Synthesis of Coordinated η^2-α,β-Unsaturated Ketone Osmacycles from an Osmium-Coordinated Alkyne Alcohol Complex

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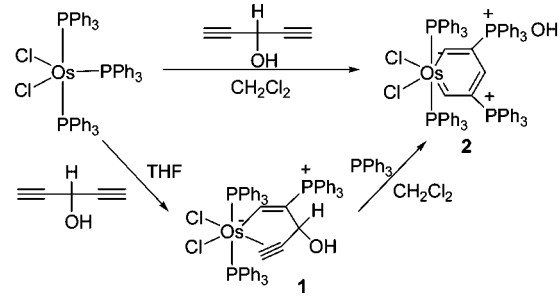
The study on the reactivity of an osmium-coordinated alkyne alcohol complex $OsCl_2(CH{=}C(PPh_3)CH(OH)$-$\eta^2$-$C{\equiv}CH)(PPh_3)_2$ (**1**) has been carried out. Treatment of **1** with acetic acid, ethylene diamine, 2,2′-bipyridine, trimethylphosphine, or tributylphosphine led to the formation of several coordinated η^2-α,β-unsaturated ketone osmacycles, including $OsCl_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PPh_3)_2$ (**3**), $[OsCl(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PPh_3)(H_2NCH_2CH_2NH_2)]Cl$ (**4**), $[OsCl(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PPh_3)(2,2'\text{-bipy})]Cl$ (**5**), $OsCl_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PMe_3)_2$ (**6**), $[OsCl(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PMe_3)_3]Cl$ (**8**), and $OsCl_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PBu_3)_2$ (**9**). Similar chemistry was also observed starting from $OsBr_2(CH{=}C(PPh_3)CH(OH)$-$\eta^2$-$C{\equiv}CH)(PPh_3)_2$ (**10**), which afforded $OsBr_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PPh_3)_2$ (**11**) on treatment with acetic acid. All these cyclic α,β-unsaturated ketone complexes are air-stable in the solid state, and most of them are also stable in solution except for $OsCl_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PMe_3)_2$ (**6**) and $[OsCl(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(PMe_3)_3]Cl$ (**8**). Complex **8** can isomerize to the osmaphenol $[OsCl(CHC(PPh_3)C(OH)CHCH)(PMe_3)_3]Cl$ (**12**) as the major product in dry chloroform, but transforms into the osmafuran $[Os(CO)(CHC(PPh_3)C(CH_3)O)(PMe_3)_3]Cl_2$ (**13**) in wet chloroform, while complex **6** is stable in dry solvent, but can convert to the osmafuran $[OsCl(CO)(CHC(PPh_3)C(CH_3)O)(PMe_3)_2]Cl$ (**14**). The remarkable thermostability and chemical stability of the coordinated α,β-unsaturated ketone osmacycles have been studied preliminarily with **3** as a representative example. The coordinated α,β-unsaturated ketone metallacyclic framework of **3** is stable in different ligand environments. For example, treatment of **3** with carbon monoxide led only to ligand substitution to produce $OsCl_2(CH{=}C(PPh_3)C(O)$-η^2-$CH{=}CH_2)(CO)(PPh_3)$ (**15**).

Introduction

Transition-metal-containing metallacycles are an important class of organometallic complexes involved in a number of reactions.[1,2] In particular, conjugated metallacycles[3] have attracted most attention due to their special reactivity and properties compared with related cyclic organics.[4]

Recently, we have reported the reaction of $OsCl_2(PPh_3)_3$ with terminal alkyne $HC{\equiv}CCH(OH)C{\equiv}CH$, resulting in the formation of the osmabenzene $[Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]OH$ (**2**) (Scheme 1).[5] During the synthesis process, we have succeeded in isolating a key intermediate, the osmacycle-containing coordinated alkyne alcohol $OsCl_2(CH{=}C(PPh_3)$-$CH(OH)$-η^2-$C{\equiv}CH)(PPh_3)_2$ (**1**) as a yellow solid from the

Scheme 1



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reaction in THF. Despite the fact that transition metals can act as coordination centers for the stabilization of many active organic compounds including some alkyne alcohols,[6] **1** was still highly reactive, which can readily react with PPh_3 to produce osmabenzene **2** via nucleophilic attack at the coordinated alkyne by PPh_3.[5] It could only remain unchanged at −18 °C under nitrogen atmosphere as a solid for several weeks or in solution for about two weeks, but only survived for several minutes in solution at room temperature.

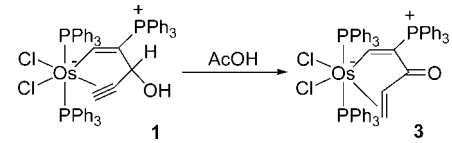
During our investigation of the reactivity of **1**, we reported more recently in a preliminary communication the reaction of **1** with acetic acid produced the coordinated α,β-unsaturated ketone osmacycle $OsCl_2(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PPh_3)_2$ (**3**).[7] It is well known that α,β-unsaturated ketones are useful in organic synthesis.[8] An available method to produce α,β-unsaturated ketones is the Meyer−Schuster rearrangement of alkyne alcohols, which was first reported in 1922[9] and continued to be the subject of extensive investigation.[10] In contrast, metallacycles bearing coordinated η^2-α,β-unsaturated ketones are still rare. To the best of our knowledge, complex **3** and the related PMe_3-substituted analogue reported in our preliminary communication represent the only examples up to now.

To further study the reactivity of **1**, we have investigated the reactions of **1** with different reagents such as ethylene diamine, 2,2′-bipyridine, PMe_3, and PBu^n_3 and successfully synthesized several stable metallacycles bearing coordinated η^2-α,β-unsaturated ketone. These products have excellent air stability and thermostability. The chemical stability of some representative complexes have also been studied. Herein, we reported these results in detail.

Results and Discussions

Reaction of $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (1) with Acetic Acid. Treatment of a suspension of **1** in dichloromethane with acetic acid for 4 h led to the precipitation of **3** as a red solid, which could be isolated in 90% yield (Scheme 2).[7]

Scheme 2



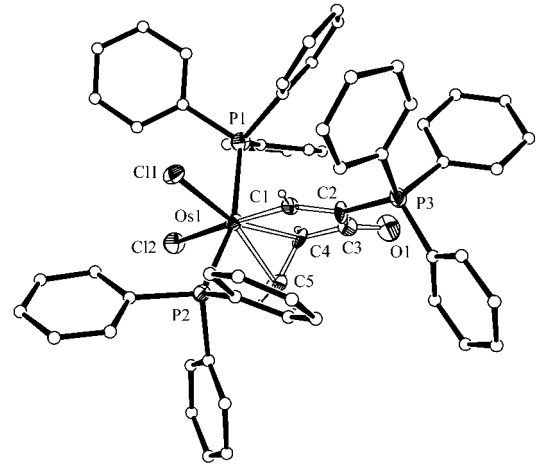


Figure 1. ORTEP plot of **3** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 1.987(7), Os1−C5 = 2.140(7), Os1−C4 = 2.159(7), O1−C3 = 1.235(11), C1−C2 = 1.367(12), C2−C3 = 1.482(12), C3−C4 = 1.465(11), C4−C5 = 1.435(12); C1−Os1−C5 = 90.7(3), C1−Os1−C4 = 78.9(3), C4−Os1−C5 = 39.0(3), C1−C2−C3 = 114.8(7), C2−C3−C4 = 113.2(7), C3−C4−C5 = 114.5(7), O1−C3−C4 = 122.5(8), O1−C3−C2 = 124.5(8).

The X-ray crystal structure of **3** has been reported briefly previously,[7] showing a cyclometalated pentadienone complex (Figure 1). The geometry of the osmium center can be viewed as a distorted octahedron with two PPh_3 ligands at the axial positions. The two chloride ligands, the vinyl carbon (C1), and the olefin double bond (C4═C5) occupied the equatorial coordination sites. Coplanarity of the five-membered ring (Os1/C1/C2/C3/C4) is reflected by the small deviations (0.0272 Å) from the rms planes of the best fit. C5 deviates from the plane with the dihedral angle between the Os1−C4−C5 plane and the Os−C1−C2−C3−C4 plane of 105.1°. The C3−O1 distance of 1.235(11) Å is typical of a normal carbon−oxygen double bond, which is very close to that in the analogous complex,[11] for example, (1,2,5-η-2,4-dimethylpenta-1,3-dien-5-oyl)Ir-$(PMe_3)_3$ (1.235(8) Å) reported by Bleeke.[11a] The bond distance between C4 and C5 is 1.435(12) Å, which is longer than typical C═C double bonds (∼1.35 Å) and shorter than typical C−C single bonds (∼1.55 Å),[12] consistent with the value of a coordinated olefin.[13] This fact aslo indicates a significant back-bonding from the metal center to the π^* orbital of the coordinated double bond, which suggests the contribution of the resonant form **3′** for the structure of **3** (Scheme 3). It appears that the resonant structures contribute almost equally to the bonding. The structure of η^2-coordinated alkenes can vary

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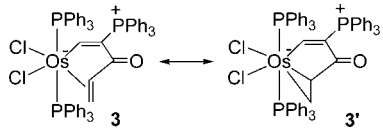
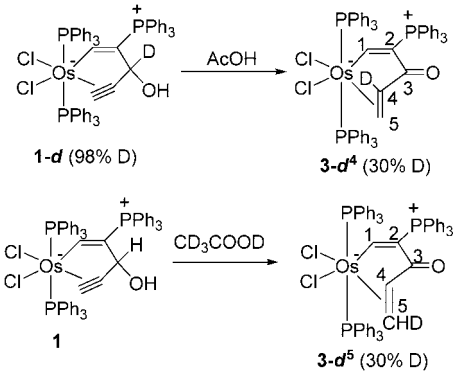
Scheme 3



Scheme 4



between the limiting resonance forms of an olefin complex and a metallacyclopropane, which is dependent on a number of factors.[14]

The NMR spectra of **3** are consistent with the solid state structure. In the ^{1}H NMR spectrum, the signal attributed to OsC*H* was observed at $\delta = 12.9$ ppm, which was significantly downfield due to the effect of the metal atom and phosphonium group on C2. The three proton signals of the C4−C5 bond were at $\delta = 3.6$, 3.2, and 2.8 ppm, which were also consistent with those of a coordinated olefin.[13b,13c] The ^{31}P{^{1}H} NMR spectrum showed the C*P*Ph$_3$ signal at $\delta = 7.1$ ppm, while signals of the two PPh$_3$ ligands on the metal atom were remarkably different, observed at $\delta = -3.9$ and −15.2 ppm, respectively.

