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Synthesis of Five-Membered Osmacycles with Osmium−Vinyl Bonds from Hydrido Alkenylcarbyne Complexes

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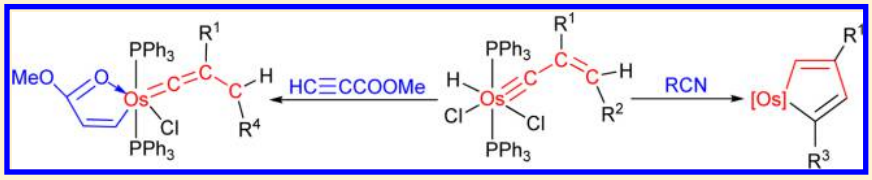
Supporting Information



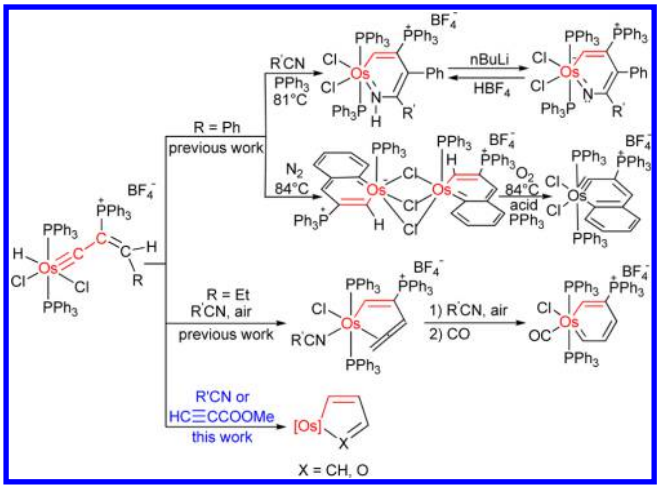
ABSTRACT: Treatment of the osmium hydrido butenylcarbyne complex $[OsH\{\equiv CC(PPh_3)=CH(Et)\}(PPh_3)_2Cl_2]BF_4$ (**1**) with excess 2-chloro-4-cyanopyridine in the presence of H_2O_2 generates the fused osmacyclopentadiene **2**. A detailed mechanism of the conversion has been investigated with the aid of in situ NMR experiments and the isolation of intermediates **3** and **4**. In contrast, reaction of **1** with the propiolic acid ester HC≡CCOOMe produces the osmafuran **5**. Analogous reactions of the osmium hydrido phenylethenylcarbyne complex $[OsH\{\equiv CC(PPh_3)=CH(Ph)\}(PPh_3)_2Cl_2]BF_4$ (**6**) with nitriles/CO or HC≡CCOOMe were also studied, which result in the formation of five-membered osmacycles $[Os\{CHC(PPh_3)CH(Ph)(OH)\}(CH_3CN)(PPh_3)_2CO](BF_4)_2$ (**7**) and $[Os\{CHC(PPh_3)CH(Ph)(OH)\}(PhCN)(PPh_3)_2CO](BF_4)_2$ (**8**). In the presence of NEt_3, **6** can convert to the osmium hydrido phenylethenylcarbyne complex $OsH\{\equiv CC=CH(Ph)\}(PPh_3)_2Cl_2$ (**9**) in wet acetonitrile, presumably involving P−C bond cleavage. Similarly, **9** can react with HC≡CCOOMe with the aid of HBF_4 to give osmafuran **10**.

INTRODUCTION

Carbyne (or alkylidyne) complexes with formal metal−carbon triple bonds have attracted considerable attention, resulting in a focus of fundamental research on structure, bonding, and reactivity.[1] For example, osmium hydride alkenylcarbyne complexes have been demonstrated to be versatile intermediates in various organometallic syntheses.[2] In the literature,[2a,e,g,3] osmium hydride alkenylcarbyne complexes can be transformed into alkenylcarbene species by means of a 1,2-hydrogen shift from the osmium to the carbyne carbon atom.

In the search of new substrates for the preparation of metallacycles, especially those with metal−vinyl bonds, we have explored the reactions of osmium hydride alkenylcarbyne complexes.[2a,e] As shown in Scheme 1, we found that the hydrido phenylethenylcarbyne complex $[OsH\{\equiv CC(PPh_3)=CH(Ph)\}(PPh_3)_2Cl_2]BF_4$ could react with nitriles to form osmapyridines through a formal [4 + 2] cycloaddition[2e,3a] and could undergo intramolecular C−H activation of the phenyl ring to form the osmanaphthalene and osmanaphthalyne.[3b] Recently, we demonstrated that the synthesis of η^2-allene-coordinated complexes and osmabenzenes can be achieved from the hydrido butenylcarbyne complex $[OsH\{\equiv CC(PPh_3)=CH(Et)\}(PPh_3)_2Cl_2]BF_4$ via triple hydrogen eliminations in the presence of nitriles in air (Scheme 1).[2a] With the aid of DFT calculations and further experimental proof, we thought that the lability of the nitrile ligand was crucial for the conversion of the osmium hydrido butenylcarbyne complex into metallabenzene. These observations prompted us to construct other osmacycles containing osmium−vinyl fragments by the reactions of osmium hydrido alkenylcarbyne complexes with unsaturated substrates. In this paper, we report the reactions of osmium hydrido alkenylcarbyne complexes with nitriles or alkynes, which afford the formation of a series of five-membered rings with osmium−vinyl bonds.

