

## Synthesis

***m*-Metallaphenol: Synthesis and Reactivity Studies**

Feifei Han, Tongdao Wang, Jinhua Li, Hong Zhang,\* and Haiping Xia\*[a]

**Abstract:** Treatment of the osmium complex  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{OH})-\eta^2\text{-C}\equiv\text{CH}\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (**1**) with excess triethylamine produces the first *m*-metallaphenol complex  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{OH})\text{CH}\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (**2**). The NMR spectroscopic and structural data as well as the nucleus-independent chemical-shift (NICS) values suggest that osmaphenol **2** has aromatic character. The reactivity studies demonstrate that **2** can react with different isocyanates to form the annulation reaction products  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{O}-\text{C}=\text{ONR})\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (R = Ph (**3**), *i*Pr (**7**), Bn (**8**)) via the carbamate intermediates  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{O}-\text{C}=\text{ONHR})\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (R = Ph (**4**), *i*Pr (**5**), Bn (**6**)). In addition, the simi-

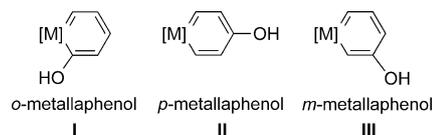
lar annulation reactions can be extended to other unsaturated compounds containing N–C multiple bonds, for example, isothiocyanates, pyridine, and sodium thiocyanate, which can produce the corresponding fused osmabenzene complexes. In contrast, the reactions of **2** with common electrophiles, such as  $\text{NOBF}_4$ ,  $\text{NO}_2\text{BF}_4$ , *N*-bromosuccinimide, and *N*-chlorosuccinimide only led to the decomposition of the metallaphenol ring. The experimental results suggest that **2** is very electrophilic and readily reacts with nucleophiles, which is mainly due to the metal center and the strong electron-withdrawing phosphonium group.

## Introduction

As new aromatic heterocycles, metallaaromatics have attracted considerable attention because of their aromatic properties and organometallic reactivities.<sup>[1]</sup> Most studies in this field concern the synthesis and the reactivity study of stable metallaaromatics. It is now well established that metallaaromatics can undergo characteristic aromatic reactions, such as electrophilic aromatic substitution ( $S_{\text{E}}\text{Ar}$ ),<sup>[2]</sup> nucleophilic aromatic substitution ( $S_{\text{N}}\text{Ar}$ )<sup>[3]</sup> reactions, and forming half-sandwich,<sup>[4a]</sup> sandwich,<sup>[4b]</sup> and triple-decker complexes<sup>[4c]</sup> as  $\eta^6$  ligands. These studies not only provide strong evidence for the aromaticity of these aromatic heterocycles, but also allow us to obtain new interesting organometallic complexes.

Since the first examples of stable metallaaromatics, that is, metallabenzene, reported in 1982,<sup>[5]</sup> the synthesis of various metallaaromatics has been widely investigated.<sup>[1]</sup> However, the isolation of metallaphenols, which can be viewed as closely related derivatives of metallabenzene, has met with limited success.<sup>[6]</sup> The reported examples of metallaphenols are *o*-metallaphenols (**I**)<sup>[6a,b]</sup> and *p*-metallaphenols (**II**)<sup>[6c,d]</sup> in which the hydroxyl group takes up a position *ortho* or *para* to the transition metal. In this contribution we present the synthesis of the first

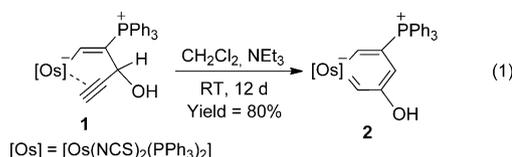
example for *m*-metallaphenols (**III**) as well as the reactivity studies of the complex.



## Results and Discussion

**Synthesis of *m*-osmaphenol from  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{OH})-\eta^2\text{-C}\equiv\text{CH}\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (**1**)**

Treatment of complex **1** with excess triethylamine in dichloromethane led to the formation of complex **2**, which can be isolated as a green solid in 80% yield [Eq. (1)]. Complex **2** was characterized by NMR spectroscopy and elemental analysis, and the structure was further confirmed by single-crystal X-ray diffraction.



The crystallographic details of the osmaphenol complex **2** are given in Table 2. Selected bond lengths and angles are given in Table 1. As shown in Figure 1, **2** contains a nearly planar metallabenzene unit and the hydroxyl group is attached to C4 of the metallacycle. The mean deviation from the least-squares plane through Os1 and C1–C5 is 0.0632 Å, and the

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Supporting information for this article is available on the WWW under  
<http://dx.doi.org/10.1002/chem.201304957>.

Table 1. Selected bond lengths and angles for 2, 3, and 4.			
	2	3	4
Bond lengths [Å]			
Os1–C1	1.975(9)	1.968(9)	1.974(3)
Os1–C5	1.937(10)	1.940(10)	1.941(3)
C1–C2	1.385(11)	1.407(12)	1.398(4)
C2–C3	1.400(13)	1.425(12)	1.425(5)
C3–C4	1.363(13)	1.372(13)	1.358(5)
C4–C5	1.422(12)	1.456(15)	1.401(5)
Bond angles [°]			
C1–Os1–C5	89.2(4)	89.5(4)	89.54(13)
Os1–C1–C2	128.4(7)	131.6(7)	128.5(2)
C1–C2–C3	123.4(8)	121.1(8)	123.0(3)
C2–C3–C4	124.6(8)	121.6(8)	123.7(3)
C3–C4–C5	124.1(9)	129.7(8)	125.7(3)
C4–C5–Os1	127.9(7)	123.7(6)	128.0(2)

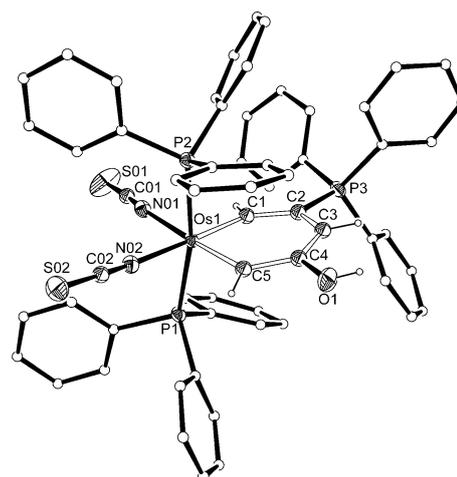


Figure 1. Molecular structure of 2. The hydrogen atoms of PPh<sub>3</sub> are omitted for clarity.

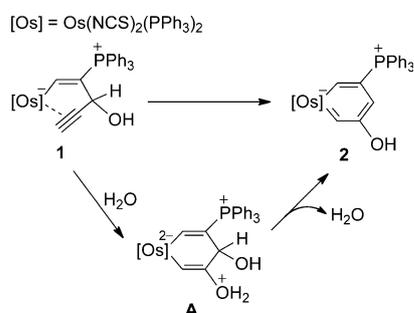
sum of angles in the six-membered ring is 717.6°, which is close to the ideal value of 720°. All bond distances within the metallacycle fall within the range observed for other typical metallabenzenes.<sup>[1]</sup> The C–C bond lengths of the metallabenzene ring are in the range of 1.363(13)–1.422(12) Å. The coplanarity and lack of significant alternations in the C–C bond lengths suggests that complex 2 has a delocalized structure. The C–O bond lengths (1.396(11) Å) are close to those found in other metallaphenol systems.<sup>[6]</sup>

The osmaphenol structure feature is also clearly evident by NMR spectroscopy. In particular, the <sup>1</sup>H NMR (in CD<sub>2</sub>Cl<sub>2</sub>) spectrum shows three <sup>1</sup>H signals of the metallabenzene ring at δ = 15.8 (C1H), 7.3 (C3H), 17.8 ppm (C5H). With the aid of the <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>13</sup>C-dept 135 spectra, the five carbon signals of the metallabenzene ring are observed at δ = 218.2 (C1), 112.0 (C2), 127.6 (C3), 157.9 (C4), and 247.0 ppm (C5) in the

