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Heterocycles

Key Intermediates of Iodine-Mediated Electrophilic Cyclization: Isolation and Characterization in an Osmabenzene System**

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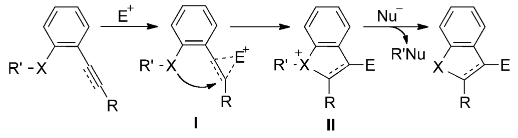
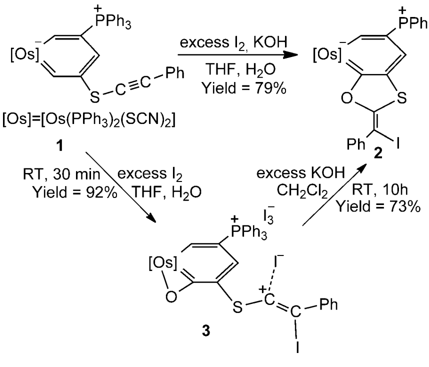
Electrophilic cyclization of alkynes or alkenes mediated by electrophiles such as I_2, ICl, or organochalcogen derivatives, has been increasingly exploited as attractive route to heterocycles during the last few years.[1] It is generally believed that the cyclization reactions proceed through addition of an electrophile to an unsaturated carbon–carbon multiple bond, followed by nucleophilic addition of a heteroatom to the activated multiple bond and subsequent removal of the group bonded to the heteroatom. Iodonium species **I** has often been hypothesized as the key intermediate in iodine-mediated electrophilic cyclization reactions (Scheme 1). However, during the course of iodine-mediated electrophilic cyclization reactions, iodonium intermediates have never been isolated or structurally characterized.



Scheme 1. Typical processes of the electrophilic cyclizations.

Metallaaromatic compounds are currently attracting considerable attention.[2] These compounds are organometallic species derived from replacement of a (hydro)carbon unit in aromatic hydrocarbons with a transition-metal fragment. Extensive studies have shown that while many reactive and short-lived aromatic hydrocarbons, for example benzyne, pyridyne, and isobenzene, are normally difficult to study experimentally, their organometallic counterparts can be stable and easy to prepare and characterize.[3–5] Thus, we speculated that electrophilic cyclization reactions of metallabenzenes (an interesting class of metallaaromatic compounds) having an alkynyl substituent might allow us to capture certain key intermediates. Herein, we report the first iodine-mediated electrophilic cyclizations of a metallabenzene complex bearing a phenylethynylthio substituent, from which we isolated a key intermediate in this cyclization reaction. Instead of the frequently described iodonium form, this intermediate is an intimate ion pair.

We first studied the reactions of the metallabenzene complex **1**,[5] which contains a phenylethynylthio substituent, under the conditions similar to the reported iodine-mediated electrophilic cyclization reactions of alkynes.[6] When the metallabenzene complex **1** was treated with I_2 (5 equiv) in the presence of KOH (3 equiv) and THF as solvent, as indicated by in situ NMR spectroscopy, it was consumed completely within one hour to give a dark-brown solution containing several products. The air-stable green complex **2** can be isolated from the reaction mixture by column chromatography in 15% yield.



Scheme 2. Electrophilic cyclization reactions of metallabenzene **1**.

The structure of the green complex **2** has been confirmed by X-ray diffraction.[7] The unit cell contains two independent molecules **2A** and **2B** (molecule **2A** is shown in Figure 1). Compound **2** contains a fused metallabenzenoid configuration, possessing a C=C bond located outside the five-membered ring. The Os1–C1 and Os1–C5 bond lengths are 1.971(8) and 1.923(9) Å, respectively. The C1–C2, C2–C3, C3–C4, and C4–C5 bond lengths are 1.400(12), 1.404(12), 1.393(12), and 1.446(12) Å, respectively.

The structural parameters associated with the metallacycle are similar to those of related fused metallabenzenes.[8] The solution NMR spectroscopic data is fully consistent with

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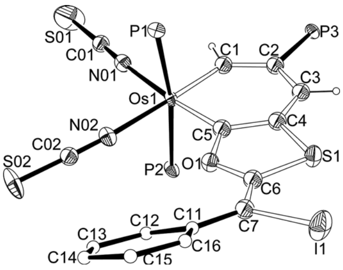


Figure 1. X-ray structure of complex **2A** (ellipsoids set at 50% probability). Phenyl rings in PPh_3 groups and some of the hydrogen atoms are omitted for clarity.

the solid-state structure. For example, the ^1H NMR spectrum of **2** shows the OsC*H* signal at $\delta = 15.7$ ppm and the OsCHC-(PPh_3)C*H* signal at $\delta = 7.3$ ppm. The $^{31}P\{^1H\}$ NMR spectrum shows two signals at 18.5 and −8.0 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the seven carbon signals of the fused metallabenzene ring at $\delta = 228.1$ (C1), 105.4 (C2), 134.3 (C3), 127.5 (C4), 232.2 (C5), 158.9 (C6), and 73.8 (C7) ppm.

