CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201200231

Interconversion of Metallabenzenes and Cyclic η^2-Allene-Coordinated Complexes

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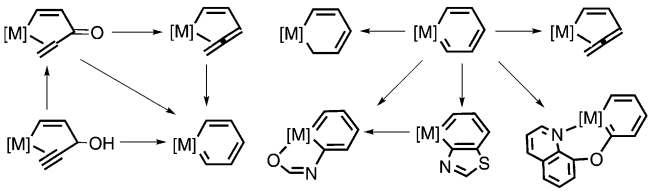
Abstract: Treatment of the osmabenzene [Os{CHC(PPh$_3$)CHC(PPh$_3$)CH}Cl$_2$(PPh$_3$)$_2$]Cl (**1**) with excess 8-hydroxyquinoline produces monosubstituted osmabenzene [Os{CH C(PPh$_3$)CHC(PPh$_3$)CH}(C$_9$H$_6$NO)Cl(PPh$_3$)]Cl (**2**) or disubstituted osmabenzene [Os{CHC(PPh$_3$)CHC(PPh$_3$)CH}(C$_9$H$_6$NO)$_2$]Cl (**3**) under different reaction conditions. Osmabenzene **2** evolves into cyclic η^2-allene-coordinated complex [Os{CH=C(PPh$_3$)CH=(η^2-C=CH$_2$)}(C$_9$H$_6$NO)(PPh$_3$)$_2$]Cl (**4**) in the presence of excess PPh$_3$ and NaOH, presumably involving a P–C bond cleavage of the metallacycle. Reaction of **4** with excess 8-hydroxyquinoline under air affords the S_NAr product [(C$_9$H$_6$NO)Os{CHC(PPh$_3$)CHCHC}(C$_9$H$_6$NO)(PPh$_3$)]Cl (**5**). Complex **4** is fairly reactive to a nucleophile in the presence of acid, which could react with water to give carbonyl complex [Os{CH=C(PPh$_3$)CH=CH$_2$}(C$_9$H$_6$NO)(CO)(PPh$_3$)$_2$]Cl (**6**). Complex **4** also reacts with PPh$_3$ in the presence of acid and results in a transformation to [Os{CHC(PPh$_3$)CHCHC}(C$_9$H$_6$NO)Cl(PPh$_3$)$_2$]Cl (**7**) and [Os{CH=C(PPh$_3$)CH=(η^2-C=CH(PPh$_3$))}(C$_9$H$_6$NO)Cl(PPh$_3$)]Cl (**8**). Further investigation shows that the ratio of **7** and **8** is highly dependent on the amount of the acid in the reaction.

Keywords: allenes · interconversion · metallabenzene · metallacycles · aromatic substitution

Introduction

The chemistry of metallabenzenes is a field of great current interest because they can display aromatic properties and mediate organometallic reactions.[1] Several approaches have been developed to construct a remarkable number of stable metallabenzene rings.[2] Common strategies previously employed are the formation of metallabenzenes from various unsaturated metallacycles, including four-,[3] five-,[4] and six-membered metallacycles.[5] Reactivity studies of metallabenzenes demonstrated that the converse transformation could also be feasible.[6–9] However, only the interconversion of metallacyclopentadienes or metallacyclohexadienes to metallabenzenes could be achieved.[7,8] Paneque et al. reported that iridabenzenes with electron-withdrawing CO_2Me groups could be prepared from iridacyclopentadienes or iridacyclohexadienes; the reactions are reversible in these examples.[7,8a] Chin and Lee reported the facile interconversion between iridacyclohexadienes and iridabenzenes through the elimination or addition of H^+.[8b] Roper, Wright, and coworkers have demonstrated the first intermolecular nucleophilic aromatic substitution of metallabenzenes to give the isolated metallacyclohexadienes and showed that the subsequent oxidation of these compounds could yield the corresponding substituted metallabenzenes.[8c]

We have recently prepared a series of new metallabenzenes from unsaturated metallacycles,[10] thus contributing a valuable addition to previous synthetic methodologies. In our investigation of the reactivity of metallabenzenes, we found that they could be easily transformed to the monocyclic or polycyclic species.[9] As a part of our recent studies on metallabenzene chemistry, we have studied the relationship between metallabenzenes and various metallacycles and found that the former is an excellent material to generate new metallacycles with different metals and substituents (Scheme 1). In this paper, we report the interconversion of metallabenzenes and cyclic η^2-allene-coordinated complexes.



Scheme 1. Transformation of metallabenzenes to other metallacycles.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200231.

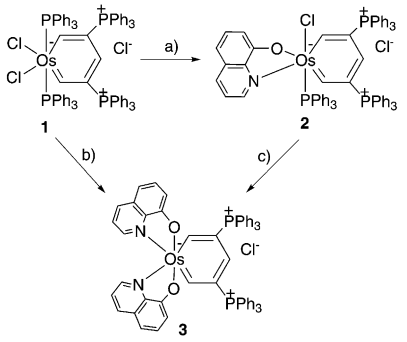
Results and Discussion

Reactions of Osmabenzene and 8-Hydroxyquinoline

We have previously reported the first nucleophilic aromatic substitution (S_NAr) reaction of ruthenabenzene [Ru{CHC(PPh$_3$)CHC(PPh$_3$)CH}Cl$_2$(PPh$_3$)$_2$]Cl, which was attacked by

8-hydroxyquinoline and generated a multicyclic complex with highly stability.[9a] Thus, we envisioned that the introduction of 8-hydroxyquinoline to our osmabenzenes might give new access to the interconversion of metallabenzenes and related metallacycles.

Treatment of a solution of **1** in dichloromethane with 1.5 equivalents of 8-hydroxyquinoline under reflux for 4 hours led to the formation of the corresponding monosubstituted osmabenzene **2** (Scheme 2). As complex **2** has good solubility in organic solvents, it is difficult to obtain single crystals of **2** to determine its solid-state structure. Fortunately, the counter anion Cl^- in **2** can be easily replaced with BPh_4^- by treatment of **2** with $NaBPh_4$ to give osmabenzene **2′**. The structure of **2′** was confirmed unambiguously by X-ray diffraction. The crystallographic details are listed in Table 1. The molecular structure of **2′** (Figure 1) reveals that it is a metallabenzene complex formed through the replacement of one Cl and one PPh_3 ligand in **1** by one 8-hydroxyquinoline ligand. The metallacycle of complex **2′** deviates significantly from planarity. The osmium center lies 0.5072 (73) Å out of the plane of the metallacyclic carbon atoms (C1–C5). The dihedral angle between this plane and the C1-Os-C5 plane is 21.9°. However, the carbon–carbon bond distances of the metallacycle are in the range of 1.389(9)–1.422(9) Å. A similar delocalized metallabenzene structure without a planar metallacycle was observed in our previously reported metallabenzene with a 2,2′-dipyridyl ligand.[10b,11]



Scheme 2. Reactions of osmabenzene **1** with 8-hydroxyquinoline. Conditions: a) 8-hydroxyquinoline (1.5 equiv), CH_2Cl_2, reflux, 4 h, yield 50%; b) 8-hydroxyquinoline (2.5 equiv), NaOH (5 equiv), CH_2Cl_2, reflux, 4 h, yield 45%; c) 8-hydroxyquinoline (1.5 equiv), NaOH (5 equiv), CH_2Cl_2, reflux, 4 h, yield 53%.