Transformation of **1** to **3** can be viewed as isomerization of the coordinated alkyne alcohol to the intramolecular-coordinated α,β-unsaturated ketone. In fact, for an organic tertiary alkyne alchol, a protic acid could be used as a simple reagent to drive the Meyer−Schuster reaction, which afforded α,β-unsaturated ketones or aldehydes as byproducts.[10a] The mechanism for the conversion of **1** to **3** has been probed by the deuterium labeling experiments. Reaction of OsCl$_2$(CH═C(PPh$_3$)CD(OH)-η^2-C≡CH)(PPh$_3$)$_2$ (**1-*d***, 98% D) with acetic acid led to the formation of partially deuterated product **3-*d*^{4}** with deuterium content of 30% at the C4 position, while treatment of nondeuterated **1** with CD$_3$COOD led to ca. 30% incorporation of deuterium at the C5 position (Scheme 4). On the basis of these observations, an acid-catalyzed hydrogen shift process shown in Scheme 5 has been proposed as the mechanism using **1-*d*** as reactant. The isomerization process may be initiated by protonation of the coordinated terminal alkyne to give intermediate **A**, which undergoes β-D elimination to give **B**. An insertion reaction could produce intermediate **C**, which followed by dissociation of the hydroxy proton and subsequent coordination of the terminal double bond to the metal center produces **3-*d*^{4}**. The low deuterium content in the product (30%) can be attributed to the H−D exchange of intermediate **B** with the acid present in the solution, which consequently gives rise to the formation of the nondeuterated product **3**.

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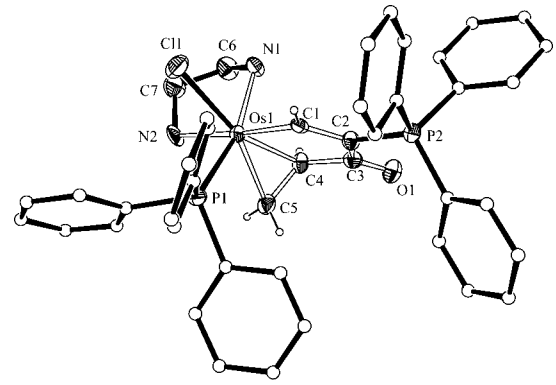
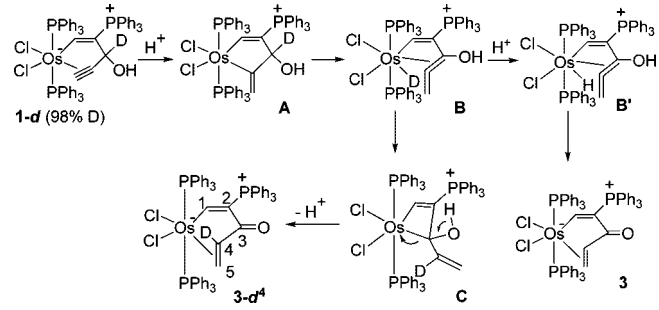
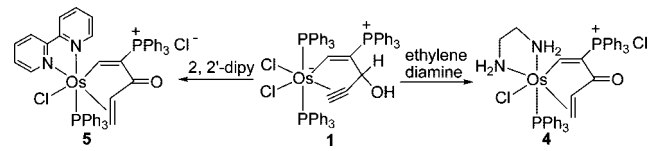


Figure 2. Molecular structure for the complex cation of **4** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 1.971(6), Os1−C5 = 2.135(6), Os1−C4 = 2.124(5), Os1−N1 = 2.153(4), Os1−N2 = 2.234(5), O1−C3 = 1.222(6), C1−C2 = 1.365(7), C2−C3 = 1.451(8), C3−C4 = 1.484(8), C4−C5 = 1.391(8); C1−Os1−C5 = 94.4(2), C1−Os1−C4 = 78.3(2), C4−Os1−C5 = 38.1(2), N1−Os1−N2 = 77.5 (2), C1−C2−C3 = 114.5(5), C2−C3−C4 = 112.4(5), C3−C4−C5 = 120.2(5), O1−C3−C4 = 121.7(5), O1−C3−C2 = 125.9(5).

Scheme 5. Possible Mechanism for the Conversion of 1 to 3



Scheme 6



Reaction of OsCl$_2$(CH═C(PPh$_3$)CH(OH)-η^2-C≡CH)(PPh$_3$)$_2$ (1) with Basic Ligand. In order to see whether the acidic condition is necessary for the transformation of the coordinated alkynol to coordinated α,β-unsaturated ketone osmacycle, we carried out the reaction of **1** with basic reagent. Whereas treatment of **1** with inorganic base such as NaOH, NaHCO$_3$, and K$_2$CO$_3$ or with organic base such as LDA and Et$_3$N did yield mixtures of unidentified decomposed products, the reaction of **1** with excess ethylene diamine in CH$_2$Cl$_2$ indeed generated complex **4**, analogous to **3**, which could be isolated in 53% yield (Scheme 6).

The structure of **4** has also been established by X-ray diffraction. As shown in Figure 2, the complex cation of **4** contains a coordinated α,β-unsaturated ketone osmacycle with one Cl and one PPh$_3$ ligand in **3** replaced by the ethylene diamine ligand. The similar conjugated delocalization of the five-membered osmacycle Os1−C1−C2−C3−C4 was confirmed by the bond distances of the penta-1,4-dien-3-one ligand. The dihedral angle between the Os1−C4−C5 plane and the Os1−C1−C2−C3−C4 plane is 113.2°.

In agreement with the solid state structure, the ^{31}P{^{1}H} NMR spectrum showed one C*P*Ph$_3$ signal at $\delta = 9.6$ ppm and one

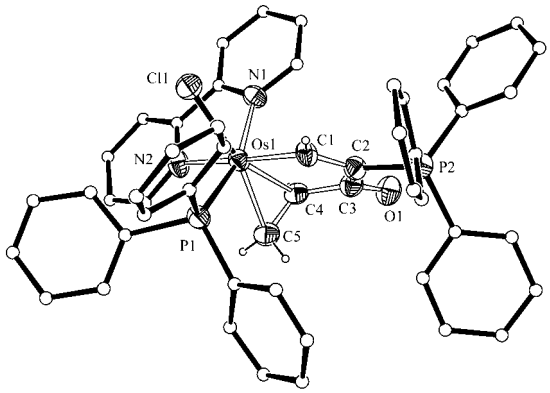


Figure 3. Molecular structure for the complex cation of **5** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 1.985(7), Os1−C5 = 2.141(8), Os1−C4 = 2.153(7), Os1−N1 = 2.163(6), Os1−N2 = 2.111(6), O1−C3 = 1.216(9), C1−C2 = 1.365(11), C2−C3 = 1.457(10), C3−C4 = 1.495(11), C4−C5 = 1.395(11), C1−Os1−C5 = 89.8(3), C1−Os1−C4 = 79.1(3), C4−Os1−C5 = 37.9(3), N1−Os1−N2 = 75.4(3), C1−C2−C3 = 116.1(6), C2−C3−C4 = 112.2(6), C3−C4−C5 = 118.7(7), O1−C3−C4 = 123.2(7), O1−C3−C2 = 124.6(7).

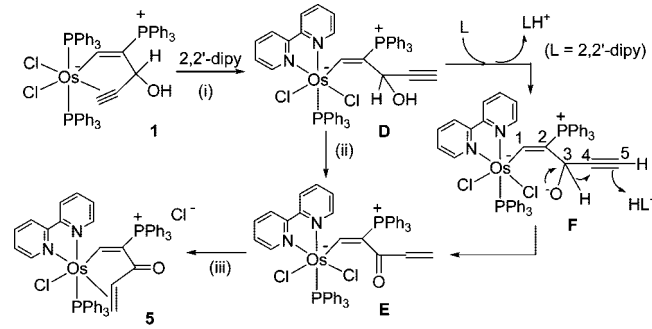
Os*P*Ph$_3$ signal at 0.2 ppm. In the ^{1}H NMR spectrum, the signal attributed to Os*CH* appeared at δ = 13.9 ppm. The signals of protons of the C4−C5 bond appeared at δ = 4.5, 2.8, and 2.4 ppm. In an osmahexatriene complex having a similar terminal coordinated double-bond structure, the three proton signals were observed at comparable chemical shifts (δ = 4.6, 3.7, and 2.6 ppm).[13c] The signals of $H_2NCH_2CH_2NH_2$ were observed at δ = 2.1−4.2 ppm (close to those of $H_2NCH_2CH_2NH_2$-coordinated osmium complexes[15]). In the ^{13}C{^{1}H} NMR spectrum, signals of the five carbons within the central osmallacycle ring were observed at δ = 228.4 (Os*C*H), 210.6 (*C*(O)), 117.9 (*C*(PPh$_3$), 65.1 (*C*HCH$_2$), and 47.9 (s, CH*C*H$_2$) ppm, respectively.

In order to gain some clue to better understand the mechanism for the transformation and to see whether the active hydrogens in $H_2NCH_2CH_2NH_2$ are critical for the transformation, we have performed the reaction of **1** with the weakly basic bidentate ligand 2,2′-bipyridine (2,2′-bipy) without any active hydrogens. In the same way, the reaction led to the formation of a similar 2,2′-bipy-substituted α,β-unsaturated ketone osmacycle **5**, which was isolated in 67% yield (Scheme 6). The structure of **5** has also been confirmed by X-ray diffration (Figure 3).

