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Synthesis and Characterization of an Osmapentalene Derivative Containing a β-Agostic Os···H–C(sp^3) Interaction

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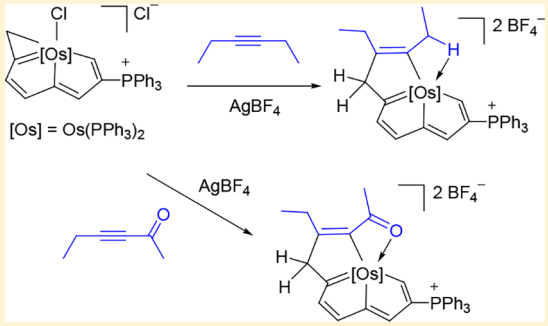
Supporting Information

ABSTRACT: Treatment of cyclopropaosmapentalene (**1**) with EtC≡CEt in the presence of $AgBF_4$ gave a new type of polycyclic metallaaromatic complex with a structure containing an sp^3 carbon and a β-agostic Os···H–C(sp^3) interaction. This result strongly supported our proposed intermediate in the reaction of cyclopropaosmapentalene **1** with alkynes that produced photothermal osmium carbolong complexes. When EtC≡CCOMe was used, the reaction gave a more thermally stable ketone-coordinated complex as the major product. The DFT study indicated that the difference in the two reactions is of thermodynamic origin.



INTRODUCTION

Metallacycles that are conjugated with carbon ring(s) have received considerable attention from chemists both experimentally and theoretically. For example, many efforts contributed by experimental chemists have led to the isolation of metallabenzenes,[1,2] metallabenzynes,[3,4] metallaannulenes,[5] and other metallacycles.[6,7] Meanwhile, the concept of metallaaromaticity has been extended from Hückel aromaticity[8] to Möbius aromaticity,[9] σ-aromaticity,[10] and spiro-aromaticity.[11] In addition, these interesting metallacycles are also expected to possess interesting properties owing to their large conjugated systems. For instance, osmium carbolong complexes **2** and **3**[12] show excellent photothermal properties.

These photothermal osmium carbolong complexes (**2** and **3**)[13] can be prepared by the reaction of cyclopropaosmapentalene **1**[10b] with two equivalent terminal alkynes (Scheme 1). A plausible mechanism for this reaction has been proposed, as shown in Scheme 1:[12] First, intermediate **A** with a vacant site was generated from complex **1** in the presence of $AgBF_4$. The coordination of a terminal alkyne (HC≡CR) to intermediate **A** followed by a migration insertion gave intermediate **C**. **C** released HBF_4 to give intermediate **D**, which reacted with another alkyne to give **E**. Finally, **E** rearranged to complex **2** or **3** via intermediates **F** and **G**.

Recently, when the terminal alkynes were replaced by alkynones, the reactions gave osmium carbolong complexes **4** and **5**[14] (Scheme 2), supporting the presence of proposed intermediate **D** in the reaction mechanism. However, we did not observe intermediate **C** in these reactions. Herein, we report the reaction of cyclopropaosmapentalene **1** with alkyne EtC≡CEt to give osmapentalene derivative **7** containing a β-agostic Os···H–C(sp^3) interaction, which supports the formation of intermediate **C** in the reaction mechanism of complex **1** with terminal alkynes to give photothermal carbolong complexes.[12]

RESULTS AND DISCUSSION

Reaction of Cyclopropaosmapentalene 1 with 3-Hexyne. The 18e cyclopropaosmapentalene **1** has been shown to have reactivity toward alkynes or allenes to give ring-growing osmapentalene derivatives. For example, the reactions of complex **1** with terminal alkynes (HC≡CR, R = 3-thiophenyl, phenyl) or 4,4,5,5-tetramethyl-2-(propa-1,2-dienyl)-1,3,2-dioxaborolane gave osmapentalene derivatives (**2**, **3**, and **6** in Schemes 1 and 2) containing CCCCC pentadentate chelates with planar Möbius aromaticity.[12] Complexes **2**, **3**, and **6**, which we call 12-carbon carbolong complexes, exhibited excellent photothermal behavior, and complex **2** has been demonstrated to be a photothermal therapy reagent for killing tumors in vivo.[12] Further studies on their formation mechanism by using alkynones (R′C≡CCOR) to react with cyclopropaosmapentalene **1** have led to the isolation of complexes **4** and **5** with 10-atom carbon chains[14] (Scheme 2). The observation of these complexes supported the formation of the proposed intermediate **D** in the reaction mechanism shown in Scheme 1.