When the reaction was performed in the presence of excess NaOH and the proportion of 8-hydroxyquinoline in this reaction was increased, it produced the disubstituted osmabenzene **3** instead of the expected S_NAr product (Scheme 2).[9a] The reaction of isolated **2** with excess 8-hydroxyquinoline and NaOH under the same conditions gave the same result.

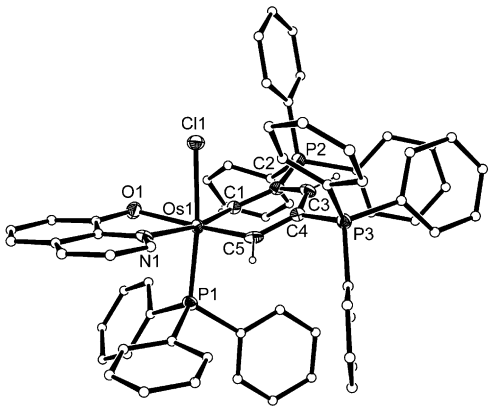


Figure 1. Molecular structure of complex **2′** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Cl1: 2.4661(14), Os1–P1: 2.3082(15), Os1–N1: 2.182(5), Os1–O1: 2.130(4), Os1–C1: 1.922(6), Os1–C5: 1.944(6), C1–C2: 1.413(9), C2–C3: 1.389(9), C3–C4: 1.422(9), C4–C5: 1.393(8), P2–C2: 1.789(6), P3–C4: 1.793(6); Cl1-Os1-P1: 173.13(6), N1-Os1-O1: 76.70(18), C1-Os1-C5: 91.0(3), Os1-C1-C2: 125.1(5), C1-C2-C3: 124.5(6), C2-C3-C4: 123.7(6), C3-C4-C5: 123.2(6), C4-C5-Os1: 125.5(5).

Complex **3** was characterized by multinuclear NMR spectroscopy and elemental analysis. The ^1H NMR spectrum (in $CDCl_3$) shows a downfield signal at 16.8 ppm, which can be assigned to the Os*CH* protons. The $^{13}C\{^1H\}$ NMR spectrum of **3** (in $CDCl_3$) displays the three signals of the metallabenzene ring at 215.5, 142.3, and 111.0 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) shows a singlet at 21.9 ppm. The counter anion Cl^- in **3** can also be easily replaced with BPh_4^- to generate osmabenzene **3′**, the structure of which was established by X-ray crystallography. As shown in Figure 2, complex **3′** contains an essentially planar metallabenzene unit. The co-planarity is reflected by the small mean deviation (0.0363 Å) from the least-squares plane through the six atoms Os1, C1, C2, C3, C4, and C5. The C–C bond lengths of the C1–C5 chain are in the range of 1.395(10)–1.409(10) Å, and the lack of significant variation in the C–C bond lengths suggests that **3′** has a delocalized structure.

Interconversion of Metallabenzenes and Cyclic η^2-Allene-Coordinated Complexes

When the reaction of osmabenzene **2** with NaOH was performed in a protic solvent under refluxing temperature for two hours, traces of cyclic η^2-allene-coordinated complex **4** were identified by in situ NMR. Conversion of complex **2** into **4** seems to be promoted by the addition of PPh_3. When a solution of **2** and excess NaOH in H_2O/CH_3OH (1:20) was heated at 60 °C in the presence of purposely added PPh_3, the reaction could be completed within 5 hours to give **4** as the dominant product (Scheme 3).

Abstract in Chinese:

本文通过8-羟基喹啉配体的引入，实现了金属苯与环状配位联烯化合物的相互转换。此研究有望进一步开拓制备金属杂环的简便新途径。

Table 1. Crystal Data and Structure Refinement for **2′**, **3′**, **4**, **5**, **6′**, **7**, and **8**.

	2′·$2CH_2Cl_2$	**3′**·$0.25CH_2Cl_2$	**4**·$2H_2O$	**5**	**6′**·CH_2Cl_2	**7**·$C_2H_4Cl_2$·$0.5CH_2Cl_2$·$1.5H_2O$	**8**·CH_2Cl_2·$0.25CHCl_3$
formula	$C_{94}H_{78}BCl_5NOP_3Os$	$C_{83.25}H_{65.50}BCl_{0.50}N_2O_2P_2Os$	$C_{68}H_{59}ClNO_3P_3Os$	$C_{59}H_{45}ClN_2O_2P_2Os$	$C_{69}H_{57}Cl_2F_6NO_2P_4Os$	$C_{70.50}H_{62}Cl_5NO_{2.5}P_3Os$	$C_{69.25}H_{56.25}Cl_{4.75}NOP_3Os$
Mr	1708.74	1406.55	1256.72	1101.56	1431.14	1423.57	1369.90
wavelength [Å]	0.71073	0.71073	1.54178	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2/c$	$P21/c$	$P\bar{1}$	$P21/n$
a [Å]	10.63560(10)	9.9993(3)	34.9194(4)	25.9776(11)	12.9376(6)	12.687(3)	17.0256(7)
b [Å]	17.0231(3)	18.3447(5)	15.2141(2)	8.6114(3)	38.1212(14)	16.761(3)	20.1970(6)
c [Å]	23.4742(4)	20.2956(5)	24.6165(3)	22.6944(8)	14.5517(10)	18.381(4)	19.8694(8)
α [°]	87.392(2)	84.148(2)	90	90	90	112.48(3)	90
β [°]	82.0750(10)	87.366(2)	102.4340(10)	113.414(5)	121.941(4)	101.78(3)	113.091(5)
γ [°]	81.9680(10)	75.235(2)	90	90	90	103.32(3)	90
V [Å^3]	4166.65(11)	3580.44(17)	12771.2(3)	4658.8(3)	6090.2(6)	3323.7(18)	6285.0(4)
Z	2	2	8	4	4	2	4
ρ_{calcd} [gcm^{-3}]	1.362	1.305	1.307	1.571	1.561	1.422	1.448
μ [mm^{-1}]	1.796	1.892	5.207	2.911	2.353	2.237	2.351
F(000)	1736	1429	5088	2208	2872	1436	2754
crystal size [mm^3]	0.50×0.40×0.40	0.30×0.30×0.15	0.28×0.15×0.15	0.25×0.15×0.15	0.28×0.25×0.20	0.25×0.20×0.15	0.40×0.30×0.30
θ range [°]	2.42-25.00	2.29-25.00	3.18-60.13	2.85-25.00	2.74-25.00	3.07-25.00	2.79-25.00
reflns collected/unique	52686/14647	24848/12161	26429/9433	20431/8190	29597/10721	41056/11639	30041/11058
data/restraints/params	14647/51/992	12161/102/856	9433/54/721	8190/66/606	10721/0/766	11639/63/794	11058/60/766
GOF on F^2	1.000	0.998	1.000	0.809	0.997	1.000	0.999
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0519/0.1505	0.0509/0.1393	0.0422/0.1613	0.0309/0.0410	0.0555/0.0959	0.0368/0.1401	0.0489/0.1243
R_1/wR_2 (all data)	0.0669/0.1563	0.0832/0.1465	0.0467/0.1708	0.0554/0.0428	0.0870/0.1015	0.0402/0.1565	0.0783/0.1302
largest peak/hole [e Å^{-3}]	2.358/−1.915	1.354/−0.603	1.673/−0.863	1.010/−1.378	1.439/−3.543	2.108/−1.079	2.150/−1.071