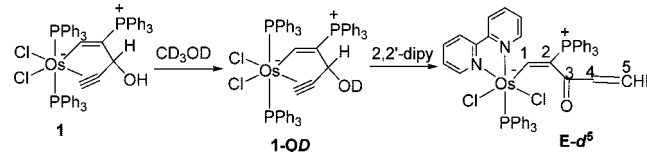
The solid state structure of **5** is also fully supported by the solution NMR spectroscopic data and elemental analysis. The ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ showed one C*P*Ph$_3$ signal at δ = 11.7 ppm and one Os*P*Ph$_3$ signal at δ = −7.6 ppm. In the ^{1}H NMR spectrum, four signals of the protons in the metallacycle were observed at δ = 14.2, 3.2, 2.8, and 1.8 ppm, respectively, which are close to those of **4**.

Thus the coordinated α,β-unsaturated ketone osmacycle could also be generated from **1** under basic conditions. According to the results of the *in situ* NMR, a multistep pathway has been presumed for the reaction of **1** with 2,2′-bipyridine, which includes (i) the replacement of one PPh$_3$ ligand and the coordinated alkyne by 2,2′-bipyridine to give intermediate **D**, (ii) transformation from alkyne alcohols to α,β-unsaturated ketones to produce **E**, and (iii) dissociation of one chloride atom from osmium and concomitant coordination of the terminal double bond (Scheme 7).

Scheme 7. Proposed Mechanism for the Formation of 5



Scheme 8



The key intermediate **E** can be successfully observed from the *in situ* NMR and remains almost unchanged for approximately 2 h. The ^{31}P{^{1}H} NMR spectrum showed one C*P*Ph$_3$ signal at δ = 11.6 ppm and one Os*P*Ph$_3$ signal at δ = −1.0 ppm. In the ^{1}H NMR spectrum in CD_2Cl_2, three proton signals attributed to CHCH$_2$ appeared at δ = 6.4 (CHC*H*$_2$), 5.8 (C*H*CH$_2$), and 4.4 (CHC*H*$_2$) ppm, respectively, which were comparable with those of a normal uncoordinated terminal double bond.[16] Another proton signal attributed to Os*CH* was observed at δ = 11.6 ppm.

Different from the acid-catalyzed hydrogen transfer process for the formation of **3**, transformation of the alkyne alcohol in **D** to the α,β-unsaturated ketone in **E** is likely initiated by the deprotonation of the hydroxyl by the basic ligand 2,2′-bipy to give intermediate **F**, which was followed by protonation at C5 and concomitant 1,2-shift of the H at C3 to C4. In fact, a similar 1,2-H shift has been proposed for the redox isomerization of propargyl alcohols to enals and enones by Trost et al.[17] Consistent with this proposal, treatment of **1** with CD_3OD (excess) and 2,2′-bipy subsequently (supposing **1-O*D*** was formed first) led to the formation of **E-*d*^{5}** exclusively (Scheme 8). As indicated by the *in situ* NMR, the peak at δ 6.4 ppm (CHC*H*$_2$) present in the protio compound **E** is almost totally missing, while the two proton signals at δ 5.8 (C*H*CH$_2$) and 4.4 (CHC*H*$_2$) ppm remain with a 1:1 integral ratio.

Reaction of OsCl$_2$(CH═C(PPh$_3$)CH(OH)-η^2-C≡CH)(PPh$_3$)$_2$ (1) with PMe$_3$ and PBu$_3$. We have reported that the reactive intermediate **1** could react with PPh$_3$ to produce the osmabenzene **2** via nucleophilic attack at the coordinated alkyne by PPh$_3$.[5] We now extend the phosphine nucleophiles to PMe$_3$ and PBu$_3$. However, the reactions took place by different paths. Again, other α,β-unsaturated ketone osmacyclic complexes were afforded as the final products.

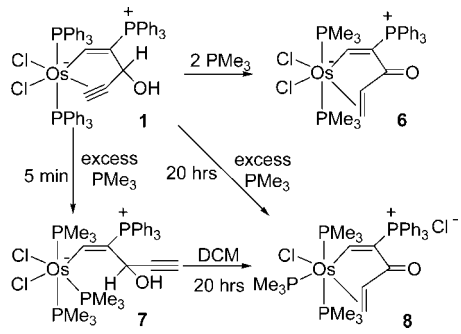
Treatment of **1** with 2 equiv of PMe$_3$ produced the bis-trimethylphosphine-coordinated complex **6** with the same ring structure as above-mentioned complexes **3**−**5** (Scheme 9) and

(15) (a) Peacock, A. F. A.; Habtemariam, A.; Fernández, R.; Walland, V.; Fabbiani, F. P. A.; Parsons, S.; Aird, R. E.; Jodrell, D. I.; Sadler, P. *J. Am. Chem. Soc.* **2006**, *128*, 1739. (b) McQueen, J. S.; Nagao, N.; Eberspacher, T.; Li, Z. W.; Taube, H. *Inorg. Chem.* **2003**, *42*, 3815. (c) Murmann, R. K.; Barnes, C. L. *Inorg. Chem.* **2001**, *40*, 6514.

(16) Zabawa, T. P.; Chemler, S. R. *Org. Lett.* **2007**, *9*, 2035.

(17) (a) Trost, B. M.; Livingston, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 9586. (b) Trost, B. M.; Livingston, R. C. *J. Am. Chem. Soc.* **2008**, *130*, 11970.

Scheme 9



was isolated in 70% yield. The structure of **6** could be readily assigned on the basis of the NMR data. The $^{31}P\{^1H\}$ NMR spectrum showed three singlet peaks at $\delta = 11.4$ (C*P*Ph$_3$), −34.7 (Os*P*Me$_3$), and −37.2 (Os*P*Me$_3$) ppm. The two PMe$_3$ signals on the osmium were different from each other due to the slightly different steric environments. In the ^1H NMR spectrum, the four signals of protons on the central ring appeared at $\delta = 13.9$ (OsC*H*), 3.4 (CHCH_2), 2.8 (*CH*CH$_2$), and 2.1 (CHCH_2) ppm, respectively, which were also close to the similar osmacycles mentioned above. In the $^{13}C\{^1H\}$ NMR spectrum, the five carbon signals on the central ring were observed at $\delta = 229.0$ (Os*C*H), 214.4 (*C*O), 110.0 (*C*PPh$_3$), 54.6 (*C*HCH$_2$), and 44.2 (CH*C*H$_2$) ppm.

When excess PMe$_3$ was added into a suspension of **1** in CH_2Cl_2, the reaction went differently. A tris-trimethylphosphine-coordinated complex **7** could be generated within 10 min and was isolated in 88% yield.

As can be judged on the basis of NMR data, **7** has a structure containing an uncoordinated terminal alkyne. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed one C*P*Ph$_3$ signal at $\delta = 11.2$ (dt, J(PP) = 27.9 Hz, 5.1 Hz) ppm and two Os*P*Me$_3$ signals at $\delta = -48.6$ (dd, J(PP) = 21.8 Hz, 5.1 Hz) and −53.8 (dt, J(PP) = 27.9 Hz, 21.8 Hz) ppm, respectively. Their integral ratio indicated the presence of three PMe$_3$ ligands on the metal atom. In the ^1H NMR spectrum, four characteristic signals could be observed at $\delta = 10.5$ (OsC*H*), 4.3 (C*H*OH), 2.3 (O*H*), and 2.0 (C≡C*H*) ppm. The ^{13}C NMR spectrum showed five signals at $\delta = 213.4$ (Os*C*H), 120.5 (*C*PPh$_3$), 92.4 (*C*≡CH), 77.2 (C≡*C*H), and 51.9 (*C*HOH) ppm for the carbons on the central structure. In particular, the ^{13}C signals of C≡CH observed at $\delta = 92.4$ and 77.2 ppm and the ^1H signal at $\delta = 2.0$ ppm were comparable with normal terminal alkyne C≡CH,[18] which clearly indicated the terminal triple bond was not coordinated to the metal atom.

The powder of **7** could only survive for several days under a nitrogen atmosphere at −18 °C. In a solution of CH_2Cl_2, **7** transformed completely to other species at room temperature within 2 h. As can be seen from the *in situ* ^1H and ^{31}P NMR spectra, more than four species were produced, from which the comparatively stable complex **8**, as the major product, could be isolated by column chromatography in 16% yield. Complex **8** could also be produced directly from the reaction of **1** with excess PMe$_3$ and isolated in comparable yield. We have previously reported that complex **8** could also be generated in high yield (92%) from the reaction of complex **3** with excess PMe$_3$ in CH_2Cl_2, which slowly isomerized in chloroform solution to the interesting *p*-osmaphenol complex **12** (see below).[7]

(18) Asano, Y.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2007**, *9*, 3901.

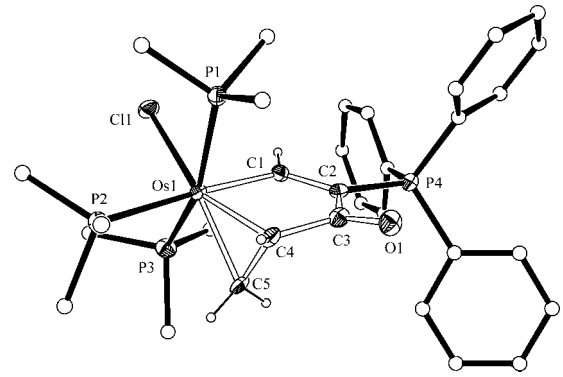
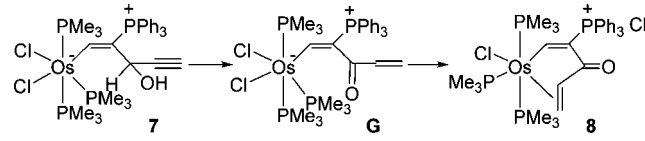
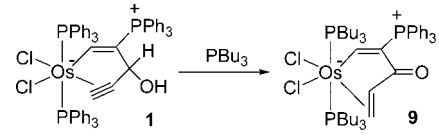


Figure 4. Molecular structure for the complex cation of **8** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 2.019(4), Os1−C5 = 2.143(3), Os1−C4 = 2.153(3), O1−C3 = 1.233(4), C1−C2 = 1.376(5), C2−C3 = 1.460(5), C3−C4 = 1.497(5), C4−C5 = 1.421(5); C1−Os1−C5 = 87.1(2), C1−Os1−C4 = 78.1(1), C4−Os1−C5 = 38.6 (1), C1−C2−C3 = 114.0(3), C2−C3−C4 = 112.8(3), C3−C4−C5 = 115.9(3), O1−C3−C4 = 123.5(3), O1−C3−C2 = 123.7(4).

