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Nine-Membered Osmacycles Derived from Metathesis Reactions between Alkynes and an Osmafuran

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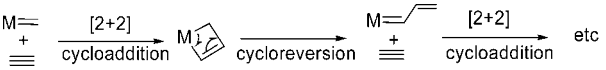
Ring-expansion reactions of the five-membered osmafuran $\mathrm{Os\{{=}CHC(PPh_3){=}C(O)\ OEt\}Cl_2(PPh_3)_2}$ (**1**) via alkyne insertion have been investigated, which lead to the formation of several nine-membered osmacycles. Reaction of **1** with PhC≡CH gives the nine-membered complexes $\mathrm{Os\{{=}CPhCH{=}CPh\text{-}\eta^2\text{-}CH{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PPh_3)}$ as a mixture of a couple of isomers **2a** and **2b** with different disposition of the two chloride ligands on the metal centers. The reaction involves a head-to-tail double insertion of PhC≡CH into osmacycle **1** via [2 + 2] cycloaddition process, which is relevant to the polymerization of alkynes by metathesis reaction. Treatment of the mixture of **2a** and **2b** with $\mathrm{PMe_3}$ gives selectively $\mathrm{Os\{{=}CPhCH{=}CPh\text{-}\eta^2\text{-}CH{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PMe_3)}$ (**3**), the $\mathrm{PMe_3}$-substituted counterpart of **2a**. These complexes might serve as the intermediates for alkyne polymerization which are stabilized by the coordination of internal olefin. Heating the mixture of **2a** and **2b** in $\mathrm{CHCl_3}$ under reflux gives complex $\mathrm{Os\{\eta^2\text{-}CHPh{=}CHCPh{=}CHCC(PPh_3)C(O)OEt\}Cl_2(PPh_3)}$ (**4**) by an intramolecular hydrogen shift. In addition, reaction of **1** with HC≡CCH(OH)Ph affords $\mathrm{[Os\{O{=}CPhCH_2\text{-}\eta^2\text{-}CH{=}CHC(PPh_3){=}C(O)OEt\}Cl(PPh_3)_2]Cl}$ (**5**) as a monoinsertion product, which can dissociate a phosphine ligand under reflux in $\mathrm{CH_2Cl_2}$ to give complex $\mathrm{Os\{O{=}CPhCH_2\text{-}\eta^2\text{-}CH{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PPh_3)}$ (**6**). The one of the α-H of the carbonyl group in complex **5** can be deprotonated by $\mathrm{NEt_3}$ to give an η^3-allylic structure $\mathrm{Os[\eta^3\text{-}CH\{CPh({=}O)\}CHCHC(PPh_3){=}C(O)OEt]Cl(PPh_3)_2}$ (**7**). Treatment of **7** in $\mathrm{CHCl_3}$ with 1 equiv of HCl regenerates **5**. All of the complexes can be prepared under mild condition in good yield. Moreover, these reactions provide convenient and efficient routes to synthesize the nine-membered osmacycles. Complexes **1**, **3**, **4**, **5′**, **6**, and **7** have been characterized by X-ray diffraction analysis.

Introduction

Over the past two decades, metathesis reactions have been extensively investigated as an efficient method for the chemo- and stereoselective formation of C−C bonds.[1−3] In particular, olefin metathesis is now a well-established and powerful tool in organic synthesis and polymer chemistry.[1] Closely related to olefin metathesis is the polymerization of alkynes via metathesis reaction as shown in Chart 1, which has also been widely reported.[4−7] Metallacyclobutene intermediates are initially formed from addition of alkynes to metal carbenes in much the same way as metallacyclobutanes from alkenes and metal carbenes. Then, through isomerization and cycloreversion,

Chart 1



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metathesis products are formed. Since the metathesis mechanism was proposed by Masuda and co-workers for the polymerization of phenylacetylene catalyzed by WCl_6 and $MoCl_5$ in 1975,[5] it has attracted much attention.[6,7] Several experiments supporting this mechanism have been reported for some catalysts containing metals such as Ta, W, and Mo. For example, a metallacyclobutene was obtained by the reaction of tantalum carbene with diphenylacetylene as reported by Schrock et al.[6] Some Fischer-type carbene complexes react with alkynes first to give a new vinylalkylidene, and then alkynes are polymerized under various conditions.[7]

It is well-known that ruthenium carbene complexes are widespread and effective catalysts for the metathesis reaction. In contrast to the ruthenium, osmium is more reducing and prefers coordination saturation.[8] Thus, although the catalytic osmium chemistry is scarce,[9] the relative osmium complexes have been used to prepare stable models of reactive intermediates proposed in reactions catalyzed by other species, such as ruthenium analogues.[10]

In our recent work, we have developed a convenient route to prepare some interesting metallcycles,[11] including metallabenzenes,[11a−e] bridged iridacycles,[11f] and metallafuran,[11e] starting from the reactions between transition-metal-containing complexes and alkynes. As an outgrowth of our long-standing interest in such reactions, we have studied the reaction of $HC{\equiv}CCOOEt$ with $OsCl_2(PPh_3)_3$. The reaction led to the formation of an osmafuran $Os\{{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PPh_3)_2$ (**1**). We find the Os−C bond in complex **1** with bond distance of 1.918(5) Å shows obvious carbenic character. It will be interesting to study the reactivity of this type of complex toward alkynes. The results show that the alkynes $PhC{\equiv}CH$ and $HC{\equiv}CCH(OH)Ph$ undergo facile double and single molecular addition into the metal−carbon double bond of osmafuran **1**, respectively, yielding several nine-membered osmacycles. These complexes might serve as intermediates for alkyne polymerization, which are stabilized by the coordination of internal olefin. The mechanisms for the formation of these products are relevant to olefin metathesis reactions, which involve [2 + 2] cycloaddition reaction between the carbon−carbon triple bond and the metal−carbon double bond via a metallacyclobutene intermediate. Moreover, these reactions also provide an efficient method to realize ring expansion from five- to nine-membered by alkynes insertion. The structural characterization and formation mechanism of these products have been discussed in detail.

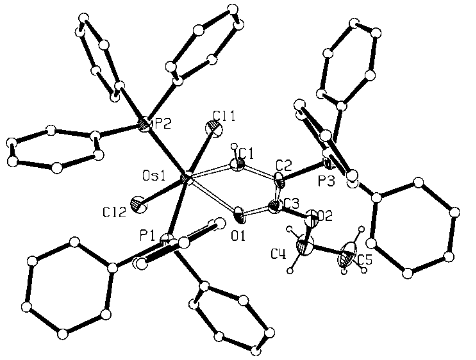
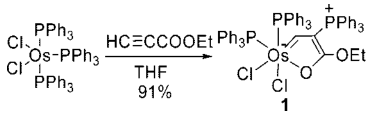


Figure 1. Molecular structure of the complex **1** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 1.918(5), Os1−O1 = 2.199(4), C1−C2 = 1.409(6), C2−C3 = 1.434(7), C3−O1 = 1.239(6), O2−C3 = 1.324(7), O2−C4 = 1.4626, C4−C5 = 1.484(8); C1−Os1−O1 = 77.5(2), C2−C1−Os1 = 118.8(3), C1−C2−C3 = 111.6(4), C2−C3−O1 = 120.0(5), C3−O1−Os1 = 110.9(3).

Scheme 1



Results and Discussion

Preparation of Osmafuran $Os\{{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PPh_3)_2$ (1). Treatment of $OsCl_2(PPh_3)_3$[12] with $HC{\equiv}CCOOEt$ in THF at room temperature for about 5 h led to the precipitation of a red solid with poor solubility, which could be isolated in 91% yield and was identified to be an osmafuran $Os\{{=}CHC(PPh_3){=}C(O)OEt\}Cl_2(PPh_3)_2$ (**1**) (Scheme 1).

The structure established by X-ray diffraction is shown in Figure 1. It confirms that complex **1** contains a planar five-membered ring incorporating osmium, oxygen, and three carbon atoms, i.e., a 2-osmafuran. In the structure of **1** the two phosphine ligands and the two chloride ligands are disposed mutually cis, respectively. It should be mentioned that the Os1−C1 bond length of 1.918(5) Å is apparently shorter than those found in osmafuran of $Os\{CHCHC(O)CH_3\}(\eta^2\text{-}H_2)(SnPh_2Cl)(PiPr_3)_2$ (2.035(2) Å)[13a] and $Os(CHCHC(O)Ph)Cl(CO)(PiPr_3)_2$ (1.971(3) Å),[13c] but is comparable to those of osmium-carbene complexes such as $[OsCl_3\{{=}C(Ph)CH_2Ph\}(CO)(PiPr_3)][HPiPr_3]$ (1.929(3) Å),[14a] $OsCl_2({=}CPh\text{-}\eta^2\text{-}CH{=}C{=}CHPh)(PPh_3)_2$ (1.894(9) Å),[14b] and $OsCl_2({=}CHPh)(CO)(PiPr_3)_2$(1.89(2) Å).[14c] These data indicate the substantial carbenic character of the Os1−C1 bond in **1**.

