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From Osmium Hydrido Vinylidene to Osmacycles: The Key Role of Osmabutadiene Intermediates

Qianyi Zhao, Xiao-Yu Cao,* Ting Bin Wen, and Haiping Xia*[a]

Abstract: Osmium hydrido vinylidene **1** shows diverse cyclization reactivity with activated terminal alkynes. Treatment of **1** with HC≡CCOR′ (R′ = OEt and Me) gave osmafurans **3a** and **3b** via osmium alkenyl/vinylidenes **2a** and **2b**. In addition, **1** reacted with HC≡CCH(OH)C≡CH to yield osmabenzene **4**, in which the alkynol acted as a C$_5$ fragment to cyclize with **1**. Mechanistic analysis indicates that these reactions and the previous formal [3+3] cycloaditions between **1** and HC≡CCH(OH)R (R = Ph, Et, and vinyl) or HC≡CCH(OEt)$_2$ all go through similar osmabutadiene intermediates. Subsequently, the intermediates either took a "coordination and cyclization" process or a "carbon–carbon coupling" path to cyclization, depending on the coordination ability of substituents on the terminal alkenyl carbon atom.

Keywords: cyclization · hydride ligands · metallacycles · osmium · vinylidene ligands

Introduction

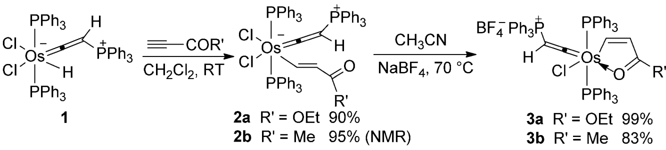
Metal vinylidene complexes have been widely used as catalysts in metathesis and coupling reactions for carbon–carbon and carbon–heteroatom bond formation.[1] These complexes are characterized by the electrophilicity of C$_\alpha$ and the nucleophilicity of C$_\beta$, and their synthesis and reactivity have been extensively studied.[2] Nonetheless, using metal vinylidene as the metal source to construct metallacycles has remained largely unexplored. Most common cyclization reactions of metal vinylidenes are [2+2] cycloadditions between the M=C$_\alpha$ fragment and alkynes or alkenes, giving four-membered metallacycles.[3] The C$_\alpha$=C$_\beta$ fragment also reacts with alkynes or alkenes in a similar manner.[4]

Metal hydrido vinylidene[5] may be regarded as an evolved metal vinylidene with a hydride ligand at the metal center. The presence of hydride ligand may allow the insertion of a terminal alkyne into the M−H bond,[6] thus creating opportunities to diversify the cyclizations for metallacycle formation. We have reported that the osmium hydrido vinylidene **1** (see Scheme 1) reacted with HC≡CCH(OH)R (R = Ph, Et, and vinyl) and HC≡CCH(OEt)$_2$ to give isoosmabenzenes and an osmabenzyne through a formal [3+3] cycloaddition.[7] Herein, we further explored the reactivities of **1** with other alkynes, such as HC≡CCOR′ (R′ = OEt and Me) and HC≡CCH(OH)C≡CH, and obtained new osmacycles. Mechanistic analysis revealed the intrinsic connections of the formation of different metallacycles from osmium hydrido vinylidene **1**. All reactions of **1** with the activated alkynes went through similar osmabutadiene intermediates.

Results and Discussion

Preparation of Osmafurans

Treatment of the osmium hydrido vinylidene **1** with ethyl propiolate in dichloromethane at room temperature (RT) led to a fast color change from light yellow to orange, giving **2a** in high yield (Scheme 1). Similarly, when 3-butyn-2-one was used, analogue **2b** was detected by in situ NMR spectroscopy. Although the metal vinylidene and the hydride ligand connected to the osmium center are both possibly reactive to alkynes, the formation of **2a** and **2b** reveals that the reaction of osmium hydrido vinylidene **1** and alkynes is initiated exclusively with the insertion of alkynes into the Os−H bond. When further heated in acetonitrile at 70 °C in the presence of NaBF$_4$, the isolated complexes **2a** and **2b** could undergo intramolecular cyclization by coordination of the oxygen atom of the carbonyl group to the osmium center to give osmafurans **3a** and **3b** (Scheme 1).



Scheme 1. Synthesis of osmafurans.