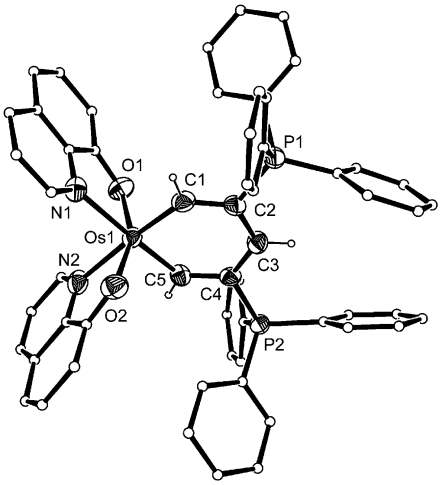
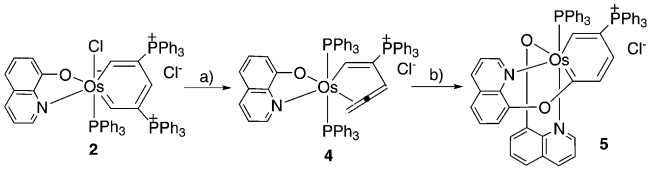


Figure 2. Molecular structure of complex **3′** (ellipsoids at the 50% probability level). Counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–O1: 2.026(5), Os1–O2: 2.030(6), Os1–N2: 2.184(6), Os1–N1: 2.184(6), Os1–C1: 1.919(8), Os1–C5: 1.927(7), C1–C2: 1.401(11), C2–C3: 1.409(10), C3–C4: 1.395(10), C4–C5: 1.397(10), P1–C2: 1.783(7), P2–C4: 1.771(7); O1-Os1-O2: 157.7(2), N1-Os1-N2: 92.5(2), C1-Os1-C5: 89.9(3), Os1-C1-C2: 129.0(6), C1-C2-C3: 124.6(7), C2-C3-C4: 121.8(7), C3-C4-C5: 124.0(6), C4-C5-Os1: 129.5(5).



Scheme 3. Interconversion of osmabenzenes and η^2-allene-coordinated complex. Conditions: a) PPh_3 (5 equiv), NaOH (15 equiv), H_2O/CH_3OH (v:v=1:20), 60 °C, 5 h, yield 76%; b) 8-hydroxyquinoline (5 equiv), $CHCl_3$, 100 °C, sealed tube, under air, 12 h, yield 60%.

Complex **4** was isolated as an orange solid. It has been characterized by elemental analysis, multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction analysis. The crystallographic details are given in Table 1. A view of the cation is shown in Figure 3. The X-ray diffraction data indicate that **4** contains a conjugated osmacycle with a terminal double bond of an allene coordinated to the metal atom. As a consequence of its coordination to the metal center, the allene unit is strongly bent with a C3-C4-C5 angle of 161.2°. In agreement with this structure, the $^{31}P\{^1H\}$ NMR spectrum displays signals at $\delta = -12.5$ (s, Os*P*Ph_3) and 9.7 (s, C*P*Ph_3) ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of Os*C*H and *C*PPh_3 appear at $\delta = 205.2$ and 118.6 ppm, while the three carbon signals of the coordinated allene backbone are observed at $\delta = 117.8$ (*C*HCCH_2), 193.1 (CH*C*CH_2), and 15.7 (CHC*C*H_2) ppm, respectively. The ^1H NMR spectrum shows the Os*CH* signal at $\delta = 11.7$ ppm and the CHCCH_2 signal at $\delta = 4.2$ ppm. On the basis of the ^1H–^{13}C HMQC spectrum, the signal of

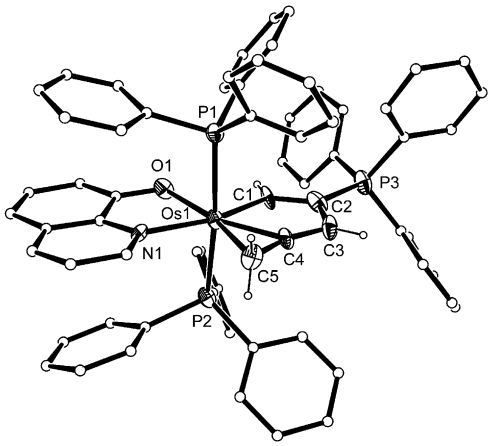
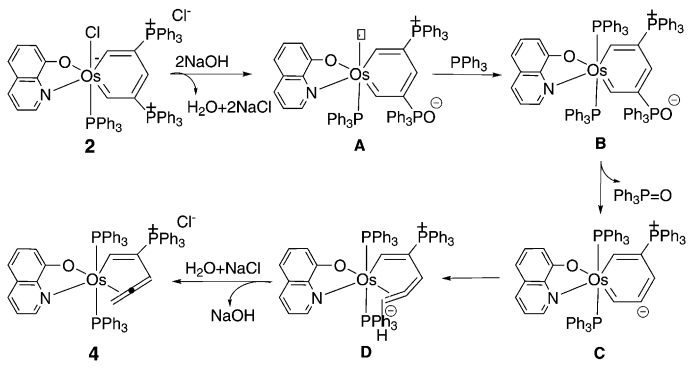


Figure 3. Molecular structure of complex **4** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1-P1: 2.4081(13), Os1-P2: 2.3903(13), Os1–N1: 2.184(4), Os1–O1: 2.105(3), Os1–C1: 2.031(5), Os1–C4: 2.058(14), Os1–C5: 2.162(5), C1–C2: 1.385(8), C2–C3: 1.465(8), C3–C4: 1.312(7), C4–C5: 1.386(7), P3–C2: 1.761(5); P1-Os1-P2: 173.04(4), N1-Os1-O1: 76.87(14), C1-Os1-C4: 72.92(19), C1-Os1-C5: 111.16(19), Os1-C1-C2: 121.3(4), C1-C2-C3: 111.3(5), C2-C3-C4: 110.6(5), C3-C4-C5: 161.2(5), C3-C4-Os1: 123.8(4), C4-C5-Os1: 66.8(3), C5-C4-Os1: 74.89(3).

C*H*CCH$_2$, which is covered by the phenyl signals in the ^{1}H NMR spectrum, can be distinguished at $\delta = 7.9$ ppm.

Allene-coordinated complexes are important intermediates that have been widely used in transition metal-catalyzed organic synthesis and mechanistic studies.[12,13] Complex **4** is a new example of metallacycles bearing an intramolecularly coordinated allene group.[9b,10c,d,14,15] A rationale that accounts for the observed result is shown in Scheme 4. The formation of **4** may involve a P–C bond cleavage of the metallacycle, followed by electron transfer to give **D** and proton capture from the solvent. A similar mechanism for the hydrolysis reaction of metallabenzene phosphonium salt has been described in our previous report.[9a] Consistent with this mechanism, the formation of **4** could not be observed when the reaction was performed with very pure sample of **2** in absence of PPh_3.



Scheme 4. Plausible mechanism for the transformation of osmabenzene **2** to η^2-allene-coordinated complex **4**.