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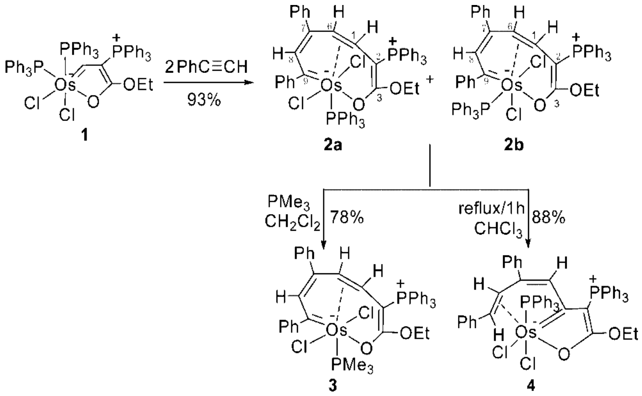
Scheme 2



The NMR spectroscopic data of **1** are consistent with the structure shown in Figure 1. In the ^{1}H NMR spectrum, the OsC*H* resonance appears at 14.3 ppm, whereas in the $^{13}C\{^1H\}$ NMR spectrum the metallacycle carbon signals are observed at 237.6 (C1), 98.2 (C2), and 181.5 (C3) ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 13.0 ppm attributed to C*P*Ph$_3$, and the two signals for Os*P*Ph$_3$ are observed at 1.5 and −6.0 ppm, respectively, with a P−P coupling constant of 16.3 Hz, which also supports the cis disposition of the two phosphine ligands.

The formation of **1** involves the nucleophilic attack of PPh_3 on the coordinated alkyne followed by coordination of the oxygen of the ester function to osmium center. Although numerous examples of metallafurans have been reported,[13] it offers another convenient route to construct metallafuran. It is also worth noting that complex **1** shows excellent air and thermal stability, in view of the fact that the solid sample remains almost unchanged when heated at 100 °C in air for 5 h.

Bis-insertion of PhC≡CH into Osmafuran. During our investigation on the reactivity of **1**, we find that complex **1** is reactive toward alkynes. The solution of **1** and PhC≡CH in a 1:4 molar ratio was stirred in $CHCl_3$ for 1 h to give a brown solution, from which the nine-membered metallacyclic complex Os{=CPhCH=CPh-η^2-CH=CHC(PPh_3)=C(O)OEt}$Cl_2(PPh_3)$ (**2**) could be isolated in 93% yield as a mixture of the isomers **2a** and **2b** (ca. 5:4 ratio) (Scheme 2). The pure complex **2a** was obtained in 45% yield as the residue after washing the mixture with methanol, whereas complex **2b** in the filtrate converted to other unidentified species. Subjecting the mixture of **2a** and **2b** to column chromatography on silica gel gave pure complex **2b** in low yield (9%), and most of **2a** and **2b** transformed to complex **4**, which will be discussed below.

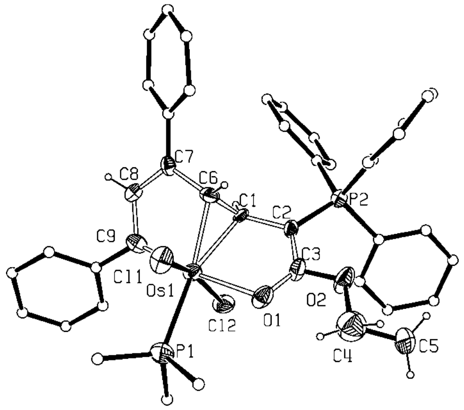


Figure 2. Molecular structure of the complex **3** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 2.165(8), Os1−C6 = 2.184(10), Os1−O1 = 2.200(7), C1−C2 = 1.484(12), C2−C3 = 1.397(13), C3−O1 = 1.254(11), C1−C6 = 1.422(13), C6−C7 = 1.475(14), C7−C8 = 1.372(13), C8−C9 =1.425(14), Os1−C9 = 1.931(11); C1−Os1−O1 = 78.3(3), C2−C1−Os1 = 109.1(6), C1−C2−C3 = 115.8(8), C2−C3−O1 = 123.7(9), C3−O1−Os1 = 112.4(6), C6−C1−Os1 = 71.6(5), C1−C6−Os1 = 70.2(5), C7−C6−Os1 = 108.7(6), C8−C7−C6 =114.3(8), C7−C8−C9 = 119.2(9), C8−C9−Os1 = 116.4(7), C9−Os1−C6 =81.0(4), C1−Os1−C6 = 38.2(3). C9−Os1−O1 = 172.9(3), C1−Os1−P1 = 159.7(3), C6−Os1−P1 = 158.2(3), Cl1−Os1−Cl2 =165.0(1).

The mixture of **2a** and **2b** is stable in the solid state under nitrogen atmosphere; however, they can convert to **4** as the main product and some other unidentified species in $CHCl_3$ solution within 2days at room temperature. As a result, the single-crystal X-ray diffraction data of **2** are unavailable, and the structure can not be assigned confidently on the basis of the NMR data. Thus, ligand substitution reaction is carried out in order to obtain stable **2** analogues.

The addition of 5.0 equiv of PMe_3 to a CH_2Cl_2 solution of the mixture of **2a** and **2b** at room temperature for 24 h produced complex Os{=CPhCH=CPh-η^2-CH=CHC(PPh_3)=C(O)OEt}-$Cl_2(PMe_3)$ (**3**) in 78% yield, which was characterized by X-ray diffraction analysis. As shown in Figure 2, complex **3** contains a nine-membered metallacycles, in which the Os atom is surrounded by a tridentate ligand (carbenic carbon, η^2-CH=CH, O sites) derived from the head-to-tail double insertion of PhC≡CH into osmafuran. It can also be viewed as two five-membered rings fused with a three-membered ring. In the structure of **3**, the geometry around the osmium atom can be described as a distorted octahedron, with the PMe_3 ligand trans to coordinated olefin (C1−Os1−P1 = 159.7(3)°, C6−Os1−P1 = 158.2(3)°). The C9 is disposed trans to O1 (C9−Os1−O1 = 172.9(3)°), and the two chloride ligands are mutually trans (Cl1−Os1−Cl2 = 165.0(1)°). The two five-membered rings consisting of Os1/C1/C2/C3/O1 and Os1/C6/C7/C8/C9 are coplanar, respectively, as reflected by the deviation of 0.0381 and 0.0234 Å from the rms planes of the best fit. The bond distance for C1−C6 (1.422(13) Å), together with those for Os1−C1 (2.165(8) Å) and Os1−C6 (2.184(10) Å), are consistent with the reported olefin-transition-metal derivatives.[11c,e,15]

The ^{1}HNMR spectrum of **3** in CD_2Cl_2 shows the characteristic protons of coordinated double bond signals at 4.2 and 4.3 ppm, respectively. The proton signal on C8 is at 7.3 ppm according to $^1H-^{13}C$ HMQC. The one quartet at 3.7 ppm and one triplet at 0.5 ppm are assigned to the ethyl group of the ester. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 18.3 (C*P*Ph$_3$) and −33.7 (Os*P*Me$_3$) ppm, with a P−P coupling constant of 4.9 Hz, indicating the weak interaction between the trimethylphosphine ligand on the metal center and the phosphonium group on the ring structure. In the $^{13}C\{^1H\}$ NMR spectrum, the

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(13) For examples of metallafurans, see:(a) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428. (b) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989. (c) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (d) Bleeke, J. R.; New, P. R.; Blanchard, J. M. B.; Haile, T.; Beatty, A. M. *Organometallics* **1995**, *14*, 5127. (e) Bleeke, J. R. *Organometallics* **2005**, *24*, 5190. (f) Bierstedt, A.; Clark, G. R.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2006**, *691*, 3846. (g) Li, X.; Chen, P.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4810. (h) Dirnberger, T.; Werner, H. *Organometallics* **2005**, *24*, 5127. (i) Grotjahn, D. B.; Hoerter, J. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 8866. (j) Li, X.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 3378.

Os=*C*(Ph) resonance appears at 245.3 ppm as a doublet with a C−P coupling constant of 4.5 Hz, also in agreement with the chemical shifts in osmium carbene complexes,[14b,d,e] while the two carbon signals of the coordinated double bond appear at 110.2 (C6) and 98.3 (C1) ppm, respectively. In addition, the signals attributed to C2 and C3 are observed at 57.3 and 178.3 ppm, whereas those attributed to C7, C8, C4, and C5 appear at 141.3, 158.2, 60.5, and 13.8 ppm, respectively.