An X-ray single-crystal diffraction experiment clarified the structure of **2a**. As shown in Figure 1, the molecular structure of **2a** is interesting, as it contains a vinylidene ligand and an alkenyl ligand. In consistence with this fea-

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[a] Q. Zhao, Dr. X.-Y. Cao, Prof. Dr. T. B. Wen, Prof. Dr. H. Xia
State Key Laboratory of Physical Chemistry of Solid Surfaces
College of Chemistry and Chemical Engineering
Xiamen University
Xiamen, 361005 (P. R. China)
Fax: (+86) 592-2186628
E-mail: xcao@xmu.edu.cn
hpxia@xmu.edu.cn

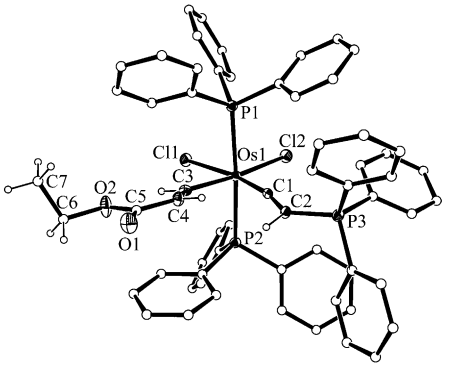


Figure 1. Molecular structure of **2a**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–Cl1 2.4779(6), Os1–Cl2 2.5099(6), Os1–P1 2.4154(7), Os1–P2 2.3951(7), Os1–C1 1.793(3), C1–C2 1.344(3), Os1–C3 2.066(3), C3–C4 1.325(3), C4–C5 1.463(4), C5–O1 1.214(3), C5–O2 1.358(3); Os1-C1-C2 167.6(2), Os1-C3-C4 133.9(2), C3-C4-C5 124.0(3), C4-C5-O2 113.4(2).

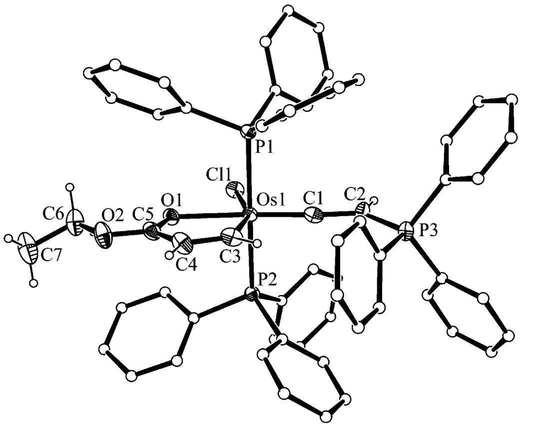


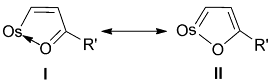
Figure 2. Molecular structure of the cation of **3a**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–Cl1 2.4256(11), Os1–P1 2.3795(11), Os1–P2 2.3888(11), Os1–C1 1.780(5), C1–C2 1.353(6), Os1–O1 2.193(3), Os1–C3 2.036(5), C3–C4 1.354(7), C4–C5 1.425(7), C5–O1 1.238(6), C5–O2 1.328(6), C6–O2 1.469(6), C6–C7 1.485(7); Os1-C1-C2 173.1(4), Os1-C3-C4 118.2(4), Os1-O1-C5 113.5(3), C3-C4-C5 113.1(4), C4-C5-O1 120.1(4).

ture, the Os1–C1 bond length (1.793(3) Å) is within the range for typical vinylidene complexes $Os{=}C{=}CRR'$ (1.78–1.95 Å).[8] The C1–C2 (1.344(3) Å) and C3–C4 bonds (1.325(3) Å) are typical carbon–carbon double bonds. The Os1–C3 bond (2.066(3) Å) is an osmium–carbon single bond.

Consistent with the solid-state structure, the ^{1}H NMR spectrum shows signals of the two alkenyl protons H3 and H4 at $\delta = 9.8$ and 4.7 ppm with a coupling constant of 16.2 Hz, which indicates a *trans* geometry. The proton linked to C2 resonates at $\delta = 0.3$ ppm. In the ^{31}P NMR spectrum, the peaks for $CPPh_3$ and $OsPPh_3$ are located at $\delta = 0.5$ and -7.0 ppm. The ^{13}C NMR spectrum shows a triplet at $\delta = 267.2$ ppm ($^{2}J_{PC} = 9.8$ Hz) for the carbene carbon atom C1. The signals for C2, C3, and C4 are found at $\delta = 69.1$, 179.5, and 121.4 ppm.

Compound **2b** is less stable than **2a**. Nonetheless, its structure can easily be deduced by NMR spectroscopy data. The signals for complex **2b** are similar to those for **2a**.