Table 2. Crystal data and structure refinement for 2, 3, 4, 9, 10, and 11.						
	2	3	4	9	10	11
formula	C <sub>62</sub> H <sub>51</sub> Cl <sub>2</sub> N <sub>2</sub> OOSp <sub>3</sub> S <sub>2</sub>	C <sub>69.5</sub> H <sub>53.5</sub> Cl <sub>4.5</sub> N <sub>3</sub> O <sub>2</sub> OsP <sub>3</sub> S <sub>2</sub>	C <sub>70.5</sub> H <sub>58</sub> Cl <sub>5</sub> N <sub>3</sub> O <sub>2</sub> OsP <sub>3</sub> S <sub>2</sub>	C <sub>67</sub> H <sub>56</sub> Cl <sub>6</sub> N <sub>3</sub> OOSp <sub>3</sub> S <sub>3</sub>	C <sub>69.75</sub> H <sub>53.5</sub> Cl <sub>8.25</sub> F <sub>3</sub> N <sub>3</sub> O <sub>5</sub> OsP <sub>3</sub> S <sub>3</sub>	C <sub>65</sub> H <sub>54</sub> Cl <sub>6</sub> N <sub>3</sub> OOSp <sub>3</sub> S <sub>3</sub>
M <sub>w</sub>	1258.18	1469.41	1503.68	1511.14	1742.41	1485.10
T [K]	173(2)	173(2)	173(2)	150(2)	173(2)	173(2)
λ [Å] (MoK <sub>α</sub> radiation)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	P21/n	Cc	P1	P21/c	C2/c	P21/c
a [Å]	12.7202(5)	19.8039(3)	12.3719(3)	13.5792(3)	47.0317(13)	13.988(2)
b [Å]	19.1661(6)	17.4152(3)	14.9614(3)	18.8412(4)	12.5667(4)	24.091(4)
c [Å]	22.6788(10)	19.7067(3)	18.9487(5)	25.5089(5)	25.0185(5)	20.018(3)
α [°]	90	90	110.217(2)	90	90	90
β [°]	97.868(4)	105.834(2)	90.007(2)	92.890(2)	101.290(2)	105.434(3)
γ [°]	90	90	98.467(2)	90	90	90
V [Å <sup>3</sup> ]	5477.0(4)	6538.73(18)	3250.54(13)	6518.1(2)	14500.6(7)	6502.2(18)
Z	4	4	2	4	8	4
ρ <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.526	1.493	1.536	1.540	1.596	1.517
μ [mm <sup>-1</sup> ]	2.634	2.319	2.354	2.417	2.275	2.422
F(000)	2528	2948	1512	3032	6954	2976
crystal size [mm <sup>3</sup> ]	0.30 × 0.20 × 0.02	0.40 × 0.20 × 0.10	0.80 × 0.60 × 0.40	0.60 × 0.40 × 0.20	0.80 × 0.60 × 0.20	0.20 × 0.20 × 0.15
θ range [°]	2.75 to 25.00	2.90 to 26.37	2.94 to 25.00	2.97 to 25.00	2.65 to 26.38	1.35 to 25.00
total reflns	25 265	18 253	26 222	28 974	38 265	32 640
unique reflns	9621	10 792	11 427	11 477	14 807	11 429
observed reflns	7181	10 154	10 622	10 119	11 808	9966
[I ≥ 2σ(I)]						
data/restraints/parameters	9621/78/677	10 792/116/821	11 427/120/821	11 477/204/831	14 807/514/995	11 429/90/786
GOF on F <sup>2</sup>	1.000	1.000	1.000	1.000	1.000	1.000
R <sub>1</sub> /wR <sub>2</sub> [I ≥ 2σ(I)]	0.0656/0.1399	0.0408/0.1094	0.0276/0.0647	0.0447/0.0996	0.0553/0.1375	0.0350/0.0871
R <sub>1</sub> /wR <sub>2</sub> (all data)	0.0961/0.1538	0.0451/0.1252	0.0315/0.0662	0.0527/0.1032	0.0734/0.1498	0.0413/0.0897
largest peak/hole [e Å <sup>-3</sup> ]	2.077/−1.791	1.411/−0.989	0.753/−1.256	1.926/−1.757	2.239/−1.332	1.522/−0.683
CCDC no.	935257	935258	964601	935261	935262	974941

$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. The presence of a hydroxyl substituent is supported by the chemical shifts in the  $^1\text{H}$  NMR spectrum ( $\delta = 3.6$  ppm).

Similar to our previously reported mechanism for the formation of osmabenzene  $[(\text{SCN})_2(\text{Ph}_3\text{P})_2\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{SCN})\text{CH}\}]$  from complex **1**,<sup>[7b]</sup> the formation of osmaphenol may also involve the nucleophilic addition and elimination process. As shown in Scheme 1, **1** could undergo intermolecular nucleophilic addition with the  $\text{H}_2\text{O}$  present in solution to give the O-protonation intermediate **A**. Subsequent elimination of  $\text{H}_2\text{O}$  could produce osmaphenol **2**. It is possible that a trace amount of water in solution initiates the reaction. When the reaction was carried out in the presence of purposely introduced  $\text{H}_2\text{O}$ , the conversion of **1** was complete within two days and gave **2** as the major product. Besides, the addition of excess triethylamine may facilitate the dehydration of intermediate **A**.

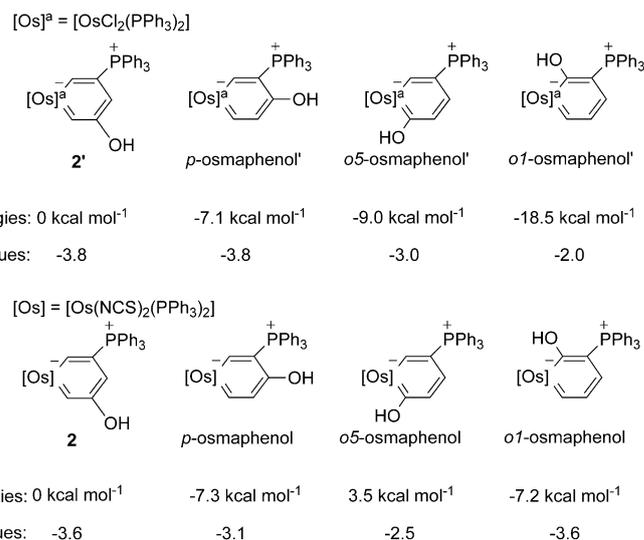


Scheme 1. Plausible mechanism for the formation of osmaphenol **2**.

It is worth mentioning that complex **2** can be viewed as the first *m*-metallaphenol (III). In addition, the osmaphenol complex **2** exhibits notable stability under an air atmosphere. After being kept for months at room temperature, it remains nearly unchanged both in the solid state and in solution. Complex **2** also has remarkable thermal stability. A solid sample of **2** could be heated at  $100^\circ\text{C}$  for at least five hours without noticeable decomposition.

DFT calculations were carried out to evaluate the aromaticity related to the metallaphenols. The optimized structure of the model complex **2** reproduces well the structural features of **2** described above. The nucleus-independent chemical shift (NICS) values were computed for the metallaphenol rings. As shown in Scheme 2, the calculated NICS(1) values of **2** are  $-3.6$  ppm. The values are comparable to other metallaphenol model complexes and those reported for other metallaaromatics.<sup>[8]</sup> The calculated negative NICS values indicate aromaticity associated with the metallaphenol ring in complex **2**.

Model DFT computations also provided estimates of the relative energies of the different osmaphenols. As shown in Scheme 2, the model complex **2'**, in which SCN substituents were replaced by Cl substituents, is the most unstable for the chloride-substituted osmaphenols, whereas complex **2** is more

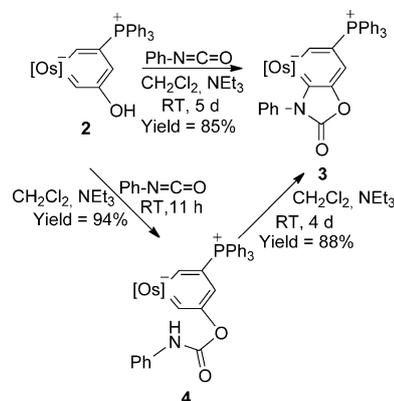


Scheme 2. Relative energies and the calculated NICS(1) values (ppm) of osmaphenols.

stable than the *ortho* isomer *o5*-osmaphenol, which is the most unstable for the thiocyanate-substituted species. Therefore, we speculate that the strong SCN ligands play important roles in the stability of osmaphenols **2**. Consistent with our calculation results, the formation of analogue *m*-osmaphenol could not be observed when the reaction was performed with starting material  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{OH})-\eta^2\text{-C}\equiv\text{CH}\}\text{Cl}_2(\text{PPh}_3)_2]$ ,<sup>[7a]</sup> that is, the chloride-substituted derivative of **1**, under the same conditions.