On the basis of the fully X-ray crystal structure and NMR characterization of complex **3** and the following spectroscopic data, we can formulate **2a** and **2b** to be a couple of isomers with different disposition of the two chloride ligands on the metal centers. Both of them contain a nine-membered ring with an internal coordinated double bond, which are statistically identical with complex **3**. Especially, **2a** is the PMe$_3$-substituted counterpart of **3**.

In the ^{1}H NMR spectrum of **2a**, the signals at 4.1 and 4.9 ppm with a H−H coupling constant of 9.6 Hz are assigned to the protons of η^2-olefin. The signals of the ethyl group of the ester appear at 3.6 ppm as a quartet and 0.4 ppm as a triplet. The proton signal on C8 is observed at 7.3 ppm, which is also confirmed by ^{1}H−^{13}C HMQC. The ^{31}P{^{1}H} NMR spectrum shows two doublets at 17.5 (C*P*Ph$_3$) and −2.9 (Os*P*Ph$_3$) ppm with a P−P coupling constant of 6.1 Hz. In the ^{13}C{^{1}H} NMR spectrum, the carbon signals associated with the metallacycles are very similar to those of complex **3**. The most downfield carbon signal is C9, which appears at 245.0 ppm. In comparison with the signals of C8 (159.4 ppm) and C7 (140.9 ppm), the signal of C6 appears at 109.8 (^3J(PC) = 14.7 Hz, ^3J(PC) = 3.4 Hz) ppm, together with C1 at 99.0 (^3J(PC) = 15.7 Hz, ^3J(PC) = 15.5 Hz) ppm, indicative of the coordination of the C1=C6 double bond to the metal center. The P−C coupling constants support that the PPh$_3$ ligand is disposed trans to the coordinated olefin.

According to the following NMR data, we confirm that in the structure of **2b** the PPh$_3$ ligand is disposed cis to coordinated olefin and the two chloride ligands are located cis to each other. The ^{1}HNMR spectrum of **2b** shows the proton signals of the coordinated olefin at 3.8 and 3.7 ppm, respectively, which are highfield compared with those of **2a** (4.9 and 4.1 ppm), probably due to the difference of the trans influence between phosphine ligand (in **2a**) and chloride ligand (in **2b**) toward the η^2-olefin. In the ^{13}C{^{1}H} NMR spectrum, the carbon signals of C1 and C6 appear as doublets at 85.6 (^3J(PC) = 13.8 Hz) and 82.2 (^3J(PC) = 5.7 Hz) ppm. They are apparently more highfield compared with those in **2a** (99.0 and 109.8 ppm), indicating the different trans influence of chloride ligand relative to that of phosphine ligand in **2a** as well. Especially, in comparison with those in **2a**, the P−C coupling of Os*P*Ph$_3$ toward C1 and C6 has not been observed. This also reflects that the chloride ligand is disposed trans to η^2-olefin rather than that of the phosphine ligand in **2a**. Other carbon signals are observed at 259.4 (C9), 156.0 (C8), 139.8 (C7), 178.3 (C3), 61.3 (C2), 60.9 (C4), and 14.0 (C5) ppm, respectively, which are very close to those of complex **2a**. The ^{31}P{^{1}H} NMR spectrum shows two singlets appear at 19.0 (C*P*Ph$_3$) and −7.5 (Os*P*Ph$_3$) ppm, whereas those in **2a** are two doublets with a P−P coupling constant of 6.1 Hz. This further supports the different disposition of phosphine ligands between **2a** and **2b**.

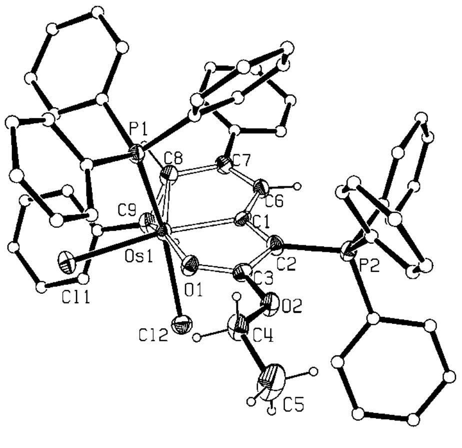

Figure 3. Molecular structure of the complex **4** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 1.981(8), Os1−O1 = 2.133(5), C1−C2 = 1.428(11), C2−C3 = 1.427(11), C3−O1 = 1.257(10), C1−C6 = 1.423(11), C6−C7 = 1.344(12), C7−C8 = 1.491(12), C8−C9 = 1.424(13), Os1−C8 = 2.153(8), Os1−C9 = 2.152(8); C1−Os1−O1 = 79.7(3), C2−C1−Os1 = 113.8(6), C1−C2−C3 = 112.8(7), C2−C3−O1 = 120.7(7), C3−O1−Os1 = 110.5(5), C6−C1−Os1 = 119.1(6), C7−C6−C1 = 115.4(7), C8−C7−C6 = 115.9(7), C7−C8−Os1 = 110.6(6), C9−C8−Os1 = 70.6(5), C8−C9−Os1 = 70.7(5), C9−Os1−C8 = 38.6(3).

The mixture of **2a** and **2b** can transfer to complex **4** and some other species in CHCl$_3$ at room temperature within 2days. Nevertheless, under reflux for 1 h in CHCl$_3$, they convert to Os{η^2-CHPh=CHCPh=CHCC(PPh$_3$)C(O)OEt}Cl$_2$(PPh$_3$) (**4**) in high yield (88%) (Scheme 2).

The structure of **4** was established by X-ray diffraction as depicted in Figure 3. In comparison with complexes **2a** and **2b**, the coordinated olefin bond in **4** shifts from internal to terminal position. The osmium-η^2-vinyl coordination exhibits Os−C bond lengths of 2.153(8) Å (Os1−C8) and 2.152(8) Å (Os1−C9), which is in agreement with those found in other osmium-olefin complexes.[11c,e] The C8−C9 distance of 1.424(13) Å is also within the range reported for the η^2-olefin compounds (1.340−1.455 Å).[15] In the metallafuran consist of C1/C2/C3/O1/Os1, the C1−C2 and C2−C3 bond distances are approximately equal (1.428(11) and 1.427(11) Å), and the Os1−C1 and Os1−O1 distance are 1.981(8) and 2.133(5) Å, respectively, indicating considerable delocalization in the metallacycle. The C6−C7 and C7−C8 distances are 1.344(12) and 1.491(12) Å, respectively, suggesting a significant alternation of single and double bonds in metallacycle of Os1/C1/C6/C7/C8. However, the eight atoms constituting the fused five-membered rings are almost coplanar, which is reflected by a deviation of 0.0824 Å from the rms planes of the best fit, while C9 deviates out of the plane of the bicyclic system by −1.2153 Å. The dihedral angle between the Os1/C8/C9 and the Os1/O1/C3/C2/C1/C6/C7/C8 plane is 66.7°.

The NMR spectroscopic data are consistent with the X-ray structure. In the ^{1}H NMR spectrum, the protons of the terminal coordinated olefin double bond are observed at 4.4 (η^2-C*H*(Ph)=CH) and 5.7 (η^2-CH(Ph)=C*H*) ppm, shifting downfield compared with those of the reported η^2-olefin,[11c,e] possibly due to the deshielding effect of the neighboring phenyl groups.

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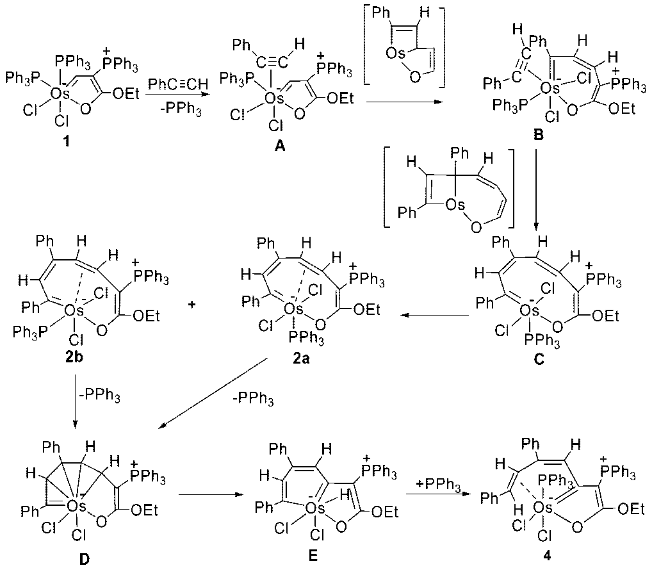
Scheme 3. Proposed Mechanism for Formation of 2 and 4



The proton signal on C6 is observed at 5.8 ppm, which is typical for the olefinic compound.[16] In the ^{13}C{^{1}H} NMR spectrum, the carbon signals of the metallacycle appear at 243.4 (C1), 88.0 (C2), 184.5 (C3), 63.3 (C4), 13.6 (C5), 137.6 (C6), 179.8 (C7), 66.3 (C8), and 62.1 (C9) ppm, respectively. The ^{31}P{^{1}H} NMR spectrum shows two singlets at 6.0 (C*P*Ph$_3$) and −2.5 (Os*P*Ph$_3$) ppm, respectively.

