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Selective Synthesis of Osmanaphthalene and Osmanaphthalyne by Intramolecular C–H Activation**

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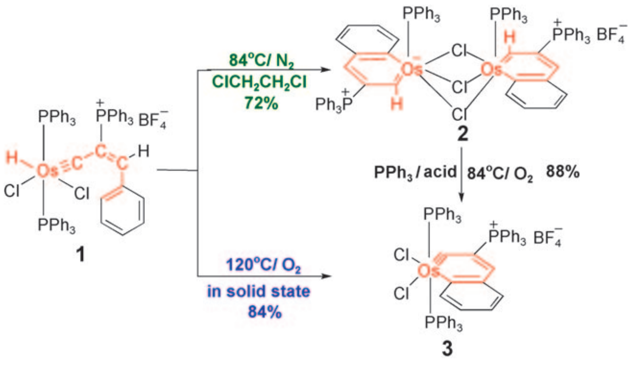
Metallabenzenes[1] and metallabenzynes[2] have attracted considerable research interest in recent years. However, their higher homologues are still very rare.[3] In fact, only two well-characterized examples have been reported. One is the metallanaphthalene prepared by Paneque et al. in 2003 by oxidation of a bicyclic iridium complex.[3a] The other is the metallanaphthalyne synthesized by Jia, Lin, and co-workers in 2007 by reduction of an osmium carbyne complex with zinc and subsequent C–Cl bond activation.[3b]

It is known that C–H activation[1a,4] is a very important method for the synthesis of organic and organometallic compounds. Recently, we reported the synthesis of osmium hydride–alkenylcarbyne complex $[OsH\{\equiv C{-}C(PPh_3){=}CHPh\}(PPh_3)_2Cl_2]BF_4$ (**1**) and its formal [4+2] cycloaddition with acetonitrile to give the first late-transition-metal-containing metallapyridine and metallapyridinium compounds.[5] From our further investigation of the reactivity of **1**, we herein report the selective formation of metallanaphthalene **2** and metallanaphthalyne **3** from **1** in high yields by intramolecular C–H activation of the phenyl ring under a N_2 or O_2 atmosphere, respectively (Scheme 1). Furthermore, the transformation of isolated **2** into **3** is also reported. As there is a metallabenzene unit in **2** and a metallabenzyne unit in **3**, the transformation of **2** into **3** represents the first example of the conversion from metallabenzene into metallabenzyne.



Scheme 1. Preparation of **2** and **3**.

Heating **1** in DCE ($ClCH_2CH_2Cl$) at reflux under a N_2 atmosphere gave the (μ-Cl)$_3$-bridged bisosmanaphthalene **2**, which was isolated as a green solid in 72% yield (Scheme 1). The structure of **2** was confirmed by X-ray diffraction. The asymmetric unit contains two independent molecules (**2A** and **2B**). A drawing of the cation **2A** is shown in Figure 1. In **2A**, two osmanaphthalene metallacycles are connected by three chlorido bridges. The Os–Cl bond lengths of the chlorido bridges are in the range 2.496(2)–2.554(2) Å, which are similar to those in reported dinuclear osmium complexes with three chlorido bridges.[6] The mean deviation from the least-squares plane through the C11, C12, C13, C14, and C15 chain is 0.035 Å, and the value through the C21, C22, C23, C24, and C25 chain is 0.026 Å. The Os1 atom is out of the plane of the metallacyclic carbon atoms by 0.736 Å (the relevant value of Os2 is 0.697 Å), which is similar to the metal atom displacement in the iridanaphthalene compound reported by Paneque et al. (0.76 Å).[3a] The dihedral angle between the plane through C11, C12, C13, C14, and C15 and the plane constructed by C11, Os1, and C15 is 31.7° (the relevant dihedral angle in the Os2-containing six-membered metallacycle is 30.4°). These values are comparable with those found in our previously reported bisruthenabenzene

