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Formation of Four Conjugated Osmacyclic Species in a One-Pot Reaction

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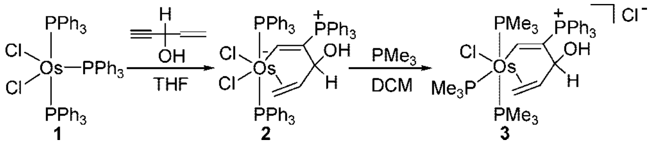
Treatment of $HC{\equiv}CCH(OH)CH{=}CH_2$ with $OsCl_2(PPh_3)_3$ in THF produced the η^2-allyl alcohol osmacycle $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)CH{=}CH_2)$ (**2**) with poor solubility and low stability, which underwent a ligand substitution reaction with PMe_3 to give the more stable analogue $[OsCl(PMe_3)_3(CH{=}C(PPh_3)CH(OH)CH{=}CH_2)]Cl$ (**3**). Heating the suspension of **2** in CH_2Cl_2 led to the formation of four interesting conjugated osmacycles in one pot, including the osmabenzene $OsCl_2(PPh_3)_2(CHC(PPh_3)CHCHCH)$ (**4**), the cyclic osmium η^2-allene complex $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH{=}C{=}CH_2)$ (**5**), the osmafuran $OsCl_2(PPh_3)_2(CHC(PPh_3)C(CH_2CH_3)O)$ (**6**), and the α,β-unsaturated ketone complex $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)C(O)C{=}CH_2)$ (**7**). All of the four products could also be produced in higher yield under appropriate conditions.

Introduction

Metallacycles containing transition metals[1–5] are an interesting class of compounds, due to their special reactivity and properties compared with those of similar cyclic organics. Over the past several decades, rapid progress has been made in research on the syntheses and properties of some archetypical aromatic metallacycles.

Scheme 1



As one class of six-membered delocalized metallacycles analogous to benzene, metallabenzenes[1−3] have attracted considerable attention, both experimentally and theoretically, in recent years. Since the first metallabenzene (osmabenzene) was isolated and characterized in 1982,[2a] both synthetic methods and different aromatic topologies of metallabenzenes have been developed. In contrast, osmabenzenes, as the pioneers of metallabenzenes, are still limited to only a few reports.[2]

Recently, we have reported some interesting reactions of the highly unsaturated C_5 dialkyne $HC{\equiv}CCH(OH)C{\equiv}CH$ with transition-metal-containing complexes bearing phosphine ligands, which led to the formation of some stable metallacycles, including osmabenzenes,[2d,e] ruthenabenzenes,[3e,f] and bridged iridacycles.[5d] These reactions were initiated by the coordination of the alkyne to the metal center and nucleophilic attack of the phosphines on the coordinated alkyne. All of the products of the above reactions contained bulky phosphoniums in the structures, which acted as protecting groups and thus improved their stability to some extent.

As an offshoot of our continuing interest in constructing stable metallacycles from C_5 units, we now set out to investigate this type of reaction using $HC{\equiv}CCH(OH)CH{=}CH_2$[6] as the starting material, expecting that the relatively lower unsaturation of the building block might lead to different chemistry. To this end, we have studied the reaction of $HC{\equiv}CCH(OH)CH{=}CH_2$ with $OsCl_2(PPh_3)_3$,[7] a readily accessible starting material for the syntheses of osmium complexes.[8] As expected, we have successfully isolated and characterized some interesting stable

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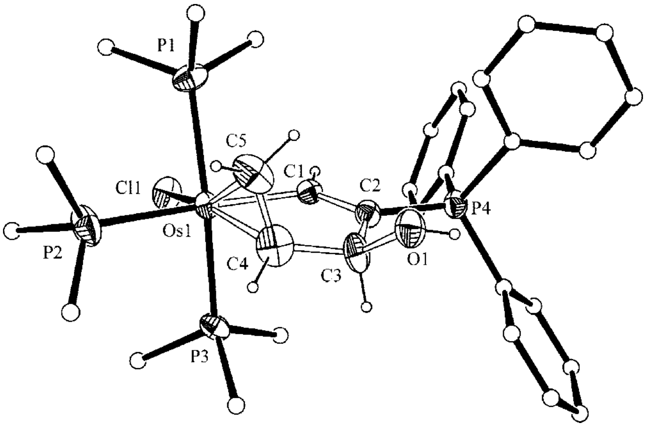


Figure 1. Molecular structure for the complex cation of **3**. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.075(4), Os1−C4 = 2.168(5), Os1−C5 = 2.135(4), C1−C2 = 1.356(6), C2−C3 = 1.497(6), C3−C4 = 1.510(7), C4−C5 = 1.342(8), O1−C3 = 1.417(5); C1−Os1−C5 = 85.5(2), C2−C1−Os1 = 118.9(3), C1−C2−C3 = 118.0(4), C2−C3−C4 = 109.8(4), C3−C4−C5 = 114.0(5), C4−C5−Os1 = 73.2(3), C3−C4−Os1 = 114.0(3).

