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# Reactivity study of a hydroxyl coordinated osmium vinyl complex OsCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>[CH=C(PPh<sub>3</sub>)CHPh(OH)]<sup>†</sup>

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We studied the reactivity of an osmium vinyl complex containing a coordinated hydroxyl group  $OsCl_2(PPh_3)_2[CH=C(PPh_3)-CHPh(OH)]$  (1) toward bidentate ligand 1,4-bis(diphenylphosphino)butane (DPPB),  $\pi$  acid ligand (CO), base (Cs<sub>2</sub>CO<sub>3</sub>) and heat. Two osmium vinyl complexes  $OsCl_2(dppb)[CH=C(PPh_3)CHPh(OH)]$  (2) and  $OsCl_2(CO)_2(PPh_3)[CH=C(PPh_3)CHPh(OH)]$  (3), as well as two relatively rare phosphonium-containing osmafuran complexes  $Os(\eta^2-OCOO)(PPh_3)_2[CHC(PPh_3)CPhO]$  (4) and  $OsCl_2(PPh_3)_2[CHC(PPh_3)CPhO]$  (5), were obtained in high yields from these reactions. All products were characterized by NMR spectroscopy, elemental analysis, and their structures were further confirmed by single crystal X-ray diffraction.

osmium vinyl complex, osmafuran, aromatic cyclization, ligand substitution, metallaaromatics

# 1 Introduction

Transition metal containing aromatic metallacycles [1] have attracted more and more attention because they possess both the reactivity of organometallic complexes and the aromaticity of ring systems. Recently, considerable progresses have been achieved in this field, and a lot of aromatic metallacycles such as metallabenzene [2], metallabenzyne [1a, 1e, 3], metallanaphthalene [4], metallapyridine [5], metallapyridinium [5a, 5b], metallapyridyne [6] and metallafuran [7] have been synthesized. In 2009, we reported the synthesis of the first osmanaphthalene [4a] and metallapyridinium [5b]. In those studies, treatment of a hydroxyl coordinated osmium vinyl complex OsCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>[CH=C(PPh<sub>3</sub>) CHPh(OH)] (1) with HBF<sub>4</sub> afforded the key intermediate hydride osmium carbyne complex [OsHCl<sub>2</sub>(PPh<sub>3</sub>)  $\{\equiv CC(PPh_3)=CHPh\}BF_4$  [4a, 5b]. As hydroxyl group is a relatively weak ligand toward the central osmium, it can be replaced by other ligands to afford ligand-exchanged products. Herein, we present a series of reactions of complex 1, which give osmium vinyl complexes  $OsCl_2(dppb)[CH=C(PPh_3) CHPh(OH)]$  (2) and  $OsCl_2(CO)_2(PPh_3)[CH=C(PPh_3) CHPh(OH)]$  (3), as well as osmafurans  $Os(\eta^2-OCOO)(PPh_3)_2$  [CHC(PPh\_3)CPhO] (4) and  $OsCl_2$  (PPh\_3)\_2[CHC(PPh\_3)CPhO] (5) in high yields.

# 2 Experimental

#### 2.1 General experimental section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium and benzophenone (diethyl ether, THF), or calcium hydride (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, ClCH<sub>2</sub>CH<sub>2</sub>Cl). The starting material complex **1** was synthesized according to our previous communication [5b]. NMR experiments were performed on Bruker AV300, AV400 or AV500 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are relative to TMS, and <sup>31</sup>P NMR chemical shifts are relative to 85% H<sub>3</sub>PO<sub>4</sub>. Elemental analyses data were obtained on Thermo Quest Italia S.P.A. EA 1110. Cs<sub>2</sub>CO<sub>3</sub> and 1,4-bis(diphenylphosphino)butane (DPPB) were purchased from Sigma-Aldrich and used as received.