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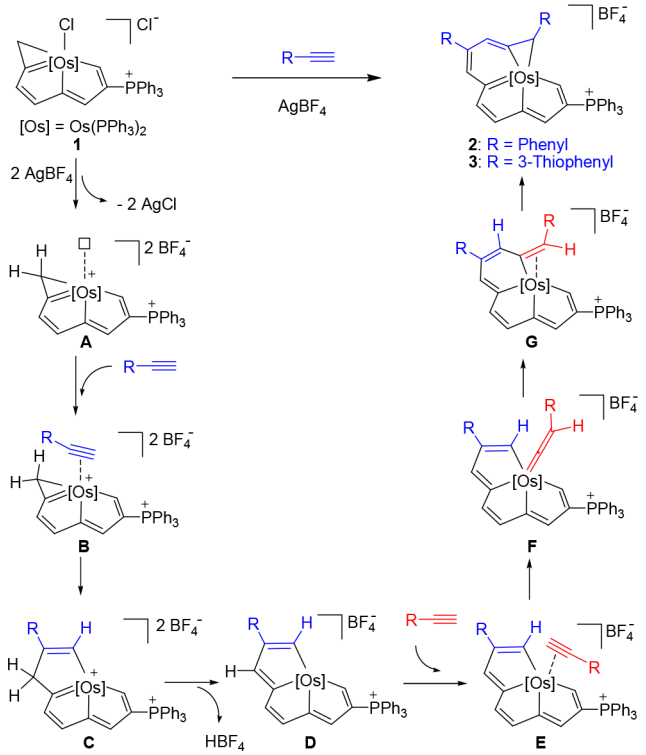
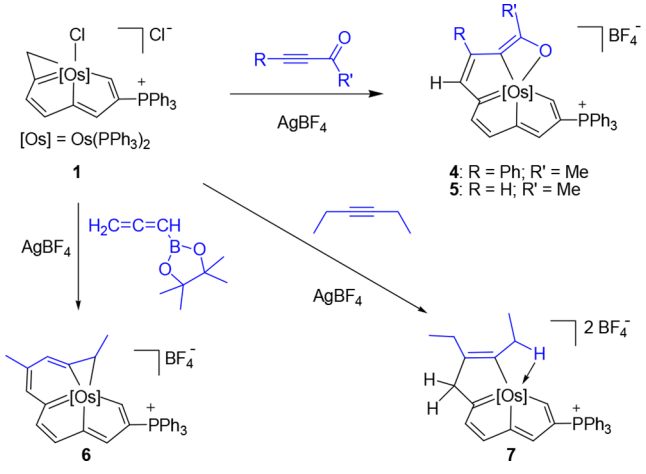
Scheme 1. Preparation of Complexes 2 and 3 and the Proposed Formation Mechanism



Scheme 2. Reactions of Cyclopropaosmapentalene 1 with Alkynes and an Allene



Interestingly, treatment of cyclopropaosmapentalene **1** with EtC≡CEt in the presence of $AgBF_4$ gave unexpected complex **7** containing an Os···H−C(sp^3) interaction (Scheme 2). Complex **7** was isolated as a brown solid in 87% yield.

Complex **7** was characterized by single-crystal X-ray diffraction, multinuclear nuclear magnetic resonance (NMR), and high-resolution mass spectrometry (HRMS). In the solid state, complex **7** exhibited remarkable thermal and air stabilities. As shown in Figure 1, complex **7** contains a near-planar metal-bridged tricyclic framework, as reflected by the small mean deviation from the least-squares plane (0.021 Å). The Os−C bond lengths of complex **7** (2.064 Å for Os1−C1, 2.085 Å for Os1−C4, and 2.081 Å for Os1−C7) are within the range of those of reported osmapentalenes (1.926−2.175 Å).[15] The