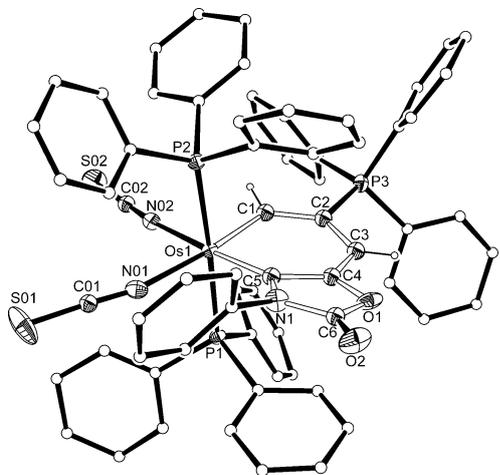
### Reactions of the osmaphenol complex **2** with phenyl isocyanate

Since the formation of the urethane linkage from the isocyanates and phenols is one of the most characteristic chemical reactions of phenols, we initially studied the reactivity of **2** with phenyl isocyanate. As shown in Scheme 3, treatment of **2** with excess phenyl isocyanate in dichloromethane in the presence of triethylamine led to the formation of the complex **3**, which can be isolated as a green solid in 85% yield.



Scheme 3. Reactions of osmabenzene **2** with phenyl isocyanate.

Complex **3** has been characterized by single-crystal X-ray diffraction. Selected bond lengths and angles are given in Table 1, and the crystallographic details are given in Table 2. The molecular structure of **3** is shown in Figure 2, which confirms that **3** is a fused metallabenzene complex, that is, metal-



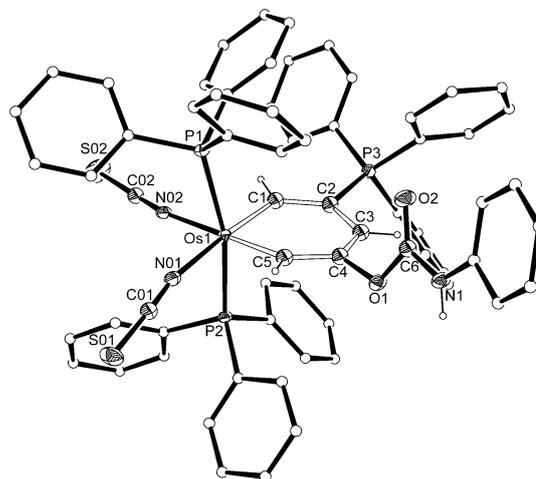
**Figure 2.** Molecular structure of **3**. The hydrogen atoms of  $\text{PPh}_3$  are omitted for clarity.

labenzoxazolone. Due to the fused five-membered ring, the metallabenzene ring of **3** deviates slightly from planarity, as reflected by the mean deviation from the least-squares plane through Os1 and C1–C5 (0.0699 Å). The C4–C5 bond length (1.456 Å) is in the high end of the observed range for the typical metallabenzenes (1.316–1.472 Å).<sup>[9]</sup> Consistent with the solid-state structure, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic chemical shifts of the six-membered ring atoms in complex **3** appear in the aromatic region. The  $^1\text{H}$  NMR spectrum displayed the OsCH signal at  $\delta = 15.9$  ppm and the OsCHC( $\text{PPh}_3$ )CH signal at  $\delta = 7.4$  ppm. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed the five carbon signals of the metallabenzene ring at 230.8 (C1), 105.6 (C2), 122.2 (C3), 147.1 (C4), and 203.9 ppm (C5). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed two singlets at 15.1 ( $\text{CPh}_3$ ) and  $-9.7$  ppm ( $\text{OsPPh}_3$ ).

On the basis of the above observations, we supposed that phenyl isocyanate may react with osmaphenol **2** to form the corresponding carbamate derivative, which then converts to osmabenzoxazolone **3** by the intramolecular  $\text{S}_\text{N}\text{Ar}$  reaction. As illustrated in Scheme 3, the conjectural carbamate intermediate **4** can be separated from the reaction as a green solid in 94% yield by shortening the reaction time. Complex **4** has been characterized by NMR spectroscopy and elemental analysis. The resonances of the osmabenzene ring in the  $^1\text{H}$  ( $\delta = 16.9$  (C1H), 7.7 (C3H), and 17.5 ppm (C5H)) and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra ( $\delta = 229.0$  (C1), 112.2 (C2), 141.5 (C3), 151.1 (C4), and 244.7 ppm (C5)) are very close to those observed for the osmaphenol complex **2** (Table 3). The presence of the urethane moiety is evident by the chemical shifts in the  $^1\text{H}$  ( $\delta = 6.6$  ppm (NH)) and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\delta = 153.5$  ppm (C=O)). The structure of **4** has been further confirmed by an X-ray diffraction study, and a view of **4** is shown in Figure 3. The X-ray

**Table 3.** Selected NMR spectroscopic data for the carbamate complexes **4**, **5**, and **6**.

Compound	$\delta$ ( $^1\text{H}$ ) [ppm]			$\delta$ ( $^{13}\text{C}$ ) [ppm]				
	H1	H3	H5	C1	C2	C3	C4	C5
<b>4</b>	16.9	7.7	17.5	229.0	112.2	141.5	151.1	244.7
<b>5</b>	16.6	7.6	17.5	228.3	111.9	141.0	151.4	246.3
<b>6</b>	16.7	7.6	17.5	228.6	112.1	141.1	151.5	245.8



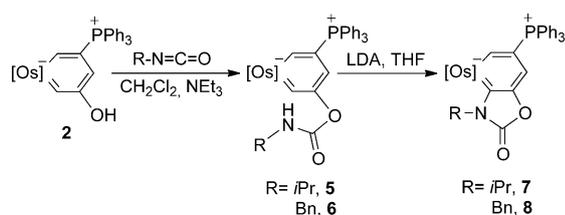
**Figure 3.** Molecular structure of **4**. The hydrogen atoms of  $\text{PPh}_3$  are omitted for clarity.

structure clearly shows that complex **4** contains an essentially planar metallabenzene ring substituted with a urethane linkage.

As indicated by the in-situ NMR spectrum, the expected conversion of **4** to the final cyclization product **3** can be observed, when a mixture of **4** and excess triethylamine in  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature for four days (Scheme 3). The conversion strongly suggests that the carbamate derivative **4** is the key intermediate for the transformation of osmaphenols **2** to osmabenzoxazolone **3**. Similar annulation reactions of metallabenzenes by intramolecular  $\text{S}_\text{N}\text{Ar}$  reactions have been demonstrated.<sup>[3d,10]</sup> Thus we envisioned that the reactivity study of the hydroxyl group in osmaphenols **2** may afford other annulation reactions to achieve new fused metallaaromatics complexes.

### Extension of the chemistry-annulation reactions of the osmaphenol complex **2**

Using different isocyanates, we carried out analogous annulation reactions and observed similar results. Thus the reaction of **2** with isopropyl isocyanate produced the expected carbamate product **5**, which can be converted to the corresponding isopropyl-substituted osmabenzoxazolone **7** in the presence of excess lithium diisopropylamide (LDA). Similarly, the carbamate product **6** was obtained from the reaction of **2** with benzyl isocyanate, which was transformed to yield benzyl-containing osmabenzoxazolone **8** (Scheme 4). These complexes have been

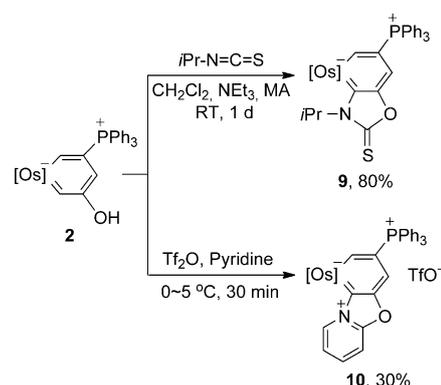


Scheme 4. Reactions of the osmabenzene complex **2** with other isocyanates.

characterized by NMR spectroscopy and elemental analysis. As shown in Table 3, the complexes **5** and **6** must have a structure similar to that of **4** as indicated by the similarity in their NMR spectroscopic data. **Due to their low solubility in common organic solvents, the attempt to obtain the full NMR spectroscopy characterization of the complexes **7** and **8** failed.** Fortunately, we get the single crystals of **7** and **8**, making it possible to determine their solid-state structure. The crystallographic details are given in Table S1 in the Supporting Information. Selected bond lengths and angles are given in Table 4. The X-ray diffraction study reveals that **7** and **8** are the annulation reaction products, which are structurally similar to osmabenzoxazone **3**.