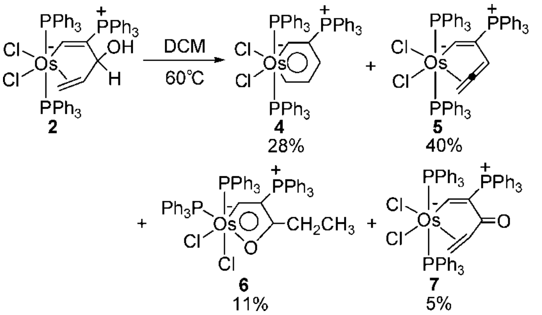
metallacycles and developed a convenient route to prepare four different conjugated osmacyclic species (an osmabenzene, a cyclic osmium η^2-allene complex, an osmafuran, and an α,β-unsaturated ketone complex) in a one-pot reaction.

Results and Discussion

Preparation of η^2-Allyl Alcohol Osmacycles. Reaction of $HC{\equiv}CCH(OH)CH{=}CH_2$with $OsCl_2(PPh_3)_3$ (**1**) in THF at 0 °C for 1 h yielded the yellow precipitate **2**, which could be isolated in 65% yield (Scheme 1). Complex **2** has poor solubility in common organic solvents. It is only slightly soluble in CH_2Cl_2 and shows very low stability in solution, transforming almost simultaneously during the dissolving process. As a result, neither the solution NMR spectroscopic characterization data nor the single-crystal X-ray diffraction data of **2** are available. However, in view of our previous experience in the reaction of $HC{\equiv}CCH(OH)CH{\equiv}CH$ with $OsCl_2(PPh_3)_3$, which led to the formation of the complex $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)\text{-}C{\equiv}CH)$ by nucleophilic attack of PPh_3 on the coordinated alkyne,[2d] we can infer that **2** is the η^2-allyl alcohol osmacycle $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)CH{=}CH_2)$ formed in a similar way. The solid-state NMR spectrum and elemental analysis data of **2** are consistent with this conjecture. Especially, in the solid-state ^{13}C NMR spectrum, signals attributed to Os*C*H, *C*(PPh$_3$), and *C*H(OH) were observed at 207.9, 110.2, and 85.8 ppm, respectively, which are comparable with those of $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)C{\equiv}CH)$ (δ 206.5, 111.2, and 77.8 ppm).[2d] In addition, the two signals (δ 45.4 and 33.4 ppm) attributed to the carbons of the terminal coordinated double bond are also close to those for reported η^2-olefin complexes.[2e]

The structural formulation of **2** was further confirmed by the synthesis of complex **3** from a simple ligand substitution reaction of **2** with excess PMe_3 (Scheme 1). Complex **3** showed better solubility and higher stability than **2** and could be structurally characterized. The crystal structure of **3** is shown in Figure 1.

Scheme 2



The single-crystal X-ray diffraction clearly revealed that complex **3** contained an η^2-allyl alcohol osmacycle. The bond distances of Os1−C1 (2.075(4) Å), Os1−C4 (2.168(5) Å), and Os1−C5 (2.135(4) Å) are within the range of typical Os−C single bonds. The C1−C2 and C4−C5 bond distances (1.356(6) and 1.342(8) Å, respectively) are typical for a C═C double bond, while the C2−C3 (1.497(6) Å) and C3−C4 (1.510(7) Å) bond distances are typical for a C−C single bond. The C3−O1 bond length (1.417(5) Å) indicates the existence of a hydroxyl group, which is close to that reported for the η^2-allyl alcohol complex $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (1.45(2) Å).[9]

One-Pot Synthesis of Four Conjugated Osmacycles by Heating Complex 2. During the process of our investigation on the reactivity of **2**, we found that heating a suspension of **2** in dichloromethane at 60 °C in a sealed tube led to the unexpected formation of the different conjugated osmacyclic species **4**−**7** in one pot (Scheme 2). After recrystallization of the crude product from dichloromethane/ether, four kinds of crystals with varied forms were collected and isolated manually.