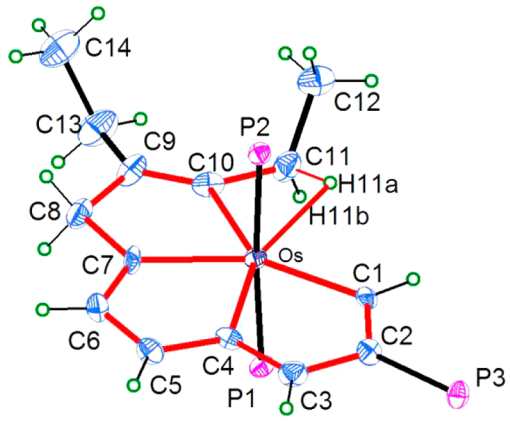


Figure 1. ORTEP drawing of complex **7** with thermal ellipsoids at the 50% probability level. The phenyl groups in PPh_3 groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1−C1 2.064(5), Os1−C4 2.085(6), Os1−C7 2.081(5), Os1−C10 2.058(6), C1−C2 1.384(9), C2−C3 1.416(8), C3−C4 1.392(7), C4−C5 1.392(8), C5−C6 1.373(9), C6−C7 1.376(9), C7−C8 1.509(8), C8−C9 1.486(9), C9−C10 1.342(8), C10−C11 1.415(8), C11−C12 1.523(1), C9−C13 1.510(10), C13−C14 1.514(9); Os1−C1−C2 118.2(4), C1−C2−C3 114.3(5), C2−C3−C4 114.2(5), C3−C4−Os1 117.2(4), C4−Os1−C1 76.1(2), Os1−C4−C5 118.9(4), C4−C5−C6 113.3(6), C5−C6−C7 114.9(5), C6−C7−Os1 118.9(4), C7−Os1−C4 73.9(2), C7−Os1−C10 71.2(2), C7−C8−C9 107.6(5), C8−C7−Os1 122.1(4), C8−C9−C10 110.1(5), C9−C10−Os1 128.9(4).

most interesting feature of this structure is the presence of an agostic interaction between the osmium and one aliphatic hydrogen (H11a) of the CH_2 group. The position of this hydrogen (H11a) was not determined exactly by single-crystal X-ray diffraction, but it was estimated by the HYDEX program[16] with an Os1−H11a distance of 2.055 Å. When the structure of **7** was optimized by density functional theory (DFT) calculation at the B3LYP/lanl2dz/6-31g level (see the Supporting Information), the Os1−H11a distance and the Os−H(11a)−C11 angle were found to be 2.036 Å and 103.7°, respectively. The calculated length of the C11−H11a bond was 1.170 Å, which was slightly longer than that of typical C−H bonds (1.06−1.12 Å),[17] confirming the agostic interaction between Os1 and H11a. Thus, complex **7** represents a new type of polycyclic metallaaromatic complex containing a *β*-agostic Os···H−C(sp^3) interaction. It is noted that there are only a few osmium complexes that contain *β*-agostic Os···H−C(sp^3) interactions.[18] The distance and angle in complex **7** are similar to those in reported complexes containing Os···H−C(sp^3) interactions.

Moreover, the distances of C8−C7 and C8−C9 in complex **7** were 1.509(8) and 1.486(9) Å, respectively. This result indicates that the carbon (C8) in the metallacycle is an sp^3 carbon, which strongly supports the formation of our proposed intermediate **C**, as shown in the mechanism for the reaction of complex **1** with alkynes (Scheme 1).

The NMR and HRMS data of complex **7** were consistent with the solid-state structure. In particular, the ^1H NMR spectrum of complex **7** showed a characteristic Os=C−H signal as a doublet at 14.96 ppm with a J_{P-H} coupling constant of 18.0 Hz. The H8 signal was located at 2.60 ppm at room temperature, which is a typical chemical shift for an allylic proton. The $^{31}P\{^1H\}$ NMR spectrum showed two resonances at 12.26 (t, J_{PP} = 4.5 Hz, CPPh_3) and −7.61 ppm (d, J_{PP} = 3.6 Hz, OsPPh_3). In the $^{13}C\{^1H\}$ NMR spectrum, the signals of C8

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and C11 were located at 68.1 and 1.1 ppm, respectively. These results confirm the sp^3 character of C8 and C11. In the ^{13}C NMR spectrum (Figure S4), the coupling constant of H11−C11 is 112.0 Hz, which is smaller than those of H8−C8 (125.7 Hz) and H13−C13 (126.9 Hz). Thus, this result confirms the β-agostic Os···H−C(sp^3) interaction.