Table 4. Selected bond lengths and angles for <b>7</b> , <b>8</b> , <b>9</b> , and <b>10</b> .				
	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
Bond lengths [Å]				
Os1–C1	2.003(4)	1.996(3)	1.993(5)	1.965(6)
Os1–C5	1.957(4)	1.965(3)	1.974(5)	1.976(6)
C1–C2	1.367(6)	1.383(5)	1.382(8)	1.392(8)
C2–C3	1.431(6)	1.436(5)	1.422(7)	1.399(8)
C3–C4	1.341(6)	1.348(5)	1.350(8)	1.375(9)
C4–C5	1.436(6)	1.438(5)	1.412(8)	1.402(9)
C4–O1	1.414(5)	1.411(4)	1.402(6)	1.404(8)
C6–O1	1.365(6)	1.361(4)	1.339(8)	1.327(8)
C5–N1	1.402(5)	1.391(4)	1.403(7)	1.437(8)
C6–N1	1.379(6)	1.388(4)	1.375(8)	1.357(9)
Bond angles [°]				
C1–Os1–C5	88.94(17)	89.48(13)	89.0(2)	87.7(2)
Os1–C1–C2	130.6(3)	130.0(2)	130.2(4)	133.2(5)
C1–C2–C3	122.0(4)	122.6(3)	122.1(5)	121.8(5)
C2–C3–C4	122.0(4)	121.9(3)	121.8(5)	121.5(6)
C3–C4–C5	129.8(4)	129.6(3)	130.5(5)	129.4(6)
C4–C5–Os1	123.2(3)	123.5(2)	122.9(4)	126.2(5)
C5–C4–O1	110.9(4)	110.9(3)	110.3(5)	112.2(5)
C4–O1–C6	106.1(3)	106.2(3)	107.5(5)	106.0(5)
O1–C6–N1	108.8(4)	108.4(3)	108.2(5)	110.4(6)
C5–N1–C6	112.0(4)	112.1(3)	111.5(5)	110.7(5)
C4–C5–N1	101.8(4)	101.8(3)	102.2(5)	100.8(5)

To further study the annulation reaction of the osmaphenol complex **2**, we also investigated its reactivities with other unsaturated compounds containing the N=C double bond. As shown in Scheme 5, isothiocyanates can also react with **2** similarly. Thus, the reaction of **2** with isopropyl isothiocyanate gave the structurally similar complex **9** (Scheme 5). The structure of complex **9** has been confirmed by an X-ray diffraction study (Figure 4). Overall, the structural parameters of **9** associated



Scheme 5. Other annulation reactions of the osmabenzene complex **2**. MA = maleic anhydride.

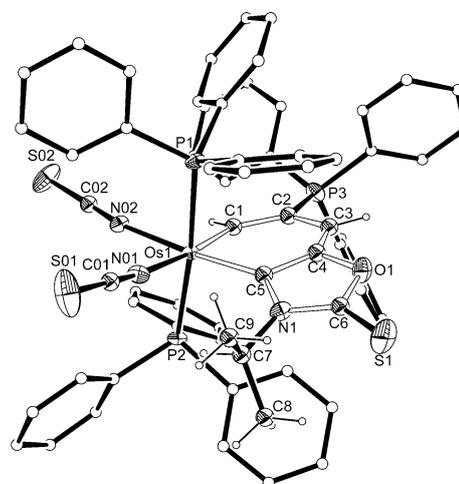


Figure 4. Molecular structure of **9**. The hydrogen atoms of PPh<sub>3</sub> are omitted for clarity.

with the fused metallabenzene ring are similar to those of **3**, **7**, and **8**. The solution NMR spectroscopic data is fully consistent with the solid-state structure, which are all in accord with the osmabenzooxazolethione formulation and comparable to those of complex **3** (Table 5). For example, the <sup>1</sup>H NMR spectrum of **9** shows the metallabenzene ring signal at δ = 16.7 and 7.4 ppm (Table 5). The <sup>13</sup>C signals of the metallabenzene ring were observed at 232.0 (C1), 106.9 (C2), 123.2 (C3), 150.8 (C4) and 204.4 ppm (C5) with the aid of the <sup>13</sup>C{<sup>1</sup>H} NMR, <sup>1</sup>H-<sup>13</sup>C HMBC, and the <sup>13</sup>C-dept 135 spectrum. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows two signals at δ = –6.3 and 15.7 ppm.

Table 5. Selected NMR spectroscopic data for the fuse metallabenzene complexes <b>3</b> , <b>9</b> , and <b>10</b> .							
Compound	δ ( <sup>1</sup> H) [ppm]		δ ( <sup>13</sup> C) [ppm]				
	H1	H3	C1	C2	C3	C4	C5
<b>3</b>	15.9	7.4	230.8	105.6	122.2	147.1	203.9
<b>9</b>	16.7	7.4	232.0	106.9	123.2	150.8	204.4
<b>10</b>	20.4	8.7	242.7	117.2	140.7	151.8	178.6

Notably, the chemistry can even be extended to using pyridine as the starting materials. Treatment of osmaphenol **2** with trifluoromethanesulfonic anhydride at 0 °C in pyridine gave rise to a brown solution. A pure sample of compound **10** can be obtained as an orange solid from the reaction mixture by column chromatography in 30% yield. The structure of **10** has been determined by an X-ray diffraction study, and selected bond lengths and angles are given in Table 4. As shown in Figure 5, complex **10** contains an essentially planar polycyclic

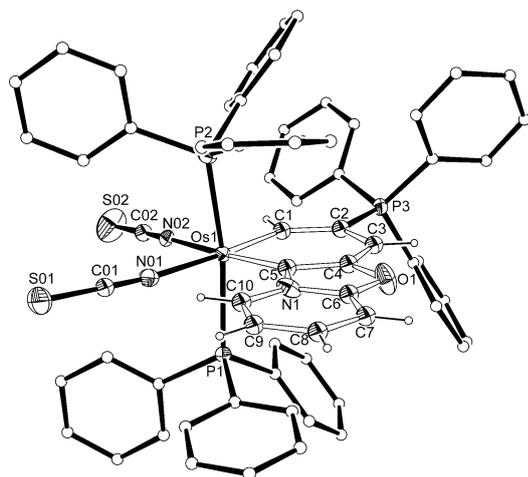
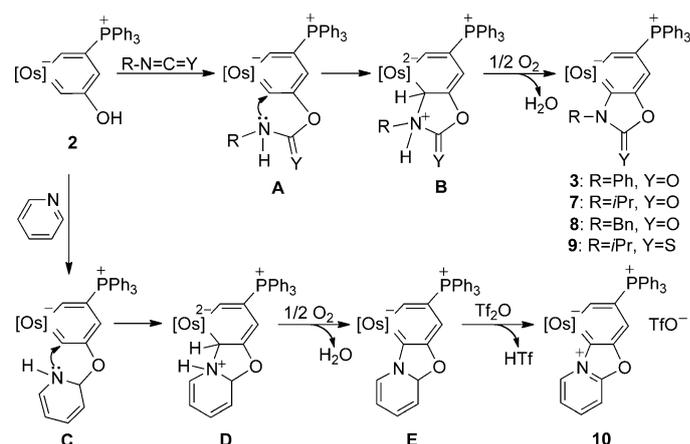


Figure 5. Molecular structure of **10**. Counteranion and the hydrogen atoms of  $\text{PPh}_3$  are omitted for clarity.

