Metallacycles

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Annulation of Metallabenzenes: From Osmabenzene to Osmabenzothiazole to Osmabenzoxazole**

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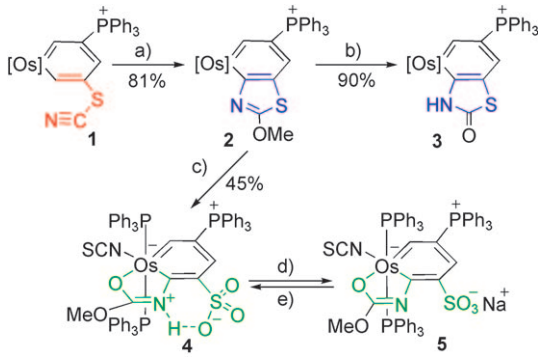
Research into transition-metal-containing metallaaromatics is attracting considerable current attention.[1] Since the first example of metallabenzenes were reported by Roper et al. in 1982,[2] a wide variety of monocyclic metallaaromatics have been successfully isolated and characterized.[3–5] However, the chemistry of fused metallaaromatics is less developed.[6–8] Most of the reported fused metallaaromatics were constructed by the cyclometalation of an unsaturated precursor.[6,7] Only one exceptional example, based on the metal insertion reaction of benzothiophene, has been reported.[8] In principle, it may be another efficient approach to construct fused metallaaromatics from monocyclic metallaaromatics; however, such a possibility has not been realized to date. Herein, we report a novel annulation reaction leading to the first metallabenzothiazole **2** based on the intramolecular nucleophilic aromatic substitution (S_NAr) reaction of metallabenzene **1**. Furthermore, transformation of **2** to the first metallabenzoxazoles **4** and **5** is also presented (Scheme 1).



Scheme 1. Preparation of compounds **2**–**5**. $[Os]=[Os(PPh_3)_2(NCS)_2]^-$. Conditions: a) MeONa/MeOH, CH_2Cl_2, RT; b) $CHCl_3/H_2O$, reflux; c) $AgNO_3/H_2O$, THF, RT; d) $NaOH/CH_2Cl_2$, RT; e) H_2O/CD_2Cl_2, RT.

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It is now well-established that arenes, and especially heteroarenes, could undergo S_NAr reaction if electron-withdrawing substituents are positioned *ortho* or *para* to the leaving group (typically a halogen) on the ring. Recently, we reported the synthesis of osmabenzene **1**[3b] bearing a phosphonium substituent and a reactive thiocyano group on the metallacycle. In this system, the metal center and the electron-withdrawing phosphonium group may exert significant influence on the electron density of the aromatic ring. In this regard, complex **1** might be expected to undergo intramolecular S_NAr reactions to construct new metallaaromatic compounds.

With this idea in mind, we studied the reaction of osmabenzene **1** with MeONa/MeOH, from which osmabenzothiazole **2** was isolated as a green solid (Scheme 1). This new product is air-stable and can be kept for several days without appreciable decomposition either in the solid state or in solution at room temperature.

The structure of **2** has been confirmed by X-ray diffraction. As shown in Figure 1, it contains a perfectly planar metallabenzothiazole unit. The maximum deviation from the least-squares plane of the whole metallabenzothiazole system is 0.0096 Å. As expected, the lengths of the Os1–C1 (1.954(7) Å) and Os1–C5 (1.953(8) Å) and the C–C bonds within the osmabenzene ring are within the range of those observed for other osmabenzenes.[2,3b–d,9] The C–N and C–S bond lengths of the thiazole moiety are similar to those

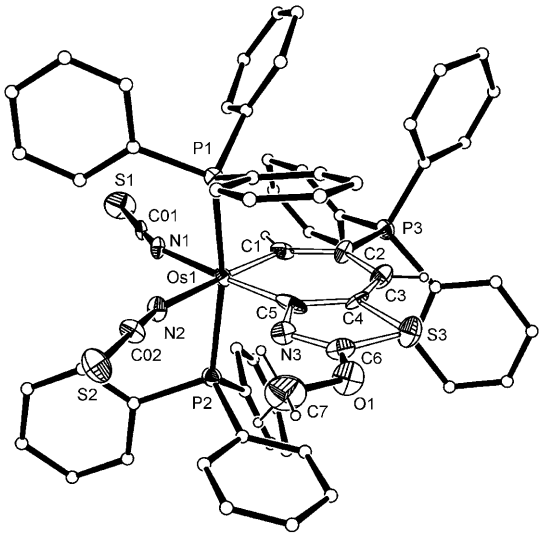
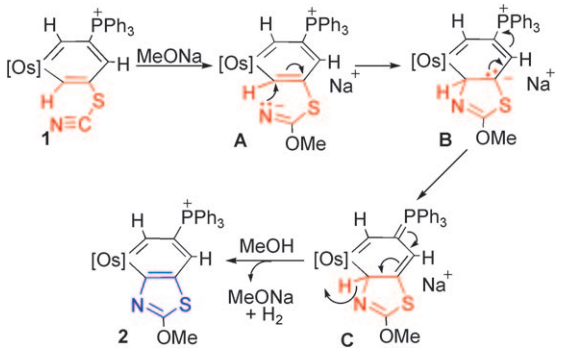