The presence of an agostic proton ligand in complex **7** is indicated by the ^1H NMR spectrum, which shows a broad hydride signal at −1.22 ppm as a broad peak due to the fast exchange of two protons (H11) at room temperature (Figure 2). The ^1H NMR spectra of **7** are temperature-dependent.

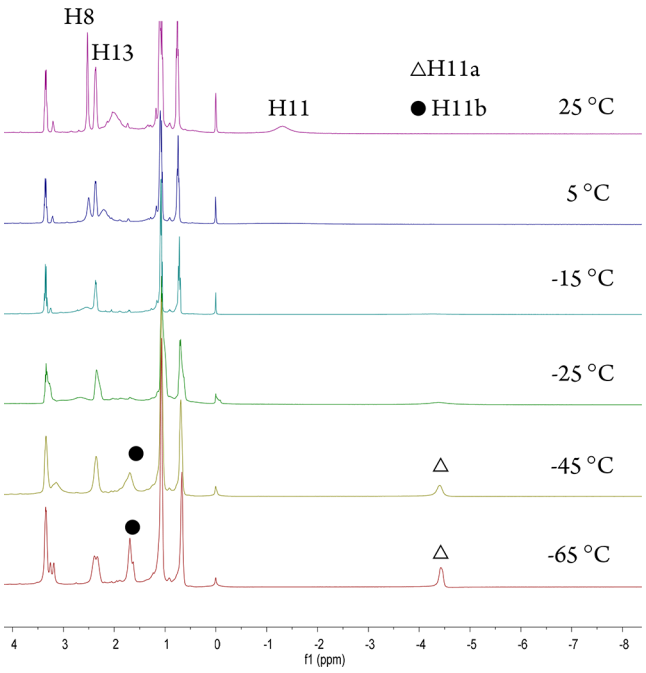


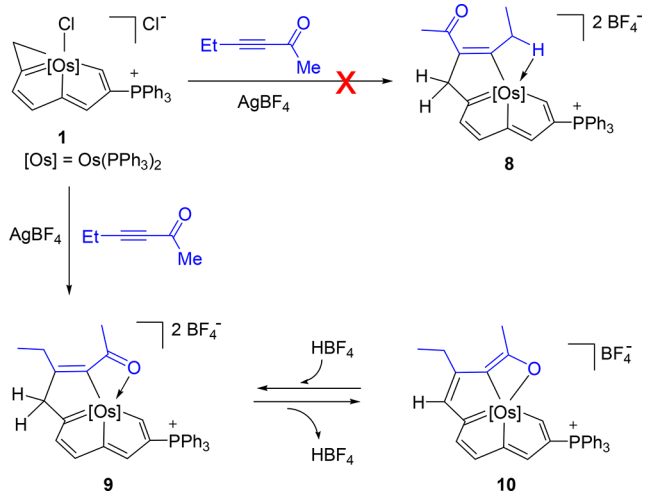
Figure 2. ^1H NMR spectra of complex **7** in the range of +4 to −8 ppm in CD_2Cl_2 at −65 to +25 °C.

When the temperature is lower than −15 °C, the agostic proton signal disappears due to the broadening of the resonance. At −65 °C, two proton signals appear at −4.42 (agostic proton, H11a) and 1.64 ppm (H11b) as sharp singlet signals.

Reaction of Cyclopropaosmapentalene 1 with 3-Hexyn-2-one. These results raised the interesting question of what complex (agostic complex **8** or ketone-coordinated complex **9** in Scheme 3) would be produced if alkyl alkynone was used in this reaction. With this in mind, we then investigated the reaction of complex **1** with EtC≡CCOMe in the presence of $AgBF_4$. Interestingly, the reaction produced complex **9** as the major product, which was observed by in situ $^{31}P\{^1H\}$ NMR at 16.02 and −4.63 ppm and was quickly converted to complex **10** during the workup process.