Scheme 10. Possible Mechanism for the Conversion of 7 to 8



Scheme 11



The structure of **8** has been confirmed by an X-ray diffraction study (Figure 4) and is similar to that of **3** with the PPh$_3$ and one of the chloride ligands replaced by PMe$_3$ to give the cationic structure.

The isolation of **7** and its conversion to **8** provide firm support for the mechanistic proposal of a noncoordinated alkyne intermediate **D** mentioned in Scheme 6 for the formation of **5** from the reaction of **1** with 2,2′-bipyridine. Consistently, the observation of the noncoordinated alkene intermediate **E** mentioned previously (Scheme 7) may indicate analogous intermediacy for the conversion of **7** to **8** (Scheme 10).

Treatment of **1** with excess PBu$_3$ produced the bis-tributylphosphine-coordinated complex **9**, which could be isolated in 78% yield by column chromatography (Scheme 11). The $^{31}P\{^1H\}$, ^1H, and ^{13}C NMR data of **9** were very similar to those of **6**, implying that the two complexes have similar structures. Even if an excess of PBu$_3$ was added in the reaction, **9** was the only isolated product in similar yield. Probably, PBu$_3$ is more bulky than PMe$_3$; it is difficult for PBu$_3$ to form the tris-coordinated species analogous to **7** or **8**.

It is interesting to note that the reaction of **1** with PPh$_3$ produces the osmabenzene complex **2**,[5] while the reactions with PMe$_3$ and PBu$_3$ take place very differently and afford the α,β-unsaturated ketone osmacyclic products instead. This might be attributed to the different steric and electronic effects as well as the coordination ability of the phosphine ligands.

Similar Chemistry of OsBr$_2$(CH═C(PPh$_3$)CH(OH)-η^2-C≡CH)(PPh$_3$)$_2$ (10). Similar chemistry was also observed starting from OsBr$_2$(CH═C(PPh$_3$)CH(OH)-η^2-C≡CH)(PPh$_3$)$_2$ (**10**).[5] Thus treatment of **10** with acetic acid for 5 h led to the

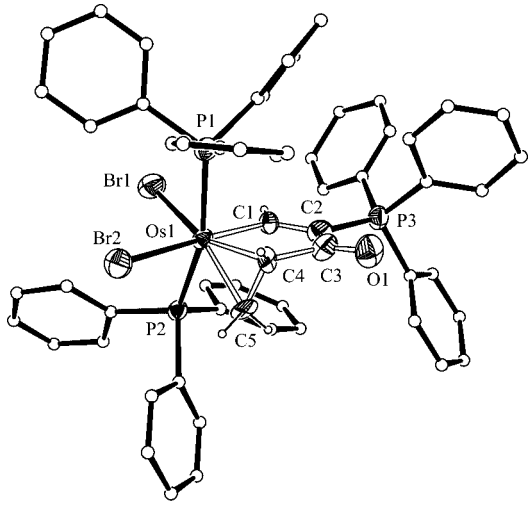
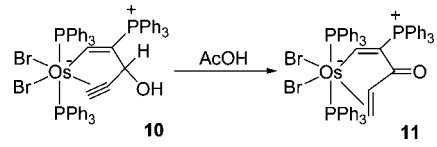


Figure 5. ORTEP plot of **11** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 2.004(8), Os1−C5 = 2.143(8), Os1−C4 = 2.151(8), O1−C3 = 1.221(13), C1−C2 = 1.373(14), C2−C3 = 1.516(14), C3−C4 = 1.519(14),C4−C5=1.417(13),C1−Os1−C5=90.1(4),C1−Os1−C4 = 80.2(4), C4−Os1−C5 = 38.5(4), C1−C2−C3 = 114.5(9), C2−C3−C4 = 112.3(9), C3−C4−C5 = 111.5(9), O1−C3−C4 = 123.2(10), O1−C3−C2 = 124.4 (10).

Scheme 12



precipitation of **11**, with a similar structure to that of **3** (Figure 5), in good yield (Scheme 12). The result indicates that different halogen atoms on the osmium do not affect the rearrangement of the coordinated alkyne alcohol to the α,β-unsaturated ketone osmacycles.

Air Stability and Solution Stability Studies on α,β-Unsaturated Ketone Osmacycles. We have investigated several uncommon classes of five- and six-membered metallacycles and recently reported the synthesis of osmabenzenes,[5] ruthenabenzenes,[19,20] bridged iridacycles,[21] and related complexes containing phosphoniums on the metallacycles.[22] It was found that the introduction of bulky phosphoniums could improve the stability of these products to some extent by the protecting effects.

In the solid state, all the α,β-unsaturated ketone osmacycles described above could be stored in air without noticeable change for several months, and most of them are also solution-stable except for complexes **6** and **8**.

Stirring a solution of **8** in dry chloroform for about five days led to the formation of the first stable *p*-metallaphenol, **12** (Scheme 13). We have reported the synthesis, characterization (Figure 6), and formation mechanism of the interesting complex in a previous communication.[7]

In sharp contrast, when **8** was dissolved in wet chloroform and stirred for five days, the osmafuran **13** could be isolated in

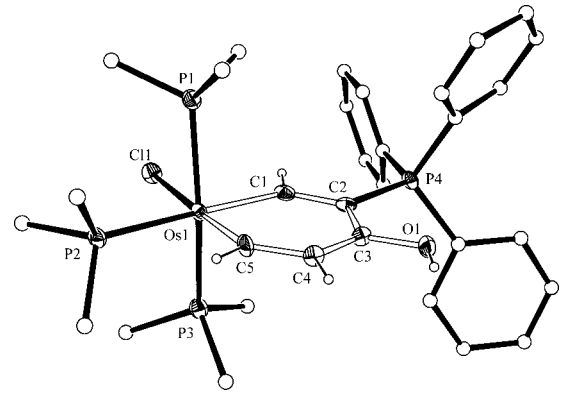


Figure 6. Molecular structure for the complex cation of **12** (50% probability displacement ellipsoids). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 = 2.032(5), Os1−C5 = 1.918(6), O1−C3 = 1.349(6), C1−C2 = 1.388(8), C2−C3 = 1.444(7), C3−C4 = 1.377(7), C4−C5 = 1.385(8); C1−Os1−C5 = 87.3(2), Os1−C1−C2 = 130.0(4), C1−C2−C3 = 121.9(5), C2−C3−C4 = 123.5(5), C3−C4−C5 = 124.6(5), C4−C5−Os1 = 132.4(4).

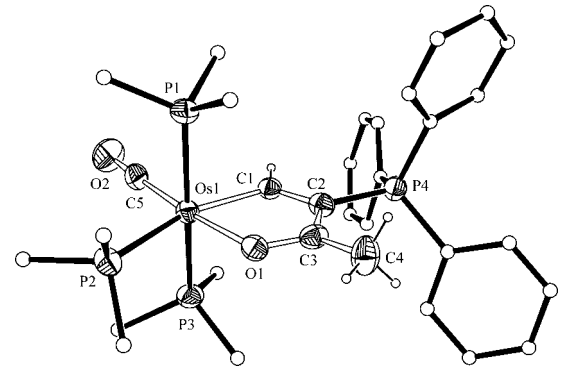
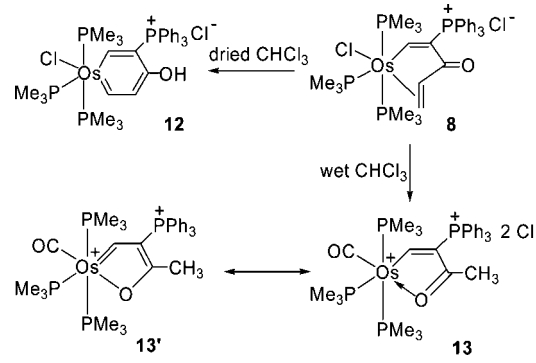


Figure 7. Molecular structure for the complex cation of **13** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 2.038(5), Os1−C5 = 1.847(6), Os1−O1 = 2.130(4), O1−C3 = 1.275(7), O2−C5 = 1.164(8), C1−C2 = 1.381(8), C2−C3 = 1.438(8), C3−C4 = 1.502(8); C1−Os1−C5 = 100.0(2), O1−Os1−C5 = 175.0(2), C1−Os1−O1 = 75.8(2), O2−C5−Os1 = 178.2(6) C1−C2−C3 = 114.3(5), C2−C3−C4 = 127.0(5), C2−C3−O1 = 115.6(5), C4−C3−O1 = 117.3(5).

Scheme 13

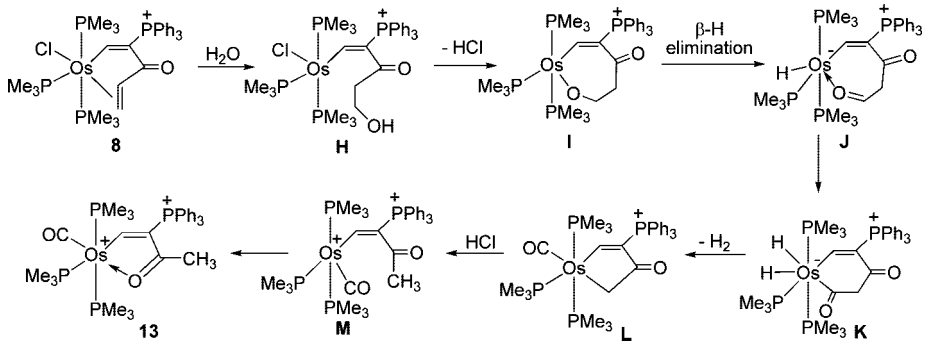


52% yield (Scheme 13), whose structure has also been determined by X-ray diffraction (Figure 7).