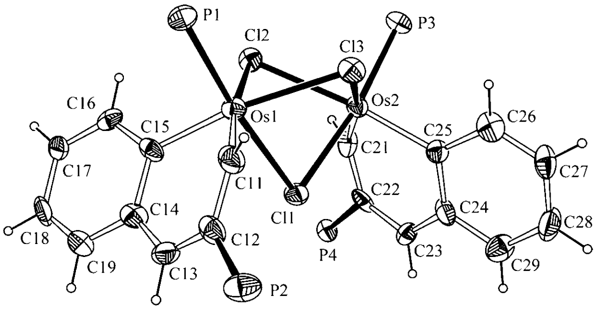


Figure 1. X-ray crystal structure of **2A** (ellipsoids at the 50% probability level).[12] Counteranion and phenyl rings in PPh_3 groups are omitted for clarity. Selected bond lengths [Å]: Os1–C11 1.923(8), Os1–C15 2.039(8), Os1–P1 2.268(2), Os1–Cl1 2.496(2), Os1–Cl2 2.520(2), Os1–Cl3 2.546(2), Os2–C21 1.914(9), Os2–C25 2.000(8), Os2–P3 2.260(2), Os2–Cl1 2.497(2), Os2–Cl2 2.554(2), Os2–Cl3 2.516(2), P2–C12 1.786(9), P4–C22 1.779(9), C11–C12 1.395(13), C12–C13 1.375(12), C13–C14 1.421(13), C14–C15 1.420(12), C21–C22 1.396(12), C22–C23 1.388(12), C23–C24 1.432(12), C24–C25 1.426(12).

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$[\{\overline{\text{Ru(CHCRCHCRCH)}}\text{R}\}_2(\mu\text{-Cl})_3](\text{BF}_4)_3$ ($R = PPh_3$) (26.4 and 30.1°).[7] The Os1–C11 (1.923(8) Å), Os1–C15 (2.039(8) Å), Os2–C21 (1.914(9) Å), and Os2–C25 (2.000(8) Å) bond lengths are similar to those observed in the reported osmabenzenes.[1h,o] All the C–C bond lengths of the fused benzene rings are comparable to those found in iridanaphthalene[3a] and naphthalene.[8] Furthermore, there is no significant C–C bond length alternation, thus indicating a delocalized structure.

The solid-state structure of **2** is fully supported by solution NMR spectroscopy. The ^{1}H NMR spectrum shows the signals of Os*CH* at $\delta = 21.42$ ppm (dd, $J_{P,H} = 12.0$ and 6.9 Hz) and OsCHC(PPh$_3$)*CH* at $\delta = 7.75$ ppm (d, $J_{P,H} = 18.2$ Hz). The ^{31}P{^{1}H} NMR spectrum shows two signals at $\delta = 21.06$ (d, $J_{P,P} = 3.5$ Hz) and -2.20 ppm (d, $J_{P,P} = 3.5$ Hz) assignable to C*P*Ph$_3$ and Os*P*Ph$_3$, respectively. The ^{13}C{^{1}H} NMR spectrum displays signals for C11 (C21) at $\delta = 239.2$ ppm (d, $J_{P,C} = 10.9$ Hz) and C15 (C25) at 189.0 ppm (d, $J_{P,C} = 7.1$ Hz).

When the transformation of **1** to **2** was carried out in the presence of a slight amount of air, another product could be detected from the NMR spectra. When **1** was heated in DCE at reflux under an O_2 atmosphere, this product could be isolated in high yield and identified as osmanaphthalyne **3**. After optimizing the reaction conditions, **3** could even be obtained in 84 % yield by heating the solid sample of **1** in air at 120 °C for 5 h (Scheme 1). This solid-state synthesis is easy to handle and environmentally benign.

The structure of **3** was confirmed by X-ray diffraction. As shown in Figure 2, **3** has an essentially planar metallacycle. The sum of angles in the ring constructed by Os1, C1, C2, C3, C4, and C5 is 719.9°, which is almost identical to the ideal value of 720°. The mean deviation from the least-squares plane through the six atoms of the Os-containing six-membered ring is 0.0117 Å, and the value through the 10 atoms of the two fused rings is 0.0421 Å. It is worth noting that the Os1–C1 (1.754(7) Å) and Os1–C5 bond lengths (2.110(6) Å) are within the range of those observed for typical Os≡C bonds (1.69–1.84 Å)[2a,9] and Os–C(aryl) bonds (2.02–2.18 Å),[10] respectively. They are also comparable to those observed for the osmanaphthalyne reported by Jia and co-workers (1.732(4) Å and 2.127(3) Å, respectively).[3b] The C–C bond lengths of the metallacycle are between those of single and double C–C bonds, without significant bond length alternation. These data suggest a delocalized structure. The Os1-C1-C2 bond angle is 151.1(5)°, which is similar to those found in Jia's osmanaphthalyne (155.0(3)°)[3b] and osmabenzynes (148.3(6)–154.9(9)°).[2a,b]

