

Protonation and Bromination of an Osmabenzynes: Reactions Leading to the Formation of New Metallabenzynes

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We have recently reported the synthesis and characterization of the first metallabenzynes [Os(≡CC(SiMe₃)=C(CH₃)C(SiMe₃)=CH)Cl₂(PPh₃)₂] (**1**).¹ The compound is interesting² because it is structurally related to metallabenzynes^{3–5} and benzyne⁶ which have attracted considerable attention of experimental and theoretical chemists. Unlike benzyne, which is thermally unstable, complex **1** can be isolated as a greenish-blue solid and can be conveniently characterized by NMR spectroscopy and X-ray diffraction. The X-ray diffraction study of **1** shows that the six-membered metallacycle has a planar delocalized structure.¹ The delocalized structural feature is similar to that of aromatic ring systems such as benzene and metallabenzynes. In these regards, it would be interesting to find out if metallabenzynes could also undergo typical reactions of aromatic compounds or benzyne.

When a mixture of **1** and 2 equiv of HBF₄ in wet dichloromethane was stirred for 8 h, the cationic osmabenzynes **2** was produced (Scheme 1). **2** is presumably formed by protonation of one of the chloride ligands followed by trapping the intermediate with water present in the reaction medium. The structure of **2** has been confirmed by X-ray diffraction.⁷ As shown in Figure 1, the complex contains an essentially planar six-membered metallacycle with a water molecule trans to the formally carbyne carbon. The Os–C(1) (1.756(5) Å) bond is slightly shorter than that (1.815(4) Å) of **1** but is still longer than Os≡C bonds in complexes such as OsHCl₂(≡CCH₂Ph)(P(*i*-Pr)₃)₂ (1.711(4) Å),⁸ OsHCl₂(≡CCH=CPh₂)(PCy₃)₂ (1.715(4) Å),⁹ and OsCl₃(≡CCH₂CMe₃)(PPh₃)₂ (1.728(3) Å).¹⁰ The Os–C(5) bond (2.016(5) Å) is slightly longer than that of **1** (1.939(5) Å) and is close to the Os–CH bonds in osmabenzynes Os(C(SMe)CHCHC(X)CH)I(CO)(PPh₃)₂ (X = NO₂, 2.011(7) Å; X = Br, 2.039(9) Å).^{4a} The Os–C(1)–C(2) angle is at 153.8(4)°, which is slightly larger than that of **1** (148.7(3)°). The solid-state structure is fully supported by the solution NMR spectroscopic data and elemental analysis. The most relevant compound to **2** is the cationic aquocarbyne osmium complex, [OsCl₂(≡CC₆H₄NMe₂)(H₂O)(PPh₃)₂]⁺.¹¹

When a mixture of **1** and 6 equiv of HBF₄ in dichloromethane was stirred for 20 h, the desilylated cationic osmabenzynes **3** was produced. Isolated **2** could also be slowly converted to **3** when treated with excess of HBF₄. If the protonation reaction was carried out in the presence of NaCl and the resulting mixture was treated with water, the neutral desilylated osmabenzynes **4** can be isolated in 73%. Treatment of isolated **3** with NaCl also gave **4**.

The structure of complex **3** can be inferred from its NMR spectroscopy. The ³¹P{¹H} NMR spectrum (in CD₂Cl₂) showed a singlet at 10.5 ppm. The ¹³C{¹H} NMR spectrum displayed the Os≡C signal at 309.3 ppm, the OsCH signal at 210.3 ppm, the CH signals at 125.2 and 107.7 ppm, and the CCH₃ signal at 176.6