metallacycle unit. The mean deviation from the least-squares plane through metallabenzene ring (Os1 and C1–C5) is 0.0173 Å, and the maximum deviation from the least-squares plane through all six atoms is –0.0325 Å for C5. It is interesting that even the thirteen atoms (Os1, C1–C10, N1, and O1) of the three rings are approximately coplanar, which is reflected by the small mean deviation (0.0204 Å) from the least-squares plane. Besides, the Os1–C1 bond length (1.965(6) Å) is very close to the Os1–C5 bond length (1.976(6) Å). The ring C–C distances of the metallacycle are in the range of 1.375(9)–1.402(9) Å, which are intermediate between single and double carbon–carbon bonds. The structural data together with its planar nature indicate that **10** has a delocalized structure. Consistent with the solid-state structure, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic chemical shifts of the metallacycle atoms appear in the aromatic region. As shown in Table 5, the  $^1\text{H}$  NMR spectrum displays the OsCH signal at  $\delta = 20.4$  ppm and the  $\gamma\text{-CH}$  signal at  $\delta = 8.7$  ppm. On the basis of the  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $^1\text{H}\text{-}^{13}\text{C}$  HSQC,  $^1\text{H}\text{-}^{13}\text{C}$  HMBC, and  $^{13}\text{C}$ -dept 135 spectra, the five carbon signals of the metallacycle are identified at 242.7 (C1), 117.2 (C2), 140.7 (C3), 151.8 (C4) and 178.6 ppm (C5), respectively.

#### Mechanistic consideration for the annulation reactions of the osmaphenol complex **2**

Based on above experimental observations, we postulate a reaction mechanism shown in Scheme 6 for the annulation reac-

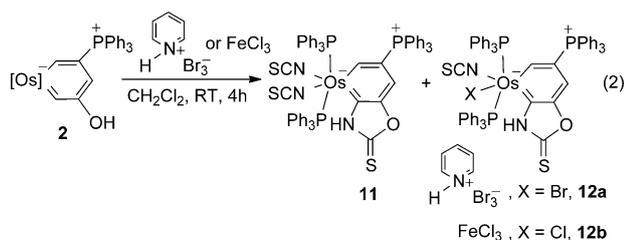


Scheme 6. Proposed mechanism for the annulation reactions of the osmaphenol complex **2**.

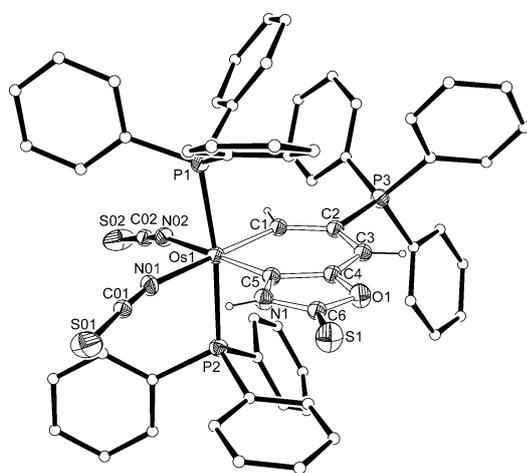
tions of the osmaphenol complex **2**. For isocyanates or isothiocyanates, osmaphenol **2** can undergo characteristic nucleophilic addition reactions to form intermediate **A**. This step is fully proven by the isolation and the characterization of the complexes **4**, **5**, and **6**. Then, nucleophilic addition of the urethane linkage at the C5-position of metallabenzene ring may result in formation of the  $\sigma^{\text{H}}$  adduct **B**. Subsequent dehydration reactions of **B** in the presence of oxygen can yield the fused metallabenzene derivatives **3**, **7**, **8**, or **9**. For pyridine, a similar reaction of the hydroxyl group of **2** leads to the formation of the intermediate **C**, which can also undergo the intermolecular  $\text{S}_{\text{N}}\text{Ar}$  reaction to generate the polycyclic intermediate **E** by intermediate **D**. With the aid of trifluoromethanesulfonic anhydride, deprotonation of the azacycle of **E** restores the aromatic pyridine ring, affording the final product **10**.

#### Other reactions of the osmaphenol complex **2**

In general, phenol is highly reactive toward electrophiles to undergo  $\text{S}_{\text{E}}\text{Ar}$  reactions due to the strong electron donation effect of hydroxyl. To further compare the similarity of metallaphenol and phenol, reactivity of osmaphenol **2** was also tested against a number of electrophiles. As indicated by in situ NMR spectra, the reactions of **2** with common electrophiles, such as  $\text{NOBF}_4$ ,  $\text{NO}_2\text{BF}_4$ , *N*-bromosuccinimide, and *N*-chlorosuccinimide, only led to the decomposition of the metallaphenol ring, giving the unidentified species at room temperature. In addition, osmaphenol **2** is reactive towards pyridinium tribromide although we have failed to isolate or identify the expected  $\text{S}_{\text{E}}\text{Ar}$  product from the reaction mixtures. As suggested by NMR spectroscopy (in  $\text{CD}_2\text{Cl}_2$ ), reaction of **2** with pyridinium tribromide produces a mixture of the complex **11** and the complex **12a** in a molar ratio of 3:2 at room temperature (Eq. (2)). The  $^1\text{H}$  NMR spectrum of the mixture shows two sets of characteristic signals of OsCH ( $\delta = 16.9$  and 16.7 ppm) and NH ( $\delta = 9.7$  and 9.7 ppm). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows two OsPPh<sub>3</sub> signals at  $\delta = -8.6$  and  $-12.5$  ppm and two CPPH<sub>3</sub> signals at  $\delta = 20.4$  and 20.0 ppm. The two sets of signals are similar to those of the fused metallabenzene rings described above.



Our attempts to separate the products by recrystallization or column chromatography were unsuccessful due to the similarity of the two products. Fortunately, after recrystallization of the crude reaction mixture from  $\text{CH}_2\text{Cl}_2$ /hexane, a single crystal of **11** was obtained, making it possible to determine its solid-state structure. The crystallographic details are given in Table 2. The X-ray diffraction study reveals that **11** is an osmabenzooxazothione complex (Figure 6). The bond lengths of



**Figure 6.** X-ray structure of complex **11** (ellipsoids at the 50% probability level). Some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Os1–C1 1.981(4), Os1–C5 1.944(3), C1–C2 1.380(5), C2–C3 1.432(5), C3–C4 1.353(5), C4–C5 1.412(5), C4–O1 1.409(4), C6–O1 1.344(5), C6–S1 1.635(4), C6–N1 1.357(5), C5–N1 1.386(5); C1–Os1–C5 88.43(15), C2–C1–Os1 130.8(3), C1–C2–C3 123.4(3), C2–C3–C4 120.9(3), C3–C4–C5 128.5(4), C4–C5–Os1 127.5(3), C5–C4–O1 109.8(3), C4–O1–C6 107.5(3), O1–C6–N1 107.4(3), C5–N1–C6 113.4(3), C4–C5–N1 101.9(3).

the fused metallabenzene rings compare well with those found in the complex **9**. On the basis of the characterized structure of **11**, we assume the formation of **11** presumably proceed through the partly decomposition of osmaphenol **2** to release the free  $\text{SCN}^-$ , followed by the annulation reaction of the osmaphenol ring. Thus, the other unseparated product was supposed to be the ligand substitution product of **11** with pyridinium tribromide. Consistent with our assumption, when the reaction was carried out in the presence of excess  $\text{NaSCN}$ , complex **11** was exclusively formed, which can be isolated in 81% yield. Besides, the conversion of **2** to **11** doesn't occur in the absence of pyridinium tribromide.