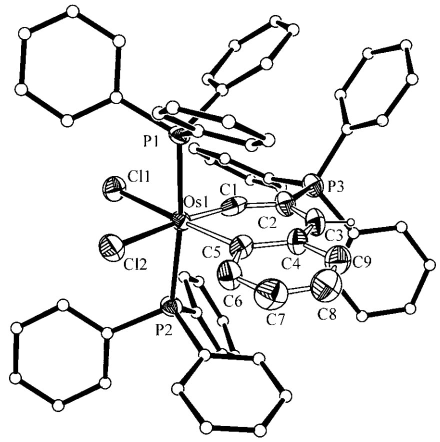
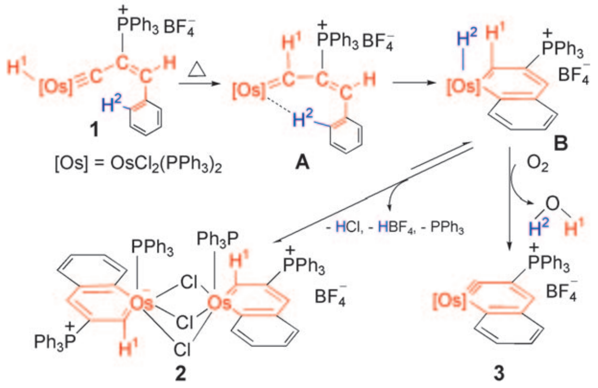


Figure 2. X-ray crystal structure of **3** (ellipsoids at the 50% probability level).[12] Anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Os1–P1 2.418(1), Os1–P2 2.419(2), Os1–Cl1 2.459(2), Os1–Cl2 2.442(2), Os1–C1 1.754(7), Os1–C5 2.110(6), C1–C2 1.385(9), C2–C3 1.369(9), C3–C4 1.395(9), C4–C5 1.450(8), C5–C6 1.420(8), C6–C7 1.373(9), C7–C8 1.362(10), C8–C9 1.370(10), C9–C4 1.416(9).

The NMR spectroscopic data of **3** are consistent with its solid-state structure. The ^{1}H NMR spectrum shows a signal at $\delta = 8.19$ ppm assignable to Os≡CC(PPh$_3$)*CH*. The ^{31}P{^{1}H} NMR spectrum shows two signals at $\delta = 14.33$ and -9.11 ppm assignable to C*P*Ph$_3$ and Os*P*Ph$_3$, respectively. The ^{13}C{^{1}H} NMR spectrum displays signals for C1 and C5 at $\delta = 264.9$ and 174.2 ppm, respectively.

A plausible mechanism for the formation of **2** and **3** is shown in Scheme 2. The migration of the hydride ligand (H^1) from osmium to the carbyne carbon atom should afford an osmium carbene[5,9a,11] intermediate (**A**) with an agostic form. The *ortho* C–H^2 bond of the phenyl ring of **A** is further activated to give intermediate **B** containing a hydride ligand (H^2). Under a N_2 atmosphere, dimerization of **B** through the loss of PPh$_3$, HCl, and HBF$_4$ should give **2**, whereas in the presence of O_2, **B** is oxidized to osmanaphthalyne **3** and H_2O.



Scheme 2. Proposed mechanism for the formation of **2** and **3**.

Consistent with the proposed mechanism, when some weak bases such as NaHCO$_3$ or PhNH$_2$ were purposely added to the reaction system, the in situ NMR experiment showed that the formation of **2** was indeed facilitated, even in air. The reaction was also monitored by ^{31}P and ^{1}H NMR spectroscopy when **1** was heated at reflux in DCE under an O_2 atmosphere. Both **2** and **3** could be observed in the NMR spectra at the initial stage (Figure S1 in the Supporting Information). Then, the signal of **3** increased gradually, accompanied by the decrease of the signal of **2**. Eventually, **3** was obtained as the main product and isolated in 76 % yield. This phenomenon indicates that **2** could transform into **3** under suitable conditions. To further confirm the mechanism, the isolated compound **2** was heated at reflux in DCE under an O_2

atmosphere in the presence of HCl (1 equiv), HBF_4 (1 equiv), and excess PPh_3 (to balance the equation for the conversion of **2** into **3**). As indicated by in situ ^{31}P NMR spectroscopy (Figure S2 in the Supporting Information), the amount of **3** increased gradually while that of **2** decreased. Although some unidentified species were observed at the early stages, 35 min later, **3** became the main product along with excess PPh_3. In sharp contrast, when the reaction was performed under a N_2 atmosphere, no appreciable reaction could be observed. These results strongly support the indispensable role of O_2 in the formation of **3**.

