Direct amidation of metallaaromatics: access to N-functionalized osmapentalynes via a 1,5-bromoamidated intermediate†

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The direct C–H amidation or imidation of metallaaromatics with N-bromoamides or imides has been achieved under mild conditions and leads to the formation of a family of N-functionalized metallapentalyne derivatives. A unique 1,5-bromoamidated species has been identified, and can be viewed as a $\sigma^1$-adduct intermediate in a nucleophilic aromatic substitution. The 1,5-addition of both electrophilic and nucleophilic moieties into the metallaaromatic framework demonstrates a novel pathway in contrast to the typical radical process of arene C–H amidation involving N-haloamine reagents. iridabenzo[3,4]iridabenzo[6,7]benzo[3,4]furan via multiple consecutive reactions. As an alternative, by pre-installation of a functional group on the metallaarene, intramolecular nucleophilic aromatic substitutions and $\text{NH}$-substitution reactions can be realized to access N-functionalization metallaaromatics. Despite these impressive advances, approaches to amido-substituted metallaaromatics usually require multistep pathways or prefunctionalized starting materials. Direct C–H amidation has emerged as a step- and atom-economical alternative, but is elusive and its successful completion is challenging.

Herein we report the direct amidation of metallaaromatics with N-bromoamides and N-bromooimides, respectively. A planar Möbius metallaaromatic, osmapentalyne, was employed as a model substrate and a series of N-functionalized metallaaromatic derivatives have been synthesized under mild conditions at room temperature (rt) (Scheme 1). The identified 1,5-bromoamidation metallaaromatic intermediate suggests that the reaction proceeds a unique pathway involving electrophilic

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**Scheme 1** Direct amidation of metallaaromatics via 1,5-bromoamidated intermediate.
addition and nucleophilic attack. This is quite different from the typical radical process of organic arene C–H amidation involving N-haloamidine reagents.

**Results and discussion**

**Synthesis and characterization of osmapentalyne 1**

We have previously reported some interesting metallalaaromatics, i.e. metallapentalynes containing a metal–carbon triple bond in a five-membered ring, which exhibit the rare planar Möbius aromaticity.\(^{6,8,9}\) In order to investigate the direct amidation strategy to obtain its N-functionalized derivatives, we envisioned that metallapentalyne with relatively electron-deficient groups would participate in the substitution of hydrogen by the amidating reagent. Accordingly, we designed and synthesized the tri-substituted osmapentalyne 1. Details of the synthesis and characterization are in the ESI (see ESI, p. S5). As shown in Fig. 1, the metallacycle contains an osmium shared by two fused five-membered rings. The eight atoms (Os1, C1–C7) are coplanar as reflected by the mean deviation of 0.010 Å from the least squares plane and the sum of angles in the fused five-membered rings, which are both 540.0°. The coplanarity as well as the Os–C and C–C bond distances in the fused five-membered ring indicates it is a delocalized metallabicyclic compound, which resembles our previously reported aromatic osmapentalynes.\(^{6,8,9}\)

**Direct C–H amidation or imidation of osmapentalyne 1: procedure, scope and characterization of products**

We investigated the reactions of osmapentalyne 1 with various amidating reagents (Table 1). When 1 was reacted with N-bromophthalimide (NBP) in the presence of aluminium oxide in air at rt for 12 h, complex 2a was formed in 92% yield. The product 2a can also be obtained in 81% yield when the reaction mixture was treated with CH₃COONa instead of Al₂O₃ (see ESI, p. S5†). Treatment of compound 1 with N-bromosuccinimide (NBS) under similar conditions led to the formation of 2b in 90% yield. Complexes 2a and 2b were characterized by X-ray crystallographic analysis. As shown in Fig. 2, the metallacyclic

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**Table 1** Scope of amidation reagents

| Entry | [N] | Yield (%) | Entry | [N] | Yield (%) |
|-------|-----|-----------|-------|-----|-----------|
| 2a    | 2d  | 92        | 2e    | 80  | 85        |
| 2b    | 2f  | 90        | 2g    | 76  | 71        |
| 2c    | 2h  | 93        |       |     |           |

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a) Reaction conditions: 1 (0.20 mmol) with N-bromosuccinimide (0.60 mmol) and Al₂O₃ (5.0 mmol) in CH₂Cl₂ (10.0 mL) for 12 h at rt in air.

b) Isolated yield. [Os] = OsCl(PPh₃)₂.