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#### 2.2 Synthesis of complex 2

A red solution of complex 1 (400 mg, 0.34 mmol) in dichloromethane (10 mL) was treated with 1,4-bis(diphenylphosphino)butane (DPPB) (724 mg, 1.7 mmol). After the mixture was stirred for 5 h at room temperature, it was filtered and the filtrate was evaporated. Addition of diethyl ether gave complex 2 as a yellow precipitate, which was washed with diethyl ether and dried in vacuo. Yield: 329 mg, 90%. <sup>1</sup>H NMR (500.17 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 11.70 (d,  ${}^{3}J(PH) = 23.5 \text{ Hz}, 1H, OsCH), 8.09-6.70 (m, 40H, other)$ aromatic protons), 5.43 (d,  ${}^{4}J(PH) = 7.5$  Hz, 1H, OH), 4.46 (m, 1H,  $Ph_2PCH$ ), 2.66(t,  ${}^{2}J(PH) = 14$  Hz, 1H,  $Ph_2PCH$ ), 2.90 (q,  ${}^{2}J(PH) = 26.5 \text{ Hz}$ ,  ${}^{2}J(PH) = 13.5 \text{ Hz}$ , 1H, Ph<sub>2</sub>PCH), 1.53 (br, 1H, Ph<sub>2</sub>PCH), 3.72 (d,  ${}^{3}J(PH) = 7.5$  Hz, 1H, OsCHCPPh<sub>3</sub>CH), 2.16 (br, 4H, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.47 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.40 (s, CPPh<sub>3</sub>), 9.71 (d,  ${}^{2}J(PP) = 16.2 \text{ Hz}, Ph_{2}P$ ), -2.06 (d,  ${}^{2}J(PP) = 16.2 \text{ Hz},$ Ph<sub>2</sub>P). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  212.5 (br, OsCH), 139.4-122.9 (m, other aromatic carbon atoms), 104.2 (d,  ${}^{1}J(PC) = 82.1$  Hz, OsCHCPPh<sub>3</sub>), 87.3 (d,  ${}^{2}J(PC) =$ 32.8 Hz, OsCHCPPh<sub>3</sub>CH), 27.5 (s, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>), 18.4 (s, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>). Anal. Calcd for C<sub>55</sub>H<sub>51</sub>OCl<sub>2</sub>P<sub>3</sub>Os: C, 61.05; H, 4.75. Found: C, 61.32; H, 5.05.

#### 2.3 Synthesis of complex 3

A red solution of complex 1 (400 mg, 0.34 mmol) in dichloromethane (10 mL) was stirred in CO atmosphere at room temperature for 10 h. The solvent was removed in vacuo. Addition of methanol to the resulting residue provided complex 3 as a pale solid, which was washed with methanol and dried in vacuo. Yield: 280 mg, 85%. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  9.94 (d, <sup>3</sup>J(PH) = 30.4 Hz, 1H, OsCH), 7.91-6.65 (m, 35 H, other aromatic protons), 3.49  $(d, {}^{3}J(PH) = 4.4 \text{ Hz}, 1H, \text{ OsCHCPPh}_{3}CH). {}^{31}P{}^{1}H} \text{ NMR}$ (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  18.6 (d, <sup>4</sup>*J*(PP) = 32.4 Hz, CPPh<sub>3</sub>), -6.4 (d,  ${}^{4}J(PP) = 32.4$  Hz, OsPPh<sub>3</sub>).  ${}^{13}C{}^{1}H{}$  NMR and Dept 135 (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  186.0 (dd, <sup>2</sup>*J*(PC) = 85.4 Hz,  ${}^{2}J(PC) = 4.1$  Hz, OsCH), 177.0 (d,  ${}^{2}J(PC) = 5.2$  Hz, CO), 175.6 (d,  ${}^{2}J(PC) = 5.7$  Hz, CO), 141.4–122.0 (m, other aromatic carbon atoms), 120.3 (d,  ${}^{1}J(PC) = 87.1$  Hz, OsCHCPPh<sub>3</sub>), 77.4 (dd,  ${}^{2}J(PC) = 16.6$  Hz,  ${}^{4}J(PC) = 3.7$  Hz, OsCHCPPh<sub>3</sub>CH). Anal. Calcd for C<sub>47</sub>H<sub>38</sub>O<sub>3</sub>Cl<sub>2</sub>P<sub>2</sub>Os: C, 57.96; H, 3.93. Found: C, 57.91; H, 4.49.