The structure of **3a** in the solid state was also characterized by X-ray diffraction. As shown in Figure 2, the molecule structure contains an osmafuran and a vinylidene group. The Os1–C1 (1.780(5) Å) and C1–C2 (1.353(6) Å) bonds are similar to those in **1**, indicating a vinylidene segment. The Os1–C3 (2.036(5) Å) bond length is between those for osmium–carbon single and double bonds. The C3–C4 (1.354(7) Å), C4–C5 (1.425(7) Å), C5–O1 (1.238(6) Å) and Os1–O1 (2.193(3) Å) bond lengths reveal two resonance forms of the metallaheterocycle, with **I** as the dominant contributor.[9]



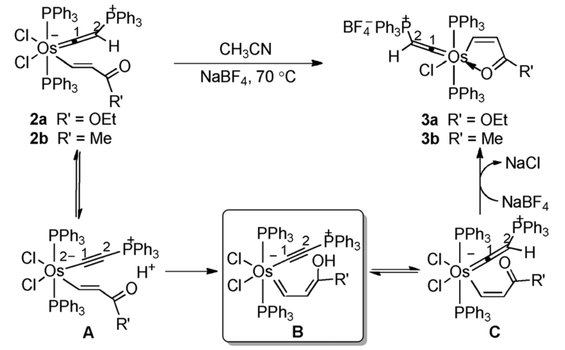
Abstract in Chinese:

本文系统总结了锇亚乙烯 ***1*** *与炔类的关环反应，发现这些反应均经过了锇顺丁二烯中间态，合成了新型的锇苯和锇呋喃化合物，拓展了金属亚乙烯的反应化学。*

The NMR spectra of **3a** are consistent with its solid-state structure. The ^{1}H NMR spectrum shows two alkenyl proton signals at $\delta = 10.5$ (H3) and 6.1 ppm (H4), with an H–H coupling constant of 8.0 Hz, indicating a *cis* geometry. The vinylidene proton resonates at $\delta = 2.3$ ppm. In the ^{31}P NMR spectrum, two kinds of signals are observed, $\delta = 3.5$ ppm for $OsPPh_3$ and $\delta = 0.9$ ppm for $CPPh_3$. In the ^{13}C NMR spectrum, the ring carbon signals ($\delta = 197.2$ (C3), 117.2 (C4), and 180.4 ppm (C5)) are comparable to those reported for other osmafurans.[9,10] The vinylidene carbon atoms C1 and C2 resonate at $\delta = 273.6$ and 78.0 ppm. The NMR spectra of **3b** are almost identical to those of **3a**.

The insertion of alkynes bearing ester functional groups into the M–X (X = H, I, Hg) bond is an efficient approach to synthesize metallafurans.[10,11] In general, the stereochemistry of the insertion of terminal alkynes into metal hydrides is *syn*,[12] creating complexes with an *E*-alkenyl group, such as **2a** and **2b**. In the subsequent transformation, nonetheless, the *E*-alkenyl group in **2a** or **2b** is changed to a *Z*-alkenyl group in **3a** or **3b**. Such configurational change can occur in some 16-electron metal complexes.[12] However, the osmium centers of **2a** and **2b** are 18-electron centers. Deuterium-labeling studies indicate the acidity of the vinylidene protons. When **2a** was treated with D_2O at RT, in situ ^{1}H NMR spectroscopy showed that the resonance of the vinylidene proton ($\delta = 0.3$ ppm) disappeared quickly, indicating a hydrogen–

deuterium exchange. Thus we propose a mechanism in Scheme 2. The reaction starts with the equilibrium of vinylidene–alkynyl interconversion. Once the proton dissociates from C2 in **2a** or **2b** to form **A**, it tends to attack the oxygen atom of the carbonyl group, followed by keto–enol isomerization to give osmabutadiene intermediate **B**. The configuration of the *E*-vinyl ketone group is changed to *s-cis* alkenyl carbene during this process. Then **B** undergoes equilibriums of keto–enol tautomerization and vinylidene–alkynyl interconversion with **C**. Finally, the carbonyl oxygen atom in **C** coordinates to the osmium center to furnish **3a** or **3b**.

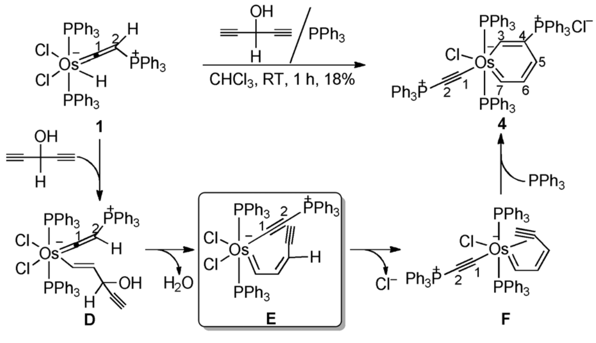


Scheme 2. Proposed mechanism for the formation of osmafurans **3a**, **b**.