Scheme 1. Previous Work and Initial Attempt



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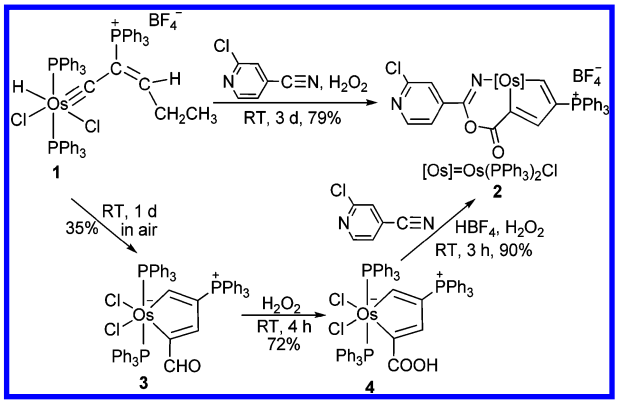
RESULTS AND DISCUSSION

Reaction of the Osmium Hydrido Butenylcarbyne Complex $[OsH\{\equiv CC(PPh_3)=CH(Et)\}(PPh_3)_2Cl_2]BF_4$ with 2-Chloro-4-cyanopyridine. As shown in Scheme 2, treatment of the osmium hydrido butenylcarbyne complex **1** with 2-chloro-4-cyanopyridine in the presence of the oxidant H_2O_2 led to the formation of **2**, which can be isolated as a yellow solid in 79% yield. The complex **2** has been characterized by multinuclear NMR spectroscopy and elemental analysis.

Scheme 2. Synthesis of Complex 2



The structure of **2** has been verified by X-ray diffraction. Selected bond lengths and angles are given in Table 1. As shown in Figure 1, the fused metallacyclopentadiene ring of **2** is almost planar. The mean deviation from the least-squares plane is only 0.0232 Å. The bond lengths of Os1−C1 (2.072(7) Å) and Os1−C4 (2.133(7) Å) are comparable with the Os−C bond lengths in our previous reported osmapentalenes (1.926−2.139 Å)[4] and osmacyclopentadiene (Os−C1 (1.977(2) Å), Os−C4 (2.082(2) Å)).[5] The C−C bond distances (1.327(10)−1.462(11) Å) of the five-membered ring are typical for carbon−carbon double- or single-bond lengths. The Os1−N1 bond length (1.883(6) Å) is within the range of reported values of Os−N single bonds (1.635−2.543 Å).[6] The C5−O1 (1.198(10) Å) and C5−O2 bond lengths (1.377(11) Å) are between the typical carbon−oxygen double- or single-bond distances. In agreement with the solid-state structure, the ^{1}H NMR spectrum displays the signals of osmabicycle at δ 11.6 (OsC*H*) and 8.4 (γ-*H*) ppm. The ^{31}P NMR spectrum shows signals at δ −5.4 (s, Os*P*Ph$_3$) and 11.6 (s, C*P*Ph$_3$) ppm, respectively. In the ^{13}C NMR spectrum, the signals of C1, C2, C3, C4, C5, and C6 appear at δ 218.4, 119.1, 151.6, 151.5, 158.5, and 160.6 ppm, respectively.

Table 1. Selected Bond Lengths and Angles for 2−4

	2	3	4
	Bond Lengths (Å)		
Os1−C1	2.072(7)	2.039(7)	2.024(10)
Os1−C4	2.133(7)	2.074(7)	2.177(9)
Os1−N1	1.883(6)		
C1−C2	1.327(10)	1.348(10)	1.363(13)
C2−C3	1.461(10)	1.444(9)	1.442(14)
C3−C4	1.388(11)	1.373(10)	1.355(14)
C4−C5	1.462(11)	1.449(11)	1.427(14)
C5−O1	1.198(10)	1.206(11)	1.219(12)
C5−O2	1.377(11)		1.336(12)
C6−O2	1.377(10)		
C6−N1	1.250(9)		
	Bond Angles (deg)		
Os1−C1−C2	121.5(6)	118.7(5)	118.0(8)
C1−Os1−C4	74.5(3)	76.6(3)	77.4(4)
C1−C2−C3	113.6(7)	114.2(6)	115.5(9)
C2−C3−C4	113.5(7)	113.6(7)	116.3(9)
Os1−C4−C3	116.8(5)	116.8(5)	112.7(7)
Os1−C4−C5	129.5(6)		
C4−C5−O2	120.7(7),		
C5−O2−C6	122.3(6)		
O2−C6−N1	122.6(7)		
Os1−N1−C6	145.6(6)		

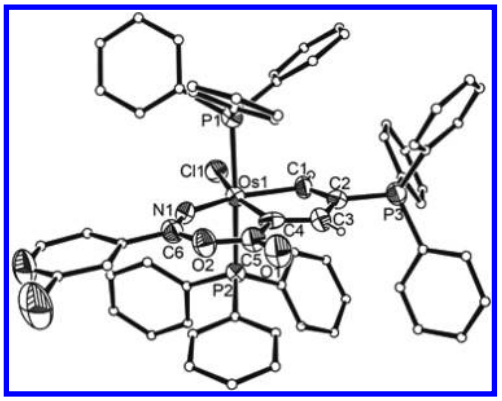


Figure 1. X-ray molecular structure for the cation of complex **2** drawn with 50% probability ellipsoids. The counteranion and some of the hydrogen atoms are omitted for clarity.

In order to understand the mechanistic aspects for the formation of complex **2**, we undertook the stepwise pathway to trap the key intermediates of the reaction. As shown in Scheme 2, when a solution of osmium hydrido butenylcarbyne complex **1** was stirred in air at room temperature for 1 day, **1** was completely consumed to afford paramagnetic complex **3**, which could be further oxidated by H_2O_2 to generate paramagnetic complex **4**. The structures of the two complexes **3** and **4** have been confirmed by X-ray diffraction. Selected bond lengths and angles are given in Table 1.

As shown in Figures 2 and 3, the osmacyclopentadiene rings of the two complexes are almost the same. The only difference

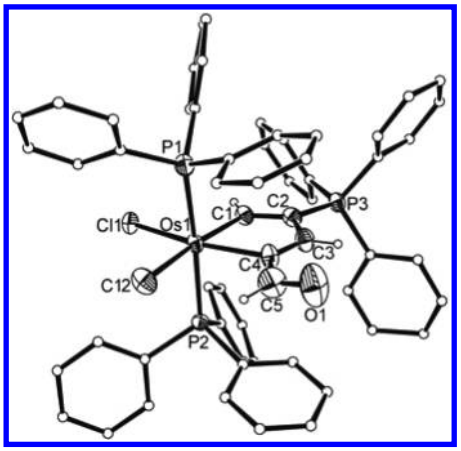


Figure 2. X-ray molecular structure of complex **3** drawn with 50% probability ellipsoids. The hydrogen atoms in PPh$_3$ groups are omitted for clarity.