We have demonstrated that a similar cyclic η^2-allene complex, $[Os\{CH{=}C(PPh_3)C(CH_3){=}(\eta^2\text{-}C{=}CH_2)\}(PhCN)_2(PPh_3)_2]Cl_2$, could isomerize to metallabenzene when $CHCl_3$ was employed as solvent in the reaction.[10c] By contrast, complex **4** is very stable in $CHCl_3$ under refluxing condition. When the solution of **4** in $CHCl_3$ was heated in sealed tube at 100 °C (oil bath temperature), it decomposed to form a mixture of species with triphenylphosphine oxide as the major decomposition product. We presumed that the conversion of complex **4** to metallabenzene might occur and that the product was not stable under the reaction conditions. When the reaction was performed with additional 8-hydroxyquinoline (5 equiv) in $CHCl_3$ in a sealed tube under air for 12 hours at 100 °C (oil bath temperature), metallabenzene **5** was isolated as a brownish solid in 60% yield (Scheme 3).

The structure of **5** has been determined by X-ray diffraction, and a view of the cation of **5** is shown in Figure 4. The X-ray structure clearly shows that complex **5** contains an es-

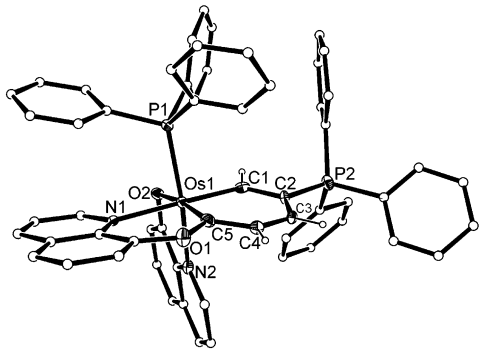
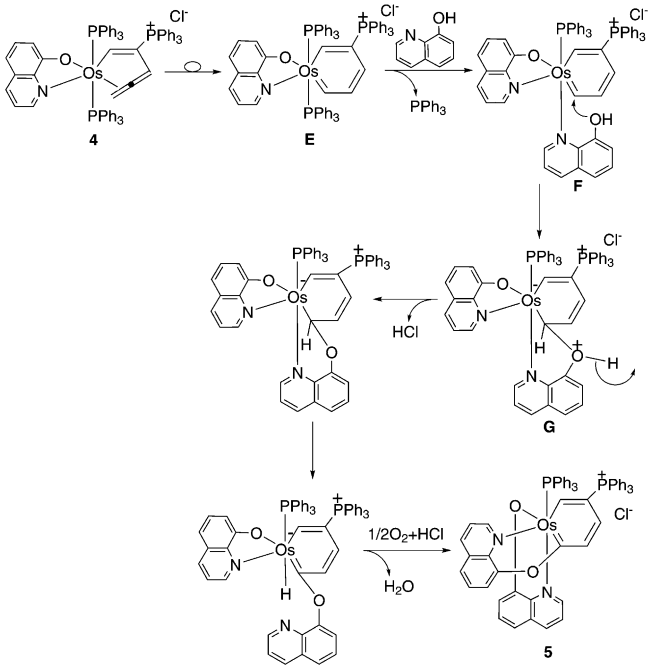


Figure 4. Molecular structure of complex **5** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–P1: 2.3499(13), Os1–N1: 2.177(3), Os1–N2: 2.128(4), Os1–O2: 2.166(2), Os1–C1: 1.959(4), Os1–C5: 1.900(4), C1–C2: 1.387(5), C2–C3: 1.419(5), C3–C4: 1.365(5), C4–C5: 1.427(5), P2–C2: 1.768(4); P1-Os1-N2: 168.84(9), N1-Os1-O2: 89.47(11), C1-Os1-C5: 90.00(16), Os1-C1-C2: 129.5(3), C1-C2-C3: 121.9(4), C2-C3-C4: 124.2(4), C3-C4-C5: 124.8(4), C4-C5-Os1: 128.2(3).

sentially planar metallabenzene unit. The mean deviation from the least-squares plane through Os1 and C1–C5 is 0.0475 Å, and the sum of the angles in the six-membered ring is 718.6°, which is very close to the ideal value of 720°. It is interesting that even the seventeen atoms of the metallacycle (Os1, C1–C5) and the 8-hydroxyquinoline ring (N1, O1, and C11–C19) are approximately coplanar, which is reflected by the mean deviation (0.0721 Å) from the least-squares plane. The Os1-C5 bond (1.900(4) Å) is appreciably shorter than the Os1-C1 bond (1.959(4) Å). The lengths of the carbon–carbon bonds in the metallacycle (1.365(5)–1.427(5) Å) are between those of normal single and double bonds and close to the length of the C–C bonds in benzene (1.400 Å). The structural feature associated with the metallacycle of **5** is very similar to that of the ruthenabenzene

$[(C_9H_6NO)Ru\{CHC(PPh_3)CHCHC\}(C_9H_6NO)(PPh_3)]Cl$ previously reported by us.[9a] Consistent with the solid-state structure, the ^1H and ^{13}C NMR chemical shifts of the ring atoms appear in the aromatic region. The ^1H NMR spectrum displays the OsC*H* signal at $\delta = 15.1$ ppm, the OsCHC(PPh_3)C*H* signal at $\delta = 7.5$ ppm, and the OsCHC(PPh_3)CHC*H* signal at $\delta = 7.0$ ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the five carbon signals of the metallacycle at $\delta =$ 232.0 (Os*C*H), 110.2 (*C*(PPh_3)), 144.6 (γ-*C*H), 124.1 (OsCHC(PPh_3)CH*C*H), and 246.5 (Os*C*) ppm.

The above observations led us to propose the mechanism depicted in Scheme 5. The transient metallabenzene **E**, resulting from the isomerization of allene complex **4**, appears



Scheme 5. Plausible mechanism for the transformation of η^2-allene-coordinated complex **4** to osmabenzene **5**.

to be a key intermediate of this rearrangement that involves a hydrogen-transfer process. Ligand substitution of **E** with additional 8-hydroxyquinoline gives **F** and subsequent intermolecular S_NAr reaction and oxidation reaction could generate osmabenzene **5**. Although we have failed to observe the intermediate **E**, the formation of metallabenzene from a cyclic η^2-allene-coordinated complex has been previously reported and DFT calculations have also been performed before to elucidate the mechanism.[10c] In addition, increasing the stability of metallabenzene by introducing 8-hydroxyquinoline substitution to the metallabenzene ring has also been confirmed by our recent study.[9a]

Reactions of Complex 4 with Nucleophiles

As mentioned above, excess NaOH has been regarded as one of the essential conditions for the formation of complex **4**. Thus, complex **4** is stable in solution with alkali. However, complex **4** is very electrophilic in the presence of a weak acid and even water can react with it as a nucleophile. A solution containing complex **4** and excess NH_4Cl in wet chloroform in a sealed tube at 100 °C gave complex **6** as the major product (all reactions of **4** were carried out under air).

Complex **6** was isolated as a brown solid in 60% yield and characterized by elemental analysis and NMR spectroscopy. In particular, the ^1H NMR spectrum (in $CDCl_3$) shows the signals of OsCH=C(PPh_3)CH=CH_2 at $\delta = 11.3$ (OsC*H*), 7.0 (*CH*CH_2), 6.5 (CHC*H*$_2$), and 5.0 (CHC*H*$_2$) ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the signals of the vinyl ligand OsCH=C(PPh_3)CH=CH_2 at $\delta = 198.5$ (Os*C*H), 113.8 (*C*(PPh_3)), 140.0 (*C*H), 115.6 (*C*H_2) ppm and the *C*O signal at 186.6 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at $\delta = 15.8$ (C*P*Ph_3) and -5.9 (Os*P*Ph_3) ppm. The complex of the same cation as **6** in association with the counter anion PF_6^- (**6′**) is obtainable by simple anion metathesis. A view of the molecular geometry of **6′** is shown in Figure 5.