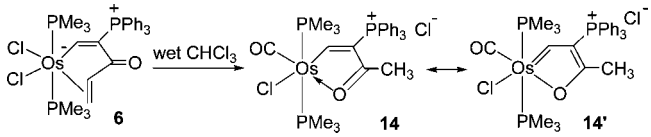
The X-ray structure clearly shows that the complex has an essentially planar five-membered metallacycle with one phosphonium and one methyl substituent (Figure 7). The perfect coplanarity is reflected by the small rms deviation (0.0095 Å) from the least-squares plane through the five atoms Os1/C1/

(19) Zhang, H.; Xia, H. P.; He, G. M.; Wen, T. B.; Gong, L.; Jia, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2920.
(20) Zhang, H.; Feng, L.; Gong, L.; Wu, L.; He, G.; Wen, T. B.; Yang, F.; Xia, H. *Organometallics* **2007**, *26*, 2705.
(21) Gong, L.; Wu, L.; Lin, Y.; Zhang, H.; Yang, F.; Wen, T.; Xia, H. *Dalton Trans.* **2007**, 4122.
(22) Gong, L.; Lin, Y.; Wen, T. B.; Zhang, H.; Zeng, B.; Xia, H. *Organometallics* **2008**, *27*, 2584.

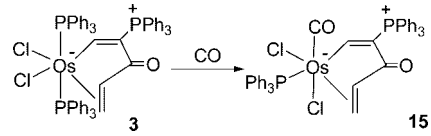
Scheme 14



Scheme 15



Scheme 16



C2/C3/O1. The Os1−C1 bond length is 2.038(5) Å, which is comparable to that of Os{CHCHC(CH$_3$)O}(η^2-H$_2$)(SnPh$_2$Cl)-(P^{i}Pr$_3$)$_2$ (2.035(2) Å).[23a] The C1−C2 and C2−C3 distances are 1.381(8) and 1.438(8) Å, respectively. These values are between those expected for single and double carbon−carbon bonds. The O1−C3 (1.275(7) Å) and Os1−O1 (2.130(4) Å) values are quite similar to those found in the osmafuran Os(CHCHC(O)Ph-)Cl(CO)(P^{i}Pr$_3$)$_2$ (1.283(4) and 2.130(4) Å, respectively). The two resonance forms **13** and **13′** shown in Scheme 13 should be taken into account to describe the bonding pattern of the heterocycle.[23b] The solution NMR spectroscopic data are consistent with the solid state structure. The ^{1}H NMR spectrum showed a characteristic Os*CH* proton signal at δ = 12.2 ppm. The ^{13}C{^{1}H} NMR spectrum showed the three carbon signals of the metallacycle at δ = 213.7 (Os*C*H), 180.1 (*C*(CH$_3$)), and 120.7 (*C*PPh$_3$) ppm. Those for CO on the metal atom and methyl substituent could be observed at δ = 260.1 (*C*O) and 32.0 (*C*H$_3$) ppm.

A plausible mechanism for the formation of **13** is shown in Scheme 14. The process may be initiated by the addition reaction of water to the coordinated terminal double bond to give **H**, which then undergoes dehydrochlorination to generate **I**. β-H elimination produces the metal hydride **J**. Oxidative addition of the aldehyde C−H to the osmium center gives the dihydride-acyl intermediate **K**, which was followed by loss of H$_2$ together with deinsertion of the carbonyl from the acyl to give **L**. Protolysis of the alkyl by the initially eliminated HCl and subsequent coordination of the lone pair electrons of the oxygen atom in the carbonyl group to the osmium center produces the osmafuran **13**.

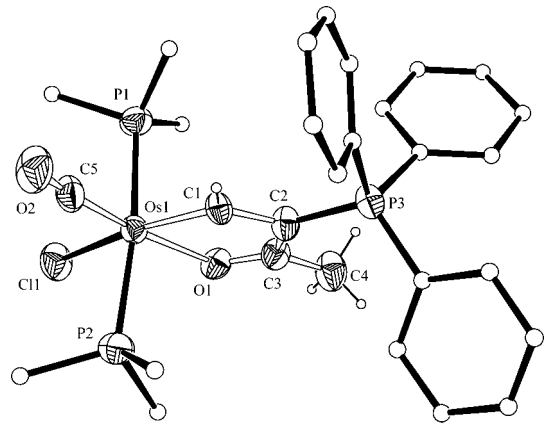


Figure 8. Molecular structure for the complex cation of **14** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 1.960(6), Os1−C5 = 1.858(7), Os1−O1 = 2.147(5), O1−C3 = 1.251(10), O2−C5 = 1.135(8), C1−C2 = 1.402(9), C2−C3 = 1.430(9), C3−C4 = 1.500(10); C1−Os1−O1 = 77.0(2), C3−O1−Os1 = 114.8(4), C2−C1−Os1 = 117.6(5), O1−C3−C2 = 117.3(7), O1−C3−C4 = 117.3(6), C2−C3−C4 = 125.3(7), O2−C5−Os1 = 173.3(6).

As compared to **8**, complex **6** was stable in dry solvent and remained almost unchanged for several days. In a similar manner, it also transformed into the similar osmafuran complex **14** in wet chloroform (Scheme 15). The structure of **14** has been confirmed by X-ray diffraction (Figure 8).

As one class of aromatic five-membered metallacycles, metallafurans have been prepared by various routes.[24] The hydrolysis reactions of α,β-unsaturated ketone osmacycles mentioned above provide available and efficient synthesis methods for osmafurans.

Thermoanalysis of α,β-Unsaturated Ketone Osmacycles. The thermostability of the complexes has been studied. As a representative example, **3** has excellent thermal stability and air stability, which were confirmed by thermoanalysis (TG) in air.[25] The powder of **3** remained almost unchanged until 240 °C. **3** was also stable in the refluxed solution of CHCl$_3$ under nitrogen atmosphere within two weeks.

Chemical Stability of α,β-Unsaturated Ketone Osmacycles. Complex **3** has also been studied as a typical example in its chemical stability. When complex **3** was treated with other 2*e* donor ligands, the metallacyclic framework remained unchanged. For example, as shown in Scheme 16, treatment of **3** with CO led only to the substitution of one PPh$_3$ ligand by a CO ligand. Complex **15** was isolated in 85% yield. The structure of product **15** has also been determined by X-ray diffraction

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(25) See Supporting Information.

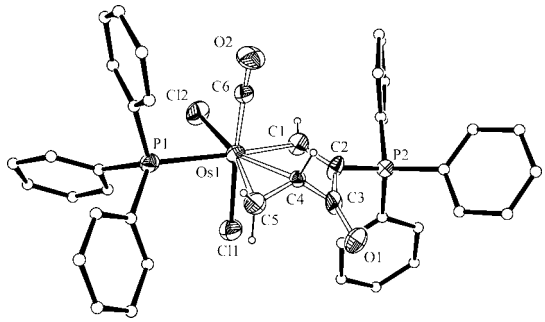

Figure 9. ORTEP plot of **15** (50% probability displacement ellipsoids). Selected distances (Å) and angles (deg): Os1−C1 = 2.053(12), Os1−C5 = 2.194(13), Os1−C4 = 2.106(11), Os1−C6 = 1.842(11), O1−C3 = 1.200(16), O2−C6 = 1.099(14), C1−C2 = 1.224(19), C2−C3 = 1.462(18), C3−C4 = 1.520(18), C4−C5 = 1.404(16); C1−Os1−C5 = 107.0(5), C1−Os1−C4 = 71.5(4), C4−Os1−C5 = 38.1(4), C1−C2−C3 = 112.6(12), C2−C3−C4 = 104.6(10), C3−C4−C5 = 124.7(11), O1−C3−C4 = 126.0(13), O1−C3−C2 = 129.4(14), O2−C6−Os1 = 177.3(11).

(Figure 9). Compared with the former complexes, the five-membered ring Os1−C1−C2−C3−C4 was distorted remarkably with a dihedral angle of 32.1° between the two planes passing through Os1−C1−C4 and C1−C2−C3-C4. This nonplanarity might reflect the strong influence exerted by the CO group, whose position of substitution could be readily rationalized. Because the CO ligand is a strong π-acceptor, it favors occupying the position trans to the donor ligand Cl. Such results also suggested the good chemical stability of the coordinated α,β-unsaturated ketone metallacyclic framework of **3**.

Conclusion

During our investigation on the reactivity of the osmacycle-containing coordinated alkyne alcohol $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**1**) toward different reagents, we have studied the reactions of **1** with acetic acid, ethylene diamine, 2,2′-bipyridine, PMe_3, and PBu^n_3, respectively. These reactions led to the formation of several conjugated osmacycles bearing coordinated η^2-α,β-unsaturated ketone. All these cyclic α,β-unsaturated ketone complexes are air stable in the solid state, and most of them are also stable in solution except for $OsCl_2(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PMe_3)_2$ (**6**) and $[OsCl(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PMe_3)_3]Cl$ (**8**). Complex **8** can isomerize to the osmaphenol $[OsCl(CHC(PPh_3)C(OH)CHCH)(PMe_3)_3]Cl$ (**12**) as the major product in dry chloroform, but transforms into the osmafuran $[Os(CO)(CHC(PPh_3)C(CH_3)O)(PMe_3)_3]Cl_2$ (**13**) in wet chloroform, while complex **6** was stable in dry solvent, but can convert to the osmafuran $[OsCl(CO)(CHC(PPh_3)C(CH_3)O)(PMe_3)_2]Cl$ (**14**). The remarkable thermostability of the coordinated α,β-unsaturated ketone osmacycles has been studied preliminarily with **3** as a representative example. The coordinated α,β-unsaturated ketone metallacyclic framework of **3** is stable in different ligand environments. Treatment of **3** with carbon monoxide led only to ligand substitution to produce $OsCl_2(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(CO)(PPh_3)$ (**15**).