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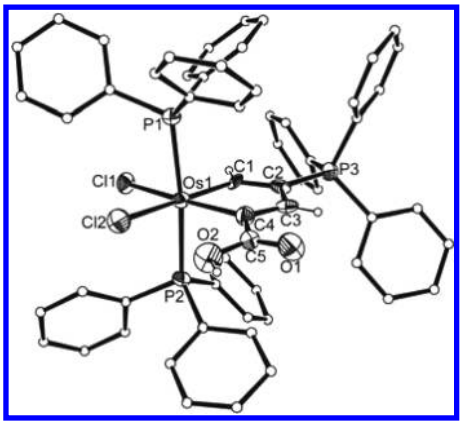
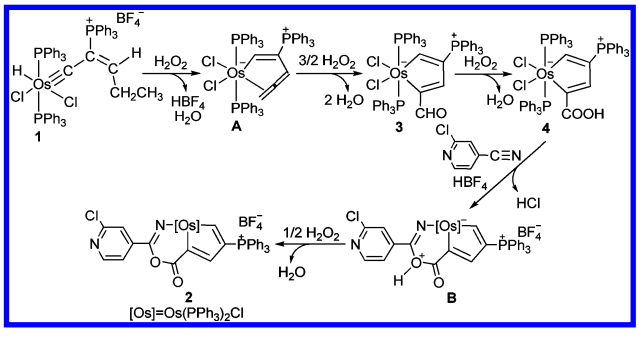


Figure 3. X-ray molecular structure of complex **4** drawn with 50% probability ellipsoids. The hydrogen atoms in PPh_3 groups are omitted for clarity.

is the exocyclic carbonyl group. Both of the five-membered rings of **3** and **4** are nearly coplanar, as reflected by the mean deviation from the least-squares plane through Os1 and C1−C4 (0.0010 Å for **3** and 0.0050 Å for **4**). The C1−C4 bond distances in complex **3** (1.348(10)−1.444(9) Å) and in complex **4** (1.355(14)−1.442(14) Å) are between the typical carbon−carbon single-bond and double-bond lengths, indicating a certain degree of delocalization within the metallacycle. The exocyclic aldehyde group of complex **3** is clearly evidenced by the C4−C5 (1.449(11) Å) and C5−O1 bond lengths (1.206(11) Å). In addition, the C4−C5 (1.427(14) Å), C5−O1 (1.219(12) Å), and C5−O2 bond lengths (1.336(12) Å) of complex **4** indicate its exocyclic carboxyl group. Experimentally, complex **4** can be converted to the final fused osmacyclopentadiene product **2** by stirring a DCM (dichloromethane) solution of **4** and excess 2-chloro-4-cyanopyridine at room temperature for about 3 h in the presence of HBF_4 and H_2O_2 additives. The experimental observations strongly suggest that complexes **3** and **4** can be regarded as intermediates for the reaction.

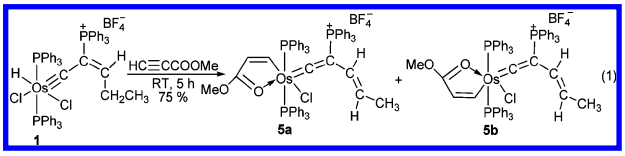
On the basis of the characterized structures of the isolated intermediates, we propose a reaction mechanism for the formation of complex **2**. As shown in Scheme 3, in the presence

Scheme 3. Proposed Mechanism for the Formation of Complex 2



of H_2O_2, the osmium hydrido butenylcarbyne complex **1** can convert to the η^2-allene-coordinated osmium complex **A**, which has been demonstrated in our previous report.[7] Subsequent oxidation of the terminal carbon in the allene fragment results in the formation of **3**. **3** could be further oxidized by H_2O_2 to generate **4**, which may undergo nucleophilic addition with the nitrile to produce intermediate **B**. The deprotonation of **B** in the presence of H_2O_2 would give the final product **2**.

Reaction of Osmium Hydrido Butenylcarbyne Complex $[OsH\{\equiv CC(PPh_3)=CH(Ph)\}(PPh_3)_2Cl_2]BF_4$ with HC≡CCOOMe. Inspired by the above observations, we next studied the reactions of **1** with propiolic acid ester with the hope of obtain the corresponding fused osmapentadienes. The reaction of osmium hydrido butenylcarbyne complex **1** with HC≡CCOOMe in the presence of H_2O_2 resulted in a mixture of species in low yields. When the reaction was performed without H_2O_2, two inseparable isomers (**5a**,**b**; eq 1) were produced in a molar ratio of 1:1, as suggested by the ^1H NMR spectrum.



Formation of the two isomers from the reaction is not surprising, due to the presence of a methoxyl group in the five-membered osmacycle (eq 1). Supporting evidence for the existence of the two isomers is that the ^1H NMR spectrum (in CD_2Cl_2) shows two sets of characteristic signals of OCH_3 (2.9 and 3.0 ppm), CH(COOMe) (5.9 and 6.3 ppm), $CHC(PPh_3)$ (5.1 and 6.2 ppm), and $OsCH$ (9.6 and 10.8 ppm). The ^{31}P NMR spectrum (in CD_2Cl_2) shows two $OsPPh_3$ signals at 0.6 and 0.8 ppm and two $CPPh_3$ signals at 5.1 and 2.5 ppm.