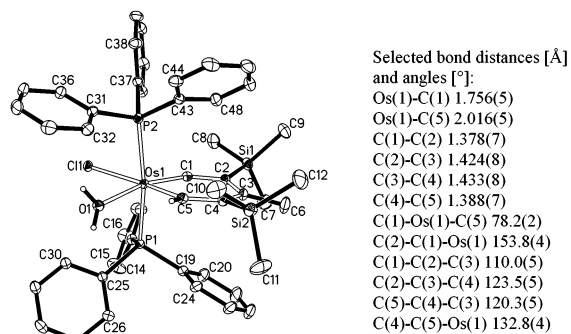
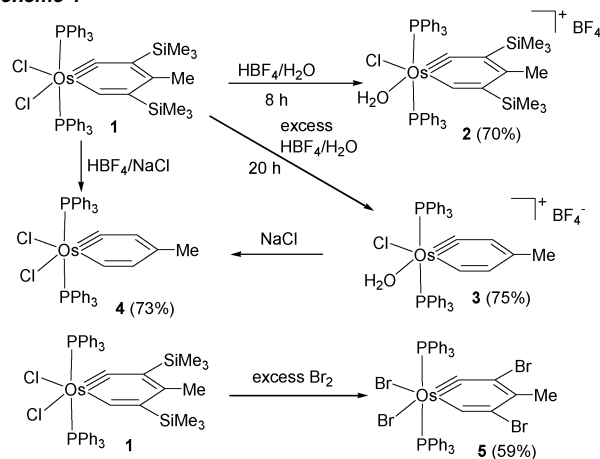


Figure 1. Molecular structure for the complex cation of **2**.

Scheme 1



ppm. In the ¹H NMR spectrum, the three CH signals were observed at 12.65 (d, *J*(HH) = 8.2 Hz, OsCH), 6.33 (d, *J*(HH) = 8.2 Hz, OsCH=CH), and 4.26 ppm (Os≡CCH). The ≡CCH signal appeared in relatively high field, presumably because the CH group is adjacent to the carbyne carbon.

The structure of **4** has also been determined by X-ray diffraction (Figure 2).⁷ The structural features associated with the metallacycle are very similar to those of **1**. Consistent with the structure, the ¹H NMR spectrum showed three CH signals at 12.19 (OsCH), 5.66 (OsCH=CH), and 4.03 ppm (OsCCH). In the ¹³C{¹H} NMR spectrum, the five carbon signals of the metallacycle were observed at 302.2 (Os≡C), 212.4 (OsCH), 175.9 (CCH₃), 125.2 (OsCH=CH), and 107.6 (Os≡CCH) ppm.

The reactions of **1** with HBF₄ to give **3** and **4** are similar to the reactions of C₆H₅SiMe₃ with acids¹² in that the Me₃Si groups of the six-membered ring are replaced with hydrogens. Like the reactions of C₆H₅SiMe₃ with acids, replacement of the Me₃Si groups in the metallacycle with hydrogens in the protonation reactions most

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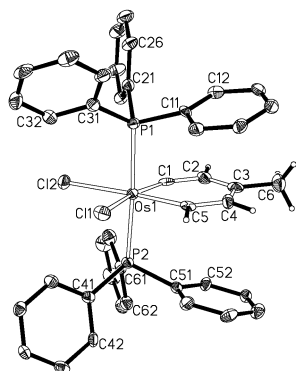


Figure 2. Molecular structure of 4.

Selected bond distances [Å] and angles [°]:
 Os(1)-C(1) 1.805(7)
 Os(1)-C(5) 2.008(7)
 C(1)-C(2) 1.363(9)
 C(2)-C(3) 1.413(9)
 C(3)-C(4) 1.405(9)
 C(4)-C(5) 1.372(8)
 C(1)-Os(1)-C(5) 79.8(3)
 C(2)-C(1)-Os(1) 148.3(6)
 C(1)-C(2)-C(3) 114.9(6)
 C(4)-C(3)-C(2) 121.3(6)
 C(5)-C(4)-C(3) 123.5(6)
 C(4)-C(5)-Os(1) 132.1(5)

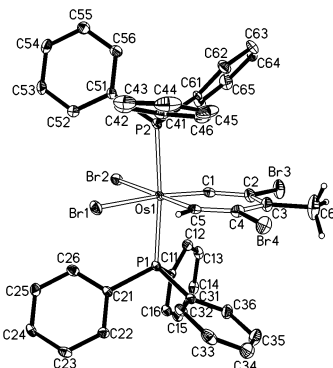


Figure 3. Molecular structure of 5.