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**Fig. 1** X-ray crystal structure of the cation of 1 (thermal ellipsoids are set at the 50% probability level and the phenyl groups in the PPh₃ moieties are omitted for clarity). Selected bond lengths [Å] and angles [°]: Os1–C1: 1.858(3), Os1–C4: 2.106(3), Os1–C7: 2.045(3), C1–C2: 1.398(4), C2–C3: 1.398(5), C3–C4: 1.398(5), C4–C5: 1.397(5), C5–C6: 1.410(5), C6–C7: 1.396(5), C4–Os1–C1: 72.31(13), C7–Os1–C4: 75.01(13).

**Fig. 2** X-ray crystal structure of the cation of 2a (thermal ellipsoids are set at the 50% probability level and the phenyl groups in the PPh₃ moieties are omitted for clarity). Selected bond lengths [Å] and angles [°]: Os1–C1: 1.842(2), Os1–C4: 2.111(2), Os1–C7: 2.044(2), C1–C2: 1.404(3), C2–C3: 1.404(3), C3–C4: 1.414(3), C4–C5: 1.397(3), C5–C6: 1.397(3), C6–C7: 1.388(3), C5–N1: 1.430(3), C4–Os1–C1: 72.32(9), C7–Os1–C4: 75.89(9).
skeleton of 2a is similar to that of 1, with the exception of the phthalimido substitute attached to C5. The length of the C5–N1 bond (1.430(3) Å) indicates its single-bond character, and is similar to the reported N-aryl single bond (1.464(4) Å) in the imide-substituted metallaromatics.\(^\text{15}\) The dihedral angle between the metallabicyclic unit and the imide group is 62.40°. The Os1–C1 bond length (1.842(2) Å) suggests that it maintains the Os≡C triple bond character. The C–C bond lengths (1.388–1.414 Å) in the fused five-membered rings are intermediate between the lengths of C–C and C≡C bonds and show no significant bond-length alternation. The planarity and the bond lengths in the fused five-membered rings indicate it is a delocalized metallabicyclic compound. All these parameters are consistent with 2a being a C5-phthalimido-substituted osmapentalyne derivative.

The solid-state structure of 2a is fully supported by NMR spectroscopy. In the \(^1\)H NMR spectrum, the characteristic signal of H3 (δ = 8.30 ppm) appears in the aromatic region. Carbon C5 bearing the phthalimido substitute has a peak at δ = 140.3 ppm. In the \(^{31}\)P\(^{1}\)H\) NMR spectrum of 2a, only one singlet (δ = −0.18 ppm) is observed for the two PPh\(_3\) ligands, indicating that the two phosphorus atoms are equivalent.

Encouraged by the effective imidation of osmapentalyne with NBP and NBS, we then examined other amidating reagents. N-Bromocarboxamides substituted with different groups were subjected to the standard reaction conditions. The methyl, phenyl, benzyl, \(n\)-propyl and cyclohexyl groups were all well-tolerated, yielding the corresponding products in moderate to excellent yields (71–93%, 2c–2g) (Table 1). Complexes 2c, 2d and 2e have been fully characterized by X-ray crystallographic analysis and all the structures were further supported by NMR spectroscopy and high-resolution mass spectrometry (HRMS) (see ESI p. S44–S53†).

The structural parameters of the fused rings in compound 2c resemble those in 2a (Fig. 3). The acetamide group attached at C5 position is indicated by the N1–C5 bond length (1.387(11) Å), which is close to that of the reported N-aryl single bond (1.391(4) Å) in osmapentalyne.\(^\text{16}\) The intramolecular hydrogen bonds N1H···O1 (2.107 Å) and H3···O2 (2.105 Å) were also observed in the acetamide-substituted osmapentalyne.