The molecular structure of one of the isomers has been confirmed by X-ray diffraction. Crystals of **5a** suitable for X-ray diffraction were grown from a dichloroethane (DCE) solution of the **5a**,**b** mixture layered with hexane. The X-ray structure shows that the five-membered rings of **5a** are almost coplanar (Figure 4). The mean deviation from the least-squares plane through Os1/C6/C7/C8/O1 is only 0.0022 Å, and the sum of angles in the five-membered ring is 540.1°, which is very close to the ideal value of 540°. The Os1−C1 (1.791(6) Å) and C1−

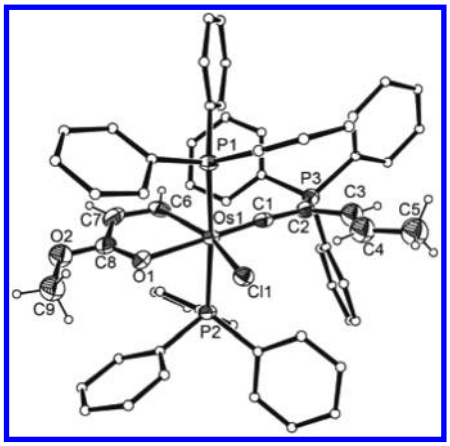


Figure 4. X-ray molecular structure for the cation of complex **5a** drawn with 50% probability ellipsoids. The counteranion and hydrogen atoms in PPh_3 groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 1.791(6), C1−C2 = 1.361(8), C2−C3 = 1.485(9), C3−C4 = 1.281(11), C4−C5 = 1.515(11), Os1−C6 = 2.058(6), C6−C7 = 1.351(9), C7−C8 = 1.441(10), C8−O1 = 1.258(8), Os1−O1 = 2.213(4); Os1−C1−C2 = 172.6(5), C1−C2−C3 = 123.4(6), C2−C3−C4 = 129.7(7), C6−Os1−O1 = 75.6(2), Os1−C6−C7 = 117.8(5), C6−C7−C8 = 114.1(6), C7−C8−O1 = 119.7(6), Os1−O1−C8 = 112.9(4).

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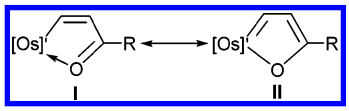
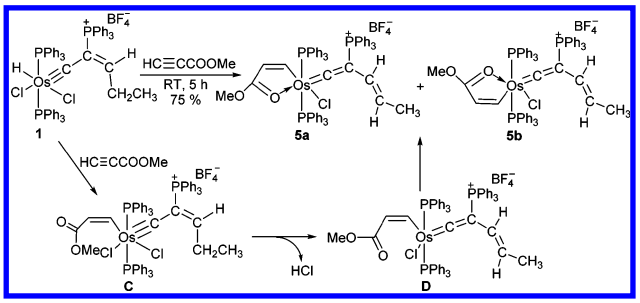
C2 bond lengths (1.361(8) Å) compare well with those found in our previously reported metallacycles containing osmium−vinylidene fragments.[8] The Os1−C6 bond length (2.058(6) Å) is in the range of osmium−carbon single and double bonds. Although there is a considerable bond distance alternation, the C6−C7 (1.351(9) Å), C7−C8 (1.441(10) Å), C8−O1 (1.258(8) Å), and Os1−O1 bond lengths (2.213(4) Å) are comparable to those of previously reported osmafurans.[8,9] The structural parameters indicate that the metallacycles of **5a** could be represented by the two resonance structures **I** and **II**, with **I** being more important.



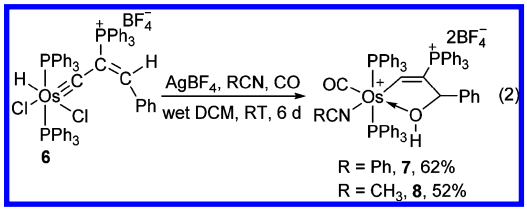
Similar to our previous reported mechanism for the formation of osmafurans from osmium hydrido vinylidene,[8] the formation of the osmafuran **5a,b** may also involve the insertion of alkynes into the Os−H bond and an elimination process. As shown in Scheme 4, the insertion of terminal alkyne

Scheme 4. Proposed Mechanism for the Formation of Osmafuran 5



into the Os−H bond of **1** could generate the intermediate **C**. Subsequent deprotonation might lead to the formation of the alkenyl vinylidene complex **D**. Finally, coordination of the oxygen atom of carbonyl in **D** to the osmium center could result in the final product **5a,b**.

Reaction of the Osmium Hydrido Phenylethenylcarbyne Complex [OsH{≡CC(PPh$_3$)=CH(Ph)}(PPh$_3$)$_2$Cl$_2$]BF$_4$ with Nitriles in the Presence of CO. As shown in Scheme 1, the hydrido phenylethenylcarbyne complex [OsH{≡CC(PPh$_3$)=CH(Ph)}(PPh$_3$)$_2$Cl$_2$]BF$_4$ (**6**) could react with nitriles to produce osmapyridines.[2e,3a] To further study the influence of the coligands on the reactions, the reactions of **6** with nitriles were investigated in the presence of CO at room temperature. Although **6** was unreactive to benzonitrile or acetonitrile under carbon monoxide atmosphere at room temperature, the addition of AgBF$_4$ led to the isolation of **7** or **8** (eq 2).



The molecular structure of **7** has been confirmed unambiguously by X-ray diffraction (Figure 5). As shown in Table 2, the Os1−C1 distance (2.045(7) Å) agrees well with

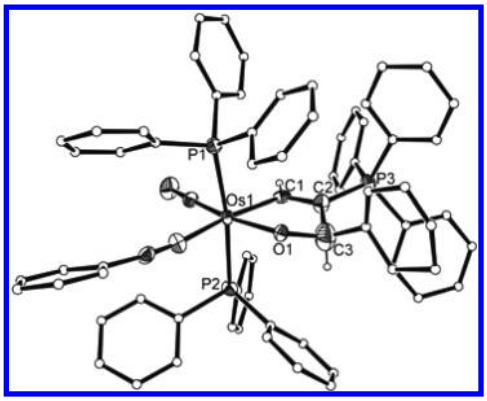


Figure 5. X-ray molecular structure for the cation of complex **7** drawn with 50% probability ellipsoids. The counteranion and hydrogen atoms in PPh$_3$ groups are omitted for clarity.