According to the above experimental results, we think that pyridinium tribromide may act as an oxidant in the conversion

to facilitate the intermolecular  $\text{S}_\text{N}\text{Ar}$  reaction step. To test this idea, we also studied the conversion in the presence of different oxidants. As suggested by in situ NMR spectroscopy, **2** is unreactive towards  $\text{Ag}_2\text{O}$  while the decomposition of the osmaphenol ring was observed when the reaction was performed with the oxidant  $\text{H}_2\text{O}_2$ . Similar conversion can be achieved when the osmaphenol complex **2** was allowed to react with  $\text{FeCl}_3$  (Eq. (2)). The reaction produced the expected annulation products **11** and **12b** in a molar ratio of 1:3. Supporting evidence for the existence of the two products is the similarity in the NMR spectroscopic (in  $\text{CD}_2\text{Cl}_2$ ) data. The two products exhibit the  $\text{OsPPh}_3$  signals at  $\delta = -8.6$  and  $-7.5$  ppm and the  $\text{CPh}_3$  signals at  $\delta = 20.4$  and  $20.1$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The signals at  $\delta = 16.9$  and  $16.0$  ppm are assignable to  $\text{OsCH}$  protons of the osmabenzene rings in the  $^1\text{H}$  NMR spectrum. The molecular structure of **12b** has been confirmed by X-ray diffraction. Selected bond distances and angles are given in Table S2 in the Supporting Information.

In view of the reactivity study results, we consider that the metal center and the strong electron-withdrawing phosphonium group might play a more important role than the hydroxyl in osmaphenol **2**, and therefore **2** is very electrophilic and readily reacts with nucleophiles.

## Conclusion

In summary, the first example of *m*-metallaphenol has been synthesized and fully characterized. Both experimental and theoretical studies suggest that its metallacycle has an aromatic character. It can undergo typical reactions of aromatic systems (e.g. nucleophilic substitution reactions) as well as phenols (e.g. formation of urethane linkages with isocyanates). Further advances in the chemistry of this novel metallaaromatic compound are expected especially in the study of its properties and applications.

## Experimental Section

### General comments

All manipulations were carried out at room temperature under a nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, and tetrahydrofuran) or calcium hydride (dichloromethane and triethylamine). The starting material  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{OH})-\eta^2\text{-C}\equiv\text{CH}\}(\text{PPh}_3)_2(\text{NCS})_2]$  (**1**) was synthesized by literature procedures.<sup>[7b]</sup> Column chromatography was performed on neutral alumina gel (200–300 mesh). NMR spectroscopic experiments were performed on a Bruker AV-500 spectrometer ( $^1\text{H}$ : 500.2;  $^{13}\text{C}$ : 125.8,  $^{31}\text{P}$ : 202.5 MHz), or a Bruker AV-300 spectrometer ( $^1\text{H}$ : 300.1,  $^{13}\text{C}$ : 75.5,  $^{31}\text{P}$ : 121.5 MHz).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic chemical shifts are relative to TMS and  $^{31}\text{P}$  NMR spectroscopic chemical shifts are relative to 85%  $\text{H}_3\text{PO}_4$ . Elemental analysis data were obtained on an Elementar Analysen system GmbH Vario EL III instrument.

### Preparation and characterization of complex 2

A solution of  $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CH}(\text{OH})\text{-}\eta^2\text{-C}\equiv\text{CH}\}\{\text{PPh}_3\}_2(\text{NCS})_2]$  (**1**) (504 mg, 0.43 mmol) in dichloromethane (15 mL) and triethylamine (3 mL) was stirred at room temperature for about 12 days to give a dark-green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of hexane (20 mL) to the residue produced a green solid. This was then washed with chloroform (5 mL) and hexane (20 mL) and the product collected by filtration, and dried under vacuum. Yield: 404 mg, 80%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 17.8$  (s, 1H,  $\text{C}^5\text{H}$ ), 15.8 (d,  $J(\text{P,H}) = 24.0$  Hz, 1H,  $\text{C}^1\text{H}$ ), 7.3 (1H,  $\text{C}^3\text{H}$  obscured by the phenyl signals and confirmed by  $^1\text{H-}^{13}\text{C}$  HSQC), 6.9–7.7 (m, 45H; Ph), 3.6 ppm (s, 1H, OH);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 18.3$  (s,  $\text{C}^1\text{PPh}_3$ ),  $-6.5$  ppm (s,  $\text{OsPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$  plus  $^1\text{H-}^{13}\text{C}$  HSQC and  $^{13}\text{C-dept}$  135):  $\delta = 247.0$  (br,  $\text{C}^5$ ), 218.2 (br,  $\text{C}^1$ ), 157.9 (d,  $J(\text{P,C}) = 16.4$  Hz,  $\text{C}^4$ ), 148.8, 142.0 (s, SCN), 121.8–134.8 (m, Ph), 127.6 (d,  $J(\text{P,C}) = 22.6$  Hz,  $\text{C}^3$ ), 112.0 ppm (d,  $J(\text{P,C}) = 75.5$  Hz,  $\text{C}^2$ ); elemental analysis calcd (%) for  $\text{C}_{61}\text{H}_{49}\text{N}_2\text{O}_5\text{OsP}_3\text{S}_2$ : C 62.44, H 4.21, N 2.39; found: C 62.19, H 4.53, N 2.35.

### Preparation and characterization of complex 3

**Method A:** Phenyl isocyanate (0.49 mL, 4.5 mmol) was added to a solution of **2** (505 mg, 0.43 mmol) in dichloromethane (25 mL) and triethylamine (5 mL). The reaction mixture was stirred at room temperature for about 5 days to give a dark-green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a dark-green solid. This solid was washed with chloroform (5 mL) and diethyl ether (20 mL), giving a green solid, which was collected by filtration, and dried under vacuum. Yield: 472 mg, 85%.

**Method B:** A solution of **4** (245 mg, 0.19 mmol) in dichloromethane (15 mL) and triethylamine (3 mL) was stirred at room temperature for about 4 days to give a green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a green solid, which was collected by filtration, washed with diethyl ether ( $2 \times 10$  mL) and dried under vacuum. Yield: 216 mg, 88%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.9$  (d,  $J(\text{P,H}) = 23.0$  Hz, 1H,  $\text{C}^1\text{H}$ ), 7.4 (d,  $J(\text{P,H}) = 10.5$  Hz, 1H,  $\text{C}^3\text{H}$ ), 6.8–7.7 ppm (m, 50H, Ph);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.1$  (s;  $\text{C}^1\text{PPh}_3$ ),  $-9.7$  ppm (s,  $\text{OsPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$  plus  $^1\text{H-}^{13}\text{C}$  HSQC and  $^{13}\text{C-dept}$  135):  $\delta = 230.8$  (br,  $\text{C}^1$ ), 203.9 (br,  $\text{C}^5$ ), 158.3 (s,  $\text{C}^6$ ), 147.1 (d,  $J(\text{P,C}) = 16.4$  Hz,  $\text{C}^4$ ), 145.3, 142.3 (s, SCN), 122.2 (d,  $J(\text{P,C}) = 24.0$  Hz,  $\text{C}^3$ ), 120.9–137.1 (m, Ph), 105.6 ppm (d,  $J(\text{P,C}) = 77.0$  Hz,  $\text{C}^2$ ); elemental analysis calcd (%) for  $\text{C}_{68}\text{H}_{52}\text{N}_3\text{O}_2\text{OsP}_3\text{S}_2$ : C 63.29; H 4.06; N 3.26; found: C 63.34; H 4.41; N 3.27.

### Preparation and characterization of complex 4

Phenyl isocyanate (0.22 mL, 2.0 mmol) was added to a solution of **2** (235 mg, 0.20 mmol) in dichloromethane (15 mL) and triethylamine (3 mL). The reaction mixture was stirred at room temperature for about 11 h to give a dark-green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a dark-green solid. This solid was washed with chloroform (5 mL) and diethyl ether (20 mL) to produce a green solid, which was collected by filtration, and dried under vacuum. Yield: 243 mg, 94%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 17.5$  (s, 1H,  $\text{C}^5\text{H}$ ), 16.9 (d,  $J(\text{P,H}) = 22.5$  Hz, 1H,  $\text{C}^1\text{H}$ ), 7.7 (d,  $J(\text{P,H}) = 12.5$  Hz, 1H,  $\text{C}^3\text{H}$ ), 6.9–7.7 (m, 50H, Ph), 6.6 ppm (br, 1H, NH);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 19.2$  (s,  $\text{C}^1\text{PPh}_3$ ),  $-4.5$  ppm (s,  $\text{OsPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 244.7$  (br,  $\text{C}^5$ ),

229.0 (br,  $\text{C}^1$ ), 153.5 (s,  $\text{C}^6$ ), 151.1 (d,  $J(\text{P,C}) = 15.1$  Hz,  $\text{C}^4$ ), 147.3, 143.4 (s, SCN), 141.5 (d,  $J(\text{P,C}) = 21.4$  Hz,  $\text{C}^3$ ), 119.4–138.6 (m, Ph), 112.2 ppm (d,  $J(\text{P,C}) = 76.7$  Hz,  $\text{C}^2$ ); elemental analysis calcd (%) for  $\text{C}_{68}\text{H}_{54}\text{N}_3\text{O}_2\text{OsP}_3\text{S}_2$ : C 63.19, H 4.21, N 3.25; found: C 62.72, H 3.92, N 3.44.

