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

Bin Liu, Hujun Xie, Huijuan Wang, Liqiong Wu, Qianyi Zhao, Jinxiang Chen, Ting Bin Wen, Zexing Cao,* and Haiping Xia*

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/{C17/C0C(PPh3)=CHPh}(PPh3)2Cl2]BF4 (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 mettlanaphthalene 2 and metallanaphthalyne 3 from 1 in high yields by intramolecular C–H activation of the phenyl ring under a N2 or O2 atmosphere, respectively (Scheme 1). Furthermore, the transformation of isolated 2 into 3 is also reported. As there is a metallabenzen unit in 2 and a metallabenzyne unit in 3, the transformation of 2 into 3 represents the first example of the conversion from metallabenzen into metallabenzyne.

Heating 1 in DCE (CICH2CH2Cl) at reflux under a N2 or O2 atmosphere gave the (μ-Cl)2-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 chloride bridges. The Os–Cl bond lengths of the chloride bridges are in the range 2.496(2)–2.554(2) Å, which are similar to those in reported dinuclear osmium complexes with three chloride bridges.[6] The mean deviation from the least-squares plane through the Os1–C1–C12 is 0.736(8) 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 chain is 0.035 Å, and the value through the C11, C12, C13, and C15 chain is 0.026 Å. The Os1 atom is out of the plane of the metallacyclic carbon atoms by 0.736 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

** This work was financially supported by the National Science Foundation of China (No. 20872123 and No. 20873105).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200902238.
The solid-state structure of 2 is fully supported by solution NMR spectroscopy. The $^1$H NMR spectrum shows the signals of OsCH at $\delta = 21.42$ ppm (dd, $J_{HH} = 12.0$ and 6.9 Hz) and OsCHC(PPh$_3$)CH at $\delta = 7.75$ ppm (d, $J_{HH} = 18.2$ Hz). The $^{31}$P($^1$H) NMR spectrum shows two signals at $\delta = 21.06$ (d, $J_{PP} = 3.5$ Hz) and $-2.20$ ppm (d, $J_{PP} = 3.5$ Hz) assignable to CPP$_3$ and OsPP$_3$, respectively. The $^{13}$C($^1$H) NMR spectrum displays signals for C1 and C5 at $9.11$ ppm and $264.9$ and $174.2$ ppm, respectively. The $^{13}$C($^1$H) NMR spectrum shows two signals at $\delta = 14.33$ and $-9.11$ ppm assignable to CPP$_3$ and OsPP$_3$, 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 ($^1$H) from osmium to the carbonyl carbon atom should afford an osmium carbene[5,9a,11] intermediate (A) with an agostic form. The ortho C–H bond of the phenyl ring of A is further activated to give intermediate B containing a hydride ligand ($^1$H). 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 Os$_2$, B is oxidized to osmanaphthalyne 3 and H$_2$O.

Consistent with the proposed mechanism, when some weak bases such as NaHCO$_3$ or PhNH$_2$ were purposely added to the reaction system, the initial 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$_2$
respectively). From the 18-electron reactant (path a, Scheme 3). As the transformation of metallabenzyne into metallabenzenes was reported by Jia’s group in 2006 (path b, Scheme 3).\[24\] the interconversion between these two kinds of interesting metallarenes, namely, metallabenzenes and metallabenzenoids, would now be feasible.

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 N2 or O2). Compound 3 can also be obtained by solid-state synthesis. The formation of metallanaphthalyne 3 from metellanaphthalene 2 provides a valuable method for the transformation of metallabenzenoids employing this convenient method are ongoing. alkenylcarbene), the reaction proceeds to an agostic intermediate A‘ (alkenylcarbene) via the first transition state (TS1) 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 carbene complex into an osmium carbene has already been reported\[3,9a,11\]. Followed by the ortho C–H activation of the phenyl ring via the second transition state (TS2) with a barrier of 17.6 kcal mol\(^{-1}\), A‘ can be converted into B’, which contains a hydride ligand. Under a N2 atmosphere, intermediate B’ can evolve to 2’ through subsequent H2–Cl bond coupling and HCl removal as well as dimerization or to 3’ through H–H’ 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 O2 atmosphere, the involvement of O2 in the removal of two H atoms (H’ and H” in Figure 3) can facilitate the formation of 3’ with an overall exothermicity of 40.3 kcal mol\(^{-1}\). Presumably, under an O2 atmosphere, the transformation of 2’ into 3’ is driven thermodynamically through the reaction of the intermediate B’ with O2. Such results are consistent with our present experiments.

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 PPh3 substituent or ligands\[10\] and their aromaticity.

The transformation of 2 into 3 represents the first example of the conversion of metallabenzyne to metallabenzenoid (Figure 3). As indicated by in situ \(^{31}\)P NMR spectroscopy, and excess PPh3 (to balance the equation for the conversion of 1 into 3, \(2009\), 5461–5464 /C23 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**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 N2. 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%;\(\text{\(^{1}\)H NMR plus HMQC (300.1 MHz, CDCl}_3\)}; \(\delta = 21.42\) (dd, \(J_{(PH)} = 12.0\) Hz, \(J_{(PH)} = 6.9\) Hz, 2H, OsCH), 7.75 (d, \(J_{(PH)} = 18.2\) Hz, 2H, OsCH(PPh3)CH), 7.85–6.89 ppm (m, 68H, other aromatic atoms); \(\text{\(^{31}\)P[H] NMR (121.5 MHz, CDCl}_3\)}; \(\delta = 21.06\) (d, \(J_{(PP)} = 3.5\) Hz, C(PPh3)), \(-2.20\) ppm (d, \(J_{(PP)} = 3.5\) Hz, Os(PPh3)); \(\text{\(^{13}\)C[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=CH(PPh3)=CH), 143.3 (d, \(J_{(PC)} = 13.7\) Hz, Os=CH(PPh3)=CH), 120.1 (d, \(J_{(PC)} = 86.7\) Hz, Os=CH(PPh3)), 147.1–121.7 ppm (m, other aromatic carbon atoms). Anal. calc (\%) for C\(_{66}\)H\(_{42}\)Cl\(_3\)P\(_3\)BF\(_4\)Os: 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 O₂ 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: 237 mg, 88%; 1H NMR (CDCl₃): δ = 18.6 m, 1H, C; 4.04; found: C 60.18, H 4.26.

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


[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.