On the basis of the characterized structure of **2** and the reaction conditions, we conjectured that **2** should be the product of iodocyclization, and the oxygen atom of the five-membered ring may derive from KOH. However, the reaction failed to afford the expected complex **2** when the proportion of KOH in this reaction was increased. We then assumed that trace water in the reaction is the source of the oxygen atom in **2**. To test this hypothesis, we performed the reaction in THF/water (30:1, v/v), which afforded the best result, with **2** being formed in 79% yield of isolated product (Scheme 2). Furthermore, the reaction of **1** with excess I_2 in absence of KOH only generated the complex **3** (Scheme 2) without any detectable amount of the complex **2**, as indicated by in situ NMR spectroscopy. When a solution of **1** and excess I_2 (5 equiv) in THF/water (30:1, v/v) was stirred at room temperature for 30 min, the complex **3** was formed, which can be isolated as a brownish-red solid in 92% yield (Scheme 2). We also carried out isotopic labeling experiments with ^{18}O labeled water. The results indicate that trace water is the source of the oxygen atom in the complexes **2** and **3**.[9]

The complex **3** is only sparingly soluble in dichloromethane, slightly soluble in acetone and chloroform, and almost insoluble in methanol and THF. Its structure has been confirmed by X-ray diffraction studies.[7] As shown in Figure 2, **3** has a distorted pentagonal bipyramidal geometry around the metal center, which contains an essentially planar metallabenzene unit. The coplanarity is reflected by the mean deviation (0.0134 Å) from the least-squares plane through the six atoms Os1, C1, C2, C3, C4, and C5. There is a very slight but significant alternation in the C−C distances within the osmabenzene ring (C1−C2 1.361(14), C2−C3 1.415(14), C3−C4 1.344(15), C4−C5 1.398(14) Å), although all the distances clearly fall in the aromatic range and are typical of those observed in related metallabenzenes.[2] The Os1−C5 bond (1.971(9) Å) is much shorter than the Os1−C1 bond (2.061(9) Å). Furthermore, an oxygen atom is attached at the C5 position and the C5−O1 unit is bonded to the osmium center in an η^2 bonding mode. The C5−O1 bond (1.229(12) Å) is very close in length to the average C=O bond (1.227 Å) for corresponding non-coordinated carbonyl groups, and the Os1−O1 bond (2.159(6) Å) is considerably longer than the average Os−O single bond (2.047 Å).[10] The structural parameters related to the η^2-C(O) unit are similar to those reported η^2-C(O,S)-containing metallabenzenes, such as $[Os(C(O)C(R^1)C(CH_3)C(R^2)CH)Cl_2(PPh_3)_2]$ ($R^1 = Cl$, $R^2 = Cl$; $R^1 = Cl$, $R^2 = SiMe_3$; $R^1 = H$, $R^2 = NO_2$),[11a] $[Os(C(S)CHCHCHCH)(CO)(PPh_3)]$,[11b] and iridabenzene $[Ir(C(S)CHCHCHCH)(MeCN)(PPh_3)_2][CF_3SO_3]$.[11c]

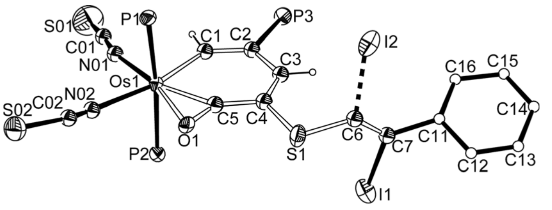
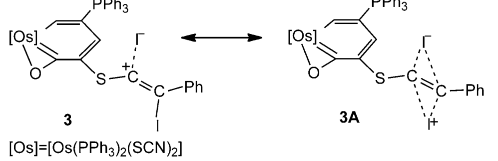


Figure 2. X-ray structure of complex **3** (ellipsoids set at 50% probability). Phenyl rings in PPh_3 groups, some of the hydrogen atoms, and the counteranion are omitted for clarity. Selected bond distances [Å] and angles [°]: Os–C1 2.061(9), Os–C5 1.971(9), Os1–O1 2.159(6), C1–C2 1.361(14), C2–C3 1.415(14), C3–C4 1.344(15), C4–C5 1.398(14), C5–O1 1.229(12), C4–S1 1.768(10), C6–S1 1.713(14), C6–C7 1.17(2), C7–C11 1.55(2), C7–I1 2.098(17), C6–I2 2.362(19); C1-Os1-C5 78.8(4), Os1-C1-C2 133.4(7), C1-C2-C3 124.1(9), C2-C3-C4 123.5(9), C3-C4-C5 117.9(9), C4-C5-Os1 142.3(8), C5-O1-Os1 64.5(5), O1-C5-Os1 81.3(6), C5-Os1-O1 34.2(3), C6-S1-C4 101.5(6), C7-C6-S1 136.9(17).