Furthermore, complexes **3a** and **3b** show high stability. Although they contain a vinylidene group at the osmium center, unlike most air-sensitive metal vinylidene complexes, the solid samples of **3a** and **3b** can be stored in air for months without decomposition. In addition, **3a** and **3b** can resist strong acids such as HCl and HBF_4. This unexpected stability may due to the stabilization effect and electron-withdrawing property of the phosphonium group.

Preparation of Osmabenzene

The reaction of **1** with HC≡CCH(OH)C≡CH gave osmabenzene **4** (Scheme 3), in which HC≡CCH(OH)C≡CH acted as a C_5 fragment to cyclize with **1**. In situ NMR spectroscopy indicated the formation of two products in a molar ratio of about 1:1, yet only osmabenzene **4** could be isolated by column chromatography. The other product was too unstable to be separated.



Scheme 3. Synthesis of osmabenzene **4**.

The structure of **4** can be inferred from NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **4** exhibit characteristic chemical shifts of an osmabenzene: H3 and H7 show characteristic low-field resonances at $\delta = 14.7$ and 17.7 ppm, and the metal-bound carbon atoms C3 and C7 show typical low-field signals at $\delta = 243.7$ and 262.0 ppm. The ^{31}P NMR spectrum of **4** consists of three signals: $\delta = 16.3$ and -15.7 ppm for two $CPPh_3$ groups and $\delta = -5.6$ ppm for $OsPPh_3$. Two carbon signals of the alkynylphosphonium group are found at $\delta = 188.7$ ppm for C1 and $\delta = 94.2$ ppm for C2.

By changing the counteranion Cl^- of **4** into BPh_4^-, complex **4′** was prepared, and X-ray diffraction further confirmed its solid-state structure (Figure 3). The metallacycle (Os1, C3–C7) and C1, C2 are almost coplanar, with the osmium atom deviating the most (0.023 Å) from the mean plane. The C1−C2 bond length (1.243(10) Å) is typical for that of a carbon–carbon triple bond. The Os1−C3 bond length (2.005(8) Å) is a little longer than that of Os1−C7 (1.923(7) Å). Presumably the alkynylphosphonium group (*trans* to C3) has a greater influence than the chloride ligand (*trans* to C7). The C−C distances within the cycle (C3−C4 1.393(9) Å, C4−C5 1.409(9) Å, C5−C6 1.368(9) Å and C6−C7 1.427(9) Å) are between those for carbon–carbon single and double bonds, with a slight alternation comparable to that of reported metallabenzenes.[13] The sum of angles in the osmabenzene cycle is 719.9°—almost identical to the ideal value of 720°. All these structural features suggest a delocalized π-electron system.

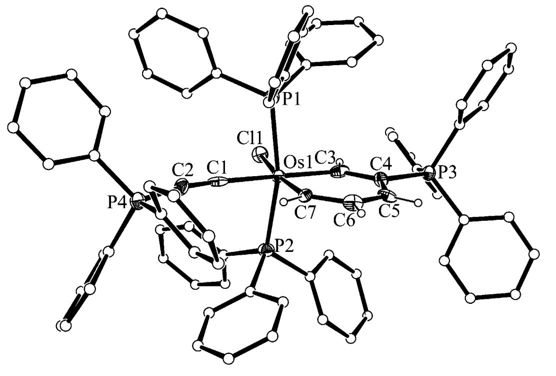
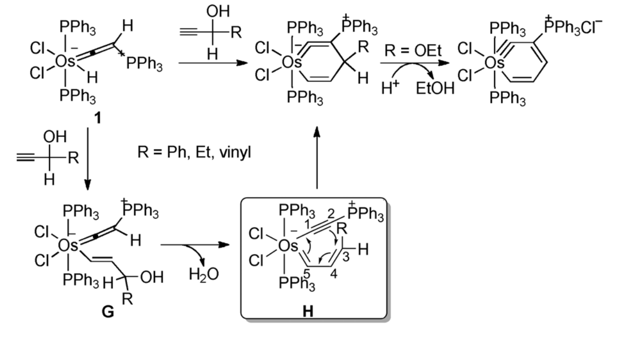


Figure 3. Molecular structure of the cation of **4′**. Thermal ellipsoids are drawn at the 50% probability level. Counteranion BPh_4^- and hydrogen atoms in the phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–Cl1 2.536(2), Os1–P1 2.388(2), Os1–P2 2.381(2), Os1–C1 2.008(9), Os1–C3 2.005(8), Os1–C7 1.923(7), C1–C2 1.243(10), C3–C4 1.393(9), C4–C5 1.409(9), C5–C6 1.368(9), C6–C7 1.427(9); Os1-C1-C2 172.4(7), C3-Os1-C7 87.4(3), Os1-C3-C4 131.7(6), C3-C4-C5 120.9(7), C4-C5-C6 125.2(7), C5-C6-C7 124.0(7), C6-C7-Os1 130.7(6).

