacyclopentadienes: Unusual C-C Bond Formation between Unsaturated Hydrocarbyl Ligands. *Organometallics* **2005**, *24*, 4849–

4852. (g) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. Isolation of a Stable 1-Iridabicyclo[3.2.0]hepta-1,3,6-triene and Its Reversible Transformation into an Iridacycloheptatriene. *J. Am. Chem. Soc.* **2004**, *126*, 1610–1611. (h) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. An Osmabenzofuran from Reaction between $\text{Os}(\text{PhC}\equiv\text{CPh})(\text{CS})(\text{PPh}_3)_2$ and Methyl Propiolate and the C-Protonation of this Compound to Form a Tethered Osmabenzene. *Organometallics* **2006**, *25*, 1771–1777. (i) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. Reaction of the Iridacyclopentadiene $\text{TpMe}_2\text{Ir}(\text{C}(\text{R})-\text{C}(\text{R})\text{C}(\text{R})-\text{C}(\text{R}))(\text{H}_2\text{O})(\text{R} = \text{CO}_2\text{Me})$ with Alkynes. *Organometallics* **2009**, *28*, 172–180. (j) Clark, G. R.; Johns, P. M.; Roper, W. R.; Söhnle, T. L.; Wright, J. Regioselective Mono-, Di-, and Trifunctionalization of Iridabenzofurans through Electrophilic Substitution Reactions. *Organometallics* **2011**, *30*, 129–138. (k) Vivasco, Á.; Hernández, Y. A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Álvarez, E. Formation of β -Metallanaphthalenes by the Coupling of a Benzo-Iridacyclopentadiene with Olefins. *Organometallics* **2015**, *34*, 177–188.
- (10) Roh, S. W.; Choi, K.; Lee, C. Transition Metal Vinylidene and Allenylidene-Mediated Catalysis in Organic Synthesis. *Chem. Rev.* **2019**, *119*, 4293–4356.
- (11) Zhu, C.; Xia, H. Carbolong Chemistry: A Story of Carbon Chain Ligands and Transition Metals. *Acc. Chem. Res.* **2018**, *51*, 1691–1700.
- (12) (a) Luo, M.; Zhu, C.; Chen, L.; Zhang, H.; Xia, H. Halogenation of Carbyne Complexes: Isolation of Unsaturated Metallaodirenium Ion and Metallabromirenium Ion. *Chem. Sci.* **2016**, *7*, 1815–1818. (b) Luo, M.; Long, L.; Zhang, H.; Yang, Y.; Hua, Y.; Liu, G.; Lin, Z.; Xia, H. Reactions of Isocyanides with Metal Carbyne Complexes: Isolation and Characterization of Metallacyclopentenimine Intermediates. *J. Am. Chem. Soc.* **2017**, *139*, 1822–1825.
- (13) Zhu, C.; Luo, M.; Zhu, Q.; Zhu, J.; Schleyer, P. v. R.; Wu, J. I. C.; Lu, X.; Xia, H. Planar Möbius Aromatic Pentadienes Incorporating 16 and 18 Valence Electron Osmiums. *Nat. Commun.* **2014**, *5*, 3265.
- (14) (a) Wang, T.; Zhang, H.; Han, F.; Long, L.; Lin, Z.; Xia, H. Cine-Substitution Reactions of Metallabenzynes: An Experimental and Computational Study. *Chem. - Eur. J.* **2013**, *19*, 10982–10991. (b) Chen, J.; Huang, Z.; Hua, Y.; Zhang, H.; Xia, H. Synthesis of Five-Membered Osmacycles with Osmium-Vinyl Bonds from Hydrido Alkenylcarbyne Complexes. *Organometallics* **2015**, *34*, 340–347. (c) Li, J.; Lin, Y.-M.; Zhang, H.; Chen, Y.; Lin, Z.; Xia, H. Access to Metal-Bridged Osmathiazine Derivatives by a Formal $[4 + 2]$ Cyclization. *Chem. - Eur. J.* **2019**, *25*, 5077–5085.
- (15) Based on a search of the Cambridge Structural Database, CSD version 5.36 (December 2018).
- (16) For reviews, see: (a) Jia, G. Progress in the Chemistry of Metallabenzynes. *Acc. Chem. Res.* **2004**, *37*, 479–486. (b) Landorf, C. W.; Haley, M. M. Recent Advances in Metallabenzene Chemistry. *Angew. Chem., Int. Ed.* **2006**, *45*, 3914–3936. (c) Wright, L. J. Metallabenzynes and metallabenzenoids. *Dalton Transactions* **2006**, 1821–1827. (d) Bleeker, J. R. Aromatic Iridacycles. *Acc. Chem. Res.* **2007**, *40*, 1035–1047. (e) Jia, G. Recent progress in the chemistry of osmium carbyne and metallabenzene complexes. *Coord. Chem. Rev.* **2007**, *251*, 2167–2187. (f) Paneque, M.; Poveda, M. L.; Rendón, N. Synthesis and Reactivity of Iridacycles Containing the TpMe_2Ir Moiety. *Eur. J. Inorg. Chem.* **2011**, *2011*, 19–33. (g) Chen, J.; Jia, G. Recent development in the chemistry of transition metal-containing metallabenzynes and metallabenzynes. *Coord. Chem. Rev.* **2013**, *257*, 2491–2521. (h) Cao, X.-Y.; Zhao, Q.; Lin, Z.; Xia, H. The Chemistry of Aromatic Osmacycles. *Acc. Chem. Res.* **2014**, *47*, 341–354. (i) Frogley, B. J.; Wright, L. J. Fused-ring metallabenzynes. *Coord. Chem. Rev.* **2014**, *270*–271, 151–166. (j) Wei, J.; Zhang, W.-X.; Xi, Z. Dianions as Formal Oxidants: Synthesis and Characterization of Aromatic Dilithionickeloles from 1,4-Dilithio-1,3-butadienes and $[\text{Ni}(\text{cod})_2]$. *Angew. Chem., Int. Ed.* **2015**, *54*, 5999–6002. (k) Wei, J.; Zhang, Y.; Zhang, W.-X.; Xi, Z. 1,3-Butadienyl Dianions as Non-Innocent Ligands: Synthesis and Characterization of Aromatic Dilithio Rhodacycles. *Angew. Chem., Int. Ed.* **2015**, *54*, 9986–9990.