Figure 1. X-ray structure of **2**. Ellipsoids set at 50% probability; phenyl group hydrogen atoms omitted for clarity.

reported for organic benzothiazole.[10] Consistent with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum has signals for the osmabenzene ring at 236.5 (Os*C*H), 233.6 (Os*C*), 140.9 (OsCHC(PPh_3)*C*H), 132.3 (OsC*C*), and 105.8 ppm (OsCH*C*-(PPh_3)), and the signals of the thiazole moiety at 188.6 (*C*OCH_3) and 60.1 ppm (O*C*H_3). In the $^{31}P\{^1H\}$ NMR spectrum, the signal of C*P*Ph_3 appears at 19.5 ppm and the two equivalent Os*P*Ph_3 appears at −6.3 ppm. The ^1H NMR spectrum shows the characteristic signals at 17.5 (OsC*H*), 7.9 (OsCHC(PPh_3)C*H*), and 3.5 ppm (OCH_3), respectively.

A plausible mechanism for the formation of **2** is proposed in Scheme 2. Xi et al. recently reported that N-containing



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

heterocycles could be constructed by the cycloaddition of 1-lithio-1,3-dienes with nitriles.[11] Similar to that cyclization mechanism, the addition reaction of **1** with MeONa may initially give intermediate **A**, which could undergo intramolecular nucleophilic attack to afford intermediate **B**. This intermediate **B** can be viewed as a form of Jackson–Meisenheimer complex, and a similar compound has been reported by Paneque et al.,[7d] which is formed from the metallanaphthalene undergoing ring attack by the nucleophile OH^-. Owing to the phosphonium substituent of the metallacycle, **B** could be resonance-stabilized, resulting in relatively stable intermediate **C**. Subsequent loss of the hydride ion, which combines with MeOH in solution, gives the aromatic osmabenzothiazole **2** and H_2. The production of H_2 was confirmed by the GC chromatograms of the gaseous products of this reaction (see Figure S3 in the Supporting Information). This speculative mechanism involves an addition–elimination pathway, which is similar to the classical S_NAr reaction of arenes.

In contrast to arenes, which are well-known for their stability and could hardly undergo S_NAr reaction under ordinary conditions, osmabenzene **1** undergoes an intramolecular S_NAr reaction at ambient temperature and pressure to form a new fused metallaaromatic compound, namely osmabenzothiazole **2**. This reaction shows that nucleophilic reactivity of the metallacycle can be promoted when the electron density of the aromatic ring is significantly decreased in the presence of the transition metal center and the electron-withdrawing phosphonium group. Furthermore, this unprecedented intramolecular S_NAr reaction makes the annulation reaction of metallabenzenes possible, giving a potentially useful approach to synthesize fused metallaaromatics.

When a solution of **2** in moisture-bearing chloroform was heated at reflux for about 24 h, osmabenzothiazolone **3** was isolated in high yield (Scheme 1). The formation of **3** can be accounted for by the hydrolysis of the methoxy group on the thiazole ring; such reactivity is well-known in organic chemistry.

The structure of **3** has also been confirmed by X-ray diffraction (see Figure S1 in the Supporting Information). The fundamental structure of **3** is similar to **2**, but remarkably the C6–O1 bond (1.207(9) Å) is shorter than that of **2** (C6–O1 1.302(8) Å, Figure 1), which is indicative of a carbon–oxygen double bond. The solution NMR spectroscopic data are consistent with the solid-state structure. In particular, the ^1H NMR spectrum has a characteristic signal of OsC*H* at 16.2 ppm and N*H* at 8.0 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the five carbon signals of the metallacycle were found at 231.4, 211.1, 138.8, 121.6, and 104.7 ppm, and the signal of the *C*O carbon atom at 176.2 ppm.