Another important aspect of the structure of **3** is related to the iodo-substituted phenylethenylthio substituent on the metallacycle. Within this substituent, the C6−C7 bond (1.17(2) Å) is remarkable shorter than normal double bonds. The C7−I1 bond distance (2.098(17) Å) is close to those reported for an iodo-substituted ethenyl (2.078–2.133 Å),[12] whereas the C6−I2 bond distance (2.362(19) Å) is unexpectedly much longer and beyond the range of typical single-bond length, which indicates I2 does not interact as strongly with C6 as I1 does with C7. Equation (1) shows two resonance forms contributing to the overall structure of complex **3**: the intimate ion pair form **3** and the iodonium ion form **3A**. In view of the fact that the C7−I1 bond is significantly shorter than the C6−I2 bond, we consider that the intimate ion pair resonance form **3** is dominant, although **3A** was widely described as the key intermediate in iodine-mediated electrophilic cyclization reactions. DFT calculations further support the notion that the intimate ion pair resonance form **3** makes a greater contribution to the overall structure of the complex **3**. The calculated Wiberg bond indices (bond orders, which are a measure of bond strength)

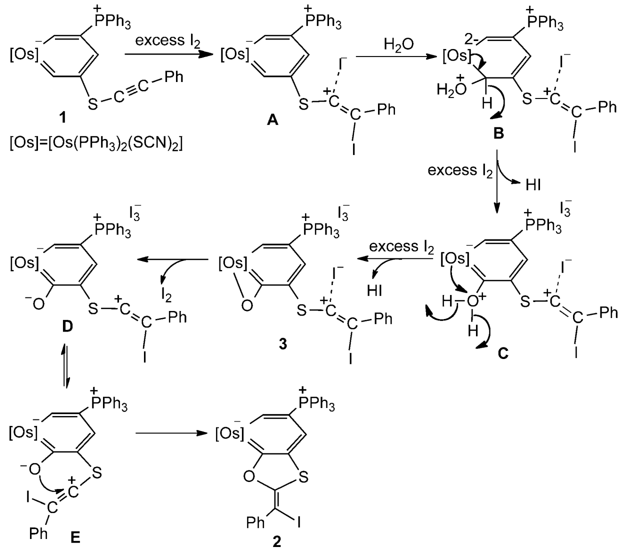


(1)

of C7–I1 and C6–I2 are 0.87 and 0.70, respectively (see the Supporting Information for the bond indices calculated for the remaining bonds in the metallacycle). The triflate salts of bromonium and iodonium ions of the highly sterically hindered olefin adamantylideneadamantane have been structurally characterized.[13] In these structures, the bromonium and iodonium ions are approximately symmetrically bonded to the two olefin carbons. In the iodonium ion, the C–I bond distances were 2.338 and 2.362 Å, which are similar to that of C6–I2 in **3**.

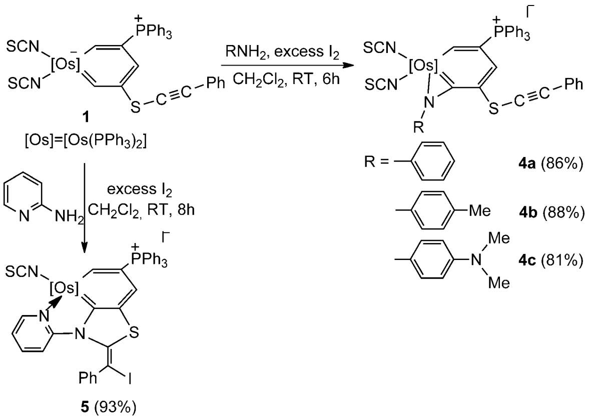
In the intimate ion pair resonance form **3**, the cationic carbon center (C6) is stabilized by the p_π lone pair on the adjacent S atom, as seen by the fact that S1–C6 (1.713(14) Å) is relatively short. S1–C4 (1.768(10) Å) is appreciably longer than S1–C6, suggesting that the conjugation of the thio substituent with the metallabenzene ring has been compromised owing to the interaction between the p_π lone pair and cationic carbon center. We expect that the electron-donating bridging oxygen makes C4 π-electron-rich, lengthens the S1–C4 bond, allows more effective interaction between the p_π lone pair and cationic carbon center, and stabilizes the cationic carbon center. The C6–C7 (1.17(2) Å) bond is unexpectedly short, which is likely due to the charge effect, that is, the positive charge associated with C6 makes the atom smaller in size.