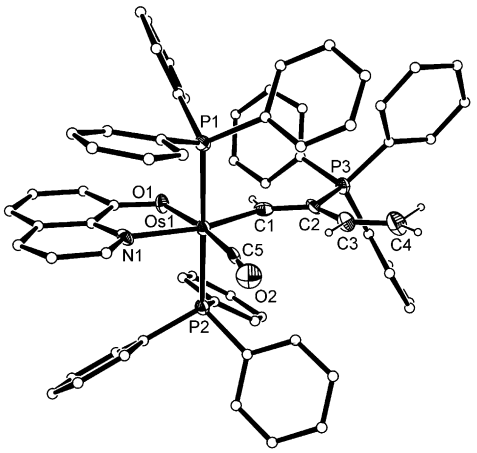
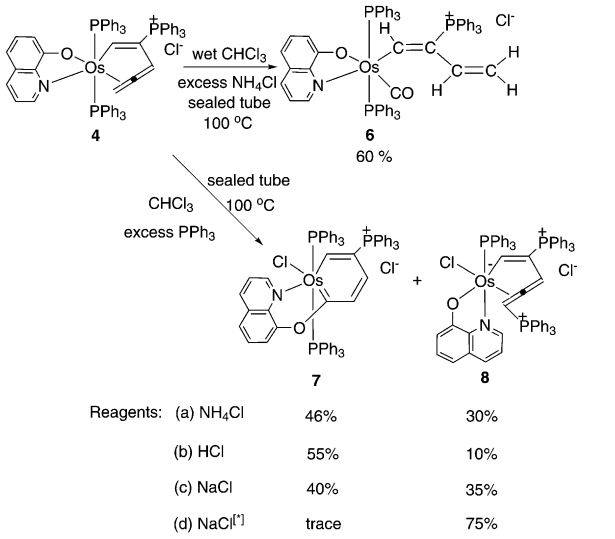


Figure 5. Molecular structure of complex **6′** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–P1: 2.3991(16), Os1–P2: 2.4071(17), Os1–O1: 2.091(4), Os1–N1: 2.152(5), Os1–C1: 2.032(6), Os1–C5: 1.810(8), C1–C2: 1.361(9), C2–C3: 1.467(9), C3–C4: 1.316(9), P3–C2: 1.798(6), O2–C5: 1.177(8); P1-Os1-P2: 176.62(6), O1-Os1-N1: 77.65(18), C1-Os1-C5: 101.4(3), Os1-C1-C2: 142.0(5), C1-C2-C3: 123.8(6), C2-C3-C4: 131.8(7).

It has been reported that osmaphenol [Os(=C(OH)CH=C(Me)C($SiMe_3$)=CH)(bipy)(PPh_3)$_2$]OTf could be converted into the carbonyl osmium complex [Os(CH=C($SiMe_3$)C(Me)=CH_2)(CO)(bipy)(PPh_3)$_2$]OTf in the presence of acid/H_2O.[5a] Our previously reported metallabenzenes were highly electrophilic at the α-carbon atom.[9] Thus, in view of the structural similarities of complex **6** and the carbonyl osmium complex [Os(CH=C($SiMe_3$)C(Me)=CH_2)(CO)(bipy)(PPh_3)$_2$]OTf,[5a] we assume that the formation of **6** proceeds through the isomerization of allene complex **4** to metallabenzene intermediate **E**, followed by nucleophilic attack of H_2O on the α-carbon to generate the met-

allaphenol intermediate (see Scheme S1 in the Supporting Information).

To further study the electrophilic nature of **4**, we also investigated the reaction of **4** with PPh_3. In contrast to the reaction of **4** with excess NH_4Cl, the reaction of complex **4** with excess PPh_3 afforded a 3:2 mixture of **7** and **8** (Scheme 6) under the above experimental conditions (excess



Scheme 6. Reactions of complex **4** with acids. [*] Reaction performed in $CHCl_3$ that was stored with K_2CO_3 in the dark prior use to avoid the photochemical formation of HCl.

NH_4Cl, sealed tube, 100 °C, $CHCl_3$, air atmosphere). Attempts to obtain a single product by using hydrochloric acid in diethyl ether instead of NH_4Cl failed and only led to a decrease in the amount of **8**. Further studies showed that the ratio of **7** to **8** is highly dependent on the amount of acid in the reaction. The results are summarized in Scheme 6. In the presence of excess NaCl, the reaction produced **7** and **8** in the molar ratio of 1:2. When the reaction was carried out in the absence of acid (the solvent $CHCl_3$ was treated beforehand with K_2CO_3 to remove acid), only a trace amount of **7** was observed, while complex **8** could be isolated in 75% yield. According to these results, it is likely that excess chloride is essential for the formation of **7** and **8**. In addition, the formation of **7** also requires the presence of acid.

Complexes **7** and **8** can be separated by chromatography. The structure of **7** has been confirmed by X-ray diffraction analysis. As shown in Figure 6, the structural features of the six-membered metallacycle are nearly identical to those of osmabenzene **5**. The solid-state structure of **7** is fully consistent with the solution NMR data.

Complex **8** was isolated as a yellow solid. The molecular structure of **8** has also been unambiguously confirmed by X-ray diffraction (Figure 7). The X-ray diffraction study proves that the allene unit of **8** is coordinated to the metal center as a η^2-ligand through the carbon–carbon double bond connected with PPh_3 substitution. Similar to complex **4**, the

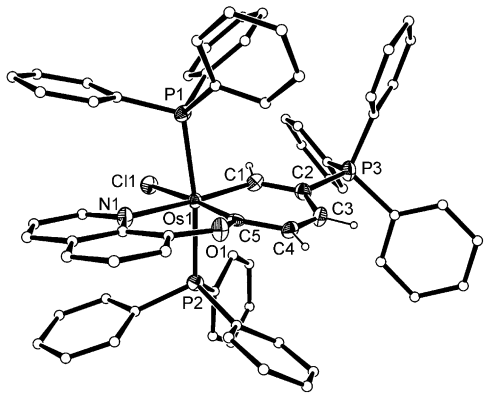


Figure 6. Molecular structure of complex **7** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–P1: 2.4128(14), Os1–P2: 2.3972(14), Os1–Cl1: 2.5234(15), Os1–N1: 2.206(5), Os1–C1: 1.995(6), Os1–C5: 1.910(5), C1–C2: 1.371(8), C2–C3: 1.433(7), C3–C4: 1.360(7), C4–C5: 1.447(7), P3–C2: 1.785(5); P1-Os1-P2: 169.84(5), Cl1-Os1-N1: 91.60(13), C1-Os1-C5: 89.4(2), Os1-C1-C2: 128.9(4), C1-C2-C3: 122.6(5), C2-C3-C4: 124.7(5), C3-C4-C5: 123.6(4), C4-C5-Os1: 128.3(4).