Selected bond distances [Å] and angles [°]:
 Os(1)-C(1) 1.766(3)
 Os(1)-C(5) 2.048(3)
 C(1)-C(2) 1.368(5)
 C(2)-C(3) 1.391(5)
 C(3)-C(4) 1.432(5)
 C(4)-C(5) 1.352(5)
 C(1)-Os(1)-C(5) 78.95(14)
 C(2)-C(1)-Os(1) 150.8(3)
 C(1)-C(2)-C(3) 116.4(3)
 C(2)-C(3)-C(4) 116.8(3)
 C(5)-C(4)-C(3) 128.1(3)
 C(4)-C(5)-Os(1) 128.9(3)

likely proceeded by initial protonation of the 3,5 positions of the metallacycle. In principle, protons could also attack on the carbon atoms of OsC or OsCH of the metallacycle. To test the possibility, we have treated **1** with CF₃SO₃D in the presence of NaCl. The reaction produced partially deuterated osmabenzynes **4**. The ²D NMR of the isolated product suggests that deuteria are only incorporated at the 3,5-positions. The result indicates that the carbons of OsC or OsCH were not attacked by the acid under the protonation condition.

Complex **1** readily reacts with bromine. Treatment of **1** with ca. 15 equiv of Br₂ rapidly produced the new osmabenzynes **5** as the predominant species. Thus, both the Me₃Si and Cl in **1** have been replaced by Br. When a lesser amount of Br₂ was used, a complicated mixture was produced, as indicated by the in situ NMR, probably due to partial displacements of the Me₃Si and Cl groups. Reactions of ArSiMe₃ with bromine are known to give Ar-Br.¹³ Therefore metallabenzynes **1** and ArSiMe₃ have similar chemical properties in terms of their reactions with bromine. Electrophilic substitution reactions of a metallabenzene have been reported by Roper et al.^{4a}

Complex **5** has been characterized by MS, NMR spectroscopy, and elemental analysis. In particular, the FAB-MS displayed the expected molecular ion peak at *m/z* = 1109.9; the ³¹P{¹H} NMR spectrum (in CD₂Cl₂) showed a singlet at -4.0 ppm. The ¹³C{¹H} NMR spectrum displayed the Os≡C signal at 288.7 ppm, the OsCH signal at 199.4 ppm, the CBr signals at 109.6 and 107.3 ppm, and the CCH₃ signal at 167.3 ppm. The structure has also been confirmed by X-ray diffraction (Figure 3).⁷

In both the protonation and bromination reactions, only the C3 and C5 carbon atoms of the metallacycle were attacked by electrophiles. A preliminary computational study¹⁴ shows that the regioselectivity can be related to the electron density of the HOMO. As shown in Figure 4, the HOMO has significant contribution from the p_π orbitals at these two positions. Thus, it is not surprising that

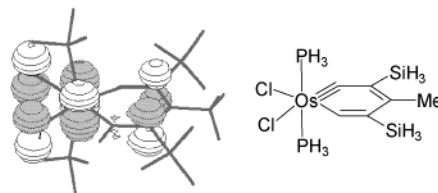


Figure 4. The contour plots of the highest occupied molecular orbital.

substitution reactions only occurred at these carbons. The HOMO also contains an Os(d) orbital and p_π orbitals from the chloride ligands. The observed protonation of one of the chloride ligands, which leads to the water coordination in **2** and **3**, can be also conveniently related to the electron density of the HOMO. The protonation at the metal center does not occur, probably due to the crowded coordination environment. The metal-carbyne π-bonding molecular orbitals are located in energy below the chloride p lone pair orbitals, suggesting the high stability of the metal-carbyne π bonds toward the electrophiles.

In summary, we have demonstrated for the first time that metallabenzynes can also undergo electrophilic substitution reactions. The reactions allowed us to prepare new types of metallabenzynes. The reactions reported in the work are unusual, especially when the reactivities of benzynes are considered. The reactivities of benzynes are usually associated with the C≡C triple bond. Electrophilic substitutions reactions of benzynes, to our knowledge, have not been demonstrated. We are now in the process of extending the chemistry by using other reagents and metallabenzynes.

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Supporting Information Available: Experimental procedures and characterization data (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- In the B3LYP calculations, Lan2dz was used for Os, P, and Cl, while 6-31G was used for all other atoms. Polarization functions were added for Cl ($\zeta = 0.514$), P ($\zeta = 0.34$), and Si ($\zeta = 0.262$).

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