The structure of complex **10** was assigned on the basis of NMR and HRMS data. The $^{31}P\{^1H\}$ NMR spectrum of complex **10** showed two resonances at 12.04 (t, J_{P-P} = 5.5 Hz, C*P*Ph$_3$) and −5.78 ppm (d, J_{P-P} = 4.9 Hz, Os*P*Ph$_3$), which are similar to those of reported complexes **4** and **5**. The ^1H NMR spectrum of complex **10** also showed a characteristic Os=C−H signal as a doublet at 11.52 ppm with a J_{P-H} coupling constant of 21.0 Hz. For comparison, this signal was observed as a doublet at 11.83 ppm (J_{P-H} = 20.3 Hz) for **4** and 11.50 ppm (J_{P-H} = 20.6 Hz) for **5**.[14] In the $^{13}C\{^1H\}$ NMR spectrum

Scheme 3. Reaction of Cyclopropaosmapentalene 1 with 3-Hexyn-2-one



of **10**, the signals of metal-bonded C1 (215.54 ppm) and C7 (215.49 ppm) appeared downfield relative to those of C4 (190.31 ppm) and C10 (147.39 ppm). These values are also similar to those of **4** and **5**, indicating that complex **10** has a metallacyclic structure similar to that of **4** and **5**.

In the presence of excess HBF_4, complex **10** was converted to complex **9**, as indicated by in situ multinuclear NMR. In the in situ ^1H NMR spectrum, complex **9** showed a characteristic H8 signal at 1.95 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of C8 was located at 84.10 ppm. The $^{31}P\{^1H\}$ NMR spectrum also showed two signals at 16.28 (br, C*P*Ph$_3$) and −4.36 ppm (br, Os*P*Ph$_3$). These values are similar to those of complex **7**, suggesting that complex **9** has a ring structure similar to that of **7**. However, attempts to isolate pure complex **9** by recrystallization or chromatography failed. During purification, complex **10** was always isolated as the final product, indicating that the release of HBF_4 from complex **9** to form complex **10** is inevitable.

To understand why the reaction gave complex **9** and then **10** instead of complex **8**, we performed DFT calculations. The computational results revealed that complex **9-Cl** (a model complex of **9**) had a lower free energy (ca. 3.6 kcal/mol) than complex **8-Cl** (a model complex of **8**), indicating that complex **9** is thermodynamically more stable than complex **8**. The result is understandable, as the ketone oxygen, which is more basic than the agostic hydrogen, will donate more electron density to the metal center, which will help stabilize complex **9**. However, in situ generated complex **9** will be deprotonated quickly to give complex **10**, which is also driven by thermodynamics (ca. 23.7 kcal/mol, Figure 3). As previously studied,[14] we believe that the aromaticity of complex **10** is the strong driving force for the deprotonation of complex **9** to give complex **10**. In contrast, deprotonation of complex **7** would not give product **11**, as our DFT calculations revealed that deprotonation of complex **7-Cl** (a model complex of **7**) to give complex **11** is thermodynamically unfavorable (ca. 2.3 kcal/mol, Figure 3). This result, which is consistent with the isolation of complex **7** instead of **11**, is also understandable because complex **11**, which has a three-fused five-membered ring, has been shown to be less aromatic[14] than complex **10**.

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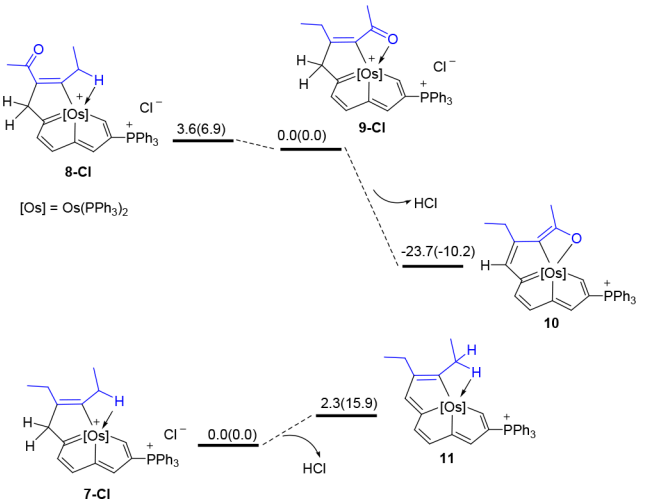

Figure 3. Free energy changes for complex **9-Cl** (a model complex of **9**) to complexes **8-Cl** (a model complex of **8**) and **10** and for complex **7-Cl** (a model complex of **7**) to complex **11** (a hypothetical complex). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