Experimentally, **3** can be converted to the final electrophilic cyclization product **2**, providing strong evidence for **3** as the key intermediate for the reaction. When a mixture of **3** and KOH (10 equiv) in CH_2Cl_2 was stirred at room temperature for about ten hours, the expected complex **2** was isolated in 73% yield (Scheme 2). The conversion of **3** to **2** does not occur in absence of KOH, even when we increased the reaction temperature up to 60°C. However, when treated with tetrabutylammonium iodide for seven hours at room temperature, **3** was completely converted into **2** in the absence of KOH. This result suggests that the role of KOH is to generate free I^- ions from I_3^-. Based on all of our experimental observations, we postulate a reaction mechanism shown in Scheme 3 for the formation of the cyclization product **2** from the metallabenzene complex **1** via the key intermediate **3**. Addition of the electrophile I_2 across the carbon–carbon triple bond of the phenylethynylthio substituent generates the intermediate **A**, which would facilitate nucleophilic addition of H_2O at the C5 position to form the σ^H adduct **B**. The precedent of intermolecular nucleophilic attack at metallabenzene carbon centers in cationic metallabenzenes rather than neutral metallabenzenes have been previously reported.[14] With the aid of excess I_2, a hydride removal restores the aromatic system, giving the intermediate **C**. Subsequent oxidative deprotonation followed by oxygen coordination to the metal center produces the intermediate **3**. Then, in the presence of KOH, the triiodide anion in **3** releases I^-, together with I^- of the intimate ion pair, to reduce the metal center and disassociate the dihapto acyl oxygen to give the intermediate **D** and I_2. **D** can easily undergo conformational isomerization to generate the intermediate **E**. Finally, an intramolecular electrophilic cyclization in **E** yields the five-membered-ring-fused metallabenzene **2**.



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

Additional supporting evidence for the mechanism is from the reaction of **1** with amines under the similar iodocyclization reaction condition. As shown in Scheme 4,



Scheme 4. Other related reactions of **1**.

treatment of **1** with excess I_2 and RNH_2 in CH_2Cl_2 at room temperature for 6 h led to the formation of the osmabenzene complexes **4** (R = Ph (**4a**), *p*-tolyl (**4b**), *p*-(dimethylamino)phenyl (**4c**)), instead of the expected iodocyclization products. The three osmabenzene complexes were characterized by NMR spectroscopy and HRMS, and the structure of **4a** was determined unambiguously by X-ray crystal structure analysis.[7] We assume that the stronger Os–N interaction in these compounds may prevent further iodocyclization reaction of **4**, compared with the Os–O interaction in the acyl analogues **3**. Interestingly, the desired iodocyclization product **5** was obtained when 2-aminopyridine was used as the nucleophile (Scheme 4). The structure of **5** was confirmed by single-crystal X-ray diffraction.[7] In this case, the coordination ability of the pyridyl substituent at N atom may play an important role in the conversion of **1** to **5**. A possible reason for the formation of **5** could be that the pyridine nitrogen atom displaces the iminoacyl nitrogen (of an initially formed complex similar to **4**) from the metal center, thereby allowing it to form the fused ring. This hypothesis does not gain further support because when we treated **4a–c** with excess pyridine or iodide, we did not find their further transformation.

In summary, we have reported the isolation and characterization of key intermediate in the iodine-mediated electrophilic cyclization reactions of metallabenzenes, which is different to the general accepted iodonium form. These reactions are also the first successful examples of employing this valuable method in metallacycle chemistry. This finding also allows us to expand the metallabenzene chemistry and open up new approach to higher π-electron metallaaromatic compounds.

Experimental Section

3: A solution of iodine (343 mg, 1.35 mmol) in THF (30 mL) was added to a suspension of **1** (345 mg, 0.27 mmol) in water (1 mL). The mixture was stirred at room temperature for about 30 min to give a brown solution. The solvent was removed under vacuum and washed with methanol (3 × 5 mL) to give a brownish-red solid. Yield: 477 mg, 92 %. ^{1}H NMR (500.2 MHz, CD_2Cl_2): $\delta = 13.5$ (d, $J(\mathrm{PH}) = 24.1$ Hz, 1H, C^1H), 7.9 (d, $J(\mathrm{PH}) = 10.2$ Hz, 1H, C^3H), 6.6–7.9 ppm (m, 50H, Ph). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta = 22.8$ (s, $CPPh_3$), −8.5 ppm (s, $OsPPh_3$). Unfortunately, the poor solubility of **3** prevented $^{13}C\{^1H\}$ NMR characterization. HRMS (ESI): *m*/*z* calcd for $C_{69}H_{52}N_2S_3P_3I_2OOs$: 1559.0153 $[M-I_3]^+$; found: 1559.0156.

Details of the preparation and characterization of **2**, **4a**, **4b**, **4c**, and **5** can be found in the Supporting Information.

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