### Investigation of the mechanism: identification of key intermediates and control experiments

Control experiments were performed to elucidate the mechanism of the reaction (Table 2). It is well known that NBS or NBP can generally participate either in radical or ionic pathways depending on the cleavage of the N–Br bond.\(^\text{17}\) When the reaction was conducted in the dark, no influence on the reaction efficiency and yield was observed (entry 2). Addition of the radical scavenger BHT (2,6-di-tert-butyl-4-methylphenol) to the reaction mixture under the standard conditions had no obvious effect on the product yield (entry 3). This result suggests that a radical pathway is unlikely.

The \(\textit{in situ}\) NMR showed that compound 3a can be identified from the reaction of 1 with NBP within 15 min (Scheme 2). HRMS spectrometry showed a dominant peak at \(m/z = 1380.1864\), consistent with the adduct of cationic 1 and NBP [C\(_{27}H_{32}BrClN\O\O\)O(PPh\(_3\)]\(^+\) (1380.1855) (see ESI p. S56†). The structure can be inferred from the NMR spectra, which indicates that it is a bromoamidation product with bromide and nitrogen moieties at C1 and C5 positions, respectively. The \(^1\)H NMR spectrum of 3a displays a signal for the H5 proton at δ = 6.12 ppm determined by \(^1\)H–\(\text{¹}^\text{C}\) heteronuclear single quantum coherence (HSQC) spectroscopy, which is significantly shifted to a higher field when compared to that of 1 (δ = 9.46 ppm). The
signal from C5 (δ = 57.5 ppm) is dramatically shifted upward when compared to the corresponding resonance observed in 1 (δ = 147.0 ppm) and 2a (δ = 140.3 ppm). The values strongly support the sp³ hybridization state of C5. In addition, the H3 proton signal (δ = 6.22 ppm) is also moved upward compared with that of 1 (δ = 8.11 ppm) and previously reported metal-lapentalenes (ca. 7–9 ppm), but is comparable with those observed in osmacyclopentadiene derivatives (δ = 6.41 ppm). Notably, the 31P{1H} NMR and DEPT-135 spectra confirmed the C1 as a quaternary carbon at δ = 198.3 ppm. The chemical shift is upward compared with those found for related osmacyclopentadienes (ca. δ = 218–235 ppm) due to the bromide attached at C1. The resonances of the two carbonyl carbons in the substituted imide group were observed at δ = 169.7 and 166.2 ppm, respectively. The 31P{1H} NMR spectrum shows signals from the two phosphorus atoms at δ = –22.68 and –21.11 ppm, respectively. These data all suggest that 3a is a deaeromatization product derived from the 1,5-addition of NBP to 1 (Table 3).

The reaction of 1 with NBS could also give rise to the analogous 1,5-addition product 3b. Complex 3a and 3b could be recognized as the intermediate δ¹-adduct in nucleophilic aromatic substitution reactions. Strong nucleophiles such as RO⁻, H²⁺, NH₂⁻ have participated in the formation of the isolated δ¹-adducts. It is challenging however for weak nucleophiles such as an imide anion to attack the aromatic ring. The isolation of a δ¹-adduct involving imide anion is limited to extremely electron-deficient aromatics.

Haloamidation of an unsaturated bond using an electrophilic halogen source such as NBS is an important and well documented synthetic route to vicinal haloamide compounds. In contrast, the reactions of amide reagents toward arenes or heteroarenes usually result in either imidation or halogenation. In our case, the unique feature of osmapentalyne permits the bromine addition to the Os=C=C bond (2.7241(5) Å and St=–Br1 (1.896(5) Å) was slightly shorter than that of 1 (δ = 140.3 ppm). The values strongly support the sp³ hybridization state of C5. In addition, the H3 proton signal (δ = 6.22 ppm) is also moved upward compared with that of 1 (δ = 8.11 ppm) and previously reported metal-lapentalenes (ca. 7–9 ppm), but is comparable with those observed in osmacyclopentadiene derivatives (δ = 6.41 ppm). Notably, the 31P{1H} NMR and DEPT-135 spectra confirmed the C1 as a quaternary carbon at δ = 198.3 ppm. The chemical shift is upward compared with those found for related osmacyclopentadienes (ca. δ = 218–235 ppm) due to the bromide attached at C1. The resonances of the two carbonyl carbons in the substituted imide group were observed at δ = 169.7 and 166.2 ppm, respectively. The 31P{1H} NMR spectrum shows signals from the two phosphorus atoms at δ = –22.68 and –21.11 ppm, respectively. These data all suggest that 3a is a deaeromatization product derived from the 1,5-addition of NBP to 1 (Table 3).