Possible mechanisms for the formation of **2** and **3** are shown in Scheme 3. Replacement of the PPh$_3$ ligand by the alkyne in **1** gives π-alkyne intermediate **A**, which undergoes the first alkyne insertion into the osmium-carbon double bond followed by cycloreversion of the metallacyclobutene to form a seven-membered osmacycle **B**. Then, [2 + 2] cycloaddition of the second molecule of alkyne with the Os=C in **B** gives a nine-membered intermediate **C**. Coordination of the internal double bond to the metal center affords the 18-e products **2a** and **2b**. We note that the related process on the formation of osmium-η^3-allenylcarbene,[14b,e,17] ruthenium-η^3-vinylcarbene,[18a] ruthenium-η^3-allenylcarbene,[18b,c] and tungsten-η^3-vinylcarbene[19] have been reported. Isomerization of **2a** and **2b** to **4** is presumably driven by the dissociation of PPh$_3$, coordination of another olefin double bond, electronic tautomerization, and subsequent α-H elimination to give hydride-osmabenzene **E**. Finally, reductive elimination of the vinyl and the hydride from **E** as well as the recoordination of PPh$_3$ ligand produces complex **4**. It is worth noting that the mechanism for the isomerization of **2** to **4** involves an intramolecular hydrogen shift process.

In the metal carbene catalyzed polymerization of alkynes, a metallacyclobutene is produced by the reaction of an alkylidene and an alkyne, which is followed by rearrangement to give a new alkylidene. If the process continues, a growing polymer chain forms.[18a] However, in the case of **2**, after two molecular of alkynes addition to osmafuran, the osmium in the nine-membered intermediate **C** is apparently saturated by intramolecular coordination of the vinyl group. Thus, a third or more alkynes addition process is disfavored. Nevertheless, these complexes might serve as intermediates trapped after two turnovers of alkynes polymerization by internal coordinated olefin to the metal center. It should also be mentioned that it is a head-to-tail double insertion of PhC≡CH molecular into the osmafuran. A head-to-head double insertion of PhC≡CH into a Rh−O bond have been reported.[22g]

Furthermore, metallacycles are attracting increasing attention in chemical research, as they are seem to be promising reagents and catalysts in organic and organometallic chemistry as well as intermediates in sorts of reactions.[20,21] The insertion of unsaturated molecular into organometallic compounds can not only construct various of metallacycles but also undergo ring expansion.[22] In particular, the alkynes insertion into various of transition-metal-containing metallacycles with ring expansion have been reported. [23−27] The ongoing work provides an efficient method to realize the ring expansion from five- to nine-membered by alkynes insertion.

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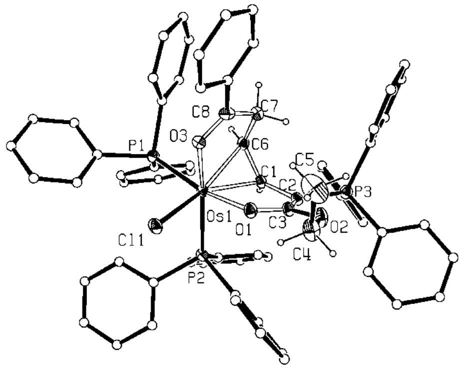
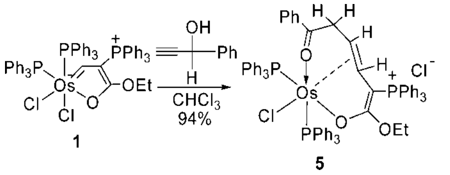


Figure 4. Molecular structure of the complex cation of **5′** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 2.217(7), Os1−C6 = 2.176(7), Os1−O1 = 2.146(5), C1−C2 = 1.513(9), C2−C3 = 1.383(11), C3−O1 = 1.258(9), C1−C6 = 1.410(9), C6−C7 = 1.515(10), C7−C8 = 1.487(12), C8−O3 = 1.241(8), Os1−O3 = 2.091(5); C1−Os1−O1 = 76.5(2), C2−C1−Os1 = 109.1(5), C1−C2−C3 = 113.8(7), C2−C3−O1 = 122.6(6), C3−O1−Os1 = 116.8(5), C6−C1−Os1 = 69.7(4), C1−C6−Os1 = 72.8(4), C7−C6−Os1 = 108.4(5), C8−C7−C6 = 111.6(6), C7−C8−O3 = 117.9(7), C8−O3−Os1 = 119.5(5), O3−Os1−C6 = 76.9(2), C1−Os1−C6 = 37.4(2), P2−Os1−O3 = 163.6(1), P1−Os1−O1 = 166.7(1), Cl1−Os1−C6 = 157.5(2), Cl1−Os1−C1 = 154.6(2).

Scheme 4



Mono-insertion of HC≡CCH(OH)Ph into Osmafuran. Even when the reaction was performed with a ratio of osmafuran and PhC≡CH of 1:1, there was still no evidence for formation of the corresponding monoinserted derivatives. In order to study the mechanism further, the comparison research on the reactions of osmafuran Os{=CHC(PPh_3)=C(O)OEt}$Cl_2(PPh_3)_2$ (**1**) and HC≡CCH(OH)Ph bearing a hydroxyl group was carried out. In this case, mono-insertion product was obtained.

Treatment at room temperature of Os{=CHC(PPh_3)=C(O)-OEt}$Cl_2(PPh_3)_2$ (**1**) with HC≡CCH(OH)Ph in $CHCl_3$ for 1 h led to [Os{O=C(Ph)CH_2-η^2-CH=CHC(PPh_3)=C(O)OEt}Cl-$(PPh_3)_2$]Cl (**5**), which was isolated as a yellow solid in 94% yield (Scheme 4).

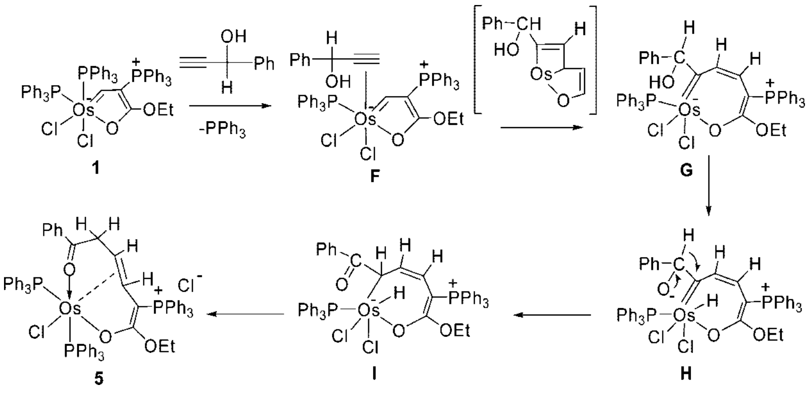
Complex **5** was characterized by solution NMR spectroscopy. In particular, the ^{1}H NMR spectrum shows the proton signals of η^2-olefin at 5.1 and 4.8 ppm, respectively. The CH_2C(Ph) signals are observed at 3.3 and 2.8 ppm. The ^{13}C{^{1}H} NMR spectrum shows the carbon signals of *C*(Ph)=O and *C*(OCH_2-CH_3) at 216.5 and 179.7 ppm, respectively. The signals attributed to the *C*HC(PPh_3), *C*HCH$_2$, *C*(PPh_3), and *C*H$_2$C(Ph) are observed at 62.0, 60.7, 49.1, and 44.1 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ shows three signals at 15.5 (C*P*Ph$_3$), −21.0 (Os*P*Ph$_3$), and −27.1 (Os*P*Ph$_3$) ppm, respectively.