Experimental Section

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 (hexane, ether, THF) or calcium hydride (CH_2Cl_2, $CHCl_3$). The starting complex $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**1**) was prepared by treatment of $OsCl_2(PPh_3)_3$ and $HC{\equiv}CCH(OH)C{\equiv}CH$ in THF for 15 min.[5] $OsCl_2(CH{=}C(PPh_3)CD(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**1-*d***) was prepared by the same procedure as **1**, with the use of $HC{\equiv}CCD(OH)C{\equiv}CH$ instead of $HC{\equiv}CCH(OH)C{\equiv}CH$. $HC{\equiv}CCD(OH)C{\equiv}CH$ was in turn prepared according to the literature method using DCOOEt instead of HCOOEt.[26] $OsBr_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**10**) was prepared by treatment of $OsBr_2(PPh_3)_3$ and $HC{\equiv}CCH(OH)C{\equiv}CH$ in THF for 15 min.[5] Column chromatography was performed on silica gel (300−400 mesh) or alumina gel (200−300 mesh). NMR experiments were performed on a Bruker ARX-300 spectrometer (^1H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz) or a Varian Unity Plus-500 spectrometer (^1H 500.40 MHz; ^{13}C 125.7 MHz; ^{31}P 202.4 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 data were obtained on a Thermo Quest Italia SPA EA 1110.

$OsCl_2(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PPh_3)_2$ (3). Glacial acetic acid (0.10 mL, 1.7 mmol) was added dropwise to a suspension of $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**1**) (1.6 g, 1.4 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for ca. 4 h to give a red precipitate, which was collected by filtration, washed with dichloromethane (5 × 2 mL), and dried under vacuum. Yield: 1.5 g, 90%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 7.1 (s, C*P*Ph_3), −3.9 (d, J(PP) = 256.9 Hz, Os*P*Ph_3), −15.2 (d, J(PP) = 256.9 Hz, Os*P*Ph_3) ppm. ^1H NMR (CD_2Cl_2, 300.1 MHz): δ 12.9 (d, J(PH) = 15.3 Hz, 1H, Os*CH*), 3.6 (m, 1H, CHC*H*$_2$), 3.2 (m, 1H, C*H*CH$_2$), 2.8 (m, 1H, CHC*H*$_2$), 6.8−7.9 (m, 45H, PPh_3) ppm. Anal. Calcd for $C_{59}H_{49}OP_3Cl_2Os$: C, 62.82; H, 4.38. Found: C, 62.55; H, 4.86.

$[OsCl(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PPh_3)(H_2NCH_2CH_2NH_2)]Cl$ (4). To a suspension of $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C‘CH)(PPh_3)_2$ (**1**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL) was added distilled $H_2NCH_2CH_2NH_2$ (en) (0.15 mL, 2.3 mmol) dropwisely. The reaction mixture was stirred at room temperature for about 12 h to give a brown solution. The volume of the mixture was reduced to approximately 1−2 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol, 8:1) to give **4** as a brownish-red solid. Yield: 0.35 g, 53%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 9.6 (d, J(PP) = 1.2 Hz, CPPh_3), 0.2 (d, J(PP) = 1.2 Hz, Os*P*Ph_3) ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 13.9 (dd, J(PH) = 18.3 Hz, J(PH) = 4.5 Hz, 1 H, Os*CH*), 7.1−7.9 (m, 30 H, PPh_3), 4.5 (m, 1 H, CHC*H*$_2$), 2.8 (m, 1 H, C*H*CH$_2$), 2.4 (m, 1 H, CHC*H*$_2$), 2.1−4.2 ppm (m, 8 H, en) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 228.4 (d, J(PC) = 3.8 Hz, Os*C*H), 210.6 (dd, J(PC) = 16.6 Hz, 1.5 Hz, *C*(O)), 123.5−135.0 (m, PPh_3), 117.9 (d, J (PC) = 77.0 Hz, OsCH*C*(PPh_3), 65.1 (dd, J(PC) = 11.3 Hz, 1.5 Hz, *C*HCH$_2$), 47.9 (s, CH*C*H$_2$), 48.7 (d, J(PC) = 11.3 Hz, en), 44.0 (s, en) ppm. Anal. Calcd for $C_{43}H_{42}ON_2Cl_2P_2Os$: C, 55.78; H, 4.57; N, 3.03. Found: C, 56.00; H, 4.85; N, 2.66.

$[OsCl(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PPh_3)(2,2'\text{-bipy})]Cl$ (5). A mixture of $OsCl_2(CH{=}C(PPh_3)CH(OH)\text{-}\eta^2\text{-}C{\equiv}CH)(PPh_3)_2$ (**1**) (0.80 g, 0.71 mmol) and 2,2′-bipyridine (0.17 mg, 1.1 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for ca. 20 h to give a brownish-red solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol, 5:1) to give **5** as a red solid. Yield: 0.48 g, 67%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 11.7 (d, J(PP) = 1.2 Hz, CPPh_3), −7.6 (d, J(PP) = 1.2 Hz, Os*P*Ph_3) ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 14.2 (dd, J(PH) = 18.3 Hz, J(PH) = 4.5 Hz, 1H, Os*CH*), 3.2 (m, 1 H, CHC*H*$_2$), 2.8 (m, 1 H, C*H*CH$_2$), 1.8 (m, 1 H, CHC*H*$_2$), 7.8−9.0 (m, 8 H, 2,2′-bipy), 7.1−7.7 (m, 30 H, PPh_3)

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ppm. Anal. Calcd for $C_{51}H_{42}O\,N_2Cl_2P_2Os$: C, 59.94; H, 4.14; N, 2.74. Found: C, 59.53; H, 4.42; N, 2.99.

Observation of [$OsCl_2$(CH═C(PPh_3)C(O)CH═CH_2)(PPh_3)(2,2′-bipy)] (E). To an NMR tube charged with $OsCl_2$(CH═C(PPh_3)CH-(OH)-η^2-C≡CH) (PPh_3)$_2$ (**1**) (20 mg, 0.018mmol) and 2,2′-bipyridine (2.9 mg, 0.018 mmol) was added $CDCl_3$ (0.5 mL) under argon atmosphere. The NMR tube was shaken for a while, and the solution was allowed to stand for 2 h and monitored by ^{31}P and ^{1}H NMR. The ^{31}P{^{1}H} spectrum indicated formation of [$OsCl_2$(CH═C-(PPh_3)C(O)CH═CH_2)(PPh_3)(2,2′-bipy)] (**E**) as the predominant product. Storage of the solution for 20 h led to the formation of **5** as the major product. Characteristic NMR data of **E**: ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 11.6 (d, *J*(PP) = 3.6 Hz, CPPh_3), −1.0 (d, *J*(PP) = 3.6 Hz, Os*P*Ph_3) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 11.6 (d, *J*(PH) = 18.0 Hz, 1H, OsC*H*), 6.4 (m, 1 H, CHCH_2), 5.8 (m, 1 H, C*H*CH_2), 4.4 (m, 1 H, CHCH_2).

$OsCl_2$(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PMe_3)$_2$ (6). A solution of PMe_3 in THF (1.0 M; 1.5 mL, 1.5 mmol) was added to a suspension of $OsCl_2$(CH═C(PPh_3)CH(OH)-η^2-C≡CH) (PPh_3)$_2$ (**1**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for about 24 h to give a brownish-red solution. Brown, crude product was collected after the solvent was evaporated to dryness under vacuum. Purification by column chromatography (silica gel, eluent: dichloromethane/methanol, 6:1) gave **6** as a red solid. Yield: 0.37 g, 70%. ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$): δ 11.4 (s, C*P*Ph_3), −34.7 (d, *J*(PP) = 253.0 Hz, Os*P*Me_3), −37.2 (d, *J*(PP) = 253.0 Hz, Os*P*Me_3) ppm. ^{1}H NMR (500.40 MHz, $CDCl_3$): δ 13.9 (d, *J*(PH) = 15.0 Hz, 1 H, OsC*H*), 3.4 (m, 1 H, CHCH_2), 2.8 (m, 1 H, C*H*CH_2), 2.1 (m, 1 H, CHCH_2), 7.3−7.7 (m, 15 H, PPh_3), 1.2−1.5 (m, 18 H, PMe_3) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 229.0 (t, *J* (PC) = 8.4 Hz, Os*C*H), 214.4 (d, *J*(PC) = 16.8 Hz, *C*O), 133.9−122.0 (m, PPh_3), 110.0 (d, *J*(PC) = 76.2 Hz, *C*(PPh_3)), 54.6 (q, *J*(PC) = 8.2 Hz, *C*HCH$_2$), 44.2 (d, *J*(PC) = 8.1 Hz, CH*C*H$_2$), 12.4−14.3 (m, PMe_3) ppm. Anal. Calcd for $C_{29}H_{37}OCl_2P_3Os$: C, 46.09; H, 4.94. Found: C, 45.60; H, 5.42.

[OsCl(CH═C(PPh_3)CH(OH)C≡CH)(PMe_3)$_3$]Cl (7). A solution of PMe_3 in THF (1.0 M; 6.0 mL, 6.0 mmol) was added to the suspension of $OsCl_2$(CH═C(PPh_3)CH(OH)-η^2-C≡CH) (PPh_3)$_2$ (**1**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 5 min to give a brownish solution. Brown product was collected after the solvent was evaporated to dryness under vacuum, and the resulting residue was washed with ether (5 × 3 mL) then dried under vacuum. Yield: 0.51 g, 88%. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 11.2 (dt, *J*(PP) = 27.9 Hz, 5.1 Hz, C*P*Ph_3), −48.6 (dd, *J*(PP) = 21.8 Hz, 5.1 Hz, Os*P*Me_3), −53.8 (dt, *J*(PP) = 27.9 Hz, 21.8 Hz, Os*P*Me_3) ppm. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.5 (dd, 1 H, *J*(PH) = 22.2 Hz, 5.7 Hz, OsC*H*), 4.3 (d, 1 H, *J*(PH) = 14.4 Hz, C*H*OH), 2.3 (d, 1 H, *J*(PH) = 14.4 Hz, O*H*), 2.0 (s, 1 H, C≡C*H*), 1.2−1.8 (m, 27 H, PMe_3), 7.4−8.0 (m, 15 H, PPh_3) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 213.4 (ddt, *J*(PC) = 63.5 Hz, 4.5 Hz, 11.5 Hz, Os*C*H), 120.5 (d, *J*(PC) = 87.4 Hz, *C*PPh_3), 92.4 (d, *J*(PC) = 21.4 Hz, *C*≡CH), 77.2 (d, *J*(PC) = 25.9 Hz, C≡*C*H), 51.9 (d, *J*(PC) = 14.7 Hz, *C*HOH), 120.7−134.5 (m, PPh_3), 13.5−18.9 (m, PMe_3) ppm. Anal. Calcd for $C_{32}H_{46}OCl_2P_4Os$: C, 46.21; H, 5.57. Found: C, 45.79; H, 5.66.