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Treatment of 3a with excessive amounts of NBP as an oxidant in the presence of HBF₄·Et₂O, led to the formation of the oxidation product 4a (Scheme 2). The solid-state structure of 4a was characterized by X-ray single-crystal diffraction (Fig. 4). The bond lengths of Os1–C1 (1.949(5) Å and C1–Br1 (1.896(5) Å as well as Br1–C1–Os1 bond angle (90.2(2)°) are comparable to those of the reported metallabromirenium compound (1.935 (11) Å, 1.872(10) Å and Br1–C7–Os1 95.8(5)°, respectively). The Os1–Br1 bond length (2.7241(5) Å was slightly shorter than that of the reported metallabromirenium (2.8254(12) Å), demonstrating the stronger interaction between the bromide atom and the metal center. The other metal–carbon bonds, Os1–C4 (2.146(5) Å) and Os1–C7 (2.023(5) Å and the C–C bond lengths

### Table 3: Selected NMR spectroscopic data for the complexes 1, 2a, 3a, and 4a

| Compound | δ¹(H) (ppm) | δ¹(C) (ppm) |
|----------|-------------|-------------|
|          | H3         | H5         | C1     | C5     |
| 1        | 8.11       | 9.46       | 324.4  | 147.0  |
| 2a       | 8.30       | —          | 327.1  | 140.3  |
| 3a       | 6.22       | 6.12       | 198.3  | 57.5   |
| 4a       | 8.13       | —          | 270.7  | 151.0  |
(1.366–1.425 Å) are within the range observed for 2a and other osmapentalenes, suggesting the rearomatization of 4a. The NMR data are consistent with the crystal structure. In particular, the signal from C1 appears at δ = 270.7 ppm, suggesting the carbene character of C1. This differs from the Os–C single bond observed in 3a (198.3 ppm). Signals from the remaining ring carbon atoms are observed at δ = 159.8 (C2), 125.4 (C3), 174.1 (C4), 151.0 (C5), 164.3 (C6) and 220.2 (C7) ppm, respectively. The 1H NMR spectrum of 4a also shows the signal for H3 at δ = 8.13 ppm in the aromatic region. The singlet peak of the two PPh3 ligands at δ = −5.11 ppm in the 31P(1H) NMR spectrum of 4a reflects the reconstruction of a molecular mirror plane.

Experimentally, N-halogen imides other than NBS were used in the reactions (Table 2). No reaction was observed with N-iodosuccinimide (NIS), which might only reflect the poor reactivity of N-iodoimides (entry 4). When NCS was used in the reaction, a mixture of unidentified species was produced (entry 5). The smaller atomic size of the chlorine atom is known to play a vital role in the reaction.

Elimination of the bromine cation from 4a could generate the osmapentalyne 2a in high yield upon the addition of Al2O3 under an argon atmosphere in the presence of NaPF6 (Scheme 2). In this context, a reasonable mechanism was proposed for the direct amidation reaction (Scheme 3). Initially, the addition of a bromine cation derived from the N-bromoamide to the metal–carbon triple bond produces an extremely electron-deficient cationic metallabromirenium A. Subsequently, nucleophilic addition of imide anion afforded the stabilized intermediate σH-adduct 3a, and this is followed by elimination of hydride ion by oxidation to accomplish the SNAr reaction giving the metallaaromatic product 4a. Elimination of the bromine cation by Al2O3 affords the final amido-substituted product 2a.