Complex **5′** was prepared by treatment of **5** with $NaBPh_4$ in methanol, and the BPh_4^- anion of **5′** was confirmed by X-ray diffraction. Figure 4 shows a view of the structure of the cation of **5′**. The cation contains a distorted nine-membered metallacycle, in which the Os atom is surrounded by a tridentate ligand (O, η^2-CH=CH, O sites). The geometry around the osmium atom can be rationalized as a distorted octahedron with the P2 trans to O3 (P2−Os1−O3 = 163.6(1)°), P1 trans to O1 (P1−Os1−O1 = 166.7(1)°), and the chloride trans to η^2-olefin (Cl1−Os1−C6 = 157.5(2)°, Cl1−Os1−C1 = 154.6(2)°). The planarities of the two five-membered rings consisting of Os1/C1/C2/C3/O1 and Os1/C6/C7/C8/O3 are reflected by the deviation of 0.0436 and 0.1134 Å from the rms planes of the best fit. The dihedral angle between them is 72.8°. The C6−C7 (1.515(10) Å) and C7−C8 (1.487(12) Å) bond distances indicate that C7 is a sp^3 carbon, resulting in the distortion of the five-membered ring of Os1/C6/C7/C8/O3.

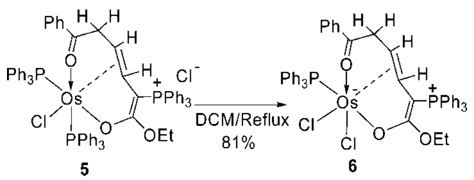
A possible mechanism for the formation of **5** is shown in Scheme 5. The addition of HC≡CCH(OH)Ph into osmafuran via a [2 + 2] cycloaddition process is similar to that of PhC≡CH, which leads to the formation of the seven-membered intermediated **G**. Then the hydroxyl is activated by the osmium center to form the hydride-osmacycle **H**, which is followed by 1,2-hydrogen shift to generate intermediate **I**. The subsequent reductive elimination and coordination of the carbonyl group, the internal alkene, and the PPh_3 ligand accompanied by dissociation of one chloride gives the 18-e complex **5**. In comparison with **2a** and **2b**, **5** could be viewed as a product of one turnover of alkyne polymerization trapped by coordination of carbonyl group and internal alkene to the metal center.

A solid sample of complex **5** could be heated at 100 °C in air for 5 h without appreciable decomposition, indicating its good thermal stability. Additionally, it is also shown resistant to oxidation since it is nearly unchanged in the presence of strong oxidants such as H_2O_2 and *t*-BuOOH in CH_2Cl_2 solution. However, the solution of **5** in CH_2Cl_2 could dissociate a phosphine ligand to produce Os{O=CPhCH$_2$-η^2-CH=CHC-

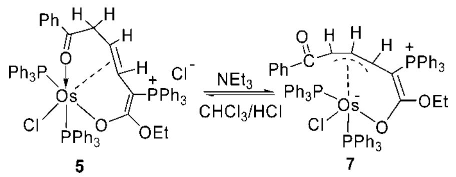
Scheme 5. Proposed Mechanism for Formation of 5



Scheme 6



Scheme 7



(PPh$_3$)=C(O)OEt}Cl$_2$(PPh$_3$) (**6**) at reflux for 12 h under nitrogen atmosphere (Scheme 6).

The structure of **6** was also confirmed by X-ray diffraction. Figure 5 clearly shows a view of the complex **6**. Similar to **5**, **6** contains a similar nine-membered structure, in this case, with the chloride Cl1 trans to O3 (Cl1−Os1−O3 = 167.5(1)°). The C1−C6 (1.405(10) Å), C6−C7 (1.502(10) Å), and C7−C8 (1.502(10) Å) bonds are similar to those found in **5**. The solution NMR spectroscopic data are in agreement with the solid-state structure. In particular, the ^{31}P{^{1}H} NMR shows two singlets at 18.9 (C*P*Ph$_3$) and −11.6 (Os*P*Ph$_3$) ppm.

It is well-known in organic chemistry that the α-H on carbonyl group could be easily deprotonated by bases. Treatment of **5** with NEt$_3$ also underwent facile deprotonation of the α-H on carbonyl group to produce Os[η^3-CH{CPh(=O)}CHCHC(PPh$_3$)=C(O)OEt]Cl(PPh$_3$)$_2$ (**7**) in 93% yield (Scheme 7).

The structure of **7** was also confirmed by X-ray diffraction, and its molecular structure is depicted in Figure 6. The X-ray diffraction study confirms that the complex **7** contains an η^3-allylic structure. The allyl moiety is bonded to the metal center in an asymmetrical fashion. The separation between the central carbon atom C6 and the osmium center Os1 (2.149(3) Å) is shorter than the separation between Os1 and the terminal carbon atoms C1 (2.169(3) Å) and C7 (2.283(3) Å). The carbon−carbon distances within the allylic skeleton are 1.406(4) Å for C1−C6 and 1.416(4) Å for C6−C7. The angle of C1−C6−C7 was 121.4(3)°. The presence of the carbonyl group is supported by the C8−O3 bond distance of 1.224(4) Å.

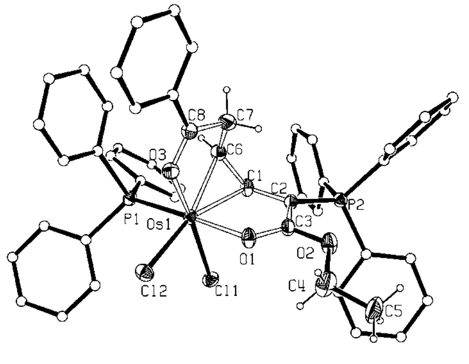


Figure 5. Molecular structure of the complex **6** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 2.159(6), Os1−O1 = 2.153(4), C1−C2 = 1.497(9), C2−C3 = 1.380(10), C3−O1 = 1.260(8), C1−C6 = 1.405(10), C6−C7 = 1.502(10), C7−C8 = 1.502(10), C8−O3 = 1.233(8), Os1−O3 = 2.074(5); C1−Os1−O1 = 78.9(2), C2−C1−Os1 = 108.2(4), C1−C2−C3 = 115.9(6), C2−C3−O1 = 123.1(6), C3−O1−Os1 = 113.4(4), C6−C1−Os1 = 70.8(4), C1−C6−Os1 = 71.1(4), C7−C6−Os1 = 107.7(4), C8−C7−C6 = 109.1(6), C7−C8−O3 = 115.7(6), C8−O3−Os1 = 120.8(4), O3−Os1−C6 = 76.1(2), C1−Os1−C6 = 38.0(3), Cl1−Os1−O3 = 167.5(1), P1−Os1−O1 = 177.0(1), Cl2−Os1−C6 = 156.7(2), Cl2−Os1−C1 = 159.9(2).

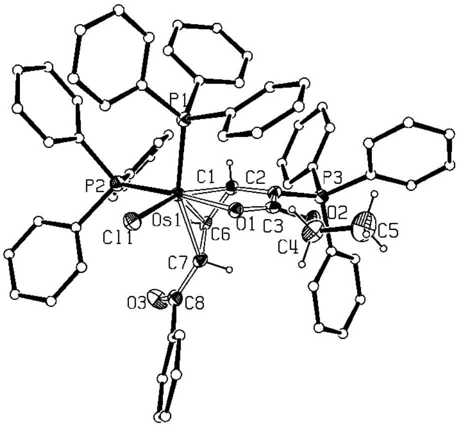


Figure 6. Molecular structure of the complex **7** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Os1−C1 = 2.169(3), Os1−C6 = 2.149(3), Os1−C7 = 2.283(3), Os1−O1 = 2.180(2), C1−C2 = 1.504(4), C2−C3 = 1.388(4), C(3)−O(1) = 1.270(4), C1−C6 = 1.406(4), C6−C7 = 1.416(4), C7−C8 = 1.466(4), C8−O3 = 1.224(4); C1−Os1−O1 = 78.54(9), C2−C1−Os1 = 108.6(2), C1−C2−C3 = 115.8(3), C2−C3−O1 = 122.8(3), C3−O1−Os1 = 113.5(2), C6−C1−Os1 = 70.2(2), C1−C6−Os1 = 71.8(2), C7−C6−Os1 = 76.6(2), C6−C7−Os1 = 66.3(2), C1−Os1−C6 = 38.0(1), C7−Os1−C6 = 37.1(1), C1−C6−C7 = 121.4(3).

The solution NMR spectroscopic data of **7** are consistent with its solid-state structure. In particular, the ^{1}H NMR spectrum shows three allylic resonances at 3.4 (C*H*C(PPh$_3$)), 4.2 (C*H*CPh(=O)), and 2.8 (η^3-CHC*H*CH) ppm. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 58.4 (C1), 45.0 (C6), and 85.9 (C7) ppm, whereas those attributed to C2, C3, and C8 appear at 49.1, 177.5, and 196.7 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum shows one C*P*Ph$_3$ signal at 16.1 ppm and two Os*P*Ph$_3$ signals at −6.2 and −9.5 ppm.