### Preparation and characterization of complex 5

Isopropyl isocyanate (0.29 mL, 3.0 mmol) was added to a solution of **2** (355 mg, 0.30 mmol) in dichloromethane (15 mL) and triethylamine (3 mL). The reaction mixture was stirred at room temperature for about 9 h to give a dark-green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a dark-green solid. This solid was washed with chloroform (5 mL) and diethyl ether (20 mL) to produce a green solid, which was collected by filtration, and dried under vacuum. Yield: 359 mg, 94%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 17.5$  (s, 1H,  $\text{C}^5\text{H}$ ), 16.6 (d,  $J(\text{P,H}) = 22.0$  Hz, 1H,  $\text{C}^1\text{H}$ ), 7.0–7.6 (m, 45H, Ph), 7.6 (1H,  $\text{C}^3\text{H}$  obscured by the phenyl signals and confirmed by  $^1\text{H-}^{13}\text{C}$  HSQC), 4.5 (br, 1H, NH), 3.7 (m, 1H,  $\text{C}^7\text{H}$ ), 1.1 ppm (d,  $J(\text{P,H}) = 5.0$  Hz, 6H,  $\text{C}^8\text{H}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 19.0$  (s,  $\text{C}^1\text{PPh}_3$ ),  $-4.2$  ppm (s,  $\text{OsPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$  plus  $^1\text{H-}^{13}\text{C}$  HSQC and  $^{13}\text{C-dept}$  135):  $\delta = 246.3$  (br,  $\text{C}^5$ ), 228.3 (br,  $\text{C}^1$ ), 155.4 (s,  $\text{C}^6$ ), 151.4 (d,  $J(\text{P,C}) = 16.4$  Hz,  $\text{C}^4$ ), 147.1, 143.0 (s, SCN), 141.0 (d,  $J(\text{P,C}) = 20.1$  Hz,  $\text{C}^3$ ), 121.6–135.0 (m, Ph), 111.9 (d,  $J(\text{P,C}) = 76.7$  Hz,  $\text{C}^2$ ), 43.7 (s,  $\text{C}^7$ ), 23.7 ppm (s,  $\text{C}^8$ ); elemental analysis calcd (%) for  $\text{C}_{65}\text{H}_{56}\text{N}_3\text{O}_2\text{OsP}_3\text{S}_2$ : C 62.04, H 4.48, N 3.34; found: C 62.24, H 4.42, N 2.98.

### Preparation and characterization of complex 6

Benzyl isocyanate (0.26 mL, 2.1 mmol) was added to a solution of **2** (246 mg, 0.21 mol) in dichloromethane (15 mL) and triethylamine (3 mL). The reaction mixture was stirred at room temperature for about 15 min to give a dark-green solution. The volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a dark-green solid. This solid was washed with chloroform (5 mL) and diethyl ether (20 mL) to produce a green solid, which was collected by filtration and dried under vacuum. Yield: 269 mg, 98%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 17.5$  (s, 1H,  $\text{C}^5\text{H}$ ), 16.7 (d,  $J(\text{P,H}) = 22.5$  Hz, 1H,  $\text{C}^1\text{H}$ ), 7.6 (1H,  $\text{C}^3\text{H}$  obscured by the phenyl signals and confirmed by  $^1\text{H-}^{13}\text{C}$  HSQC), 6.9–7.7 (m, 50H, Ph), 5.1 (br, 1H, NH), 4.3 ppm (d,  $J(\text{H,H}) = 5.5$  Hz, 2H,  $\text{C}^7\text{H}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 19.0$  (s,  $\text{C}^1\text{PPh}_3$ ),  $-4.5$  ppm (s,  $\text{OsPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$  plus  $^1\text{H-}^{13}\text{C}$  HSQC):  $\delta = 245.8$  (br,  $\text{C}^5$ ), 228.6 (br,  $\text{C}^1$ ), 156.4 (s,  $\text{C}^6$ ), 151.5 (d,  $J(\text{P,C}) = 16.4$  Hz,  $\text{C}^4$ ), 147.2 and 143.2 (s, SCN), 141.1 (d,  $J(\text{P,C}) = 21.4$  Hz,  $\text{C}^3$ ), 121.5–139.2 (m, Ph), 112.1 (d,  $J(\text{P,C}) = 75.5$  Hz,  $\text{C}^2$ ), 45.5 ppm (s,  $\text{C}^7$ ); elemental analysis calcd (%) for  $\text{C}_{69}\text{H}_{56}\text{N}_3\text{O}_2\text{OsP}_3\text{S}_2$ : C 63.43, H 4.32, N 3.22; found: C 63.56, H 4.33, N 3.16.

### Preparation and characterization of complex 7

LDA (0.25 mL, 2.0 M solution in THF, 0.50 mmol) was added to a solution of **5** (629 mg, 0.50 mmol) in THF (40 mL). The reaction mixture was stirred at room temperature for about 15 min to give a dark-green suspension. The volume of the mixture was reduced to about 2 mL under vacuum and was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 50:1) to give complex **7** as a green solid sequentially. Yield: 503 mg, 80%;  $^1\text{H NMR}$  (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 15.5$  (d,  $J(\text{P,H}) = 23.0$  Hz, 1H,  $\text{C}^1\text{H}$ ), 6.8–7.7 (m, 46H, Ph,  $\text{C}^3\text{H}$ ), 4.9 (m, 1H,  $\text{C}^7\text{H}$ ), 0.4 ppm (d,  $J(\text{P,H}) = 6.6$  Hz, 6H,  $\text{C}^8\text{H}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 16.2$  (s,  $\text{C}^1\text{PPh}_3$ ),  $-7.0$  ppm (s,  $\text{OsPPh}_3$ ); elemental analysis calcd (%) for

$C_{65}H_{54}N_3O_2OsP_3S_2$ : C 62.14, H 4.33, N 3.34; found: C 62.35, H 4.33, N 2.97.

### Preparation and characterization of complex 8

LDA (0.25 mL, 2.0 M solution in THF, 0.50 mmol) was added to a solution of **6** (650 mg, 0.50 mmol) in THF (40 mL). The reaction mixture was stirred at room temperature for about 15 min to give a dark-green suspension. The volume of the mixture was reduced to about 2 mL under vacuum and was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 50:1) to give complex **8** as a green solid sequentially. Yield: 535 mg, 82%;  $^1H$  NMR (500.2 MHz,  $CD_2Cl_2$ ):  $\delta$  = 15.8 (d,  $J(P,H)$  = 23.0 Hz, 1H,  $C^1H$ ), 6.6–7.7 (m, 51H, Ph and  $C^3H$ ), 4.6 ppm (s, 2H,  $C^7H$ );  $^{31}P\{^1H\}$  NMR (202.5 MHz,  $CD_2Cl_2$ ):  $\delta$  = 17.1 (s,  $CPPh_3$ ),  $-8.3$  ppm (s,  $OsPPh_3$ ); elemental analysis calcd (%) for  $C_{69}H_{54}N_3O_2OsP_3S_2$ : C 63.53, H 4.17, N 3.22; found: C 63.76, H 4.35, N 3.23.