# 2.4 Synthesis of complex 4

A red solution of complex **1** (400 mg, 0.34 mmol) in dichloromethane (10 mL) was treated with  $Cs_2CO_3$  (554 mg, 1.7 mmol). After the mixture was stirred for 5 h at room temperature, the suspension was filtered, and the filtrate was evaporated. Addition of diethyl ether gave complex **4** as a green precipitate, which was washed with diethyl ether and dried in vacuo. Yield: 317 mg, 80%. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  15.35 (dd, <sup>3</sup>*J*(PH) = 15.0 Hz, <sup>3</sup>*J*(PH) = 4.4 Hz, 1H, OsC*H*), 7.75–6.55 (m, 50 H, other aromatic protons). <sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  14.98 (s, *CPPh*<sub>3</sub>), 8.90 (d, <sup>2</sup>*J*(PP) = 10.4 Hz, Os*PPh*<sub>3</sub>), -4.47 (d, <sup>2</sup>*J*(PP) = 10.4 Hz, Os*PPh*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  247.6 (br, Os*C*H), 199.2 (d, <sup>2</sup>*J*(PC) = 25.8 Hz, OsO*CP*h), 169.2 (s, OCOO), 109.5 (d, <sup>1</sup>*J*(PC) = 85.2 Hz, OsCH*CPPh*<sub>3</sub>), 139.2– 121.6 (m, other aromatic carbon atoms). Anal. Calcd for C<sub>64</sub>H<sub>51</sub>O<sub>4</sub>P<sub>3</sub>Os: C, 65.86; H, 4.40. Found: C, 65.67; H, 4.25.

#### 2.5 Synthesis of complex 5

A solution of complex **1** (500 mg, 0.42 mmol) in 1,2dichloroethane (15 mL) was heated under reflux for 0.5 h. The solvent was removed in vacuo. Addition of diethyl ether to the resulting residue gave complex **5** as a pale-green solid, which was washed with diethyl ether and dried in vacuo. Yield: 374 mg, 75%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): 15.40 (d, <sup>3</sup>*J*(PH) = 12.4 Hz, 1H, OsC*H*), 7.56–6.39 (m, 50 H, other aromatic protons). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>):  $\delta$  13.05 (s, CPPh<sub>3</sub>), -0.50 (d, <sup>2</sup>*J*(PP) = 16.4 Hz, OsPPh<sub>3</sub>), -7.88 (d, <sup>2</sup>*J*(PP) = 16.4 Hz, OsPPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  242.6 (br, OsCH), 201.7 (d, <sup>2</sup>*J*(PC) = 25.1 Hz, OsOCPh), 112.5 (d, <sup>1</sup>*J*(PC) = 86.2 Hz, OsCH*C*PPh<sub>3</sub>), 139.5–121.6 (m, other aromatic carbon atoms). Anal. Calcd for C<sub>63</sub>H<sub>51</sub>Cl<sub>2</sub>OP<sub>3</sub>Os: C, 64.23; H, 4.36. Found: C, 64.47; H, 4.26.

#### 2.6 X-ray crystallography

Crystals suitable for X-ray diffraction were grown from dichloromethane (DCM) or chloroform (CHCl<sub>3</sub>) solutions layered with diethyl ether or *n*-hexane for complexes 2 (DCM/Et<sub>2</sub>O), 3 (CHCl<sub>3</sub>/Et<sub>2</sub>O), 4 (CHCl<sub>3</sub>/n-hexane), and 5 (DCM/Et<sub>2</sub>O). Selected crystals were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on an Oxford Gemini S Ultra CCD area detector or a Bruker Apex CCD area detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Multiscan or empirical absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on  $F^2$  using the Bruker SHELXTL-97 program package. All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. CCDC-900454 (2), CCDC-900455 (3), CCDC-707874 (4), and CCDC-707875 (5) 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/cgi-bin/catreq.cgi.