Table 2. Selected Bond Lengths and Angles for 7 and 8

	7	8
	Bond Lengths (Å)	
Os1−C1	2.045(7)	2.046(10)
C1−C2	1.335(11)	1.351(15)
C2−C3	1.563(13)	1.557(15)
C3−O1	1.458(11)	1.434(12)
Os1−O1	2.165(5)	2.135(7)
	Bond Angles (deg)	
Os1−C1−C2	119.9(5)	118.2(7)
C1−Os1−O1	75.2(2)	75.5(4)
C1−C2−C3	117.2(7)	120.0(9)
C2−C3−O1	102.2(7)	101.8(8)
Os1−O1−C3	117.0(5)	121.6(6)

those found in other osmium vinyl complexes.[6] The C1−C2 (1.335(11) Å) and C3−O1 bond lengths (1.458(11) Å) are in the range of C−C double bonds and C−O single bonds, respectively. The Os1−O1 distance (2.165(5) Å) is comparable to those previously reported for osmacycles containing a coordinated hydroxyl group.[2e,9a] Consistent with its solid-state structure, the ^{1}H NMR spectrum shows the signal of OsC*H* at δ 10.9 ppm and the signal of O*H* at δ 1.8 ppm. The ^{31}P NMR spectrum shows three signals at δ 12.9 (br, C*P*Ph$_3$), 11.2 (br, Os*P*Ph$_3$), and 10.8 ppm (br, Os*P*Ph$_3$). In the ^{13}C NMR spectrum, the signals of OsCH, C*P*Ph$_3$, and *C*HPh can be assigned at δ 187.3, 112.6, and 86.9 ppm, respectively.

The attempt to obtain a full NMR spectroscopic characterization of complex **8** failed due to its poor solubility in ordinary organic solvents. Fortunately, we obtained single crystals of **8** adequate for X-ray diffraction analysis (Figure 6). As shown in Table 2, the X-ray diffraction study reveals that **8** is structurally similar to complex **7**.

Scheme 5 shows a plausible mechanism for the formation of the five-membered osmacycles **7** and **8**. With the aid of AgBF$_4$, ligand substitution of **6** could generate the intermediate **E**. Then, a 1,2-hydrogen shift from the metal center to the carbyne carbon atom of **E** followed by the coordination of the nitrile ligand results in the formation of the alkenylcarbene intermediate **F**. The influence of the coligands on the process of the 1,2-hydrogen migration has been comprehensively studied by Esteruelas et al.[2g,10] The nucleophilic attack of water (coming probably from the solvent) on the terminal double bond of **F** would lead to the osmium vinyl intermediate **G**. Elimination of a proton together with the coordination of

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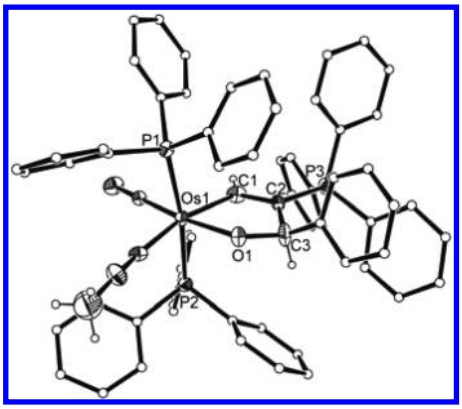
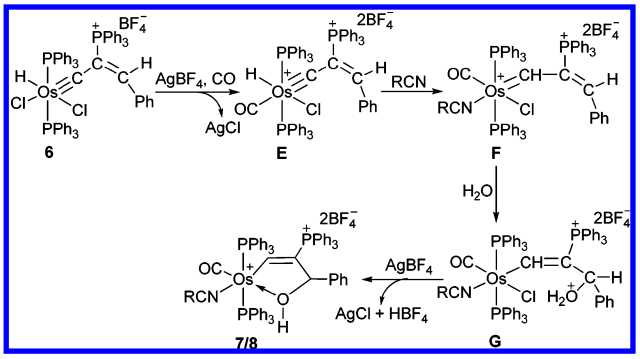


Figure 6. X-ray molecular structure for the cation of complex **8** drawn with 50% probability ellipsoids. The counteranion and hydrogen atoms in PPh_3 groups are omitted for clarity.

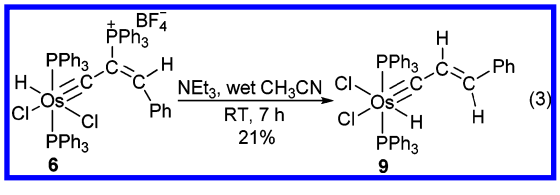
Scheme 5. Proposed Mechanism for the Conversion of 6 to 7 and 8



the hydroxyl in the presence of $AgBF_4$ could yield the final five-membered osmacycles **7** and **8**.

Reactions of **6** with propiolic acid ester were also tested under different reaction conditions. As indicated by in situ NMR, **6** was unreactive to the propiolic acid ester at room temperature. Also, the addition of $AgBF_4$ only led to the decomposition of **6**, giving unidentified species at room temperature.

Synthesis and Reactions of the Osmium Alkenylcarbyne Complex OsH{≡CC═CH(Ph)}$(PPh_3)_2Cl_2$. During our effort to study the reactivity of the hydrido phenylethenylcarbyne complex **6**, we found it was not stable in the solution with alkali. As shown in eq 3, another osmium alkenylcarbyne complex, **9**, could be isolated as a red solid in 21% yield from the reaction of **6** and excess NEt_3 in aqueous acetonitrile.