A proposed mechanism for the formation of osmabenzene **4** is shown in Scheme 3. Like the generation of **2a** and **2b**, insertion of a terminal alkyne into the Os−H bond produces *E*-vinyl intermediate **D**. The acidic hydrogen atom on the vinylidene carbon atom C2 then eliminates with the hydroxy group, leaving a molecule of H_2O to give osmabutadiene **E**, along with the transformation from an *E*-alkenyl group to an *s-cis* alkenyl carbene. Coordination of the alkyne triple bond to the osmium center gives **F**. Nucleophilic addition of PPh_3 at the 2-position of the coordinated alkyne produces osmabenzene **4**, similar to our previous metallabenzenes.[14]

Synthetic methods for metallabenzenes have now been well developed.[14–21] Among them, one-pot reaction between an organic C_5 skeleton and a transition-metal complex is the major approach, including 1) reactions of $[IrCl(PR_3)_3]$ with potassium 3,5-dimethylpentadienide followed by deprotonation of the formed pentadienediyl iridium species, found by Bleeke et al.;[16] 2) reactions of $[L_nMCl]$ with lithiated 3-vinyl-1-cyclopropenes, reported by Haley et al.;[17] and 3) reactions of $[MX_2(PPh_3)_3]$ (M = Os, Ru) with $HC{\equiv}CCH(OH)C{\equiv}CH$ by Jia and us,[14c,d] and $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CCH(OH)CH{=}CH_2$ or $HC{\equiv}CC(CH_3)(OH)CH{=}CH_2$ by us.[13b,14a,b,18] The cyclization reaction reported herein starts with a metal hydrido vinylidene complex instead of a simple transition-metal complex, creating a metallabenzene with an alkynyl group bound to the metal center.

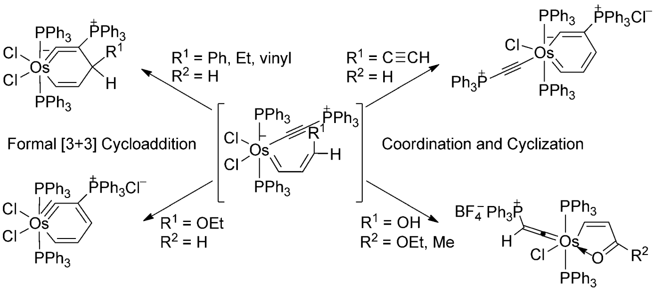
As reported, the osmium hydrido vinylidene **1** could undergo a formal [3+3] cycloaddition with $HC{\equiv}CCH(OH)R$ (R = Ph, Et, and vinyl) and $HC{\equiv}CCH(OEt)_2$ to give isoosmabenzenes and an osmabenzyne.[7] However, neither isoosmabenzene nor osmabenzyne signals were observed by in situ NMR spectroscopy when **1** was treated with the above-mentioned $HC{\equiv}CCOR'$ (R′ = OEt and Me) or $HC{\equiv}CCH(OH)C{\equiv}CH$, suggesting that the former [3+3] cycloaddition may not be involved in these reactions. In order to understand the remarkable scope of the reactions of **1** with alkynes, and with lessons learned in this work, we revisited the process of previous [3+3] cycloaddition[7b] in Scheme 4.



Scheme 4. Proposed mechanism for the formal [3+3] cycloaddition reaction to form isoosmabenzenes and an osmabenzyne.

First, migratory insertion of alkynes gives **G**. Subsequent dehydration provides the osmabutadiene intermediate **H** (similar to **B** in Scheme 2 and **E** in Scheme 3). Then C2 couples with C3 to generate an isoosmabenzene. Note that the first isometallabenzene was formed via an intermediate similar to **H**.[22] For the osmabenzyne, the cyclization reaction occurs by elimination of a molecule of EtOH to give an isoosmabenzene intermediate initially. Then, in the presence of a catalytic amount of acid, the isoosmabenzene intermediate eliminates another molecule of EtOH and eventually converts to the osmabenzyne.

Through analysis of the mechanisms for the reactions of **1** with activated alkynes, it is easy to find that the different R^1 groups on the terminal alkenyl carbon atoms in the intermediates lead to different results. As shown in Scheme 5, when R^1 are non-coordinating or weakly coordinating groups such as Ph, Et, vinyl, and OEt, carbon–carbon coupling and formal [3+3] cycloaddition dominate. By contrast, when R^1 are coordinating groups such as $C{\equiv}CH$ and OH, the coordination of R^1 to the osmium center is favored, leading to corresponding cyclization products.



Scheme 5. Osmabutadiene as the key intermediate to osmacycles.