Complex **4** could be isolated as dark green bulky crystals. The structure established by X-ray diffraction (Figure 2) indicates that **4** is a typical osmabenzene containing an essentially planar six-membered metallacycle. The mean rms (root mean square) deviation from the least-squares plane through Os1/C1/C2/C3/C4/C5 is 0.0592 Å. Within the metallacycle, the C−C bond distances are observed in the range

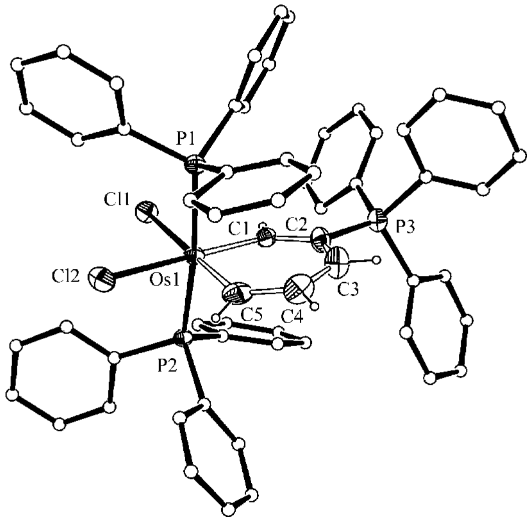


Figure 2. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): Os1−C1 = 1.977(6), Os1−C5 = 1.971(5), C1−C2 = 1.383(7), C2−C3 = 1.412(8), C3−C4 = 1.358(9), C4−C5 = 1.417(9); C1−Os1−C5 = 89.4(2), C2−C1−Os1 = 128.0(4), C1−C2−C3 = 124.5(6), C2−C3−C4 = 123.6(5), C3−C4−C5 = 125.7(6), C4−C5−Os1 = 126.8(5).

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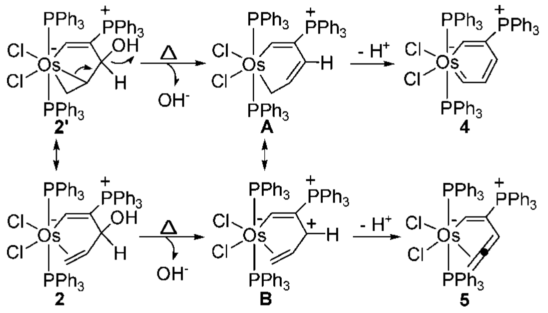
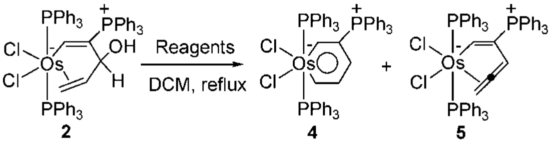
Scheme 3



Scheme 4



Reagents:	4	5
(a) $NaHCO_3$	43%	40%
(b) AcOH	0%	76%
(c) Ac_2O	5%	85%

1.358(9)−1.417(9) Å, and the Os−C bond distances in the ring are approximately equal (1.977(6) and 1.971(5) Å). The lack of significant alternations in the C−C bond distances, together with the planarity of the ring, indicates that the metallacycle has a delocalized nature. The monophosphonium-substituted osmabenzene **4** is structurally similar to our previous osmabenzene $[OsCl_2(PPh_3)_2(CHC(PPh_3)CHC(PPh_3)CH)]OH$, bearing two phosphonium substituents.[2d]

The NMR spectroscopic data of **4** are consistent with its solid-state structure. In particular, the ^1H NMR spectrum showed the two characteristic OsCH signals at 20.6 and 18.9 ppm. The proton opposite to the phosphonium group is more downfield compared with that at the ortho position. The OsCH signals for our previously reported iodoosmabenzene $OsI_2(PPh_3)_2(CHC(PPh_3)CHC(I)CH)$ appeared at 20.1 and 19.0 ppm.[2d] The two proton signals on C3 and C4 can be observed at 6.6 and 6.9 ppm, which are close to those of organic aromatic rings. The facts also suggest that the metallacycle of **4** is delocalized.

A plausible mechanism for the formation of **4** is proposed as shown in Scheme 3. The process may involve that dissociation of OH^- from **2** gives intermediate **A** followed by deprotonation of the α-H to form osmabenzene **4**. In addition, we found that addition of $NaHCO_3$ to the heating system would increase the yield of **4**(Scheme 4), which indicates deprotonation of the α-H are more facile in the presence of base.