Complex **9** has been characterized by elemental analysis and , multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction analysis. The crystallographic details are given in Table S1 (Supporting Information). The molecular structure of **9** is shown in Figure 7, which reveals that it is a new osmium hydrido phenylethenylcarbyne complex without a phosphonium substituent. The Os1−C1 bond length of 1.612(8) Å is

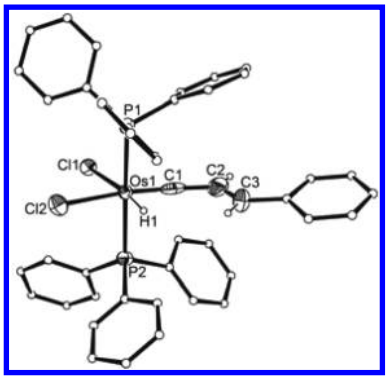
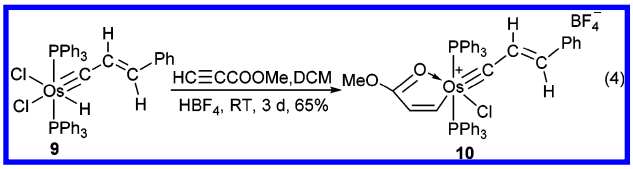


Figure 7. X-ray molecular structure for the cation of complex **9** drawn with 50% probability ellipsoids. The hydrogen atoms in PPh_3 groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 1.612(8), C1−C2 = 1.494(9), C2−C3 = 1.329(7); Os1−C1−C2 = 169.9(5), C1−C2−C3 = 120.5(7).

shorter than those reported for Os−C triple bonds.[6] The Os1−C1−C2 bond angle (169.9(5)°) obviously deviated from 180°, which is comparable to those reported for hydrido phenylethenylcarbyne complexes, such as $[OsHCl_2(≡CC(PPh_3)═CH(Ph))(PPh_3)_2]BF_4$ (172.8(7)°)[2e] and $[OsH(\kappa^2\text{-}O_2CCH_3)(≡CCH═CPh_2)(P^iPr_3)_2]BF_4$ (171.2(3)°).[10b] In agreement with the structure, the ^{31}P NMR spectrum displays only one signal at δ 5.7 (s, OsPPh_3). The ^1H NMR spectrum of **9** shows the characteristic OsH signal at −6.4 ppm (t, $^2J(PH)$ = 19.4 Hz) and alkenyl signals at δ 6.2 (β-H) and 4.2 (γ-H) ppm.

Similarly, we also studied the reactions of **9** with nitriles and propiolic acid ester. However, the reaction of complex **9** with nitriles in the presence of $AgBF_4$ at room temperature only resulted in the ligand substitution products in low yields, as suggested by the in situ NMR experiment. When complex **9** was treated with HC≡CCOOMe in DCM in the presence of HBF_4, complex **10** was isolated in 65% yield (eq 4), which has



been characterized by elemental analysis and multinuclear NMR spectroscopy. Although the solubility of **10** in ordinary organic solvents is too poor to obtain the full NMR spectroscopic characterization, the structure of **10** could be confirmed by single-crystal X-ray diffraction analysis. As shown in Figure 8, the complex has a five-membered aromatic osmafuran structure with an alkenylcarbyne fragment. The bond distances of the osmafuran ring in **10** are similar to those of **5a**, which also indicate that the resonance structure **I** contributes more to the overall structure of **10**.

■ CONCLUSIONS

The synthesis of five-membered osmacycles with osmium−vinyl bonds was achieved by the reactions of hydrido alkenylcarbyne complexes with nitriles or propiolic acid ester. For nitriles, the evolution of hydrido alkenylcarbyne to alkenylcarbene derivatives through a 1,2-hydrogen shift is crucial for the formation of the final five-membered osmacycles. For the propiolic acid ester, the insertions of a terminal triple

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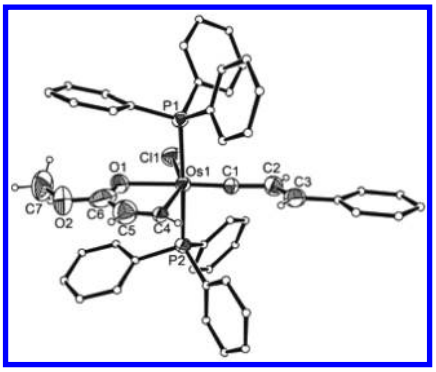


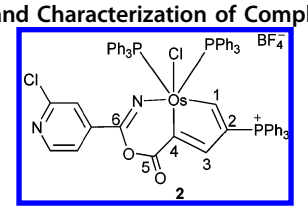
Figure 8. X-ray molecular structure for the cation of complex **10** drawn with 50% probability ellipsoids. The hydrogen atoms in PPh_3 groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 1.697(8), C1−C2 = 1.474(14), C2−C3 = 1.322(14), Os1−C4 = 2.220(8), C4−C5 = 1.238(16), C5−C6 = 1.450(19), C6−O1 = 1.256(15), Os1−O1 = 2.212(6); Os1−C1−C2 = 175.3(7), C1−C2−C3 = 119.6(8), C4−Os1−O1 = 75.7(3), Os1−C4−C5 = 111.0(9), C4−C5−C6 = 121.7(13), C5−C6−O1 = 119.3(13), Os1−O1−C6 = 112.0(8).

bond into Os−H bonds of the hydrido alkenylcarbynes are favored.

EXPERIMENTAL SECTION

General Comments. All manipulations were carried out under an inert atmosphere (Ar or N_2) unless otherwise stated. Solvents were distilled from sodium/benzophenone (tetrahydrofuran, hexane, and diethyl ether) or calcium hydride (DCM) under N_2 prior to use. Methanol and water were used as received. Other reagents were used as received from commercial sources without further purification. The starting materials $[OsH\{\equiv CC(PPh_3)=CH(Ph)\}(PPh_3)_2Cl_2]BF_4$ and $[OsH\{\equiv CC(PPh_3)=CH(Et)\}(PPh_3)_2Cl_2]BF_4$ were synthesized according to literature procedures reported by our group in 2009[2e] and 2013.[2a] NMR spectroscopic experiments were carried out on a Bruker 500 MHz spectrometer (^1H, 500.2 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz) and a Bruker 400 MHz spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses were performed on a Vario EL III elemental analyzer.