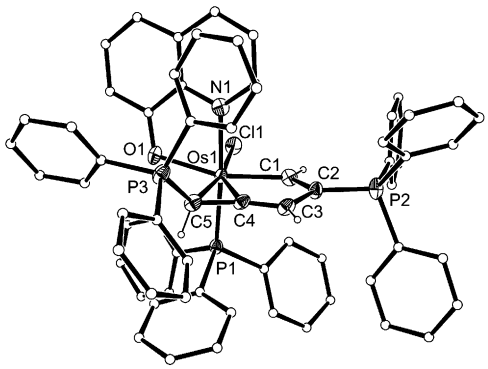
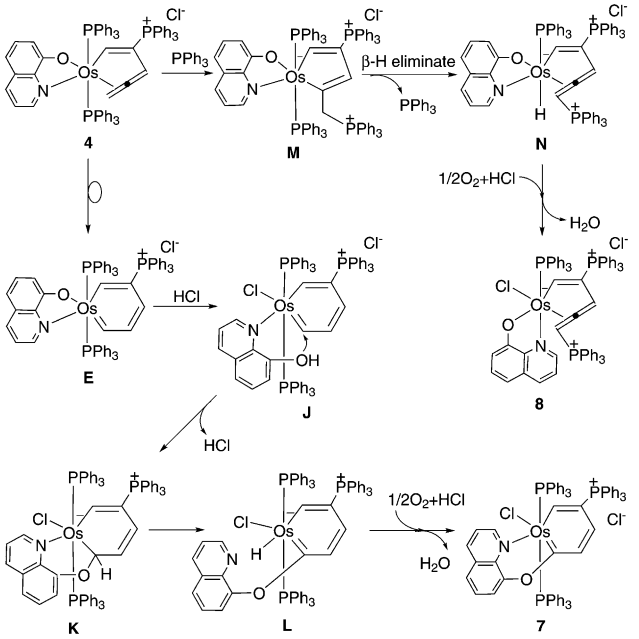


Figure 7. Molecular structure of complex **8** (ellipsoids at the 50% probability level). The counter anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–N1: 2.117(6), Os1–P1: 2.343(2), Os1–O1: 2.133(5), Os1–Cl1: 2.4268(18), Os1–C1: 2.040(7), Os1–C4: 1.999(7), Os1–C5: 2.180(7), C1–C2: 1.371(11), C2–C3: 1.465(9), C3–C4: 1.330(10), C4–C5: 1.400(10), P2–C2: 1.763(7), P3–C5: 1.766(7); N1-Os1-P1: 173.14(18), O1-Os1-Cl1: 81.38(14), C1-Os1-C4: 72.6(3), C1-Os1-C5: 111.5(3), Os1-C1-C2: 121.2(5), C1-C2-C3: 110.9(7), C2-C3-C4: 109.2(7), C3-C4-C5: 156.5(7), C4-C5-Os1: 63.6(4), C5-C4-Os1: 77.6(4).

allene unit of **8** also deviates from linearity, as reflected by the C3-C4-C5 angle of 156.5°. In addition, the characteristic spectroscopic data of **8** are consistent with the structure shown in Figure 7.

On the basis of the characterized structures of **7** and **8** and the reaction conditions, we propose a plausible mechanism for the reaction of **4** with PPh_3 in the presence of acid (Scheme 7). The intermediate **E** resulting from the isomerization of **4** is also suggested in a possible route to complex **7**. The addition of acid may facilitate the dissociation of the bidentate ligand 8-hydroxyquinoline, and then provide the possibility to undergo nucleophilic attack. The following in-



Scheme 7. Plausible mechanism for the transformation of η^2-allene-coordinated complex **4** to osmabenzene **7** and η^2-allene-coordinated complex **8** in the presence of acid.

tramolecular S_NAr reaction of 8-hydroxyquinoline to the aromatic metallacycle affords the metallabenzene **7**. As shown in Scheme 7, the formation of complex **8** may be initiated by the electrophilic addition of the coordinated carbon–carbon double bond of **4** with excess PPh_3, which could afford the osmacyclopentadiene intermediate **M**. Subsequent dissociation of the PPh_3 ligand from the metal center and β-H elimination may produce intermediate **N**. Finally, the oxidation of **N** with O_2 would yield complex **8**. When the reaction is performed in the absence of acid under air, it is also possible that the hydrogen anion could dissociate and combine with NaCl or NH_4Cl in solution to give the complex **8** and NaOH or $NH_3OH{\cdot}H_2O$ (see Scheme S2 in the Supporting Information).

It is now well established that allene-coordinated complexes show a high reactivity at the allene moiety, which could undergo several reactions to form saturated and unsaturated metallacycles.[15h–j,l,o] The reactions of cyclic η^2-allene-coordinated complex **4** with nucleophiles demonstrated that this might be another elegant way to construct metallacycles.

Conclusions

In this contribution we present the interconversion of metallabenzenes and cyclic η^2-allene-coordinated complexes. Osmabenzene **1** can react with excess 8-hydroxyquinoline to give monosubstituted osmabenzene **2** or disubstituted osmabenzene **3** under different reaction conditions. The 8-hydroxyquinoline monosubstituted osmabenzene **2** can be converted into η^2-allene-coordinated complex **4**, presumably involving a P–C bond cleavage of the metallacycle. The conversion of **4** into osmabenzene **5** could be achieved by introducing another 8-hydroxyquinoline substitution via intermolecular S_NAr reaction. Allene-coordinated complex **4** is remarkably stable both in the solid state and in solution under air, and can tolerate alkali in solution. However, complex **4** is very electrophilic in the presence of acid, and even water can react with it as a nucleophile to produce carbonyl osmium complex **6**. The reaction of complex **4** with excess PPh_3 leads to the formation of osmabenzene **7** and η^2-allene-coordinated complex **8**. It gives new access to unsaturated metallacycles with different metals and substituents starting from allene-coordinated complexes.

Experimental Section

General

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. The starting material $[Os\{CHC(PPh_3)CHC(PPh_3)CH\}Cl_2(PPh_3)_2]Cl$ **(1)** was synthesized by literature procedures.[8] NMR experiments were performed on a Bruker AV-300 spectrometer (^1H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.5 MHz) or a Bruker AV-500 spectrometer (^1H, 500.2 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 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 analysis data were obtained on a Vario EL III instrument (Elementar Analysensysteme GmbH).

*$[Os\{CHC(PPh_3)CHC(PPh_3)CH\}(C_9H_6NO)Cl(PPh_3)]Cl$ (**2**)*

A mixture of $[Os\{CHC(PPh_3)CHC(PPh_3)CH\}Cl_2(PPh_3)_2]Cl$ (**1**, 0.42 g, 0.30 mmol) and 8-hydroxyquinoline (65 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was heated to reflux for 4 h to give a brown 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 complex **2** as a brown solid. Yield: 0.18 g (50%). ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 20.0$ (dd, $J(PH) = 13.8$ Hz, $J(PH) = 5.4$ Hz, 1H, Os*CH*), 19.0 (dd, $J(PH) = 17.4$ Hz, $J(PH) = 5.4$ Hz, 1H, Os*CH*), 7.9–6.7 ppm (m, 52H, PPh_3, C_9H_6NO, $OsCHC(PPh_3)CH$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 20.6$ (s, *C*PPh_3), 20.4 (s, C*P*Ph_3), 1.2 ppm (s, Os*P*Ph_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 248.6$ (br, Os*C*H), 150.7 (t, J(PC) = 24.0 Hz, $OsCHC(PPh_3)$*C*H), 145.1–127.7 (m, PPh_3, C_9H_6NO), 120.9 ppm (dd, $J(PC) = 76.8$ Hz, $J(PC) = 12.0$ Hz, $OsCHC(PPh_3)$); elemental analysis calcd (%) for $C_{68}H_{54}NOP_3Cl_2Os$: C 65.07, H 4.34, N 1.12; found: C 65.08, H 4.63, N 0.99.