- (l) Wei, J.; Zhang, Y.; Chi, Y.; Liu, L.; Zhang, W.-X.; Xi, Z. Aromatic Dicu[10]annulenes. *J. Am. Chem. Soc.* **2016**, *138*, 60–63. (m) Zhang, Y.; Chi, Y.; Wei, J.; Yang, Q.; Yang, Z.; Chen, H.; Yang, R.; Zhang, W.-X.; Xi, Z. Aromatic Tetralithiodigalloses with a Ga-Ga Bond: Synthesis and Structural Characterization. *Organometallics* **2017**, *36*, 2982–2986. (n) Zhang, Y.; Wei, J.; Chi, Y.; Zhang, X.; Zhang, W.-X.; Xi, Z. Spiro Metalla-aromatics of Pd, Pt, and Rh: Synthesis and Characterization. *J. Am. Chem. Soc.* **2017**, *139*, 5039–5042. (o) Frogley, B. J.; Wright, L. J. Recent Advances in Metallaaromatic Chemistry. *Chem. - Eur. J.* **2018**, *24*, 2025–2038. (p) Wang, H.; Zhou, X.; Xia, H. Metallaaromatics Containing Main-group Heteroatoms. *Chin. J. Chem.* **2018**, *36*, 93–105. (q) Wei, J.; Zhang, W.-X.; Xi, Z. The aromatic dianion metalloles. *Chem. Sci.* **2018**, *9*, 560–568. (r) Zhang, Y.; Yang, Z.; Zhang, W.-X.; Xi, Z. Indacyclopentadienes and Aromatic Indacyclopentadienyl Dianions: Synthesis and Characterization. *Chem. - Eur. J.* **2019**, *25*, 4218–4224.
- (17) Examples for synthesis of osmium vinylidenes from terminal alkynes: (a) Wen, T. B.; Yang, S. Y.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. Unexpected Formation of Osmium Carbyne and Vinylidene Complexes from the Reaction of $\text{OsCl}_2(\text{PPh}_3)_3$ with $\text{HC}\equiv\text{CCMe}_3$. *Organometallics* **2000**, *19*, 3757–3761. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. Reactions of Elongated Dihydrogen-Osmium Complexes Containing Orthometalated Ketones with Alkynes: Hydride-Vinylidene- π -Alkyne versus Hydride-Osmacyclopentene. *Organometallics* **2003**, *22*, 2472–2485. (c) Wen, T. B.; Zhou, Z. Y.; Jia, G. Coupling Reaction of Phenylacetylene with $\text{OsH}_n(\text{PPh}_3)_3(2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ ($n = 1, 3$). *Organometallics* **2003**, *22*, 4947–4951. (d) Bajo, S.; Esteruelas, M. A.; López, A. M.; Oñate, E. Alkenylation of 2-Methylpyridine via Pyridylidene-Osmium Complexes. *Organometallics* **2012**, *31*, 8618–8626. (e) Batuecas, M.; Escalante, L.; Esteruelas, M. A.; García-Yebra, C.; Oñate, E.; Saá, C. Dehydrative Cyclization of Alkynals: Vinylidene Complexes with the C β Incorporated into Unsaturated Five- or Six-Membered Rings. *Angew. Chem., Int. Ed.* **2011**, *50*, 9712–9715.
- (18) (a) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. Carbene Ligand Insertion into a Metallacycle Ring: A Metallacyclopentadiene to Metallacyclobutene Conversion. *J. Am. Chem. Soc.* **1990**, *112*, 6731–6732. (b) O'Connor, J. M.; Merwin, R.; Rheingold, A. L.; Adams, M. L. Synthesis and Structural Characterization of a Diiridium μ -Acyl Complex. *Organometallics* **1995**, *14*, 2102–2105.
- (19) (a) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P. v. R.; Xia, H. Stabilization of Anti-aromatic and Strained Five-Membered Rings with a Transition Metal. *Nat. Chem.* **2013**, *5*, 698–703. (b) Zhu, C.; Zhu, Q.; Fan, J.; Zhu, J.; He, X.; Cao, X.-Y.; Xia, H. A Metal-Bridged Tricyclic Aromatic System: Synthesis of Osmium Polycyclic Aromatic Complexes. *Angew. Chem., Int. Ed.* **2014**, *53*, 6232–6236. (c) Zhuo, Q.; Zhang, H.; Hua, Y.; Kang, H.; Zhou, X.; Lin, X.; Chen, Z.; Lin, J.; Zhuo, K.; Xia, H. Constraint of a Ruthenium-Carbon Triple Bond to a Five-Membered Ring. *Sci. Adv.* **2018**, *4*, No. eaat0336.
- (20) Sheldrick, G. M. *SADABS: Program for semi-empirical absorption correction*; University of Göttingen: Göttingen, Germany, 1997.
- (21) Sheldrick, G. M. *SHELXL 97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
- (22) (a) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157*, 200–206. (d) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (23) Scalmani, G.; Frisch, M. J. Continuous Surface Charge Polarizable Continuum Models of Solvation. I. General formalism. *J. Chem. Phys.* **2010**, *132*, 114110–114115.

(24) *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, The Netherlands, 1984.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.