[OsCl(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PMe_3)$_3$]Cl (8). Method A: A solution of OsCl(CH═C(PPh_3)CH(OH)C≡CH)(PMe_3)$_3$ (**7**) (0.50 g, 0.60 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for about 20 h to give a brownish-red solution. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (silica gel, eluent: dichloromethane /methanol, 5:1) to give **8** as a brownish-red solid. Yield: 0.080 g, 16%. **Method B:** A solution of PMe_3 in THF (1.0 M; 4.3 mL, 4.3 mmol) was added to a suspension of $OsCl_2$(CH═C(PPh_3)CH(OH)-η^2-C≡CH)(PPh_3)$_2$ (**1**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for about 20 h to give a brownish-red solution. Brown, crude product was collected after the solvent was evaporated to dryness under vacuum. The volume of the mixture was reduced to approximately 1 mL under vacuum. The residue was purified by column chromatography (silica gel, eluent: dichloromethane/methanol, 5:1) to give **8** as a brownish-red solid. Yield: 0.10 g, 17%. **Method C:** A PMe_3/THF solution (1.0 M, 5.4 mL, 5.4 mmol) was dropped into the suspension of $OsCl_2$(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PPh_3)$_2$ (**3**) (1.0 g, 0.89 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 8 h. Concentrating the solution to 4 mL and addition of ether (20 mL) to the residue produced an orange solid, which was collected by filtration, washed with ether (5 mL × 3), and dried under vacuum. Yield: 0.68 g, 92%. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 10.9 (dt, *J*(PP) = 22.6 Hz, 3.1 Hz, C*P*Ph_3), −45.9 (dd, *J*(PP) = 22.6 Hz, 3.1 Hz, Os*P*Me_3), −55.7 (dt, *J*(PP) = 22.6 Hz, 22.6 Hz, Os*P*Me_3) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.9 (d, 1 H, *J*(PH) = 21.0 Hz, OsC*H*), 3.2 (br, 1 H, C*H*CH_2), 3.0 (m, 1 H, CHCH_2), 2.1 (m, 1 H, CHCH_2), 1.0−1.5 (m, 27 H, PMe_3), 7.5−7.8 (m, 15 H, PPh_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 235.5 (ddt, *J*(PC) = 75.2 Hz, 7.3 Hz, 7.9 Hz, Os*C*H), 211.8 (dd, *J*(PC) = 18.1 Hz, 6.0 Hz, *C*O), 117.7 (d, *J*(PC) = 73.8 Hz, *C*PPh_3), 52.8 (d, *J*(PC) = 11.9 Hz, *C*HCH$_2$), 36.4 (s, CH*C*H$_2$), 119.6−134.8 (m, PPh_3), 14.7−17.4 (m, PMe_3) ppm. Anal. Calcd for $C_{32}H_{46}OCl_2P_4Os$: C, 46.21; H, 5.57. Found: C, 46.07; H, 5.76.

$OsCl_2$(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PBu_3)$_3$ (9). PBu_3 (0.50 mL, 2.2 mmol) was added to the suspension of $OsCl_2$(CH═C-(PPh_3)CH(OH)-η^2-C≡CH)(PPh_3)$_2$ (**1**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for about 20 h to give a brownish-red solution. Crude product was collected after the solvent was evaporated under vacuum, and the residue was washed with *n*-hexane (5 × 3 mL). Purification by column chromatography (silica gel, eluent: dichloromethane/acetone, 1:2) gave **9** as a red solid. Yield: 0.57 g, 78%. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 10.2 (s, C*P*Ph_3), −25.4 (d, *J*(PP) = 235.7 Hz, Os*P*Bu_3), −28.9 (d, *J*(PP) = 235.7 Hz, Os*P*Bu_3) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.6 (d, *J*(PH) = 14.4 Hz, 1H, OsC*H*), 3.6 (m, 1 H, CHCH_2), 3.4 (m, 1 H, C*H*CH_2), 2.3 (m, 1H, CHCH_2), 7.3−7.8 (m, 15H, PPh_3), 0.7−2.2 (m, 54H, PBu_3) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 228.7 (t, *J* (PC) = 8.1 Hz, Os*C*H), 213.8 (d, *J*(PC) = 16.6 Hz, *C*O), 120.8−133.7 (m, PPh_3), 109.4 (d, *J*(PC) = 79.3 Hz, *C*(PPh_3)), 54.0 (q, *J*(PC) = 8.0 Hz, *C*HCH$_2$), 42.7 (d, *J*(PC) = 8.5 Hz, CH*C*H$_2$), 21.5−25.6 (m, PBu_3) ppm. Anal. Calcd for $C_{47}H_{73}OCl_2P_3Os$: C, 55.99; H, 7.29. Found: C, 56.24; H, 7.52.

Os(CH═C(PPh_3)C(O)-η^2-CH═CH_2)Br_2(PPh_3)$_2$ (11). AcOH (0.050 mL) was dropped into a suspension of $OsBr_2$(CH═C(PPh_3)CH(OH)-η^2-C≡CH)(PPh_3)$_2$ (**10**) (0.80 g, 0.67 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for about 5 h to give a brownish-red suspension. The red solid was collected by filtration, washed with CH_2Cl_2 (5 × 3 mL), and then dried under vacuum. Yield: 0.65 g, 80%. ^{1}H NMR (500.4 MHz CD_2Cl_2): δ 13.1 (dd, 1H, *J*(PH) = 15.5 Hz, *J*(PH) = 2.0 Hz, OsC*H*), 6.7−7.8 (m, 45H, PPh_3), 3.4 (dd, 1H, *J*(PH) = 8.5 Hz, *J*(PH) = 4.5 Hz, CHCH_2), 2.9 (m, 1H, C*H*CH_2), 2.6 (m, 1H, CHCH_2) ppm. ^{31}P{^{1}H} NMR (202.4 MHz, CD_2Cl_2): δ 7.7 (s, C*P*Ph_3), −9.4 (d, *J*(PP) = 244.5 Hz, Os*P*Ph_3), −20.0 (d, *J*(PP) = 244.5 Hz, Os*P*Ph_3) ppm. Anal. Calcd for $OsP_3OC_{59}H_{49}Br_2$: C, 58.23; H, 4.06. Found: C, 58.52; H, 4.40.

[OsCl(CHC(PPh_3)C(OH)CHCH)(PMe_3)$_3$]Cl (12). A solution of [OsCl(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PMe_3)$_3$]Cl (**8**) (0.30 g, 0.36 mmol) dissolved in dry $CHCl_3$ was stirred for 5 days, dried under vacuum to get a purple-red solid, and washed with acetone (2 × 2 mL). Yield: (0.24 g, 80%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 21.2 (dt, *J*(PP) = 31.6, 2.4 Hz, C*P*Ph_3), −41.1 (dd, *J*(PP) = 27.9, 2.4 Hz, Os*P*Me_3), −47.2 (dt, *J*(PP) = 27.9, 31.6 Hz, Os*P*Me_3) ppm. ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 16.5 (dd, *J*(PH) = 18.4 Hz, *J*(HH) = 8.7 Hz, 1H, OsC*H*CH), 13.3 (d, *J*(PH) = 30.9 Hz, 1H, OsC*H*CPPh_3), 12.2 (s, 1H, O*H*), 8.4 (dd, *J*(HH) = 8.7 Hz, *J*(PH)

Table 1. X-ray Diffraction Structure Summary 1

	3·1.5H_2O·0.5CH_2Cl_2	**4**·2$CHCl_3$	**5**·0.25$CHCl_3$·0.5H_2O	**8**·3$CHCl_3$	**11**·CH_2Cl_2
formula	$C_{59}H_{49}Cl_2OsO·P_3·$ 1.5H_2O·0.5CH_2Cl_2	$C_{43}H_{42}ClOs·N_2O·$ $P_2·Cl·2CHCl_3$	$C_{51}H_{42}ClOsN_2O·$ $P_2·Cl·0.25CHCl_3·$ 0.5H_2O	$C_{32}H_{46}ClOsO·$ $P_4·Cl·3CHCl_3$	$C_{59}H_{49}Br_2Os·$ $OP_3·CH_2Cl_2$
fw	1197.48	1164.56	1060.76	1189.77	1301.84
temperature, K	223(2)	223(2)	223(2)	100(2)	223(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)	$P\bar{1}$	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*m*
a, Å	11.438(2)	12.334(3)	13.738(2)	19.161 (2)	11.482(2)
b, Å	20.166(4)	12.646(3)	11.568 (2)	9.914(1)	20.300(3)
c, Å	14.170(3)	15.335(3)	30.702(4)	26.300(2)	14.120(2)
α, deg	90	87.508(4)	90	90	90
β, deg	113.80	74.564(4)	97.616(2)	105.754 (1)	113.610(2)
γ, deg	90	83.030(4)	90	90	90
V, Å^3	2990.4(11)	2288.3(8)	4836.1(12)	4808.2(7)	3015.7(8)
Z	2	2	4	4	2
calcd density, g cm^{-3}	1.330	1.690	1.457	1.644	1.434
F(000)	1204	1156	2118	2360	1288
cryst dimens, mm	0.25 × 0.12 × 0.08	0.27 × 0.20 × 0.16	0.34 × 0.24 × 0.18	0.25 × 0.10 × 0.04	0.17 × 0.14 × 0.14
θ range, deg	2.2−28.3	2.2−25.1	2.3−26.1	2.2−26.8	2.6−23.5
reflns collected	21 365	16 700	28 193	26 085	23 526
indep reflns	10 333	7996	8481	9400	11 621
obsd reflns	9867	7132	7303	7073	9940
data/restraints/params	10 333/7/640	7996/0/532	8481/24/577	9400/0/469	11 621/1/644
goodness-of-fit on F^2	1.014	1.066	1.091	1.001	1.000
final *R* (*I* > 2*σ*(*I*))	R_1 = 0.0484, wR_2 = 0.1266	R_1 = 0.0440, wR_2 = 0.1013	R_1 = 0.0562, wR_2 = 0.1665	R_1 = 0.0298, wR_2 =0.0492	R_1 = 0.0520, wR_2 = 0.1293
R indices (all data)	R_1 = 0.0507, wR_2 = 0.1284	R_1 = 0.0512, wR_2 = 0.1041	R_1 = 0.0644, wR_2 = 0.1725	R_1 = 0.0549, wR_2 =0.0527	R_1 = 0.0613, wR_2 = 0.1326
peak and hole, e Å^{-3}	1.534 and −2.096	1.499 and −1.443	3.089 and −0.860	1.218 and −0.855	1.536 and −1.119