Although osmabenzenes act as the pioneer of metallabenzenes,[2a] the preparation routes of osmabenzenes are limited.[2] The reactions described above provide new available routes to prepare osmabenzene, which represent an extension of our previously reported method to synthesize metallabenzenes via the ring closure reactions.[2d,3e,f]

Complex **5** was isolated as light green prismatic crystals. The structure of **5** (Figure 3) contains a conjugated osmacycle with a terminal double bond of an allene coordinated to the metal atom, which can also be viewed as a five-membered metallacycle with an exocyclic methylene group coordinated to the osmium center. The terminal coordinated double bond C4=C5 is almost coplanar with the osmacycle consisting of Os1, C1, C2, C3, and C4. The coplanarity is reflected by the small deviation (0.0537 Å) from the rms planes of the best fit through the six atoms. The allene unit deviates slightly from linearity with an C3−C4−C5 angle of 171.0°.

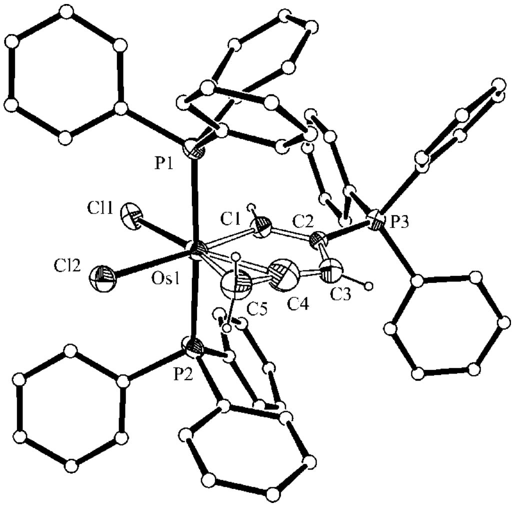


Figure 3. Molecular structure of **5**. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.014(8), Os1−C4 = 2.205(10), Os1−C5 = 2.150(9), C1−C2 = 1.382(9), C2−C3 = 1.419(10), C3−C4 = 1.282(11), C4−C5 = 1.390(12); C1−Os1−C5 = 108.2(3), C1−Os1−C4 = 71.4(4), C5−Os1−C4 = 37.2(3), C2−C1−Os1 = 122.0(6), C1−C2−C3 = 113.8(7), C2−C3−C4 = 112.2(8), C3−C4−C5 = 171.0(11), C4−C5−Os1 = 73.6(6), C3−C4−Os1 = 119.8(7).

The solid-state structure of **5** is also fully supported by the solution NMR spectroscopic data and elemental analysis. In particular, the ^1H NMR spectrum showed the OsCH signal at 12.0 ppm and the signals attributed to $C\mathit{H}CCH_2$ and $CHC\mathit{CH}_2$ at 7.6 and 2.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum showed only two singlets at 5.8 ($C\mathit{P}Ph_3$) and −11.0 ppm ($Os\mathit{P}Ph_3$), which suggested a symmetric structure. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of OsCH and CPPh₃ appeared at 208.7 and 113.0 ppm, while the three carbon signals of the coordinated allene backbone appeared at 191.1 ($CH\mathit{C}CH_2$), 114.0 ($\mathit{C}HCCH_2$), and 24.8 ($CHC\mathit{C}H_2$) ppm, respectively.

In contrast to the formation of **4**, the intermediate **A** shown in Scheme 3 can also tautomerize to **B** and then undergo deprotonation of the β-H to generate the osmium allene complex **5**. It is well-known that acid can promote the dissociation of OH^-. Consistent with this mechanism, treatment of **2** with acetic acid in refluxing dichloromethane led to the formation of **5** in 76% yield. To further optimize the reaction conditions, we also isolated **5** in 85% yield when utilizing acetic anhydride instead of acetic acid (Scheme 4).

It is now well established that allenes are useful building blocks in synthetic transformations to construct a variety of compounds.[10] Various stable coordinated allene complexes containing different metals and structures have been isolated.[11−13] However, as interesting species of these, osmium allene complexes[12,13a] and cyclic metal allene complexes[13] have been limited to a few scattered reports. Complex **5** is a rare example of a cyclic osmium η^2-allene complex, which may be compared with the allenylcarbene complexes $OsCl_2(=CPh\text{-}\eta^2\text{-}CH=C=$