While 1 was reacted with NBP in the presence of wet acetic acid, and then the mixture was treated by aluminium oxide, compound 5 can be isolated in 68% yield (Scheme 4). The X-ray crystallographic analysis confirms it is a new metallacyclic skeleton containing a five-membered metallacyclocallene (Fig. 5). Notably, carbonylation at C5 position in 5 was observed rather than N-functionalization as in 2. The proposed mechanism for the formation of 5 showed nucleophilic attack of H2O to metallabromirenium A afforded intermediate B, which would be oxidized into carbonyl complex C. The cationic C is detected by HRMS spectrometry (m/z = 1249.1461, [C64H50BrClO2OsP3]+) calculated m/z = 1249.1483 (see ESI p. S62†). The ready elimination of the bromine cation afforded the product 5 containing a metal-vinylidene moiety (see ESI p. S19†). It is presumably that the nucleophilicity of NBP in the presence of the acetic acid is dramatically reduced, thus the C5 position of 1 was prior to being attacked by H2O. The strategy provides a convenient route to access extraordinary metallaclycles with a high degree of skeletal complexity.

![Scheme 3 Proposed mechanism for the direct amidation of metallaaromatics, [Os] = OsCl(PPh3)2.](image14x290 to 26x354)

![Scheme 4 Formation of 5 by reaction of 1 with H2O, [Os] = OsCl(PPh3)2.](image52x79 to 282x307)

![Fig. 5 X-ray crystal structure of 5 (thermal ellipsoids are set at the 50% probability level and the phenyl groups in the PPh3 moieties are omitted for clarity). Selected bond lengths [Å] and angles [°]: Os1–C4: 2.111(3), Os1–C1: 1.870(3), Os1–C7: 2.059(3), O2–C5: 1.250(3), O1–C10: 1.223(4), C1–C2: 1.374(4), C3–C2: 1.450(4), C4–C3: 1.366(4), C4–C5: 1.465(4), C6–C5: 1.449(4), C6–C7: 1.382(4), C7–C8: 1.512(4), C8–C9: 1.530(4), C10–C9: 1.519(4), C6–C10: 1.464(4), C2–C1–Os1: 130.0(2), C1–C2–C3: 107.3(2), O2–C5–C4: 124.3(3), O1–C10–C6: 129.1(3).](image312x367 to 545x415)
Further, transformation of imide product 2a was performed by treatment of 2a with hydrazine hydrate, afforded amino-substituted osmapentalyne 6 in high yield (90%) (Scheme 5). Amino-substituted metallaromatics exhibit rich reactivities towards many reagents.\(^1\) Complex 6 represents the first amino-substituted metallaaromatic, which is useful for further functionalization of these unusual metallacyclic compounds.

**Thermal stability and spectroscopic properties**

The solid state of amidation products 2a–2g can be stored in air at room temperature at least for two weeks. They also exhibit good thermal stability even when heated at 100 °C in air for 5 h (see ESI p. S20\(^\dagger\)). The UV-Vis absorption spectra of the precursor 1 and its derivatives 2a–2g were investigated. As shown in Fig. 6, compound 1 displays an absorption maximum at \(\lambda_{\text{max}} = 460\) nm. The absorption bands for 2a and 2b, bearing electron-withdrawing imide groups were observed at approximately \(\lambda_{\text{max}} = 472\) nm, slightly red-shifted compared to that of 1, while 2c–2g with electron-donating amide groups at around \(\lambda_{\text{max}} = 450\) nm was slightly blue-shifted. The results show that amidation of metallaromatic compounds is a feasible methodology with which to subtly tune their photophysical properties.

**Conclusions**

We have developed a direct and efficient amidation of metallaromatics, leading to N-functionalized osmapentalynes. The successful isolation of the key intermediates, the 1,5-bromomation and metallabromirenum species, confirms that the reaction is a three-step process that first involves electrophilic addition, followed by nucleophilic attack and then oxidation.

This study provides insight into a strategy to construct functionalized metallaromatics and significantly facilitates further exploration of their properties and potential applications.

**Author contributions**

H. X. and Y.-M. L. conceived the project. H. W. performed the experiments. H. W., Y.-M. L., and Y. R. analyzed and interpreted the experimental data. Y.-M. L. and J. W. drafted the paper. All of the authors discussed the results and contributed to the preparation of the final manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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