*$[Os\{CHC(PPh_3)CHC(PPh_3)CH\}(C_9H_6NO)Cl(PPh_3)](BPh_4)$ (**2′**)*

A solution of $NaBPh_4$ (34 mg, 0.10 mmol) and CH_3OH (0.5 mL) was added slowly to a solution of complex **2** (0.10 g, 0.08 mmol) in CH_3OH (2 mL). The reaction mixture was stirred at room temperature for 5 min to give a brown suspension. The brown solid was collected by filtration, washed with CH_3OH (2×3 mL), and then dried under vacuum. Yield: 0.11 g (88%); elemental analysis calcd (%) for $C_{92}H_{74}BNOP_3ClOs$: C 71.80, H 4.85, N 0.91; found: C 71.69, H 4.98, N 1.29.

*$[Os\{CHC(PPh_3)CHC(PPh_3)CH\}(C_9H_6NO)_2]Cl$ (**3**)*

Method A (one-pot reaction). A mixture of complex **1** (0.42 g, 0.30 mmol), 8-hydroxyquinoline (0.10 g, 0.75 mmol), and NaOH (60 mg, 1.5 mmol) in CH_2Cl_2 (10 mL) was heated to reflux for 4 h to give a brown–green suspension. Following filtration, the residue was dried under vacuum, dissolved in CH_2Cl_2 (1 mL), and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give

complex **3** as a brown–green solid. Yield: 0.15 g (45%). **Method B.** A mixture of complex **2** (0.38 g, 0.30 mmol), 8-hydroxyquinoline (65 mg, 0.45 mmol), and NaOH (60 mg, 1.5 mmol) in CH_2Cl_2 (10 mL) was heated to reflux for 4 h to give a brown–green suspension. Following filtration, the residue was dried under vacuum, dissolved in CH_2Cl_2 (1 mL), and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **3** as a brow–green solid. Yield: 0.18 g (53%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ = 16.8 (d, J(PH) = 18.5 Hz, 2H, OsC*H*), 8.6–6.8 ppm (m, 43H, PPh_3, C_9H_6NO, OsCHC(PPh$_3$)C*H*); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 21.9 ppm (s, C*P*Ph$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 215.5 (s, Os*C*H), 142.3 (t, J(PC) = 25.2 Hz, OsCHC(PPh$_3$)*C*H), 170.9–113.3 (m, PPh_3, C_9H_6NO), 111.0 ppm (dd, J(PC) = 77.7 Hz, J(PC) = 15.1 Hz, OsCH*C*(PPh$_3$)); elemental analysis calcd (%) for $C_{59}H_{45}N_2O_2P_2ClOs$: C 64.33, H 4.12, N 2.54; found: C 64.72, H 4.47, N 2.18.

*[Os{CHC(PPh$_3$)CHC(PPh$_3$)CH}(C$_9$H$_6$NO)$_2$](BPh$_4$) (**3′**)*

A solution of $NaBPh_4$ (34 mg, 0.10 mmol) and CH_3OH (0.2 mL) was added slowly to a solution of complex **3** (0.1 g, 0.09 mmol) in CH_3OH (2 mL). The reaction mixture was stirred at room temperature for 5 min to give a green suspension. The green solid was collected by filtration, washed with CH_3OH (2×3 mL), and then dried under vacuum. Yield: 0.10 g (80%); elemental analysis calcd (%) for $C_{83}H_{65}BN_2O_2P_2Os$: C 71.96, H 4.73, N 2.02; found: C 71.76, H 4.77, N 2.00.

*[Os{CH=C(PPh$_3$)CH=(η^2-C=CH$_2$)}(C$_9$H$_6$NO)(PPh$_3$)$_2$]Cl (**4**)*

A solution of NaOH (0.18 g, 4.5 mmol) in H_2O/CH_3OH (5 mL, v:v = 1:20) was added to a solution of complex **2** (0.38 g, 0.30 mmol) and PPh_3 (0.39 g, 1.5 mmol) in CH_3OH(10 mL). The reaction mixture was heated for 5 h at 60 °C to give a reddish brown solution. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (3–5 mL). The solvent was reduced to about 1 mL under vacuum and the residue was purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **4** as an orange solid. Yield: 0.28 g (76%). ^{1}H NMR plus HMQC (400.1 MHz, $CDCl_3$): δ = 11.7 (d, J(PH) = 16.4 Hz, 1H, OsC*H*), 8.9–6.1 (m, 52H, PPh_3, C_9H_6NO, C*H*CCH$_2$), 7.9 (br, 1H, C*H*CCH$_2$, obscured by the phenyl signals and confirmed by ^{1}H–^{13}C HMQC), 4.2 ppm (t, J(PH) = 6.8 Hz, 2H, CHCC*H*$_2$); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = −12.5 (s, Os*P*Ph$_3$), 9.7 ppm (s, C*P*Ph$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 205.2 (t, J(PC) = 7.9 Hz, Os*C*H), 193.1 (d, J(PC) = 24.4 Hz, CH*C*CH$_2$), 167.4–120.9 (m, PPh_3, C_9H_6NO), 118.6 (d, J(PC) = 73.5 Hz, *C*(PPh$_3$)), 117.8 (d, J(PC) = 27.5 Hz, *C*HCCH$_2$), 15.7 ppm (s, CHC*C*H$_2$); elemental analysis calcd (%) for $C_{68}H_{55}NOP_3ClOs$: C 66.90, H 4.54, N 1.15; found: C 66.75, H 4.66, N 0.82.

*[(C$_9$H$_6$NO)Os{CHC(PPh$_3$)CHCHC}(C$_9$H$_6$NO)(PPh$_3$)]Cl (**5**)*

A mixture of complex **4** (0.20 g, 0.16 mmol) and 8-hydroxyquinoline (0.12 g, 0.8 mmol) in $CHCl_3$ (10 mL) was heated in sealed tube under air for 12 h at 100 °C to give a dark brown solution. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brownish precipitate which was collected by filtration. The residue was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **5** as a brownish solid. Yield: 0.11 g (60%). ^{1}H NMR plus HMQC (500.2 MHz, $CDCl_3$): δ = 15.1 (dt, J(PH) = 22.4, 2.25 Hz, 1H, OsC*H*), 9.1–6.8 (m, 42H, PPh_3, C_9H_6NO), 7.5 (br, 1H, OsCHC(PPh$_3$)C*H*, obscured by the phenyl signals and confirmed by ^{1}H–^{13}C HMQC), 7.0 ppm (br, 1H, OsCHC(PPh$_3$)CHC*H*, obscured by the phenyl signals and confirmed by ^{1}H–^{13}C HMQC); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 18.1 (s, Os*P*Ph$_3$), 10.3 ppm (s, C*P*Ph$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 246.5 (d, J(PC) = 9.0 Hz, Os*C*), 232.0 (m, Os*C*H), 144.6 (d, J(PC) = 23.0 Hz, OsCHC(PPh$_3$)*C*H), 167.9–109.6 (m, PPh_3, C_9H_6NO), 124.1 (d, J(PC) = 12.2 Hz, OsCHC(PPh$_3$)CH*C*H), 110.2 ppm (d, J(PC) = 77.7 Hz, OsCH*C*(PPh$_3$)); elemental analysis calcd (%) for $C_{59}H_{45}ClN_2O_2P_2Os$: C 64.33, H 4.12, N 2.54; found: C 64.33, H 4.43, N, 2.82.