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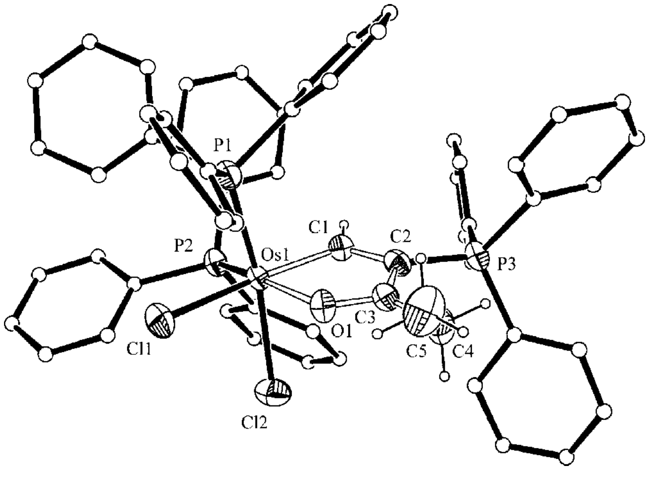
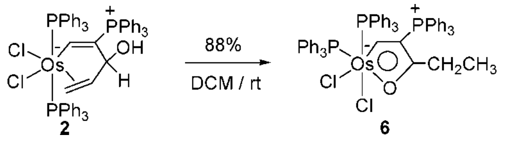


Figure 4. Molecular structure of **6**. Selected bond distances (Å) and angles (deg): Os1−C1 = 1.904(10), Os1−O1 = 2.124(7), C1−C2 = 1.395(15), C2−C3 = 1.404(15), C3−O1 = 1.262(12), C3−C4 = 1.499(15), C4−C5 = 1.480(18); C1−Os1−O1 = 78.5(4), C2−C1−Os1 = 116.5(7), C3−O1−Os1 = 113.2(6), C1−C2−C3 = 114.7(9), C2−C3−C4 = 126.9(10), C3−C4−C5 = 112.8(11), C2−C3−O1 = 116.4(9).

CH(Ph)(PPh$_3$)$_2$[13a] and [CpRu(=C(Rc)-η^2-CH=C=CH(Rc)(PPh$_3$)]PF$_6$.[13b,c] In sharp contrast to **5** which has a larger conjugated planar metallacycle with the terminal double bond of allene coordinated to osmium, the allenylcarbene complexes contain bent four-membered metallacycles with internal double bonds of allene coordinated to the metals. It is worth noting that complex **5** shows remarkable air stability; even a solution of **5** can remain unchanged for over 1 month.

Complex **6** was collected as brownish bulky crystals and identified to be a 2-osmafuran, which has been established by the solution NMR spectroscopic data as well as the solid-state structure (Figure 4). A possible mechanism for the generation of **6** may include multiple hydrogen migration steps. Formally, the alcohol is dehydrogenated, accompanied by hydrogenation of the terminal alkene in the transformation of **2** to **6**, which can be regarded as an intramolecular version of transfer hydrogenation.[14] Additionally, **6** could be isolated in higher yield (88%) when the suspension of **2** in CH$_2$Cl$_2$ was stirred at room temperature for about 30 h (Scheme 5). To the best of our knowledge, **6** could be viewed as the first phosphonium salt of metallafuran.

Scheme 5



Another product, **7**, was isolated as red prismatic crystals in 5% yield. Complex **7** was identified to be the α,β-unsaturated ketone complex OsCl$_2$(PPh$_3$)$_2$(CH=C(PPh$_3$)C(O)CH=CH$_2$), which has been reported previously by us.[2e] Formally, complex **7** was formed via elimination of H$_2$ from **2** in the reaction. The introduction of oxygen into the system could improve the yield of **7**.

According to our initial design, the introduction of phosphoniums to the metallacycles indeed improved the stability of these complexes to some extent. In the solid state, all four of the conjugated osmacycles are air-stable. Remarkably, the powders of allene complex **5** and osmafuran **6** remained almost unchanged when they were heated at 80 °C in air for several hours, and the α,β-unsaturated ketone complex **7** remained stable even when heated at 200 °C in air for 5 h.

Conclusion

We have found an efficient one-pot method to prepare four various conjugated osmacycles, which could also be prepared in higher yield under the appropriate reaction conditions. This new method allowed us to obtain interesting stable complexes containing phosphoniums in the metallacyclic rings.

Experimental Section

General Considerations. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (ether, tetrahydrofuran) or calcium hydride (dichloromethane). The starting materials HC≡CCH(OH)CH=CH$_2$ and OsCl$_2$(PPh$_3$)$_3$ were synthesized by literature procedures. Column chromatography was performed on neutral alumina gel (200−300 mesh). All of the NMR spectra were recorded with a Bruker AV300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.5 MHz) or a Bruker AV400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H$_3$PO$_4$. Elemental analysis data were obtained on a Thermo Quest Italia SPA EA 1110 instrument.