Conclusions

The reactions of osmium hydrido vinylidene **1** with terminal alkynes show great diversity, although they go through similar osmabutadiene intermediates. When **1** was treated with $HC{\equiv}CCH(OH)R$ (R = Ph, Et, and vinyl) and $HC{\equiv}CCH(OEt)_2$, it underwent a formal [3+3] cycloaddition to generate rare isometallabenzenes and an osmabenzyne. Reaction of **1** with $HC{\equiv}CCOR'$ (R′ = OEt and Me) gave osmafurans **3a** and **3b**. In addition, **1** reacted with $HC{\equiv}CCH(OH)C{\equiv}CH$ to yield osmabenzene **4**.

Some interesting results can be summarized from these reactions: 1) All reactions start with insertion of alkynes into the Os−H bond to form *E*-alkenyl complexes. 2) The acidity of the hydrogen atom on the vinylidene carbon atom C2 plays an important role in the subsequent transformations: dissociated proton either eliminates with a hydroxy group to dehydration or attacks a carbonyl oxygen atom to form enol, resulting in the formation of the key osmabutadiene intermediates. 3) The intermediates make the subsequent cyclization reactions diverse, depending on the coordination ability of substituents on the terminal alkenyl carbon atom.

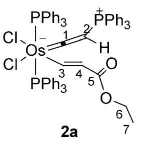
Experimental Section

General Comments

All manipulations were carried out under an inert atmosphere (Ar or N_2) by means of standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane, chloroform, acetonitrile, and 1,2-dichloroethane) under N_2 prior to use. Methanol and acetone were used as received. Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on neutral alumina in air. NMR spectroscopic experiments were carried out on a Bruker 500 MHz spectrometer (^{1}H 500.2 MHz; ^{13}C 125.8 MHz; ^{31}P 202.5 MHz) or a Bruker 300 MHz spectrometer (^{1}H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz). Elemental analyses were performed on a Vario EL III elemental analyzer.

*Compound **2a***

$HC\equiv CCOOCH_2CH_3$ (30 μL, 0.29 mmol) was added to a solution of **1** (205 mg, 0.19 mmol) in CH_2Cl_2 or $CHCl_3$ (10 mL). The reaction mixture was stirred at RT for 30 min to give an orange solution. The solvent was evaporated to dryness under vacuum. The residue was washed with hexane (3×10 mL) and dried under vacuum to give **2a** as an orange solid (202 mg, 90%).

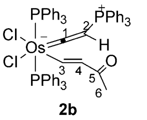


2a

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.8$ (d, $^3J_{HH} = 16.2$ Hz, 1H, H3), 8.0–6.9 (m, 45H, PPh_3), 4.7 (d, $^3J_{HH} = 16.2$ Hz, 1H, H4), 3.7 (q, $^3J_{HH} = 7.2$ Hz, 2H, H6), 1.0 (t, $^3J_{HH} = 7.2$ Hz, 3H, H7), 0.3 ppm (br, 1H, H2); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 0.5$ (s, $CPPh_3$), −7.0 ppm (s, $OsPPh_3$); ^{13}C NMR plus HMQC (75 MHz, $CDCl_3$): $\delta = 267.2$ (t, $^2J_{PC} = 9.8$ Hz, C1), 179.5 (m, C3), 165.5 (s, C5), 135.1–123.3 (m, PPh_3), 121.4 (br, C4), 69.1 (d, $^1J_{PC} = 118.8$ Hz, C2), 58.1 (s, C6), 14.8 ppm (s, C7); elemental analysis calcd (%) for $C_{61}H_{53}O_2P_3Cl_2Os$: C 62.51, H 4.56; found: C 62.80, H 4.71.

*Compound **2b***

$HC\equiv CCOCH_3$ (2 μL, 0.03 mmol) and **1** (15 mg, 0.01 mmol) were mixed in $CDCl_3$ (0.5 mL). An orange solution was obtained after 30 min at RT. The NMR spectra of **2b** were then collected (95% yield as determined by NMR spectroscopy).

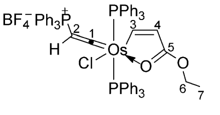


2b

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.9$ (d, $^3J_{HH} = 16.5$ Hz, 1H, H3), 8.0–6.9 (m, 45H, PPh_3), 5.3 (d, $^3J_{HH} = 16.5$ Hz, 1H, H4), 2.4 (s, 3H, H6), 0.4 ppm (br, 1H, H2); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 0.7$ (s, $CPPh_3$), −8.5 ppm (s, $OsPPh_3$).