The transformation of **5** to **7** involves the deprotonation of the α-H on carbonyl group, which undergoes ring-opening reaction by dissociation of the coordination of carbonyl from metal center to give an η^3-allylic structure. It should be noted that the conversion of **5** to **7** is reversible, as the addition of equivalent HCl to a CHCl$_3$ solution of **7** regenerates **5**.

Conclusion

Nine-membered osmacycles Os{=CPhCH=CPh-η^2-CH=CHC(PPh$_3$)=C(O)OEt}Cl$_2$(PPh$_3$) as the isomers **2a** and **2b** are obtained by a head-to-tail double insertion of PhC≡CH into the osmafuran **1**, which can be viewed as products of two turnovers of alkyne polymerization trapped by internal coordinated olefin to the metal center. The mixture of **2a** and **2b** can convert to Os{η^2-CHPh=CHCPh=CHCC(PPh$_3$)C(O)OEt}Cl$_2$(PPh$_3$) (**4**) by an intramolecular hydrogen shift. Reaction of **1** with HC≡CCH(OH)Ph affords monoinsertion osmacycle [Os{O=CPhCH$_2$-η^2-CH=CHC(PPh$_3$)=C(O)OEt}Cl(PPh$_3$)$_2$]Cl (**5**), which can be viewed as product of one turnover of alkyne polymerization. Complexes **2a**, **2b**, and **5** might be regarded as intermediates stabilized by internal coordinated olefin leading to the alkyne polymerization. The proposed mechanisms for the formation of these complexes involve [2 + 2] cycloaddition process, which are relevant to olefin metathesis and alkyne polymerization. Furthermore, current work provides an efficient method to realize the ring expansion from five- to nine-membered by alkynes insertion.

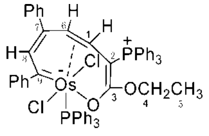
Experimental Section

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 material $OsCl_2(PPh_3)_3$ were synthesized by literature procedures.[12] HC≡CCOOEt, PhC≡CH, and HC≡CCH(OH)Ph were purchased from Sigma-Aldrich and Alfa Aesar. Column chromatography was performed on silica gel (300−400 mesh). All 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_3PO_4. Elemental analyses data were obtained on Thermo Quest Italia SPA EA 1110 instrument.

Os{=CHC(PPh₃)=C(O)OEt}Cl₂(PPh₃)₂ (1). A mixture of $OsCl_2(PPh_3)_3$ (1.00 g, 0.95 mmol) and HC≡CCOOEt (100 uL, 0.98 mmol) in THF (6 mL) was stirred at room temperature for 5 h to give a red suspension. The red solid was collected by filtration, washed with THF (2 × 2 mL), and then dried under vacuum (yield 0.99 g, 91%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 14.3 (d, ^3J(PH) = 14.1 Hz, 1 H, OsC*H*), 4.2 (m, 1 H, OC*H*$_2$), 3.7 (m, 1 H, OC*H*$_2$), 0.5 (t, ^3J(HH) = 7.2 Hz, 3 H, OCH_2CH_3), 6.9−7.8 (m, 45 H, Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 13.0 (s, C*P*Ph$_3$), 1.5 (d, ^2J(PP) = 16.3 Hz, Os*P*Ph$_3$), −6.0 (d, ^2J(PP) = 16.3 Hz, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 237.6 (s, OsCH), 181.5 (d, ^2J(PC) = 21.1 Hz, *C*(OCH_2CH_3)), 98.2 (d, ^1J(PC) = 92.9 Hz, *C*PPh$_3$), 62.3 (s, O*C*H$_2$), 13.5 (s, OCH$_2$*C*H$_3$), 120.0−138.0 (m, Ph) ppm. Anal. Calcd for $C_{59}H_{51}O_2P_3Cl_2Os$: C, 61.83; H, 4.49. Found: C, 61.50, H, 4.71.

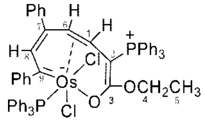
Method A: Os{=CPhCH=CPh-η^2-CH=CHC(PPh₃)=C(O)-OEt}Cl₂(PPh₃) (2a and 2b) and Os{η^2-CHPh=CHCPh=CHCC-(PPh₃)C(O)OEt}Cl₂(PPh₃) (4). A mixture of Os{=CHC(PPh$_3$)=C(O)-OEt}Cl$_2$(PPh$_3$)$_2$ (**1**) (1.15 g, 1.00 mmol) and PhC≡CH (0.44 mL, 4.00 mmol) in $CHCl_3$ (15 mL) was stirred at room temperature for 1 h to give a brown suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown precipitate, which was collected by filtration and then dried by vacuum. Yield: 1.01 g, 93% (a ratio 5:4 of the mixture complex **2a** and **2b**). The pure complex **2a** was obtained by washed the mixture with methanol. Yield: 0.49 g, 45%. The mixture of **2a** and **2b** (1.02 g) was subjected to column chromatography on silica gel using dichloromethane/acetone as eluent. The two bands were identified as complex **2b** (yield 0.092 g, 9%) and **4** (yield 0.45 g, 44%).

Spectroscopic data for **2a**. ^{1}H NMR(CD_2Cl_2, 300.1 MHz): δ 4.9 (d, ^3J(HH) = 9.6 Hz, 1 H, C^{6}H), 4.1 (d, ^3J(HH) = 9.6 Hz, 1 H, C^{1}H), 3.6 (q, ^3J(HH) = 6.6 Hz, 2 H, C^{4}H), 0.4 (t, ^3J(HH) = 6.6 Hz, 3 H, C^{5}H), 7.3 (1H, C^{8}H, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 6.8−7.6 (m, 40H, Ph) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 17.5 (d, ^4J(PP) = 6.1 Hz, C*P*Ph$_3$), −2.9 (d,^4J(PP) = 6.1 Hz, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC (CD_2Cl_2, 75.5 MHz): δ 245.0 (d, ^2J(PC) = 5.3 Hz, C9), 177.3 (dd, ^2J(PC) = 16.0 Hz, ^3J(PC) = 5.6 Hz, C3), 159.4 (s, C8), 140.9 (s, C7), 109.8 (dd, ^2J(PC) = 14.7 Hz, ^3J(PC) = 3.4 Hz, C6), 99.0 (dd, ^2J(PC) = 15.7 Hz, ^2J(PC) = 15.5 Hz, C1), 58.1 (d, ^1J(PC) = 119.3 Hz, C2), 61.0 (s, C4), 13.8 (s, C5), 122.5−136.0, 167.8−169.1 (m, Ph) ppm. Anal. Calcd for $C_{57}H_{48}O_2P_2Cl_2Os$: C, 62.92; H, 4.45. Found: C, 62.80, H, 4.59.



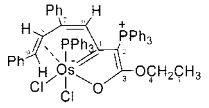
2a

Spectroscopic data for **2b**. ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 3.8 (m, 1 H, C^{6}H), 3.7(m, 1 H, C^{1}H), 3.9 (q, ^3J(HH) = 6.6 Hz, 2 H, C^{5}H), 0.4(t, ^3J(HH) = 6.6 Hz, 3 H, C^{4}H), 7.2 (1 H, C^{8}H, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 6.8−7.9 (m, 40 H, Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 19.0 (s, C*P*Ph$_3$), −7.5 (s, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC (CD_2Cl_2, 75.5 MHz): δ 259.4 (d, ^2J(PC) = 7.5 Hz, C9), 178.3 (d, ^2J(PC) = 16.9 Hz, C3), 156.0 (s, C8), 139.8 (s, C7), 85.6 (d, ^2J(PC) = 13.8 Hz, C1), 82.2 (d, ^3J(PC) = 5.7 Hz, C6), 61.3 (d, ^1J(PC) = 113.4 Hz, C2), 60.9 (s, C4), 14.0 (s, C5), 12.5−134.9, 161.5, 176.6 (m, Ph) ppm. Anal. Calcd for $C_{57}H_{48}O_2P_2Cl_2Os$: C, 62.92; H, 4.45. Found: C, 63.25, H, 4.63.