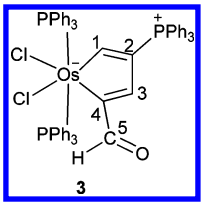
Preparation and Characterization of Complex 2.



Method A. H_2O_2 (15% in H_2O, 67.0 μL, 0.310 mmol) was added to a mixture of **1** (200 mg, 0.166 mmol) and 2-chloro-4-cyanopyridine (46.0 mg, 0.332 mmol) in DCM (10 mL), and then the mixture was stirred at room temperature for 3 days in air to give a brown solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 175 mg, 79%.

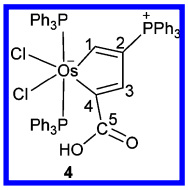
Method B. H_2O_2 (15% in H_2O, 70.0 μL, 0.323 mmol) was added to a mixture of **4** (195 mg, 0.171 mmol) and 2-chloro-4-cyanopyridine (47.9 mg, 0.346 mmol) in DCM (10 mL), and then the mixture was stirred at room temperature for 3 h in air to give a brown solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 205 mg, 90%. ^1H NMR (500.2 MHz, CD_2Cl_2): δ 11.6 (d, $^3J_{PH}$ = 15.1 Hz, 1H, C^1H), 8.4 (s, 1H, C^3H), 7.8−6.7 ppm (m, 48H, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 11.6 (s, CPPh_3), −5.4 ppm (s, OsPPh_3). ^{13}C NMR (125.8 MHz, CD_2Cl_2, plus $^1H-^{13}C$ HSQC): δ 218.4 (s, C^1), 160.6 (s, C^6), 158.5 (s, C^5), 151.6 (d, $^2J_{PC}$ = 20.1 Hz, C^3), 119.1 (d, $^1J_{PC}$ = 83.3 Hz, C^2), 151.5 (s, C^4), 150.1−117.1 ppm (m, other aromatic carbon atoms). Anal. Calcd for $C_{65}H_{50}O_2Cl_2BF_4P_3N_2Os$: C, 58.61; H, 3.78; N, 2.10. Found: C, 58.50; H, 3.96; N, 2.19.

Preparation and Characterization of Complex 3.



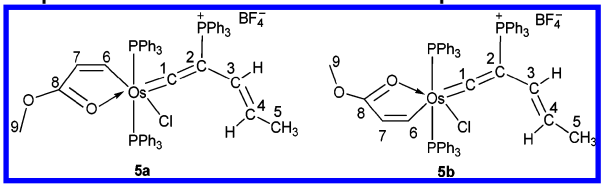
A solution of hydrido alkenylcarbyne complex **1** (421 mg, 0.350 mmol) in methanol was stirred in air at room temperature for 1 day to give a brown solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced paramagnetic complex **3** as a reddish brown solid, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 138 mg, 35%. Anal. Calcd for $C_{59}H_{48}OCl_2P_3Os$: C, 62.87; H, 4.29. Found: C, 62.44; H, 4.43.

Preparation and Characterization of Complex 4.



H_2O_2 (15% in H_2O, 50.0 μL, 0.231 mmol) was added to a solution of complex **3** (192 mg, 0.170 mmol) in DCM (10 mL), and then the mixture was stirred at room temperature for 4 h to give a brown solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced paramagnetic complex **4** as a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 140 mg, 72%. Anal. Calcd for $C_{59}H_{48}O_2Cl_2P_3Os$: C, 61.99; H, 4.23. Found: C, 62.10; H, 4.48.

Preparation and Characterization of Complex 5.



HC≡CCOOMe (74.0 μL, 0.827 mmol) was added to a suspension of complex **1** (500 mg, 0.416 mmol) in DCM (10 mL). The reaction mixture was stirred at room temperature for 5 h to give a yellow-green solution. The volume of the solution was reduced to approximately 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a yellow-green precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 390 mg, 75%. ^1H NMR (500.2 MHz, CD_2Cl_2): **5a** or **5b**, δ 9.6 (dd, $^3J_{PH}$ = 4.9 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, C^6H), 5.9 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C^7H), 5.1 (dd, apparent t, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$= 17.0 Hz, 1H, C^3H), 4.4 (m, 1H, C^4H), 2.9 (s, 3H, C^9H), 1.4 ppm (d, $^3J_{HH}$ = 4.8 Hz, 3H, C^5H); **5a** or **5b**, δ 10.8 (dd, $^3J_{PH}$ = 5.2 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, C^6H), 6.3 (d, $^3J_{HH}$ = 8.1 Hz, 1H, C^7H), 6.2 (dd, apparent t, $^3J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 16.8 Hz, 1H, C^3H), 4.8 (m, 1H, C^4H), 3.0 (s, 3H, C^9H), 1.8 (d, $^3J_{HH}$ = 5.7 Hz, 3H, C^5H), 7.6−6.7 ppm (m, 45H, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): **5a** or **5b**, δ 5.1 (s, CPPh_3), 0.6 ppm (s, OsPPh_3); **5a** or **5b**, δ 2.5(s, CPPh_3), 0.8 ppm (s, OsPPh_3). ^{13}C NMR (125.8 MHz, CD_2Cl_2, plus $^1H-^{13}C$ HSQC): **5a**

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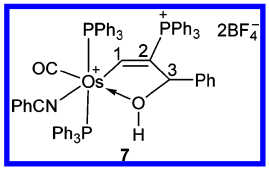
or **5b**, δ 279.5 (br, C^1), 200.3 (br, C^6), 180.5 (s, C^8), 128.9 (br, C^4), 116.9 (s, C^7), 108.6 (br, C^3), 92.6 (d, $^1J_{PC}$ = 100.0 Hz, C^2), 53.4 (s, C^9), 18.2 ppm (s, C^5); **5a** or **5b**, δ 274.9 (br, C^1). 195.6 (br, C^6), 180.7 (s, C^8),124.3 (br, C^4), 118.7 (s, C^7), 114.1 (br, C^3), 95.0 (d, $^1J_{PC}$ = 99.1 Hz, C^2), 53.6 (s, C^9), 18.6 (s, C^5), 134.6−128.0 ppm (m, other aromatic carbon atoms). Anal. Calcd for $C_{63}H_{55}P_3ClBF_4O_2Os$: C, 60.56; H, 4.44. Found: C, 60.50; H, 4.41.