### Preparation and characterization of complex 9

Isopropyl isothiocyanate (0.46 mL, 4.31 mmol) was added to a mixture of **2** (505 mg, 0.43 mmol) and maleic anhydride (422 mg, 4.30 mmol) in dichloromethane (20 mL) and triethylamine (2 mL). The reaction mixture was stirred at room temperature for about 1 day to give a brown solution. The volume of the mixture was reduced to about 2 mL under vacuum and was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone 100:1) to give complex **9** as a green solid. Yield: 438 g, 80%;  $^1H$  NMR (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 16.7 (d,  $J(P,H)$  = 21.3 Hz, 1H,  $C^1H$ ), 7.4 (d,  $J(P,H)$  = 11.7 Hz, 1H,  $C^3H$ ), 6.9–7.7 (m, 45H, Ph), 5.2 (m, 1H,  $C^7H$ ), 0.7 ppm (d,  $J(P,H)$  = 6.6 Hz, 6H,  $C^8H$ );  $^{31}P\{^1H\}$  NMR (121.5 MHz,  $CDCl_3$ ):  $\delta$  = 15.7 (s,  $CPPh_3$ ),  $-6.3$  ppm (s,  $OsPPh_3$ );  $^{13}C\{^1H\}$  NMR (75.5 MHz,  $CDCl_3$  plus  $^1H$ - $^{13}C$  HMBC and  $^{13}C$ -dept 135):  $\delta$  = 232.0 (br,  $C^1$ ), 204.4 (br,  $C^5$ ), 184.7 (s,  $C^6$ ), 150.8 (d,  $J(P,C)$  = 17.1 Hz,  $C^4$ ), 146.0, 141.9 (s, SCN), 123.2 (d,  $J(P,C)$  = 23.8 Hz,  $C^3$ ), 120.3–137.2 (m, Ph), 106.9 (d,  $J(P,C)$  = 79.6 Hz,  $C^2$ ), 53.8 (s,  $C^7$ ), 18.2 ppm (s,  $C^8$ ); elemental analysis calcd (%) for  $C_{65}H_{54}N_3O_2OsP_3S_3$ : C 61.35, H 4.28, N 3.30; found: C 61.21, H 4.44, N 3.07.

### Preparation and characterization of complex 10

Trifluoromethanesulfonic anhydride (77.4  $\mu$ L, 0.46 mmol) was added to a solution of **2** (498 mg, 0.42 mmol) in pyridine (25 mL). The reaction mixture was stirred at 0 °C for about 30 min to give a brown solution. Then the volume of the mixture was reduced to ca. 2 mL under vacuum. Addition of diethyl ether (20 mL) to the residue produced a brown solid. The solid of the mixture was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 1:1) to give complex **10** as an orange solid. Yield: 176 mg, 30%;  $^1H$  NMR (500.2 MHz,  $CD_2Cl_2$ ):  $\delta$  = 20.4 (d,  $J(P,H)$  = 20.0 Hz, 1H,  $C^1H$ ), 8.7 (d,  $J(H,H)$  = 13.0 Hz, 1H,  $C^3H$ ), 6.8–8.8 (m, 49H, Ph, Py);  $^{31}P\{^1H\}$  NMR (202.5 MHz,  $CD_2Cl_2$ ):  $\delta$  = 20.3 (s,  $CPPh_3$ ),  $-17.2$  ppm (s,  $OsPPh_3$ );  $^{13}C\{^1H\}$  NMR (125.8 MHz,  $CD_2Cl_2$  plus  $^1H$ - $^{13}C$  HSQC, HMBC and  $^{13}C$ -dept 135):  $\delta$  = 242.7 (br,  $C^1$ ), 178.6 (br,  $C^5$ ), 154.8, 146.6 (s, SCN), 151.8 (d,  $J(P,C)$  = 18.2 Hz,  $C^4$ ), 140.7 (d,  $J(P,C)$  = 21.6 Hz,  $C^3$ ), 110.1–162.5 (m, Ph, Py), 117.2 ppm (d,  $J(P,C)$  = 78.0 Hz,  $C^2$ ); elemental analysis calcd (%) for  $C_{67}H_{51}N_3F_3O_4OsP_3S_3$ : C 57.54, H 3.68, N 3.00; found: C 57.65, H 3.81, N 3.09.

### Preparation and characterization of complex 11

*Method A:* A mixture of complex **2** (305 mg, 0.26 mmol), pyridinium tribromide (249 mg, 0.78 mmol), and sodium thiocyanate (104 mg, 1.28 mmol) in dichloromethane (15 mL) was stirred at room tem-

perature for 4 h to give a dark-green solution. The volume of the mixture was reduced to about 1 mL under vacuum and was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 50:1) to give complex **11** as a green solid. Yield: 259 mg, 81%.

*Method B:* A mixture of complex **2** (203 mg, 0.17 mmol), ferric chloride (83 mg, 0.51 mmol), and sodium thiocyanate (69 mg, 0.85 mmol) in dichloromethane (15 mL) was stirred at room temperature for 4 h to give a dark-green solution. The volume of the mixture was reduced to about 1 mL under vacuum and was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone, 50:1) to give complex **11** as a green solid. Yield: 189 mg, 89%;  $^1H$  NMR (500.2 MHz,  $CD_2Cl_2$ ):  $\delta$  = 15.9 (d,  $J(P,H)$  = 24.0 Hz, 1H,  $C^1H$ ), 7.3 (1H,  $C^3H$  obscured by the phenyl signals and confirmed by  $^1H$ - $^{13}C$  HSQC), 8.4 (s, 1H, NH), 6.9–7.7 ppm (m, 45H, Ph);  $^{31}P\{^1H\}$  NMR (202.5 MHz,  $CD_2Cl_2$ ):  $\delta$  = 20.1 (s,  $CPPh_3$ ),  $-7.5$  ppm (s,  $OsPPh_3$ );  $^{13}C\{^1H\}$  NMR (125.8 MHz,  $CD_2Cl_2$  plus  $^1H$ - $^{13}C$  HSQC and  $^{13}C$ -dept 135):  $\delta$  = 226.2 (br,  $C^1$ ), 201.5 (br,  $C^5$ ), 186.7 (s,  $C^6$ ), 150.2 (d,  $J(P,C)$  = 18.9 Hz,  $C^4$ ), 144.0, 143.9 (s, SCN), 121.0–134.6 (m, Ph), 122.8 (d,  $J(P,C)$  = 23.8 Hz,  $C^3$ ), 106.2 ppm (d,  $J(P,C)$  = 81.3 Hz,  $C^2$ ); elemental analysis calcd (%) for  $C_{62}H_{48}N_3O_2OsP_3S_3$ : C 60.52, H 3.93, N 3.42; found: C 60.21, H 4.13, N 3.06.

### Crystallographic analysis

Crystals suitable for X-ray diffraction were grown from  $CH_2Cl_2$  solutions layered with hexane for **2**, **4**, and **11** and from  $CHCl_3$  solution layered with hexane for **3**, **9**, and **10**. The solvent molecules  $CH_2Cl_2$  in **2**, **4**, and **11** are disordered and were refined with suitable restraints. The solvent molecules  $CHCl_3$  in **3** and **9** are disordered and were refined with suitable restraints. The solvent molecules  $CHCl_3$  and the  $OTf^-$  groups in **10** are disordered and were refined with suitable restraints. Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector or a Bruker Apex CCD area detector with graphite-monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). All of the Data were corrected for absorption effects using the multiscan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on  $F^2$  by using Bruker SHELXTL (Version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. Further details on crystal data, data collection, and refinements are summarized in Table 2.

### Computational details

All structures were optimized at the B3LYP level of density functional theory.<sup>[11]</sup> In addition, the frequency calculations were performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double- $\zeta$  valence basis set (LanL2DZ) were used to describe the Os, P, and S atoms, whereas the standard 6–31G\* basis set was used for the C, O, and H atoms for all the compounds.<sup>[12]</sup> Polarization functions were added for Os ( $\zeta(f) = 0.886$ ), P ( $\zeta(d) = 0.34$ ), S ( $\zeta(d) = 0.421$ ), and Cl ( $\zeta(d) = 0.514$ ).<sup>[13]</sup> The calculated bond lengths in Scheme 2 using the model system are consistent with the experimental values, which indicates the reliability of our calculations. All the optimizations were performed with the Gaussian 03 software package.<sup>[14]</sup>

## Acknowledgements

We thank the 973 Program (2012CB821600), the National Natural Science Foundation of China (21174115, 21272193, 21332002) and the Natural Science Foundation of Fujian Province (No. 2011J05031).

**Keywords:** annulation reactions • metallaphenols • nucleophilic aromatic substitution • reactivity studies • synthesis

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Received: December 19, 2013

Published online on March 11, 2014