CONCLUSION

In summary, we investigated the reaction of cyclopropaosmapentalene (**1**) with EtC≡CEt in the presence of $AgBF_4$. The reaction gave a new type of polycyclic metallaaromatic complex containing a β-agostic Os···H−C(sp^3) interaction. When EtC≡CCOMe was used, the reaction gave the ketone-coordinated complex with sp^2 carbon rings owing to quick release of a proton driven by thermodynamics, as confirmed by DFT calculations. Our results enrich the family of polycyclic metallaaromatic complexes.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether), or calcium hydride (CH_2Cl_2). Complex **1** was prepared according to the procedure reported in the literature.[10b] Other commercial reagents were used as purchased from Aldrich Chemical Co. USA. NMR spectroscopic experiments were performed on a Bruker AVIII-400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz) or Bruker AVIII-500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz) spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4. Various two-dimensional and one-dimensional NMR techniques were used: 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 indicated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). HRMS experiments were performed on a Bruker En Apex Ultra 7.0T FT-MS mass spectrometer. Elemental analysis data were collected using a Vario EL III elemental analyzer.

Complex 7. 3-Hexyne (112 μL, 0.98 mmol) was injected into a mixture of complex **1** (200 mg, 0.16 mmol) and silver tetrafluoroborate ($AgBF_4$, 95 mg, 0.49 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 1 h to give a brown suspension. The precipitate was removed by filtration, and to the filtrate was added diethyl ether (20 mL) to give complex **7** as a brown solid, which was filtered, washed with diethyl ether (10 mL × 3), and dried under vacuum. Yield: 170 mg, 87%. ^{1}H NMR plus ^{1}H−^{13}C HSQC (400.1 MHz, CD_2Cl_2): δ 14.96 (d, J_{P-H} = 18.1 Hz, 1H, H1), 9.25 (s, 1H, H5), 8.02 (s, 1H, H3), 7.74 (s, 1H, H6), 2.60 (s, 2H, H8), 2.44 (q, J_{H-H} = 6.7 Hz, H13), 1.18 (s, 3H, H12), 0.831 (t, J_{H-H} = 7.5, 3H, H14), −1.22 (br, 2H, H11), 6.78−7.82 (45H, other aromatic protons) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 12.26 (t, J_{P-P} = 4.5 Hz, C*P*Ph$_3$), −7.61 (d, J_{P-P} = 3.9 Hz, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H−^{13}C HMBC, and ^{1}H−^{13}C HSQC (100.6 MHz, CD_2Cl_2): δ 251.9 (t, J_{P-C} = 7.7 Hz, C7), 211.0 (t, J_{P-C} = 9.5 Hz, C1), 192.4 (dt, J_{P-C} = 24.6 Hz, J_{P-C} = 2.6 Hz, C4), 170.7 (t, J_{P-C} = 6.3 Hz, C10), 167.4 (s, C5), 155.1 (s, C6), 142.7 (t, J_{P-C} = 3.8 Hz, C9), 151.3 (d, J_{P-C} = 22.9 Hz, C3), 138.2 (dt, J_{P-C} = 69.8 Hz, J_{P-C} = 3.8 Hz, C2), 68.1 (s, C8), 25.2 (s, C13), 13.9 (s, C14), 10.5 (s, C12), 1.1 (s, C11), 127.2−135.5 (other aromatic carbons) ppm. Anal. Calcd for $C_{68}H_{61}B_2F_8OsP_3$: C, 61.18; H, 4.61. Found: C, 61.06; H, 4.69. HRMS (ESI): m/z calcd for $[C_{68}H_{61}OsP_3]^{2+}$, 581.1795; found, 581.1802.

Observation of Complex 9. HBF_4·Et_2O (0.15 mL) was added to a green solution of complex **10** (42 mg, 0.035 mmol) in deuterated dichloromethane (0.3 mL) in an NMR tube and allowed to react for 4 h before collecting NMR data. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 10.42 (d, J_{P-H} = 21.2 Hz, 1H, H1), 8.93 (d, J_{H-H} = 3.5 Hz, 1H, H5), 8.13 (s, 1H, H3), 7.15 (d, J_{H-H} = 4.3 Hz, 1H, H6), 1.95 (s, 2H, H8), 1.93 (m, 2H, H13), 1.48 (s, 3H, H12), 0.38 (t, J_{H-H} = 6.5 Hz, 3H, H14) ppm. ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ 16.02 (br, C*P*Ph$_3$), −4.63 ppm (br, Os*P*Ph$_3$).^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 219.88 (s, C7), 205.49 (br, C4), 202.62 (t, J_{P-C} = 9.38 Hz, C1), 172.19 (s, C11), 167.74 (s, C5), 163.48 (t, J_{P-C} = 7.2 Hz, C10), 160.00 (s, C6), 152.66 (s, C3), 125.85 (d J_{P-C} = 69.8 Hz, C2), 118.0 (d, J_{P-C} = 68.5 Hz, C*P*Ph$_3$), 84.10 (s, C8), 32.88 (s, C12), 27.21 (s, C13), 11.72 (s, C14), 126.14−133.30 ppm (other aromatic carbons).