#### **3** Results and discussion

#### 3.1 Reaction of complex 1 with DPPB

Bidentate phosphine ligand 1,4-bis(diphenylphosphino)

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butane (DPPB) is widely used in organometallic synthesis and catalysis [8]. Treatment of complex **1** with DPPB afforded ligand-exchanged complex OsCl<sub>2</sub>(dppb)[CH=C(PPh<sub>3</sub>) CHPh(OH)] (**2**) (Scheme 1) in 90% yield. Complex **2** was characterized by solution NMR spectroscopy, elemental analysis, and its structure was further confirmed by single crystal X-ray diffraction.

The structure of complex **2** is shown in Figure 1. The five-membered metallacycle in complex **2** is similar to complex **1** [5b]. All bond distances and angles within the metallacycle are comparable with those of complex **1**. The Os1–C1 (1.964(7) Å) bond distance is close to the reported Os–C(vinyl) bonds (1.988(7)–2.195(5) Å) [9]. The C1–C2 (1.355(10) Å) bond is close to C–C double bonds and C3–O1 (1.465(9) Å) bond is close to C–O single bonds. The Os1–O1 (2.203(5) Å) bond length is comparable to those of reported osmium vinyl complexes containing coordinated hydroxyl group, such as  $[Os{C(Me)C(OH)PhMe}(\kappa^2-O_2C CH_3)(P^iPr_3)_2]BF_4$  (2.188(5) Å) [10] and Os{B(OEt)



Scheme 1 Synthesis of complexes 2 and 3.



**Figure 1** Molecular structure for complex **2** (ellipsoids at the 50% probability level). Some hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–P1 2.263(2), Os1–P2 2.222(2), Os1–Cl1 2.525(2), Os1–Cl2 2.487 (2), Os1–Cl 1.964(7), Os1–O1 2.203 (5), C1–C2 1.355(10), C2–C3 1.530(10), C3–O1 1.465(9); P1–Os1–P2 93.73(7), Cl1–Os1–Cl2 86.59(6), C1–Os1–O1 77.8(2), Os1–Cl-C2 120.9(5), C1–C2–C3 118.7(6), C2–C3–O1 106.9(6), C3–O1–Os1 115.0(4).

 $(OC_2H_4OH)$  Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (2.180(2) Å) [11]. Clearly, only ligand substitution occurred in this reaction, and the coordinated hydroxyl ligand remained intact.

The solution NMR data of complex 2 are consistent with its solid structure and will be discussed later together with complexes 3-5.

### 3.2 Reaction of complex 1 with CO

CO is a  $\pi$  acid ligand with stronger trans effect than the oxygen atom, thus it may facilitate the cleavage of the Os–O bond. The solution of complex **1** in dichloromethane was stirred at room temperature under CO atmosphere for 10 h to afford complex OsCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)[CH=C(PPh<sub>3</sub>)CHPh(OH)] (**3**) in 85% yield as a pale solid (Scheme 1). Complex **3** was characterized by solution NMR spectroscopy, elemental analysis and single crystal X-ray diffraction.

As shown in Figure 2, two CO ligands coordinate with the central metal in a *cis* fashion (C4–Os1–C5 = 89.7(4)°). The bond lengths of Os1–C1 (2.101(11) Å) is longer than that of complex **2** (1.964(7) Å) and within the range of the reported Os–C(vinyl) bonds [9]. The C1–C2 (1.327(14) Å) bond distance is shorter than that of complex **2** (1.355(10) Å) and close to the C–C double bond. The C2–C3 (1.494(14) Å) and C3–O1 (1.418(12) Å) bond lengths are slightly shorter than those of complex **2** (C2–C3 = 1.530(10) Å, C3–O1 = 1.465(9) Å). The bond angles of C1–C2–C3 (124.7(11)°) and C2–C3–O1 (107.7(8)°) indicate that C2 and C3 atoms are sp<sup>2</sup> and sp<sup>3</sup> hybridized, respectively.