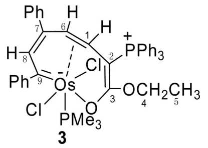
2b

Method B. Os{η^2-CHPh=CHCPh=CHCC(PPh₃)C(O)OEt}Cl₂-(PPh₃) (4). A mixture of complex **2a** and **2b**(1.00 g, 0.92 mmol) in $CHCl_3$ (15 mL) was under reflux for 1 h. Then the volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a brown precipitate, which was collected by filtration and washed with diethyl ether (2 × 5 mL), and subsequent recrystallization of the product from dichloromethane/diethyl ether yielded brownish crystals (yield 0.88 g, 88%). ^{1}HNMR ($CDCl_3$,300.1 MHz): δ 5.8 (s, 1 H, C^{6}H), 5.7 (d, ^3J(HH) = 9.6 Hz, 1 H, C^{8}H), 4.4 (dd, ^3J(HH) = 9.6 Hz, ^3J(PH) = 10.2 Hz, 1 H, C^{9}H), 4.2 (m, 1 H, C^{4}H), 3.8 (m, 1 H, C^{4}H), 0.5 (t, ^3J(HH) = 7.2 Hz, 3 H, C^{5}H), 6.9−7.8 (m, 40 H, Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 6.0 (s, C*P*Ph$_3$), −2.5 (s, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC ($CDCl_3$, 75.5 MHz): δ 243.4 (dd, ^2J(PC) = 4.5 Hz, ^2J(PC) = 3.8 Hz, C1), 184.5 (d, ^2J(PC) = 19.6 Hz, C3), 179.8 (s, C7), 137.6 (s, C6), 88.0 (d, ^1J(PC) = 91.4 Hz, C2), 66.3 (s, C8), 62.1 (s, C9), 63.3 (s, C4), 13.6 (s, C5). 119.9−144.3 (m, Ph) ppm. Anal. Calcd for $C_{57}H_{48}O_2P_2Cl_2Os$: C, 62.92; H, 4.45. Found: C, 63.33, H, 4.00.



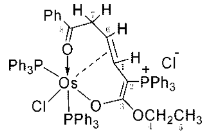
4

Os{=CPhCH=CPh-η^2-CH=CHC(PPh₃)=C(O)OEt}Cl₂(PMe₃) (3). A solution of PMe_3 in THF(1.0 M, 0.46 mL, 0.46 mmol) was added to a mixture of complex **2a** and **2b** (1.00 g, 0.92 mmol) in CH_2Cl_2 (15 mL). The suspension was stirred at room temperature for about 24 h to give a brown suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a brownish red precipitate, which was collected by filtration and washed with diethyl ether (2 × 5 mL), and subsequent recrystallization of the product from dichloromethane/hexane yielded brownish-red crystals (yield 0.65 g, 78%). ^{1}HNMR (CD_2Cl_2, 300.1 MHz): δ 4.3 (dd, ^3J(HH) = 9.3 Hz, ^3J(PH) = 3.3 Hz, 1 H, C^{6}H), 4.2 (ddd, ^3J(HH) = 9.3 Hz, ^3J(PH) = 3.0 Hz, ^3J(PH) = 2.7 Hz, C^{1}H), 3.7 (q, ^3J(HH) = 7.0 Hz, 2 H, C^{4}H), 0.5 (t, ^3J(HH) = 7.0 Hz, 3H, C^{5}H), 7.3 (1 H, C^{8}H, obscured by the phenyl signals and confirmed by ^{1}H−^{13}C HMQC), 7.0−7.6 (m, 25 H, Ph), 1.0−1.2 (m, 9 H, PMe_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 18.3 (d, ^4J(PP) = 4.9 Hz, C*P*Ph$_3$), −33.7 (d,^4J(PP) = 4.9 Hz, Os*P*Me$_3$). ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC (CD_2Cl_2, 75.5 MHz): δ 245.3 (d, ^2J(PC) = 4.5 Hz, C9), 178.3 (dd, ^2J(PC) = 16.6 Hz, ^3J(PC) = 5.3 Hz, C3), 158.2 (d, ^3J(PC) = 3.0 Hz, C8), 141.3 (s, C7), 110.2 (dd, ^2J(PC) = 15.9 Hz,^3J(PC) = 3.0 Hz, C6), 98.3 (dd, ^2J(PC) = 16.6 Hz, ^2J(PC) = 14.3 Hz, C1), 57.3 (d, ^1J(PC) = 118.5 Hz, C2), 60.5 (s, C4), 13.8 (s, C5), 10.9 (s, Me), 11.4 (s, Me), 120.1−134.0, 165.5−171.1 (m, Ph) ppm. Anal. Calcd for $C_{42}H_{42}O_2P_2Cl_2Os$: C, 55.93; H, 4.69. Found: C, 55.64; H, 4.41.



3

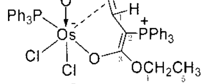
[Os{O=CPhCH$_2$-η^2-CH=CHC(PPh$_3$)=C(O)OEt}Cl(PPh$_3$)$_2$]-Cl (5). A mixture of Os{=CHC(PPh$_3$)=C(O)OEt}Cl$_2$(PPh$_3$)$_2$ (**1**) (1.15 g, 1.00 mmol) and HC≡CCH(OH)Ph (140.6 uL, 1.05 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 1 h to give a brown yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum (yield 1.20 g, 94%). ^{1}H NMR plus HMQC and H−H COSY($CDCl_3$, 300.1 MHz): δ 5.1 (dd, ^3J(PH) = 8.1 Hz, ^3J(HH) = 8.1 Hz, 1H, C^{1}H), 4.8 (br, 1 H, C^{6}H), 3.3 (dd, ^2J(HH) = 19.8 Hz, ^3J(HH) = 5.9 Hz, 1H, C^{7}H), 2.8 (d, ^2J(HH) = 19.8 Hz, 1 H, C^{7}H), 3.9 (m, 1 H, C^{4}H), 3.6 (m, 1H, C^{4}H), 0.5 (t, ^3J(HH) = 6.8 Hz, 3 H, C^{5}H), 6.9−7.7 (m, 50 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 15.5 (d, ^4J(PP) = 2.4 Hz, C*P*Ph$_3$), −21.0 (d, ^2J(PP) = 15.8 Hz, Os*P*Ph$_3$), −27.1 (dd, ^2J(PP) = 15.8 Hz, ^4J(PP) = 2.4 Hz, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC ($CDCl_3$, 75.5 MHz): δ 216.5 (s, C8), 179.7 (d, ^2J(PC) = 17.4 Hz, C3), 62.0 (d, ^2J(PC) = 13.6 Hz, C1), 60.7 (d, ^3J(PC) = 3.0 Hz, C6), 49.1 (d, ^1J(PC) = 108.7 Hz, C2), 44.1 (s, C7), 61.6 (s, C4), 13.7 (s, C5). 122.5−136.2 (m, Ph) ppm. Anal. Calcd for $C_{68}H_{59}O_3P_3Cl_2Os$: C, 63.89; H, 4.65. Found: C, 63.62, H, 4.97.



5

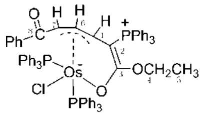
Preparation of the BPh$_4^-$ Salt of 5′. NaBPh$_4$ (148 mg, 0.43 mmol) was added to the solution of **5** (0.50 g, 0.39 mmol) in CH_3OH (10 mL). The reaction mixture was stirred for about 5 min to give an orange precipitate, which was collected by filtration, washed with methanol (2 × 2 mL), and diethyl ether and then dried under vacuum. (Yield: 0.57 g, 94%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 5.2 (dd, ^3J(PH) = 9.0 Hz, ^3J(HH) = 8.1 Hz, 1 H, C^{1}H), 4.7 (m, 1 H, C^{6}H), 3.1 (dd, ^2J(HH) = 19.9 Hz, ^3J(HH) = 7.0 Hz, 1 H, C^{7}H), 2.8 (d, ^2J(HH) = 19.9 Hz, 1 H, C^{7}H), 3.9 (m, 1 H, C^{4}H), 3.6 (m, 1 H, C^{4}H), 0.5 (t, ^3J(HH) = 6.5 Hz, 3 H, C^{5}H), 6.8−7.7 (m, 70 H, Ph). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 15.5 (d, ^4J(PP) = 2.4 Hz, C*P*Ph$_3$), −20.9 (d, ^2J(PP) = 15.8 Hz, Os*P*Ph$_3$), −27.6 (dd, ^2J(PP) = 15.8 Hz, ^4J(PP) = 2.4 Hz, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 216.5 (s, C8), 179.8 (d, ^2J(PC) = 17.4 Hz, C3), 62.1 (d, ^2J(PC) = 10.3 Hz, C1), 60.8 (s, C6), 49.1 (d, ^1J(PC) = 108.2 Hz, C2), 43.9 (s, C7), 61.7 (s, C4), 13.8 (s, C5), 163.4−165.4 (m, BPh), 122.5−136.4 (m, Ph) ppm. Anal. Calcd for $C_{92}H_{79}BO_3P_3ClOs$: C, 70.74; H, 5.10. Found: C, 70.90, H, 5.32.