Complex 10. 3-Hexyn-2-one (59.1 μL, 1.08 mmol) was injected into a mixture of complex **1** (207 mg, 0.18 mmol) and $AgBF_4$ (105.8 mg, 0.54 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 5 h to give a deep green suspension. The precipitate was removed by filtration, and the filtrate was reduced under vacuum to approximately 2 mL. The residue was loaded on a silica gel (200−300 mesh) column and eluted with dichloromethane/acetone (v/v 10/1). The blue-green band was collected, and the solvent was removed under vacuum. The resulting residue was washed with diethyl ether (2 × 10 mL) to give green complex **10**, which was dried under vacuum. Yield: 122 mg, 59%. ^{1}H NMR plus ^{1}H−^{13}C HSQC (400.1 MHz, CD_2Cl_2): δ 11.52 (d, J_{P-H} = 21.0 Hz, 1H, H1), 7.51 (d, J_{H-H} = 4.4 Hz, 1H, H5), 7.43 (s, 1H, H3), 7.07 (d, J_{H-H} = 3.5 Hz, 1H, H6), 6.79 (s, 1H, H8), 2.02 (q, J_{H-H} = 7.2 Hz, 2H, H13), 1.07 (t, J_{H-H} = 7.4 Hz, 3H, H14), 1.01 (s, 3H, H12), 6.81−7.47 (45H, other aromatic protons) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 12.04 (t, J_{P-P} = 5.5 Hz, C*P*Ph$_3$), −5.78 (d, J_{P-P} = 4.9 Hz, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H−^{13}C HMBC, and ^{1}H−^{13}C HSQC (100.6 MHz, CD_2Cl_2): δ 215.54 (dt, J_{P-C} = 10.4 Hz, J_{P-C} = 3.8 Hz, C1), 215.49 (br, C7), 190.31 (dt, J_{P-C} = 26.6 Hz, J_{P-C} = 3.7 Hz, C4), 185.96 (s, C11), 167.66 (s, C9), 152.92 (s,C5), 150.55 (s,C6), 147.39 (t, J_{P-C} = 7.8 Hz, C10), 137.31(s, C8), 132.15 (d, J_{P-C} = 24.5 Hz, C3), 124.47 (d, J_{P-C} = 66.0 Hz, C2), 28.46 (s, C12), 26.93 (s, C13), 11.75 (s, C14), 126.14−133.30 ppm (other aromatic carbons). HRMS (ESI): m/z calcd for $[C_{68}H_{58}OOsP_3]^+$, 1175.3310; found, 1175.3282.

Crystal Structure Analyses. A crystal of **7** suitable for X-ray diffraction was grown from dichloromethane solution layered with hexane. The crystal was mounted on glass fibers with epoxy glue. The diffraction intensity data of **7** were collected on an Oxford Gemini S Ultra CCD area detector with Cu Kα radiation (λ = 1.54184 Å). Using the Olex2[19] software package, the structure was solved with the SHELXTL[20] structure solution program using direct methods and refined with the SHELXTL refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically, unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Further crystallographic details are summarized in Table S1.

Computational Details. All calculations were performed with the Gaussian 09 software package.[21] The molecular geometries of all the structures presented in this study were fully optimized using the B3LYP[22] level of density functional theory (DFT) without any

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constraints. Vibrational frequency calculations were performed at the same level of theory to verify the stationary points with no imaginary frequency for the minima. The effective core potentials (ECPs) of Lanl2dz were used to describe Os, Cl, and P atoms,[23] whereas the 6-31g basis set was used for O, C, and H atoms. Polarization functions for Os (ζ_f = 0.886), Cl (ζ_d = 0.514), and P (ζ_d = 0.340) were added.[24]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00002.

Spectroscopic data for all new compounds and crystallographic details for complex **7** (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1814245 contains 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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