DFT calculations were performed to elucidate the proposed mechanism shown in Scheme 2. Figure 3 shows the relative energy profiles for the transformation of **1′** into **2′** and **3′** (**1′**, **2′**, and **3′** are the model cations of **1**, **2**, and **3**, respectively). From the 18-electron reactant **1′** (hydride–alkenylcarbyne), the reaction proceeds to an agostic intermediate **A′** (alkenylcarbene) via the first transition state (**TS$_1$**) with a barrier of 31.5 kcal mol^{-1}. Although this barrier is relatively high, it is feasible when more stable compounds such as **2** and **3** are formed. Furthermore, the transformation of an osmium hydride carbyne complex into an osmium carbene has already been reported.[5,9a,11] Followed by the *ortho* C–H activation of the phenyl ring via the second transition state (**TS$_2$**) with a barrier of 17.6 kcal mol^{-1}, **A′** can be converted into **B′**, which contains a hydride ligand. Under a N_2 atmosphere, intermediate **B′** can evolve either to **2′** through subsequent H^2–Cl bond coupling and HCl removal as well as dimerization or to **3′** through H^1–H^2 bond coupling. We note that the formation of **2′** is more favorable energetically (by 24.3 kcal mol^{-1}) than the generation of **3′** through the abstraction of dihydrogen. However, under an O_2 atmosphere, the involvement of O_2 in the removal of two H atoms (H^1 and H^2 in Figure 3) can facilitate the formation of **3′** with an overall exothermicity of 40.3 kcal mol^{-1}. Presumably, under an O_2 atmosphere, the transformation of **2′** into **3′** is driven thermodynamically through the reaction of the intermediate **B′** with O_2. Such results are consistent with our present experiments.

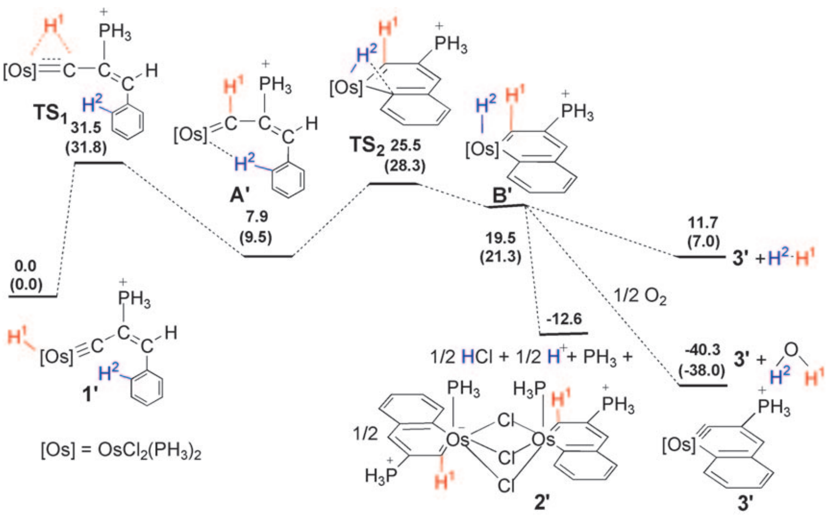
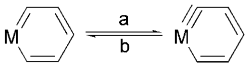


Figure 3. Relative energy and free energy (in parentheses) profiles (in kcal mol^{-1}) for the formation of the **2′** and **3′**.

Both **2** and **3** have excellent thermal stabilities. Solid samples of **2** and **3** remain nearly unchanged at 120 °C in air for 5 h. Their remarkable thermal stabilities are related to the bulky PPh_3 substituent or ligands[1f] and their aromaticity.

The transformation of **2** into **3** represents the first example of the conversion of metallabenzene to metallabenzyne (path a, Scheme 3). As the transformation of metallabenzyne into metallabenzene was reported by Jia's group in 2006 (path b, Scheme 3),[2c] the interconversion between these two kinds of interesting metallaarenes, namely, metallabenzenes and metallabenzynes, would now be feasible.



Scheme 3. Interconversion of metallabenzene and matallabenzyne.

In summary, we have selectively synthesized bismetallanaphthalene **2** and metallanaphthalyne **3** from **1** in high yields by intramolecular C–H activation by controlling the atmosphere (either N_2 or O_2). Compound **3** can also be obtained by solid-state synthesis. The formation of metallanaphthalyne **3** from metallanaphthalene **2** provides a valuable method for the transformation of metallabenzene into metallabenzyne. Investigations into the preparation of other fused ring metallabenzenoids employing this convenient method are ongoing.