Os{O=CPhCH$_2$-η^2-CH=CHC(PPh$_3$)=C(O)OEt}Cl$_2$(PPh$_3$) (6). A suspension of [Os{O=CPhCH$_2$-η^2-CH=CHC(PPh$_3$)=C(O)-OEt}Cl(PPh$_3$)$_2$]Cl (**5**) (0.50 g, 0.39 mmol) in CH_2Cl_2 (8 mL) was under reflux for 12 h to give a purple solution. The volume of the mixture was reduced to approximately 1 mL under vacuum, a purple solid deposited, which was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum (yield 0.32 g, 81%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 4.7 (dd, ^3J(PH) = 6.6 Hz, ^3J(HH) = 6.9 Hz, 1 H, C^{1}H), 4.4 (m, 1 H, C^{6}H), 4.3 (dd, ^2J(HH) = 18.0 Hz, ^3J(HH) = 6.0 Hz, 1 H, C^{7}H), 3.1 (dd, ^2J(HH) = 18.0 Hz, ^3J(HH) = 8.3 Hz, 1 H, C^{7}H), 4.0 (m, 1 H, C^{4}H), 3.7 (m, 1 H, C^{4}H), 0.5 (t, ^3J(HH) = 7.1 Hz, 3 H, C^{5}H), 7.0−7.8 (m, 35 H, Ph) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 18.9 (s, C*P*Ph$_3$), −11.6 (s, Os*P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 216.4 (s, C8), 182.8 (d, ^2J(PC) = 16.4 Hz, C3), 71.0 (d, ^2J(PC) = 14.4 Hz, C1), 58.4 (s, C6), 46.6 (d, ^1J(PC) = 114.9 Hz, C2), 44.0 (s, C7), 61.3 (s, C4), 13.9 (s, C5). 123.0−136.8 (m, Ph) ppm. Anal. Calcd for $C_{50}H_{44}O_3P_2Cl_2Os$: C, 59.11; H, 4.37. Found: C, 59.52, H, 4.74.



6

Os [η^3-CH{CPh(=O)}CHCHC(PPh$_3$)=C(O)OEt)]Cl(PPh$_3$)$_2$ (7). A solution of NEt$_3$ (0.70 mL, 5.0 mmol) was added to a suspension of [Os{O=CPhCH$_2$-η^2-CH=CHC(PPh$_3$)=C(O)OEt}Cl-(PPh$_3$)$_2$]Cl (**5**) (1.28 g, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for about 4 h to give a brown solution. The volume of the solution was reduced to approximately 2 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a orange solid, which was collected by filtration, washed with methanol (2 × 2 mL) and diethyl ether (2 × 10 mL), and dried under vacuum (yield 1.15 g, 93%). ^{1}H NMR plus HSQC (400.1 MHz, CD_2Cl_2): δ 3.4 (m, 1 H, C^{1}H), 2.8 (br, 1 H, C^{6}H), 4.2 (m, 1 H, C^{7}H), 3.8 (m, 1 H, C^{4}H), 3.7 (m, 1 H, C^{4}H), 0.3 (t, ^3J(HH) = 8.0 Hz, 3 H, C^{5}H), 6.6−8.1 (m, 50 H, Ph) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 16.1 (s, C*P*Ph$_3$), −6.2 (d, ^2J(PP) = 13.0 Hz, Os*P*Ph$_3$), −9.5 (d, ^2J(PP) = 13.0 Hz, Os*P*Ph$_3$) ppm.^{13}C{^{1}H} NMR plus DEPT-135 and HSQC (100.6 MHz, CD_2Cl_2): δ 196.7 (s, C8), 177.5 (d, ^2J(PC) = 19.1 Hz, C3), 85.9 (s, C7), 58.4 (d, ^2J(PC) = 27.2 Hz, C1), 49.1 (d, ^1J(PC) = 101.6 Hz, C2), 45.0 (d, ^3J(PC) = 8.0 Hz, C6), 60.3 (s, C4), 13.4 (s, C5). 124.1−142.2 (m, Ph) ppm. Anal. Calcd for $C_{68}H_{58}O_3P_3ClOs$: C, 65.77; H, 4.71. Found: C, 65.54, H, 5.00.



7

X-ray Crystal Structures Determination of 1, 3, 4, 5′, 6, and 7. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or $CHCl_3$ solutions layered with ether or hexane for all

Table 1. Crystal Data and Structure Refinement for 1, 3, 4, 5′, 6, and 7

	$\mathbf{1}\cdot 2\mathrm{CH_2Cl_2}$	$\mathbf{3}\cdot 0.5\mathrm{CH_2Cl_2}$	$\mathbf{4}\cdot \mathrm{H_2O}\cdot 0.5\mathrm{CH_2Cl_2}$	$\mathbf{5'}\cdot \mathrm{H_2O}$	$\mathbf{6}\cdot 1.25\mathrm{CH_2Cl_2}$	$\mathbf{7}\cdot \mathrm{CH_2Cl_2}$
empirical formula	$C_{59}H_{51}Cl_2OsP_3O_2\cdot 2CH_2Cl_2$	$C_{42}H_{42}Cl_2OsO_2P_20.5CH_2Cl_2$	$C_{57}H_{48}Cl_2OsO_2P_2H_2O\cdot 0.5CH_2Cl_2$	$C_{68}H_{59}ClOsO_3P_3B(C_6H_5)_4\cdot H_2O$	$C_{50}H_{44}Cl_2OsO_3P_2\cdot 1.25CH_2Cl_2$	$C_{68}H_{58}ClOsO_3P_3\cdot CH_2Cl_2$
formula weight	1315.86	944.26	1148.54	1579.94	1122.05	1326.63
temperature, K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	triclinic	triclinic	triclinic	monoclinic
space group	*Cc*	$Pna2_1$	*P*-1	*P*-1	*P*-1	$P2_1/n$
a, Å	12.6801(3)	12.6837(2)	13.3346(5)	13.6804(5)	12.0519(7)	14.9807(2)
b, Å	21.1499(4)	23.4194(4)	13.6669(4)	17.2308(5)	13.0418(7)	25.0138(4)
c, Å	21.4017(4)	14.1523(3)	16.7686(5)	17.5550(5)	18.7115(8)	16.0283(2)
α, deg	90	90	104.013(3)	69.765(3)	102.2530(10)	90.00
β, deg	104.597(2)	90	105.535(3)	89.334(3)	100.8660(10)	95.6750(10)
γ, deg	90	90	102.005(3)	84.897(3)	111.483(3)	90.00
V, Å^3	5554.3(2)	4203.9(1)	2732.3(2)	3866.5(2)	2557.2(2)	5976.8(2)
Z	4	4	2	2	2	4
d_{calcd}, g cm^{-3}	1.574	1.492	1.396	1.357	1.457	1.474
$F(000)$	2640	1884	1154	1616	1121	2680
crystal size, mm	0.32 × 0.23 × 0.18	0.40 × 0.38 × 0.32	0.22 × 0.20 × 0.17	0.42 × 0.31 × 0.18	0.20 × 0.18 × 0.15	0.52 × 0.25 × 0.24
θ range, deg	2.16−25.00	2.32−24.99	2.33−25.00	2.36−25.00	2.28−25.00	2.41−25.00
reflns collected	16374	14886	21566	31165	17660	31031
indep reflns	7315	4961	9496	13401	8798	10489
obsd reflns ($I > 2\sigma(I)$)	5881	4131	7587	9658	7040	7940
data/restraints/params	7315/14/656	4961/43/475	9496/24/622	13401/64/928	8798/3/572	10489/0/712
goodness-of-fit on F^2	0.876	1.000	1.095	1.010	1.067	0.995
final R ($I > 2\sigma(I)$)	$R_1 = 0.0278$, $wR_2 = 0.0372$	$R_1 = 0.0394$, $wR_2 = 0.1175$	$R_1 = 0.0510$, $wR_2 = 0.1634$	$R_1 = 0.0489$, $wR_2 = 0.1320$	$R_1 = 0.0367$, $wR_2 = 0.1198$	$R_1 = 0.0285$, $wR_2 = 0.0433$
R indices (all data)	$R_1 = 0.0386$, $wR_2 = 0.0385$	$R_1 = 0.0494$, $wR_2 = 0.1225$	$R_1 = 0.0642$, $wR_2 = 0.1695$	$R_1 = 0.0763$, $wR_2 = 0.1372$	$R_1 = 0.0492$, $wR_2 = 0.1227$	$R_1 = 0.0461$, $wR_2 = 0.0448$

complexes. 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 using graphitemonochromated Mo Kα radiation ($\lambda = 0.71073$ 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 708614 (**1**), 708615 (**3**), 708616(**4**), 708617(**5**), 708618(**6**), and 708619(**7**) 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: X-ray crystallographic files in CIF format. These materials are available free of charge *via* the Internet at http://pubs.acs.org.

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