*[Os{CH=C(PPh$_3$)CH=CH$_2$}(C$_9$H$_6$NO)(CO)(PPh$_3$)$_2$]Cl (**6**)*

A mixture of complex **4** (0.20 g, 0.16 mmol) and NH_4Cl (0.18 g. 3.4 mmol) in $CHCl_3$ (10 mL, wet) was heated for 12 h in sealed tube under air at 100 °C to give a brown solution, which was concentrated to approximately 1 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a green precipitate, which was collected by filtration. The residue was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **6** as a yellow solid. Yield: 0.12 g (60%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 11.3 (d, J(PH) = 33.0 Hz, 1H, OsC*H*), 6.4–7.6 (m, 45H, PPh_3, C_9H_6NO), 7.0 (br, 1H, C*H*CH$_2$), 6.5 (br, 1H, CHC*H*$_2$), 5.0 (d, 1H, J(HH) = 11.4 Hz, CHC*H*$_2$) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 15.8 (s, C*P*Ph$_3$), −5.9 (s, Os*P*Ph$_3$) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 198.5 (br, Os*C*H), 186.6 (s, OsCO), 166.9–111.7 (m, PPh_3, C_9H_6NO), 140.0 (d, J(PC) = 20.0 Hz, *C*HCH$_2$), 115.6 (d, J(PC) = 12.0 Hz, CH*C*H$_2$), 113.8 ppm (d, J(PC) = 70.1 Hz, *C*(PPh$_3$)); elemental analysis calcd (%) for $C_{68}H_{55}NO_2P_3ClOs$: C 66.04, H 4.48, N 1.13; found: C 65.68, H 4.75, N 1.24.

*[Os{CH=C(PPh$_3$)CH=CH$_2$}(C$_9$H$_6$NO)(CO)(PPh$_3$)$_2$](PF$_6$) (**6′**)*

A mixture of complex **6** (50 mg, 0.04 mmol) and $NaPF_6$ (68 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was stirred for 24 h at room temperature to give a yellow suspension. Following filtration, the volume of the filtrate was reduced and dried under vacuum. Yield: 51 mg (95%). Elemental analysis calcd (%) for $C_{68}H_{55}NO_2P_4F_6Os$: C 60.67, H 4.12, N 1.04; found: C 60.25, H 4.31, N 1.49.

*[Os{CHC(PPh$_3$)CHCHC}(C$_9$H$_6$NO)Cl(PPh$_3$)$_2$]Cl (**7**)*

Hydrochloric acid in diethyl ether (1.0 M, 150 μL) was added to a mixture of complex **4** (0.20 g, 0.16 mmol) and PPh_3 (0.42 g, 1.6 mmol) in $CHCl_3$ (10 mL). The reaction mixture was heated for 12 h in sealed tube under air at 100 °C to give a dark brown solution. Subsequently, the volume of the solution was reduced to approximately 1 mL in vacuum. Addition of diethyl ether (20 mL) to the solution gave a yellow precipitate, which was collected by filtration. The residue was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 20:1) to give complex **7** as a green solid. Yield: 0.11 g (55%). ^{1}H NMR plus HMQC (500.2 MHz, $CDCl_3$): δ = 15.9 (d, J(PH) = 24.1 Hz, 1H, OsC*H*), 9.1–6.8 (m, 51H, PPh_3, C_9H_6NO), 7.0 (br, 1H, OsCHC(PPh$_3$)C*H*, obscured by the phenyl signals and confirmed by ^{1}H–^{13}C HMQC), 5.9 ppm (d, J(PH) = 10.0 Hz, 1H, OsCHC(PPh$_3$)CHC*H*, confirmed by ^{1}H–^{13}C HMQC); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 17.3 (s, C*P*Ph$_3$), −1.5 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 240.4 (s, Os*C*O), 223.5 (br, Os*C*H), 142.9 (d, J(PC) = 22.1 Hz, OsCHC(PPh$_3$)*C*H), 167.9–109.6 (m, PPh_3, C_9H_6NO), 124.4 (d, J(PC) = 11.7 Hz, OsCHC(PPh$_3$)CH*C*H), 104.9 ppm (d, J(PC) = 78.6 Hz, OsCH*C*(PPh$_3$)); elemental analysis calcd (%) for $C_{68}H_{54}NOCl_2P_3Os$: C 65.07, H 4.34, N 1.12; found: C 65.24, H 4.63, N 1.27.

*[Os{CH=C(PPh$_3$)CH=(η^2-C=CH(PPh$_3$))}(C$_9$H$_6$NO)Cl(PPh$_3$)]Cl (**8**)*

A suspension of NaCl (0.19 g, 3.2 mmol), complex **4** (0.20 g, 0.16 mmol), and PPh_3 (0.42 g, 1.6 mmol) in $CHCl_3$ (10 mL) was heated for 12 h in sealed tube under air at 100 °C to give a dark brown solution. Note that prior to the reaction $CHCl_3$ should be stored with K_2CO_3 in the dark to avoid the photochemical formation of HCl. Next, the volume of the solution was reduced to approximately 1 mL in vacuum. Addition of diethyl ether (20 mL) to the solution gave a yellow precipitate, which was collected by filtration. The residue was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography (neutral alumina, eluent: acetone/methanol, 10:1) to give complex **8** as a yellow solid. Yield: 0.15 g (75%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ = 12.1 (d, J(PH) = 15.5 Hz, 1H, OsC*H*), 7.8–6.3 (m, 52H, PPh_3, C_9H_6NO), 4.8 ppm (m, 1H, CHCC*H*(PPh$_3$)); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 26.7 (C*P*Ph$_3$), 9.5 (C*P*Ph$_3$), −9.8 ppm (Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 208.3 (br, Os*C*H), 190.8 (d, J(PC) = 24.8 Hz, C*C*CH), 168.6–110.5 (m, PPh_3, C_9H_6NO), 116.7 (d, J(PC) = 76.2 Hz, OsCH*C*(PPh$_3$)), 29.4 (d, J(PC) = 19.8 Hz, OsCHC(PPh$_3$)*C*H), 9.6 ppm (d, J(PC) = 72.3 Hz, CHC*C*H-

(PPh_3)); elemental analysis calcd (%) for $C_{68}H_{54}NOCl_2P_3Os$: C 65.07, H 4.34, N 1.12; found: C 65.28, H 4.29, N 1.18.

X-ray Crystallography

Crystals of **2′**, **3′**, **4**, **5**, **6′**, **7**, and **8** suitable for X-ray diffraction were grown from CH_2Cl_2, $CHCl_3$, or CH_2ClCH_2Cl solutions layered with *n*-hexane. Data collections were performed on an Oxford Gemini S Ultra CCD Area Detector using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) (**2′**, **3′**, **5**, **6′**, and **8**) or $Cu_{K\alpha}$ radiation (λ = 1.54178 Å) (**4**) at 173 K. Data collection for **7** was collected on a Rigaku R-AXIS SPIDER IP CCD Area Detector using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at 173 K. Multi-scan 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. Further details on crystal data, data collection, and refinements are summarized in Table 1.

CCDC 849719 (**2′**), CCDC 849720 (**3′**), CCDC 849721 (**4**), CCDC 849722 (**5**), CCDC 849723 (**6′**), CCDC 849724 (**7**), and CCDC 849725 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 20801046, 20925208 and J1030415) and the Fundamental Research Funds for the Central Universities (Nos. CXB2011039 and 201112G002).

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Received: March 13, 2012
Revised: April 15, 2012
Published online: May 29, 2012