OsCl$_2$(PPh$_3$)$_2$(CH=C(PPh$_3$)CH(OH)CH=CH$_2$) (2). A mixture of OsCl$_2$(PPh$_3$)$_3$ (1.00 g, 0.96 mmol) and HC≡CCH(OH)CH=CH$_2$ (86.1 mg, 1.05 mmol) in THF (4 mL) was stirred at 0 °C for 1 h to give a brown-yellow suspension. The yellow solid was collected by filtration, washed with CH$_2$Cl$_2$ (2 × 2 mL), and then dried under vacuum (0.70 g, 65%). The solid-state NMR experiment was performed on a Bruker AV300 spectrometer operating at a MAS frequency of 11 KHz using a Bruker 4 mm probe. Solid-state ^{31}P NMR (121.5 MHz): δ 7.3 (C*P*Ph$_3$), −7.1 ppm (Os*P*Ph$_3$). Solid-state ^{13}C NMR (75.5 MHz): δ 207.9 (Os*C*H), 110.2 (*C*(PPh$_3$)), 85.8 (*C*H(OH)), 45.4 (*C*HCH$_2$), 33.4 ppm (CH*C*H$_2$). Anal. Calcd for C$_{59}$H$_{51}$OP$_3$Cl$_2$Os: C, 62.71; H, 4.55; Found: C, 62.32; H, 4.65.

[OsCl(PMe$_3$)$_3$(CH=C(PPh$_3$)CH(OH)CH=CH$_2$)]Cl (3). A solution of PMe$_3$ in THF (1.0 M, 3.0 mL, 3.0 mmol) was added to a suspension of OsCl$_2$(PPh$_3$)$_2$(CH=C(PPh$_3$)CH(OH)CH=CH$_2$) (**2**; 0.34 g, 0.30 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was stirred at room temperature for about 12 h to give a light yellow solution.

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Table 1. Crystal Data and Structure Refinement Details for 3−6

	3	**4**	**5**	**6**
empirical formula	$C_{33}H_{50}Cl_4OsOP_4$	$C_{59}H_{49}Cl_2OsP_3$	$C_{59}H_{49}Cl_2OsP_3$	$C_{59.75}H_{52.50}Cl_{3.5}OsO_{1.50}P_3$
formula wt	918.61	1111.99	1111.99	1201.70
temp, K	173(2)	223(2)	223(2)	223(2)
radiation (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	11.1653(4)	11.8066(7)	12.4030(5)	12.249(2)
b, Å	12.7631(3)	23.73951(15)	18.5440(8)	12.959(2)
c, Å	13.6141(4)	17.4227(4)	21.4896(8)	20.138(3)
α, deg	87.747(2)	90	90	98.431(3)
β, deg	85.366(2)	90.885(4)	102.065(4)	95.354(3)
γ, deg	83.153(2)	90	90	113.906(3)
V, Å^3	1919.07(10)	4882.7(4)	4833.5(3)	2849.3(8)
Z	2	4	4	2
d_{calcd}, g cm^{-3}	1.590	1.513	1.528	1.401
abs coeff, mm^{-1}	3.793	2.859	2.888	2.525
F(000)	920	2232	2232	1207
cryst size, mm	0.28 × 0.25 × 0.20	0.28 × 0.24 × 0.20	0.29 × 0.16 × 0.08	0.35 × 0.24 × 0.20
no. of rflns collected	14 019	48 489	21 519	20 698
no. of indep rflns	6592	8484	8433	9932
no. of obsd rflns ($I > 2\sigma(I)$)	5597	7035	4565	9110
no. of data/restraints/params	6592/18/388	8484/6/586	8433/25/586	9932/54/658
goodness of fit on F^2	1.009	1.031	1.061	1.039
final R ($I > 2\sigma(I)$)	R1 = 0.0280, wR2 = 0.0677	R1 = 0.0509, wR2 = 0.0804	R1 = 0.0493, wR2 = 0.0796	R1 = 0.0797, wR2 = 0.2203
R indices (all data)	R1 = 0.0353, wR2 = 0.696	R1 = 0.0663, wR2 = 0.0876	R1 = 0.1011, wR2 = 0.0861	R1 = 0.0859, wR2 = 0.2262