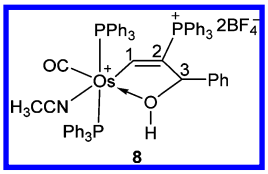
Preparation and Characterization of Complex 7.



7

Benzonitrile (85.0 μL, 0.833 mmol) was added to a mixture of **6** (200 mg, 0.160 mmol) and $AgBF_4$ (156 mg, 0.801 mmol) in DCM (10 mL), and then the mixture was stirred at room temperature for 6 days in carbon monoxide to give a white solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a white precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 141 mg, 62%. ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ 10.9 (d, $^3J_{PH}$ = 24.3 Hz, 1H, C^1H), 4.2 (br, 1H, C^3H), 1.8 (br, O*H*), 8.0−5.3 ppm (m, 55H, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 12.9 (br, C*P*Ph_3), 11.2 (br, Os*P*Ph_3), 10.8 ppm (br, Os*P*Ph_3). ^{13}C NMR (125.8 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HSQC): δ 187.3 (br, C^1), 178.7 (d, $^2J_{PC}$ = 10.8 Hz, *C*O), 112.6 (d, $^1J_{PC}$ = 81.5 Hz, C^2), 108.7 (s, Ph*C*N), 86.9 (d, $^2J_{PC}$ =31.1 Hz, C^3), 134.5−119.4 ppm (m, other aromatic carbon atoms). Anal. Calcd for $C_{71}H_{58}O_2B_2F_8P_3NOs$: C, 60.31; H, 4.13; N, 0.99. Found: C, 60.15; H, 4.06; N, 1.18.

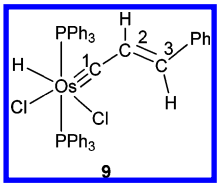
Preparation and Characterization of Complex 8.



8

CH_3CN (150 μL) was added to a mixture of **6** (200 mg, 0.160 mmol) and $AgBF_4$ (156 mg, 0.801 mmol) in DCM (10 mL), and then the mixture was stirred at room temperature for 6 days in carbon monoxide to give a white solution. The solvent was removed under vacuum and concentrated to about 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a white precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 112 mg, 52%. ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ 10.9 (d, $^3J_{PH}$ = 24.8 Hz, 1H, C^1H), 4.1 (br, 1H, C^3H), 2.0 (br, O*H*), 1.4 (s, 3H, CH_3CN), 7.7−5.2 ppm (m, 50H, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 13.0 (s, C*P*Ph_3), 11.8 (s, Os*P*Ph_3), 11.4 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{66}H_{56}O_2B_2F_8P_3NOs$: C, 58.64; H, 4.18; N, 1.04. Found: C, 58.16; H, 4.31; N, 1.40.

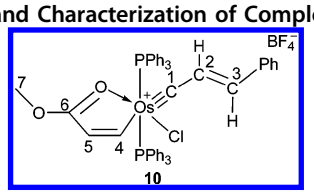
Preparation and Characterization of Complex 9.



9

To a suspension of compound **6** (600 mg, 0.480 mmol) in CH_3CN (10 mL) was added a solution of NEt_3 (140 μL, 1.01 mmol). Then the mixture was stirred at room temperature for 7 h to give a red suspension. The red solid was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 90 mg, 21%. ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ −6.4 (t, $^2J_{PH}$ = 19.4 Hz, 1H, Os*H*), 6.2 (d, $^3J_{HH}$ = 20.6 Hz, 1H, C^2H), 4.2 (d, $^3J_{HH}$ = 20.6 Hz, 1H, C^3H), 7.7−6.8 ppm (m, 35H, other aromatic protons). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 5.7 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{45}H_{38}P_2Cl_2Os$: C, 59.93; H, 4.25. Found: C, 60.34; H, 4.32.

Preparation and Characterization of Complex 10.



10

HC≡CCOOMe (97.0 μL, 1.08 mmol) and HBF_4·Et_2O (340 μL, 1.32 mmol) were added to a suspension of compound **9** (500 mg, 0.554 mmol) in DCM (10 mL). The reaction mixture was stirred at room temperature for 3 days to give a red solution. The volume of the solution was reduced to approximately 1 mL under vacuum. The addition of diethyl ether (20 mL) to the residue produced a red precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 373 mg, 65%. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 10.7 (d, $^3J_{PH}$ = 8.4 Hz, 1H, C^4H), 6.9 (d, $^3J_{HH}$ = 16.2 Hz, 1H, C^2H), 6.3 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C^5H), 5.9 (d, $^3J_{HH}$ = 16.2 Hz, 1H, C^3H), 3.0 (s, 3H, C^7H), 7.6−7.3 ppm (m, 35H, other aromatic protons). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 11.9 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{49}H_{42}P_2ClBF4O_2Os$: C, 56.74; H, 4.08. Found: C, 56.44; H, 4.46.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solutions layered with hexane or diethyl ether for **2**−**5** and **7**−**10**. Data collections were performed on an Oxford Gemini S Ultra or a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan absorption corrections (SADABS) were applied. All of the data were corrected for absorption effects using the multiscan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on F^2 using the Bruker SHELXTL (Version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. CCDC 1000199 (**2**), 1000200 (**3**), 1000201 (**4**), 1000196 (**5**), 1005002 (**7**), 1000197 (**8**), 1000198 (**9**), and 1000202 (**10**) contain supplementary crystallographic data for this paper. Further details on crystal data, data collection, and refinements are summarized in Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table and CIF files giving crystallographic data of compounds **2**−**5** and **7**−**10** and figures giving NMR spectra for complexes **2**, **5**, and **7**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

†These authors contributed equally to this paper.

Notes

The authors declare no competing financial interest.

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