Experimental Section

2: A green solution of **1** (500 mg, 0.400 mmol) in 1,2-dichloroethane (10 mL) was heated at reflux for 8 h under N_2. The solvent was removed in vacuo. Addition of diethyl ether to the resulting residue led to a brown-green solid, which was washed with a mixture of methanol and diethyl ether (1:10) and dried in vacuo. Yield: 267 mg, 72 %; ^{1}H NMR plus HMQC (300.1 MHz, $CDCl_3$): $\delta = 21.42$ (dd, J(PH) = 12.0 Hz, J(PH) = 6.9 Hz, 2 H, OsC*H*), 7.75 (d, J(PH) = 18.2 Hz, 2 H, OsCHC(PPh_3)C*H*), 7.85–6.89 ppm (m, 68 H, other aromatic atoms); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 21.06$ (d, J(PP) = 3.5 Hz, C*P*Ph_3), −2.20 ppm (d, J(PP) = 3.5 Hz, Os*P*Ph_3); ^{13}C{^{1}H} NMR plus DEPT-135 and HMQC (75.5 MHz, $CDCl_3$): $\delta =$ 239.2 (d, J(PC) = 10.9 Hz, Os=CH), 189.0 (d, J(PC) = 7.1 Hz, Os-C), 153.1 (d, J(PC) = 17.6 Hz, Os=CHC(PPh_3)=*C*H), 143.3 (d, J(PC) = 13.7 Hz, Os=CHC(PPh_3)=CH*C*), 120.1 (d, J(PC) = 86.7 Hz, Os=CH*C*(PPh_3)), 147.1–121.7 ppm (m, other aromatic carbon atoms). Anal. calcd (%) for $C_{90}H_{72}Cl_3P_4BF_4Os_2$: C 58.40, H 3.92; found: C 58.44, H 4.08.

3: Method 1: Complex **1** (106 mg, 0.085 mmol) was heated in the solid state at 120 °C in air for 5 h, then washed with a mixture of methanol and diethyl ether (1:10) and dried in vacuo. Yield: 89 mg, 84 %. Method 2: A green solution of **1** (200 mg, 0.16 mmol) in 1,2-

dichloroethane (10 mL) was heated at reflux for 15 h under an O_2 atmosphere. The solvent was removed in vacuo. Addition of diethyl ether to the resulting residue led to a green solid, which was washed with a mixture of dichloromethane and diethyl ether (1:10) and dried in vacuo. Yield: 152 mg, 76%. Method 3: A green solution of **2** (200 mg, 0.11 mmol) in 1,2-dichloroethane (10 mL) was treated with HCl (37% in H_2O, 9.0 μL, 0.11 mmol), HBF_4 (52% in diethyl ether, 18.6 μL, 0.11 mmol), and excess PPh_3, then the mixture was heated at reflux for 2 h under an O_2 atmosphere. The solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a green solid, which was washed with a mixture of dichloromethane and diethyl ether (1:10) and dried in vacuo. Yield: 237 mg, 88%; ^1H NMR plus HMQC and $^1H\{^{31}P\}$ (300.1 MHz, $CDCl_3$): $\delta = 8.19$ (d, $J(PH) = 13.5$ Hz, 1H, $OsCC(PPh_3)CH$), 7.68–5.90 ppm (m, 49H, other aromatic protons); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 14.33$ (s, $CPPh_3$), −9.11 ppm (s, $OsPPh_3$); $^{13}C\{^1H\}$ NMR plus DEPT-135 (100.6 MHz, CD_2Cl_2): $\delta = 264.9$ (br, $Os\equiv C$), 177.9 (d, $J(PC) = 8.1$ Hz, $Os\equiv CC(PPh_3)CH$), 174.2 (br, Os-C), 104.9 (d, $J(PC) = 107.2$ Hz, $Os\equiv CC(PPh_3)$), 142.0–116.3 ppm (m, other aromatic carbon atoms). Anal. calcd (%) for $C_{63}H_{50}Cl_2P_3BF_4Os$: C 60.63, H 4.04; found: C 60.18, H 4.26.

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Keywords: C—H activation · metallacycles · osmium · synthesis design

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[12] CCDC-707878 (**2A**) and CCDC-707877 (**3**) 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.