*Compound **3a***

$NaBF_4$ (36 mg, 0.33 mmol) was added to a solution of **2a** (152 mg, 0.13 mmol) in CH_3CN (10 mL). The reaction mixture was stirred at 70 °C for 30 min to give a yellow solution. After filtration to remove excess $NaBF_4$, the filtrate was evaporated under vacuum. The residue was washed with hexane (3×10 mL) and dried under vacuum to give **3a** as a yellow solid (157 mg, 99%).

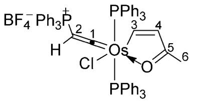


3a

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 10.5$ (br, 1H, H3), 7.8–6.8 (m, 45H, PPh_3), 6.1 (d, $^3J_{HH} = 8.0$ Hz, 1H, H4), 3.4 (q, $^3J_{HH} = 7.0$ Hz, 2H, H6), 2.3 (br, 1H, H2), 0.9 ppm (t, $^3J_{HH} = 7.0$ Hz, 3H, H7); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 3.5$ (d, $^4J_{PP} = 4.1$ Hz, $OsPPh_3$), 0.9 ppm (t, $^4J_{PP} = 4.1$ Hz, $CPPh_3$); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): $\delta = 273.6$ (t, $^2J_{PC} = 11.3$ Hz, C1), 197.2 (t, $^2J_{PC} = 6.5$ Hz, C3), 180.4 (s, C5), 135.0–122.4 (m, PPh_3), 117.2 (s, C4), 78.0 (d, $^1J_{PC} = 113.0$ Hz, C2), 62.6 (s, C6), 13.7 ppm (s, C7); elemental analysis calcd (%) for $C_{61}H_{53}O_2BF_4P_3ClOs$: C 59.88, H 4.37; found: C 59.94, H 4.24.

*Compound **3b***

$HC\equiv CCOCH_3$ (32 μL, 0.40 mmol) was added to a solution of **1** (290 mg, 0.27 mmol) in CH_2Cl_2 or $CHCl_3$ (10 mL). The reaction mixture was stirred at RT for 30 min to give an orange solution. The solvent was removed under vacuum, and the residue was redissolved in CH_3CN (10 mL). $NaBF_4$ (74 mg, 0.67 mmol) was added to this solution, and the reaction mixture was stirred at 70 °C for 1.5 h to give a yellow solution. After filtration to remove excess $NaBF_4$, the filtrate was evaporated under vacuum. The residue was washed with hexane (3×10 mL) then dried under vacuum to give **3b** as a yellow solid (267 mg, 83%).

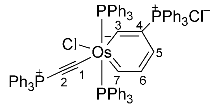


3b

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 11.8$ (br, 1H, H3), 8.0–6.8 (m, 45H, PPh_3), 6.6 (d, $^3J_{HH} = 7.5$ Hz, 1H, H4), 2.7 (br, 1H, H2), 1.2 ppm (s, 3H, H6); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 7.6$ (d, $^4J_{PP} = 4.1$ Hz, $OsPPh_3$), 0.8 ppm (t, $^4J_{PP} = 4.1$ Hz, $CPPh_3$); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): $\delta = 275.6$ (t, $^2J_{PC} = 11.3$ Hz, C1), 214.6 (br, C3), 206.2 (s, C5), 135.0–122.5 (m, PPh_3 and C4), 78.3 (d, $^1J_{PC} = 112.0$ Hz, C2), 23.5 ppm (s, C6); elemental analysis calcd (%) for $C_{60}H_{51}OBF_4P_3ClOs$: C 60.38, H 4.31; found: C 60.03, H 4.62.

*Compound **4***

$HC\equiv CCH(OH)C\equiv CH$ (31 mg, 0.39 mmol) was added to a solution of **1** (415 mg, 0.39 mmol) in $CHCl_3$ (20 mL). The reaction mixture was stirred at RT for 1 h to give a brown solution, which was then concentrated to ca. 2 mL under vacuum and purified by column chromatography on neutral alumina (acetone/methanol 15:1) to give **4** as a green solid (97 mg, 18%).

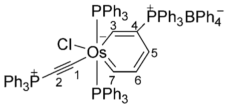


4

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 17.7$ (d, $^3J_{HH} = 8.5$ Hz, 1H, H7), 14.7 (d, $^3J_{PH} = 30.0$ Hz, 1H, H3), 8.0–6.9 (m, 61H, PPh_3 and H5), 6.8 ppm (t, $^3J_{HH} = 8.5$ Hz, 1H, H6); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 16.3$ (br, $OsCHC(PPh_3)$), −5.6 (br, $OsPPh_3$), −15.7 ppm (t, $^4J_{PP} = 4.1$ Hz, $OsCC(PPh_3)$); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): $\delta = 262.0$ (m, C7), 243.7 (m, C3), 188.7 (m, C1), 132.1 (d, $^3J_{PC} = 8.8$ Hz, C6), 140.1–120.8 (m, PPh_3 and C5), 107.5 (d, $^1J_{PC} = 70.4$ Hz, C4), 94.2 ppm (d, $^1J_{PC} = 191.2$ Hz, C2); elemental analysis calcd (%) for $C_{79}H_{64}P_4Cl_2Os$: C 73.54, H 5.03; found: C 73.37, H 5.35.