#### 3.3 Reaction of complex 1 with Cs<sub>2</sub>CO<sub>3</sub>

In 2009, we found that treatment of complex 1 with  $HBF_4$  gave a hydrido osmium carbyne complex  $[OsHCl_2(PPh_3)_2]$ 



**Figure 2** Molecular structure for complex **3** (ellipsoids at the 50% probability level). Some hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–P1 2.429(2), Os1–C11 2.443(2), Os1–C12 2.399(3), Os1–C1 2.101(11), Os1–C5 1.882(4), C5–O3 1.115(4), C1–C2 1.327(14), C2–C3 1.494(14), C3–O1 1.418(12); P1–Os1–C1 173.0(3), C11–Os1–C12 90.74(9), C4–Os1–C5 89.7(4), Os1–C5–O3 174.3(9), Os1–C4–O2 178.1(8), Os1–C1–C2 136.8(9), C1–C2–C3 124.7(11), C2–C3–O1 107.7(8).

 $\{\equiv CC(PPh_3)=CHPh\}]BF_4$  [5b]. Herein, treatment of complex 1 with  $Cs_2CO_3$  in dichloromethane at room temperature resulted in the formation of complex  $Os(\eta^2-OCOO)(PPh_3)_2$  [CHC(PPh\_3)CPhO] (4) as a green solid in 80% yield (Scheme 2). Complex 4 was characterized by NMR spectroscopy, elemental analysis and single crystal X-ray diffraction.

As shown in Figure 3, the carbonate ion coordinated with the osmium center using two oxygen atoms O2 and O3 (O2–Os1–O3 = 62.73(19)°). The C2–C3–O1 bond angle (116.1(5)°) and the disappearance of the H atom on C3 atom indicate that C3 is sp<sup>2</sup>-hybridized. The Os1–C1 (1.920(5) Å) and Os1–O1 (2.128(4) Å) bond lengths are shorter than those in complex **1** (Os1–C1 = 1.997(9) Å, Os1–O1 = 2.208(6) Å). In addition, the Os1–C1 bond length is comparable with that of the previously reported osmafuran OsCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>{CHC(PPh<sub>3</sub>)C(O)CH<sub>2</sub>CH<sub>3</sub>} (1.904(10) Å) [2i]. The C1–C2 (1.410(8) Å) and C2–C3 (1.408(9) Å) bond distances are between typical C–C single and double bonds.



Scheme 2 Synthesis of complexes 4 and 5.



**Figure 3** Molecular structure for complex **4** (ellipsoids at the 50% probability level). Some hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–P1 2.3019(17), Os1–P2 2.2558(17), Os1–O2 2.219(4), Os1–O3 2.110(4), Os1–C1 1.920(5), Os1–O1 2.128(4), C1–C2 1.410(8), C2–C3 1.408(8), C3–O1 1.281(7); P1–Os1–P2 98.77(6), O2–Os1–O3 62.73(19), C1–Os1–O1 77.6(2), Os1–C1–C2 117.6(4), C1–C2–C3 113.6(5), C2–C3–O1 116.1(5), C3–O1–Os1 114.2(3).

The bond distances of Os1–O1 (2.128(4) Å) and C3–O1 (1.281(7) Å) are close to the corresponding values in osmafuran OsCl(CO)( $P^{i}Pr_{3}$ )<sub>2</sub>{CHCHC(O)Ph} (Os1–O1 = 2.126(3) Å, C3–O1 = 1.283(4) Å) [7e]. The five-membered metallacycle constructed by Os1, C1, C2, C3, and O1 has good planarity reflected by the small rms deviation (0.0426 Å) from the least-squares plane through the five atoms. Although complex **4** can be regarded as a chelated vinyl ketone complex or oxametallacyclopentadiene complex, the structural data show that the metallacycle is delocalized and complex **4** is a metallafuran.

#### 3.4 Transformation of complex 1 at high temperature

Heating the solution of complex 1 in 1,2-dichloroethane at reflux gave osmafuran  $OsCl_2(PPh_3)_2[CHC(PPh_3)CPhO]$  (5) in 85% yield as a green solid (Scheme 2). Osmafuran 5 was characterized by solution NMR spectroscopy, elemental analysis and single crystal X-ray diffraction.