When osmabenzothiazole **2** was treated with silver nitrate in THF/H_2O solution, to our surprise, another air-stable fused metallaaromatic compound was isolated and identified as osmabenzoxazole sulfonic acid **4** (Scheme 1). As confirmed by single-crystal X-ray diffraction analysis (Figure 2), the hydrogen atom of the sulfonic acid group interacts with N2 to

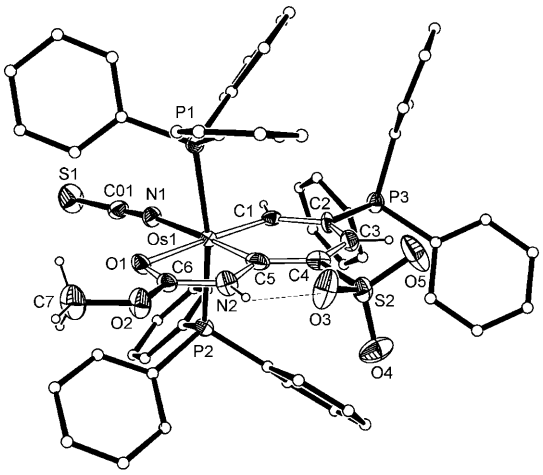


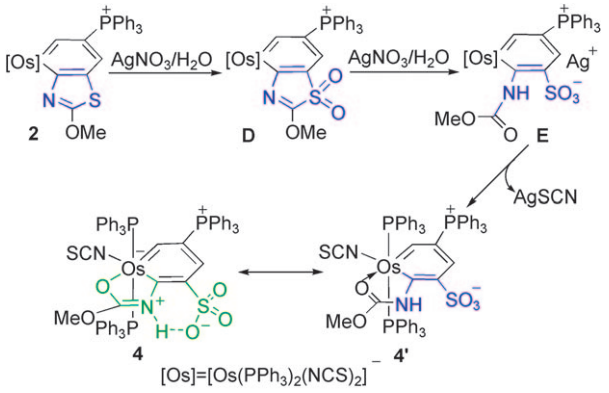
Figure 2. X-ray structure of **4.** Ellipsoids set at 50% probability; phenyl group hydrogen atoms omitted for clarity.

give a zwitterionic structure with an intramolecular hydrogen bond (N2–H···O3, 0.86 Å, 2.638(9) Å, 138.6°) which is similar to that observed in a reported sulfonic acid oxazoline.[12] The osmabenzoxazole system is essentially planar, which is reflected by the small root-mean-square deviation (0.0203 Å) from the least-squares plane through the nine atoms Os1-C1-C2-C3-C4-C5-N2-C6-O1. Again, all the bond distances within the osmabenzene ring fall between the typical lengths of single and double bonds. The Os1–O1 (2.279(5) Å) and O1–C6 bond lengths (1.235(9) Å) are comparable with the related distances found in reported

osmabenzofurans systems.[6c] The C6–O1, C5–N2 and C6–N2 bonds are also consistent with the values observed for organic benzoxazole.[13] The NMR spectroscopic data of **4** are consistent with the solid-state structure. In particular, the ^{1}H NMR spectrum shows the two characteristic signals at 16.1 (Os*CH*) and 8.2 ppm (OsCHC(PPh$_3$)*CH*), respectively. The signal at 11.9 ppm is attributed to the hydrogen atom of N2–H···O3, which can be deuterated in the presence of D_2O. In the ^{31}P{^{1}H} NMR spectrum, the signal for C*P*Ph$_3$ appears at 20.5 ppm and for the two equivalent Os*P*Ph$_3$ at 15.8 ppm. On basis of both structural data and spectroscopic data, it is reasonable to depict **4** as an osmabenzoxazole with a zwitterionic structure.

As expected, in the presence of NaOH, **4** undergoes an acid–base reaction to give the metallabenzoxazole sulfonate **5**. In situ NMR spectroscopy showed that addition of water to **5** could quantitatively regenerate **4** (Scheme 1). The structure of **5** was determined by an X-ray diffraction study (see Figure S2 in the Supporting Information). The bond distances and angles in the metallabenzoxazole unit of **5** are almost identical to those of **4**. All these results further confirm the metallabenzoxazole structure of **4**.

Mechanistically, complex **4** may be formed by initial oxidation of osmabenzothiazole **2** at the sulfur atom to give *S*,*S*-dioxide intermediate **D** (Scheme 3). Further oxidation of **D** results in the ring-opening of the thiazole moiety and thus



Scheme 3. Proposed mechanism for the formation of **4**.