The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a white precipitate, which was collected by filtration, and subsequent recrystallization of the crude product from dichloromethane/hexane yielded white crystals. Yield: 0.22 g, 88%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 9.4 (d, ^3J(PH) = 25.5 Hz, 1H, OsC*H*), 5.7 (d, ^4J(PH) = 4.5 Hz, 1H, O*H*), 5.4 (br, 1H, C*H*OH), 3.5 (m, 1H, C*H*CH_2), 2.1 (m, 2H, CHC*H*$_2$), 7.4−7.8 (m, 15H, PPh_3), 1.1−1.9 ppm (m, 27H, PMe_3). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 13.6 (dt, ^4J(PP) = 28.2, 4.7 Hz, C*P*Ph_3), −46.7 (dd, ^2J(PP) = 21.6 Hz, ^4J(PP) = 4.7 Hz, Os*P*Me_3), −55.6 ppm (dt, ^4J(PP) = 28.2 Hz, ^2J(PP) = 21.6 Hz, Os*P*Me_3). Anal. Calcd for $C_{32}H_{48}OP_4Cl_2Os$: C, 46.10; H, 5.80. Found: C, 46.07; H, 5.76.

Method A. One-Pot Reaction To Synthesize $OsCl_2(PPh_3)_2$-(CHC(PPh_3)CHCHCH) (4), $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH=C=CH_2) (5), $OsCl_2(PPh_3)_2$(CHC(PPh_3)C(CH_2CH_3)O) (6), and $OsCl_2(PPh_3)_2$(CH=C(PPh_3)C(O)CH=CH_2) (7). A suspension of $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH(OH)CH=CH_2) (**2**; 0.40 g, 0.35 mmol) in dichloromethane (8 mL) was heated to 60 °C for 6 h in a sealed tube. Then the reaction system was cooled to room temperature and depressurized to atmospheric pressure. A green solution was collected, concentrated to 3 mL under vacuum, and then layered with diethyl ether (6 mL). Dark green bulky crystals of **4** (0.11 g, 28%), light green prismatic crystals of **5** (0.16 g, 40%), brownish bulky crystals of **6** (0.044 g, 11%), and red prismatic crystals of **7** (0.020 g, 5%) were collected and isolated manually.

Method B. $OsCl_2(PPh_3)_2$(CHC(PPh_3)CHCHCH) (4). A mixture of $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH(OH)CH=CH_2) (**2**; 0.40 g, 0.35 mmol) and $NaHCO_3$ (30 mg, 0.36 mmol) in dichloromethane (10 mL) was stirred at reflux for ca. 1 h to give a green solution, which was concentrated to 3 mL under vacuum and then layered with diethyl ether (8 mL). Dark green bulky crystals of **4** (0.17 g, 43%) and light green prismatic crystals of **5** (0.16 g, 40%) could be collected and isolated manually. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 20.6 (dt, ^3J(HH) = 7.7 Hz, ^3J(PH) = 3.6 Hz, 1H, OsC*H*CH), 18.9 (dt, ^3J(PH) = 20.7 Hz, ^3J(PH) = 2.6 Hz, 1H, OsC*H*C(PPh_3)), 6.9 (dd, ^3J(PH) = 12.3 Hz, ^3J(HH) = 7.7 Hz, 1H, OsCHCHC*H*), 6.6 (t, ^3J(HH) = 7.7 Hz, 1H, OsCHC*H*), 7.0−7.9 ppm (m, 45H, PPh_3). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 18.0 (s, C*P*Ph_3), −13.0 ppm (s, Os*P*Ph_3). Anal. Calcd for $C_{59}H_{49}P_3Cl_2Os$: C, 63.72; H, 4.44. Found: C, 63.78; H, 4.70.

Method C. $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH=C=CH_2) (5). A mixture of $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH(OH)CH=CH_2) (**2**; 0.40 g, 0.35 mmol) and AcOH (0.057 mL, 1.0 mmol) in dichloromethane (10 mL) was stirred at reflux for ca. 1 h to give a green solution. The solvent was evaporated to dryness under vacuum, and the resulting residue was washed with ether (5 × 3 mL) and then dried under vacuum. Yield: 0.30 g, 76%.

Method D. $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH=C=CH_2) (5). A mixture of $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH(OH)CH=CH_2) (**2**) (0.40 g, 0.35 mmol) and Ac_2O (0.16 mL, 1.7 mmol) in dichloromethane (10 mL) was stirred at reflux for ca. 1 h to give a green solution. The solvent was evaporated to dryness under vacuum, and the resulting residue was washed with ether (5 × 3 mL) and then dried under vacuum. Yield: 0.33 g, 85%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ12.0 (d, ^3J(PH) = 16.0 Hz, 1H· OsC*H*), 7.6 (d, ^3J(PH) = 6.8 Hz, 1H, OsCHC(PPh_3)C*H*, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 2.7 (t, ^3J(PH) = 6.0 Hz, 2H, CC*H*$_2$), 6.9−7.8 ppm (m, 45H, PPh_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 5.8 (s, C*P*Ph_3), −11.0 ppm (s, Os*P*Ph_3). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 208.7 (br, Os*C*H), 191.1 (d, ^3J(PC) = 23.5 Hz, CH*C*CH_2), 114.0 (d, ^2J(PC) = 27.2 Hz, *C*HCCH_2), 113.0 (d, ^1J(PC) = 76.3 Hz, *C*(PPh_3)), 24.8 (s, C*C*H_2), 120.0−134.0 ppm (m, PPh_3). Anal. Calcd for $C_{59}H_{49}P_3Cl_2Os$: C, 63.72; H, 4.44. Found: C, 63.57; H, 4.80.