*Compound **4′***

$NaBPh_4$ (32 mg, 0.09 mmol) was added to the solution of **4** (120 mg, 0.09 mmol) in $CHCl_3/CH_3OH$ (2 mL, 1:1 v/v). Upon stirring for 5 min at RT, a green precipitate appeared, which was filtered, washed with MeOH (2×2 mL) and Et_2O (2×10 mL), and then dried under vacuum, giving **4′** as a green solid (134 mg, 93%).



4′

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 17.7$ (d, $^3J_{HH} = 8.0$ Hz, 1H, H7), 14.6 (d, $^3J_{PH} = 29.5$ Hz, 1H, H3), 7.7–6.9 (m, 61H, PPh_3 and H5), 6.8 ppm (br, 1H, H6); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 16.3$ (br, $OsCHC(PPh_3)$), −5.5 (br, $OsPPh_3$), −15.8 ppm (br, $^4J_{PP} = 4.1$ Hz, $OsCC(PPh_3)$); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): $\delta = 262.0$ (m, C7), 243.9 (m, C3), 188.5 (m, C1), 164.3 (m, BPh), 132.1 (d, $^3J_{PC} = 10.1$ Hz, C6), 140.2–120.7 (m, PPh_3 and C5), 107.4 (d, $^1J_{PC} = 69.9$ Hz, C4), 94.2 ppm (d, $^1J_{PC} = 191.8$ Hz, C2); elemental analysis calcd (%) for $C_{103}H_{84}BP_4ClOs$: C 67.85, H 4.61; found: C 67.86, H 4.85.

X-ray Crystallography

Data collection was performed on an Oxford Gemini-S Ultra charge coupled device (CCD) diffractometer at 173(2) K, with monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan absorption corrections (SADABS) were applied. Structures were solved by direct methods or the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full-matrix least-squares on F^2 with the SHELXTL program package. Non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions using the riding model. Crystals suitable for X-ray diffraction were grown from a solution in $ClCH_2CH_2Cl$ layered with hexane for **4′** and a solution in CH_2Cl_2 layered with hexane for **2a** or **3a**. Two $ClCH_2CH_2Cl$ solvent molecules in **4′** were refined with fixed C−Cl distances and Cl−C−C angles. Further details on crystal data, data collection, and refinements are summarized in Table 1.

Table 1. Crystal data and structure refinement for **2a**, **3a**, and **4′**.

	2a·$2CH_2Cl_2$	**3a**·$1.5CH_2Cl_2$	**4′**·$3C_2H_4Cl_2$
Formula	$C_{63}H_{57}Cl_6O_2P_3Os$	$C_{62.50}H_{56}BCl_4F_4O_2P_3Os$	$C_{109}H_{96}BCl_7P_4Os$
Mr	1341.90	1350.79	1978.90
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	21.6281(5)	11.9853(3)	13.0305(4)
b [Å]	14.2262(3)	12.7370(3)	43.8817(16)
c [Å]	18.8680(4)	21.9635(5)	17.3831(7)
α [°]	90	95.077(2)	90
β [°]	93.672(2)	96.011(2)	98.424(3)
γ [°]	90	113.566(2)	90
V [Å^3]	5793.5(2)	3024.93(12)	9832.4(6)
Z	4	2	4
ρ_{calcd} [gcm^{-3}]	1.538	1.483	1.337
μ [mm^{-1}]	2.605	2.418	1.599
F (000)	2696	1354	4040
Crystal size [mm^3]	0.35 × 0.30 × 0.25	0.60 × 0.42 × 0.35	0.40 × 0.20 × 0.12
θ range [°]	2.78 to 25.00	3.04 to 25.00	2.75 to 25.00
Reflns collected	27661	23777	49784
Independent reflns	10175	10624	17298
Observed reflns [$I \geq 2\sigma(I)$]	8085	9457	8228
Data/restrains/params	10175/0/676	10624/12/712	17298/250/1135
GOF on F^2	1.006	1.003	0.840
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0223/0.0346	0.0325/0.0997	0.0578/0.0865
R_1/wR_2 (all data)	0.0328/0.0355	0.0377/0.1013	0.1378/0.0958
Largest peak/hole [e Å^{-3}]	0.540/−0.477	2.100/−1.116	1.546/−1.195

CCDC 901359 (**2a**), CCDC 901360 (**3a**), and CCDC 901361 (**4′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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