As shown in Figure 4, the two Cl atoms coordinate with the central osmium atom in a *cis* fashion (Cl1–Os1–Cl2 =  $85.67(9)^{\circ}$ ). Within the five-membered metallacycle, the bond lengths are very close to those of complex 4. The planarity of the metallacycle is reflected by the small rms deviation (0.0528 Å). All these data show that complex 5 has a delocalized metallacycle.

The selected NMR data for complexes 1-5 are given in Table 1. The <sup>1</sup>H and <sup>13</sup>C chemical shifts in the metallacycle of complex 2 are very close to those of complex 1, consistent with the similar metallacycle structures in both complexes. For complex 3, the proton signal for H1 atom shifts



**Figure 4** Molecular structure for complex **5** (ellipsoids at the 50% probability level). Some hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1–P1 2.335(3), Os1–P2 2.275(2), Os1–Cl1 2.435(2), Os1–Cl2 2.514(2), Os1–Cl 1.920(9), Os1–Ol 2.128(5), C1–C2 1.413(12), C2–C3 1.424(12), C3–Ol 1.254(11); P1–Os1–P2 101.45(9), C11–Os1–Cl2 85.67(9), C1–Os1–Ol 78.0(3), Os1–Cl–C2 117.3(7), C1–C2–C3 112.3(8), C2–C3–Ol 117.8(8), C3–Ol–Os1 113.3(6), Cl2–Os1–Cl 163.7(3), P2–Os1–Ol 167.18(17).

	$\delta$ ( <sup>1</sup> H) (ppm)		$\delta$ ( <sup>13</sup> C) (ppm)			$\delta(^{31}\text{P}) \text{ (ppm)}$	
	H1	H3	C1	C2	C3	OsP	СР
1	12.22	3.21	204.9	98.1	80.9	7.74, -3.72	-0.99
2	11.70	3.72	212.5	104.2	87.3	9.71, 2.06	2.40
3	9.94	3.49	186.0	120.3	77.4	-6.4	18.6
4	15.35	-	247.6	109.5	199.2	8.90, -4.47	14.98
5	15.40	-	242.6	112.5	201.7	-0.50, -7.88	13.05

Table 1 Selected NMR data for complexes 1-5

upfield in comparison to complexes 1 and 2, presumably due to the change of the coordination environment around the metal center. The same trend is observed for C1 and C3, but the signals of C2 and CPPh<sub>3</sub> shift downfield. In complexes 4 and 5, the <sup>1</sup>H and <sup>13</sup>C chemical shifts in the metallacycle shift downfield considerably compared with complexes 1 and 2, clearly showing their aromaticity. In complex 5, the <sup>31</sup>P chemical shifts of OsPPh<sub>3</sub> shift upfield significantly in comparison to complex 4, indicating the coordination environment of the metal is changed.

A mechanism for the formation of complex **5** is proposed in Scheme 3. Complex **1** eliminates HCl from the proton of the hydroxyl group and a Cl<sup>-</sup> ligand, affording intermediate **A** (step i). The H3 atom attached to C3 atom shifts to osmium atom to give intermediate **B** (step ii). The HCl molecule formed in step i reacts with the hydride ligand in intermediate **B** to give complex **5** and H<sub>2</sub> (step iii). It is clear that the relative position of the ligands around metal center changed during the reaction. A similar mechanism has been proposed by Esteruelas and Oro et al in 1994 [7e]. In the presence of Cs<sub>2</sub>CO<sub>3</sub>, the two Cl<sup>-</sup> ligands in complex **5** can be substituted, giving complex **4** and CsCl.



Scheme 3 Proposed mechanism for the formation of complex 5.

# 4 Conclusions

In summary, we have studied the reactivity of the hydroxyl coordinated osmium vinyl complex 1 toward bidentate ligand (DPPB), CO, base ( $Cs_2CO_3$ ) and heat.In addition to the two osmium vinyl complexes 2 and 3, we obtained two osmafuran complexes 4 and 5, representing a new approach toward rare phosphonium-containing osmafurans [2i, 7a, 7b, 7f, 7k].

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