Method E. $OsCl_2(PPh_3)_2$(CHC(PPh_3)C(CH_2CH_3)O) (6). A suspension of $OsCl_2(PPh_3)_2$(CH=C(PPh_3)CH(OH)CH=CH_2) (**2**; 0.40 g, 0.35 mmol) in dichloromethane (15 mL) was stirred at room temperature for 30 h to give a brown solution. The volume of the mixture was reduced to approximately 2 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a brownish green precipitate, which was collected by filtration, and subsequent recrystallization of the crude product from dichloromethane/ether yielded green crystals. Yield: 0.35 g, 88%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ 14.9 (d, ^3J(PH) = 12.0 Hz, 1H· OsC*H*), 2.2 (dq, ^2J(HH) = 15.0 Hz, ^3J(HH) = 7.2 Hz, 1H, C*H*$_2$$CH_3$), 1.8 (dq, ^2J(HH) = 15.0 Hz, ^3J(HH) = 7.2 Hz, 1H, C*H*$_2$$CH_3$), 0.8 (dd, ^2J(HH) = 7.2, 7.2 Hz, 3H, CH_2C*H*$_3$), 6.9−7.8 ppm (m, 45H, PPh_3). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 15.1 (s, C*P*Ph_3), −2.9 (d, ^2J(PP) = 16.9 Hz, Os*P*Ph_3), −5.7 ppm (d, ^2J(PP) = 16.9 Hz, Os*P*Ph_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 241.0 (br, Os*C*H), 205.8 (d, ^2J(PC) = 10.1 Hz, *C*(O)CH_2CH_3), 113.0 (d, ^1J(PC) = 88.6 Hz, *C*PPh_3), 31.5 (s, *C*H$_2$$CH_3$), 10.1 (s, CH_2*C*H$_3$), 121.4−138.2 ppm (m, PPh_3). Anal. Calcd for $C_{59}H_{51}OP_3Cl_2Os$: C, 62.71; H, 4.55. Found: C, 62.40; H, 4.87.

Method F. $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)C(O)CH{=}CH_2)$ (7). A suspension of $OsCl_2(PPh_3)_2(CH{=}C(PPh_3)CH(OH)CH{=}CH_2)$ (**2**; 0.40 g, 0.35 mmol) in dichloromethane (8 mL) was heated at 60 °C for 6 h under an air atmosphere in a sealed tube. Then the reaction system was cooled to room temperature and depressurized to atmospheric pressure. The volume of the mixture was reduced to approximately 2 mL under vacuum. A red powder deposited, which was collected by filtration, washed with chloroform (2 mL × 2), and dried under vacuum. Yield: 0.11 g, 28%. ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 13.1 (d, ^3J(PH) = 15.0 Hz, 1 H, OsC*H*), 3.5 (m, 1 H, CHCH_2), 3.1 (m, 1 H, C*H*CH$_2$), 2.6 (m, 1 H, CHCH_2), 6.8−7.9 (m, 45 H, PPh$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 7.6 (s, C*P*Ph$_3$), −2.4 (d, ^2J(PP) = 255.2 Hz, Os*P*Ph$_3$), −14.3 (d, ^2J(PP) = 255.2 Hz, Os*P*Ph$_3$). Anal. Calcd for $C_{59}H_{49}OP_3Cl_2Os$: C, 62.82; H, 4.38. Found: C, 62.84; H, 4.52.

X-ray Crystal Structure Determination of 3−6. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or $CHCl_3$ solutions layered with ether or *n*-hexane for complexes **3**−**6**. Selected crystals were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on an Oxford Gemini S Ultra CCD area detector or a Bruker Apex CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Multiscan or empirical absorption corrections (SADABS) were applied. All 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-97 program package. All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. CCDC 675408 (**3**), 671116 (**4**), 671118 (**5**), and 671117 (**6**) contain the supplementary crystallographic data for this paper. Details on crystal data, data collection, and refinements are summarized in Table 1.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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