E may be formed as a monocyclic intermediate. The removal of AgSCN and the coordination of the ester carbonyl oxygen atom to the osmium center may result in the osmabenzoxazole having two resonance structures **4** and **4'**.

Conversion of metallabenzothiazole **2** into metallabenzoxazole **4** is interesting, especially in view of the ring-opening and the reorganization process of the metallabicycle. Compared with the annulation reaction from **1** to **2** (Scheme 1), this method may be regarded as another annulation of metallabenzenes using metal atom as a bridgehead.

In summary, we have established a convenient route for the preparation of osmabicyclic aromatic compounds starting from osmabenzenes. The first intramolecular S_NAr reaction of metallabenzenes is reported. The isolation of the first metallabenzothiazole **2** and metallabenzoxazoles **4** and **5** is interesting because it demonstrates that metallabenzenes can undergo annulation reaction to form fused metallaaromatics. We are in the process of extending the chemistry to prepare other fused metallaaromatics and studying other S_NAr reactions of metallabenzenes.

Experimental Section

2: A solution of sodium methoxide (107 mg, 1.98 mmol) in CH_3OH (5 mL) was added to a solution of complex **1** (400 mg, 0.33 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for about 15 h to give a dark green suspension. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (3 × 5 mL). The volume of the filtrate was reduced to about 3 mL under vacuum; addition of diethyl ether (30 mL) to the solution then produced a green solid that was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Yield: 332 mg, 81 %. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 17.5 (d, J(P,H) = 22.3 Hz, 1 H, Os*CH*), 7.9 (d, J(P,H) = 11.9 Hz, 1 H, OsCHC(PPh$_3$)*CH*), 6.8–7.7 (m, 45 H, PPh$_3$), 3.5 ppm (s, 3 H, O*CH*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 19.5 (s, C*P*Ph$_3$), −6.3 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 236.5 (br, Os*C*H), 233.6 (br, Os*C*), 188.6 (s, *C*OCH$_3$), 144.8 and 143.0 (s, Os(N*C*S)$_2$), 140.9 (d, J(P,C) = 23.9 Hz, OsCHC(PPh$_3$)*C*H), 135.0–121.0 (m, PPh$_3$), 132.3 (d, J(P,C) = 14.9 Hz, Os*C*C), 105.8 (d, J(P,C) = 78.2 Hz, OsCH*C*(PPh$_3$)), 60.1 ppm (s, O*C*H$_3$). Elemental analysis (%) calcd for $C_{63}H_{50}N_3OP_3S_3Os$: C 60.80, H 4.05, N 3.38; found: C 61.12, H 4.27, N 3.48.

4: A solution of silver nitrate (328 mg, 1.93 mmol) in water (3 mL) was added to a solution of complex **2** (300 mg, 0.24 mmol) in THF (30 mL). The mixture was stirred at room temperature for about 24 h to give a dark green suspension. The filtrate was collected and concentrated to about 3 mL, then diethyl ether (30 mL) was added to the solution to give a green precipitate. After filtration, THF (3 × 5 mL) was added to dissolve the precipitate. The undissolved solid was separated by filtration and the filtrate was concentrated to about 3 mL. Addition of diethyl ether (30 mL) to the filtrate gave a green solid, which washed with diethyl ether (3 × 5 mL) and dried under vacuum. Yield: 136 mg, 45 %. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 16.1 (d, J(P,H) = 19.4 Hz, 1 H, Os*CH*), 11.9 (s, 1 H, N*H*), 8.2 (d, J(P,H) = 13.6 Hz, 1 H, OsCHC(PPh$_3$)*CH*), 6.8–7.7 (m, 45 H, PPh$_3$), 3.1 ppm (s, 3 H, COC*H*$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 20.5 (s, C*P*Ph$_3$), 15.8 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 229.7 (br, Os*C*H), 231.1 (br, Os*C*), 166.7 (s, *C*OCH$_3$), 153.8 (d, J(P,C) = 22.7 Hz, OsCHC(PPh$_3$)*C*H), 142.6 (s, OsN*C*S), 134.6–121.3 (m, Os*C*C and PPh$_3$), 106.1 (d, J(P,C) = 80.2 Hz, OsCH*C*-(PPh$_3$)), 55.1 ppm (s, CO*C*H$_3$). Elemental analysis (%) calcd for $C_{62}H_{51}N_2O_5P_3S_2Os$: C 59.51, H 4.11, N 2.24; found: C 59.29, H 4.32, N 2.67.

For details of the synthesis of **3** and **5**, and an improved preparation of **1**, see the Supporting Information.

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