Table 2. X-ray Diffraction Structure Summary 2

	12·2$CHCl_3$	**13**·5H_2O	**14**·0.83H_2O	**15**·0.25H_2O
formula	$C_{32}H_{46}ClOsO·$ $P_4·Cl·2CHCl_3$	$C_{32}H_{46}OsO_2P_4·$ $2Cl·5H_2O$	C_{29} $H_{37}ClOsO_2·$ $P_3·Cl·0.83H_2O$	C_{42} $H_{34}Cl_2OsO_2·$ $P_2·0.25H_2O$
fw	1070.40	937.75	786.61	898.24
temperature, K	100(2)	223(2)	223(2)	223(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	hexagonal	orthorhombic
space group	*Pbca*	$P\bar{1}$	*R*3*c*	*P*2(1)2(1)2(1)
a, Å	16.122(2)	9.819(6)	26.911(3)	9.975(3)
b, Å	17.089(2)	10.177(7)	26.911(3)	16.527(5)
c, Å	32.257(4)	22.554(15)	25.553(5)	24.668(7)
α, deg	90	98.259(10)	90	90
β, deg	90	98.520(10)	90	90
γ, deg	90	102.861(10)	120	90
V, Å^3	8887.3(18)	2136(2)	16026(4)	4067(2)
Z	8	2	18	4
calcd density, g cm^{-3}	1.600	1.458	1.467	1.467
F(000)	4256	948	7026	1787
cryst dimens, mm	0.20 × 0.15 × 0.05	0.32 × 0.24 × 0.16	0.34 × 0.13 × 0.12	0.32 × 0.20 × 0.14
θ range, deg	2.1−28.2	2.0−28.5	2.2−28.5	1.5−28.7
reflns collected	42025	14 152	36 547	37 109
indep reflns	7734	7283	6219	7138
obsd reflns	5399	6948	5988	6769
data/restraints/params	7734/6/433	7283/0/421	6219/1/355	7138/66/451
goodness-of-fit on F^2	1.008	1.002	1.097	0.961
final *R* (*I* > 2*σ*(*I*))	R_1 = 0.0424, wR_2 = 0.0743	R_1 = 0.0479, wR_2 = 0.1309	R_1 = 0.0326, wR_2 = 0.0824	R_1 = 0.0681, wR_2 = 0.1933
R indices (all data)	R_1 = 0.0817, wR_2 = 0.0816	R_1 = 0.0493, wR_2 = 0.1322	R_1 = 0.0340, wR_2 = 0.0828	R_1 = 0.0720, wR_2 = 0.1977
peak and hole, e Å^{-3}	1.545 and −1.137	3.469 and −2.608	1.306 and −0.615	2.437 and −2.792

= 5.1 Hz, 1 H, OsCHC*H*), 7.5−7.7 (m, 15 H, PPh_3), 1.2−1.6 (m, 27H, PMe_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): *δ* 244.1 (dd, *J*(PC) = 71.0, 6.0 Hz, Os*C*HC(PPh_3)), 238.2 (s, Os*C*HCH), 171.4 (d, *J*(PC) = 11.3 Hz, *C*OH), 125.0 (s, OsCHC*H*), 106.1 (dd, *J*(PC) = 72.5, 5.3 Hz, *C*PPh_3), 105.7−135.2 (m, PPh_3), 14.1−32.2 (m, PMe_3) ppm. Anal. Calcd for $C_{32}H_{46}OP_4Cl_2Os$: C, 46.21; H, 5.57. Found: C, 45.99; H, 5.75.

[Os(CO)(CHC(PPh$_3$)C(CH$_3$)O)(PMe$_3$)$_3$]Cl$_2$ (13). A solution of [OsCl(CH═C(PPh_3)C(O)-*η*^{2}-CH═CH_2)(PMe_3)$_3$]Cl (**8**) (0.30 g, 0.36 mmol) dissolved in wet $CHCl_3$ was stirred for 5 days. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the concentrate gave a dark brownish-red precipitate, which was collected by filtration, and subsequent recrystallization of the crude product from dichloromethane/ether yielded orange-red crystals. Yield: 0.16 g, 52%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): *δ* 17.8 (d, *J*(PP) = 13.4 Hz, C*P*PPh_3), −32.4 (d, *J*(PP) = 26.7 Hz, Os*P*Me_3), −45.3 (dt, *J*(PP) = 26.7, 13.4 Hz, Os*P*Me_3) ppm. ^1H NMR ($CDCl_3$, 300.1 MHz): *δ* 12.2 (d, *J*(PH) = 19.8 Hz, 1H, Os*CH*), 2.5 (s, 3H, C*H*$_3$), 7.5−7.9 (m, 15 H, PPh_3), 1.5−1.8 (m, 27 H, PMe_3) ppm. $^{13}C\{^1H\}$ NMR

(CD_2Cl_2, 75.5 MHz): δ 260.1 (dt, *J*(PC) = 56.5, 7.8 Hz, *C*O), 213.7 (dd, *J*(PC) = 27.6, 10.6 Hz, Os*C*H), 180.1 (br, *C*C(CH_3)), 120.7 (d, *J*(PC) = 86.8 Hz, *C*(PPh_3)), 32.0 (s, *C*H_3), 116.8−135.9 (m, PPh_3), 16.8−18.5 (m, PMe_3) ppm. Anal. Calcd for $C_{32}H_{46}O_2P_4Cl_2Os$: C, 45.34; H, 5.47. Found: C, 45.99; H, 5.75.

[OsCl(CO)(CHC(PPh$_3$)C(CH$_3$)O)(PMe$_3$)$_2$]Cl (14). A solution of $OsCl_2$(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PMe_3)$_2$ (**6**) (0.30 g, 0.40 mmol) dissolved in wet $CHCl_3$ was stirred for a week. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the concentrate gave a dark brownish-red precipitate, which was collected by filtration, and subsequent recrystallization of the crude product from dichloromethane/ether yielded orange-red crystals. Yield: 0.13 g, 43%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 16.9 (s, C*P*Ph_3), −24.2 (s, Os*P*Me_3) ppm. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 13.0 (d, *J*(PH) = 15.0 Hz, 1 H, OsC*H*), 2.1 (s, 3 H, CH_3), 7.5−7.8 (m, 15 H, PPh_3), 1.5−1.8 (m, 27 H, PMe_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 246.9 (t, *J*(PC) = 17.1 Hz, *C*O), 204.1 (dd, *J*(PC) = 25.6, Os*C*H), 181.5 (s, *C*C(CH_3)), 114.2 (d, *J*(PC) = 86.1 Hz, *C*(PPh_3)), 32.0 (s, *C*H_3), 118.6−135.6 (m, PPh_3), 14.5−15.3 (m, PMe_3) ppm. Anal. Calcd for $C_{29}H_{37}O_2P_3Cl_2Os \cdot 0.5Et_2O$: C, 46.04; H, 5.24. Found: C, 46.08; H, 5.44.

OsCl$_2$ (CH═C(PPh$_3$)C(O)-η^2-CH═CH$_2$)(CO)(PPh$_3$) (15). A continuous flow of CO was pumped into the stirred suspension of $OsCl_2$(CH═C(PPh_3)C(O)-η^2-CH═CH_2)(PPh_3)$_2$ (**3**) (0.80 g, 0.71 mmol) in CH_2Cl_2 (15 mL) at room temperature for 24 h to give a brown solution. Light brown product was collected after the solvent was evaporated to dryness under vacuum, and the resulting residue was washed with ether (5 × 3 mL) then dried under vacuum. Yield: 0.54 g, 85%. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 10.4 (d, *J*(PP) = 31.6 Hz, C*P*Ph_3), −11.1 (d, *J*(PP) = 31.6 Hz, Os*P*Ph_3) ppm. ^1H NMR (300 MHz, CD_2Cl_2): δ 11.8 (dd, 1 H, *J*(PH) = 18.0 Hz, 4.2 Hz, OsC*H*), 7.3−7.8 (m, 30 H, PPh_3), 4.7 (m, 1 H, CHCH_2), 2.9 (m, 1 H, C*H*CH_2), 2.8 (m, 1H, CHCH_2) ppm. Anal. Calcd for $C_{42}H_{34}O_2Cl_2P_2Os$: C, 56.44; H, 3.83. Found: C, 56.18; H, 3.96.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or $CHCl_3$ solutions layered with ether or *n*-hexane for **3**, **4**, **5**, **8**, **11**, **12**, **13**, **14**, and **15**. Selected crystals were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on a Bruker Apex CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan 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. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Details on crystal data, data collection, and refinements are summarized in Tables 1 and 2.

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Supporting Information Available: X-ray crystallographic files (CIF) and Tg plot of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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