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Metallacycles

Reactions of Osmabenzene with Silver/Copper Acetylides: From Metallabenzene to Benzene

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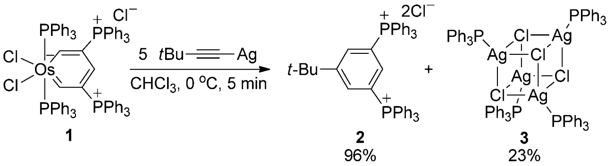
Abstract: The transformations of metallabenzene to substituted benzenes have been achieved by reactions of osmabenzenes with silver/copper acetylides. In this investigation, novel tetraphenylphosphonium salts containing two phosphonium substituents on the same benzene ring are generated.

Nowadays, the scope of heteroaromatics is not limited to cyclic conjugated π systems containing main-group atoms or related groups. Metallaaromatics[1] have emerged as special heteroaromatics and have attracted continuing interest from both theoretical and experimental chemists, since model compounds of metallaaromatics, that is, metallabenzenes, were first predicted by Thorn and Hoffmann in 1979.[2] Metallabenzenes represent a particularly interesting class of heteroaromatics derived from replacement of a (hydro)carbon unit in conventional aromatic hydrocarbons with a transition-metal fragment. In the past 35 years, a number of metallabenzenes have been reported together with their aromatic properties and reactivities.[2,3] Despite the growing interests and extensive studies, full exploitation of the potential of this class of aromatics has not yet been completely achieved. Over the past few years, we have demonstrated that metallabenzenes could act as starting materials to access many other higher π-electron metallaaromatics, such as metallabenzothiazole,[4a] metallabenzoxazole,[4a] metallaisoquinolyne,[4b] metallabenzoxazolone, and metallabenzooxazolethione.[4c] Furthermore, interesting organic molecules with novel structures and/or properties can be obtained from the reactions of metallabenzenes, such as highly stable cyclopentadienyl ions[5a,b] and a dialdehyde molecule that is compatible with nitric acid.[5c] Herein, we report new reactions of an osmabenzene with silver/copper acetylides, which lead to transformation of metallabenzene to substituted benzenes.

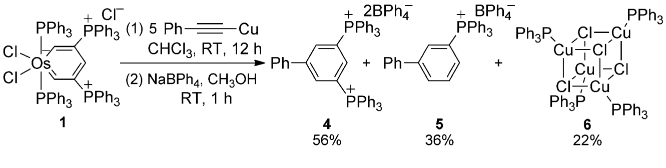
As shown in Equation (1), treatment of the osmabenzene complex **1** with excess tBuC≡CAg in chloroform at 0 °C for 5 min led to formation of the dicationic phosphonium salt **2**, which can be isolated by column chromatography as a colourless solid in 96% yield. Complex **1**[6a] and the transition-metal acetylides[6b,c] were synthesized according to literature and our previous method, and the detailed synthesis procedures are given in Supporting Information.



(1)

The dicationic phosphonium salt **2** has been characterized by NMR spectroscopy, single-crystal X-ray diffraction analysis, and elemental analysis. A 3D structural view of the dicationic phosphonium ion in **2** is shown in Figure 1. The X-ray diffraction analysis indicates that the dicationic phosphonium ion contains a benzene ring with a *tert*-butyl and two phosphonium substituents.

Attempts to capture related metal complexes from the reaction only afforded isolation of the silver complex **3** [Eq. (1)]. To gain more information for the mechanistic aspects of the reaction, we then undertook the corresponding reaction using PhC≡CCu as an alternative transition-metal acetylide. As shown in Scheme 1, when we treated **1** with five equivalents of PhC≡CCu in chloroform at room temperature, **1** was completely consumed to give a mixture of compounds in 12 h, as suggested by in situ NMR spectroscopy. Upon treatment of the reaction mixture with $NaBPh_4$, we were able to isolate two tetraphenylphosphonium salts from the mixture; one is the dicationic phosphonium salt **4** in 56% yield, and the other one is the phosphonium salt **5** in 36% yield (Scheme 1). We also isolated the copper complex **6** in 22% yield.



Scheme 1. Reaction of the osmabenzene **1** with PhC≡CCu. Isolated yields.

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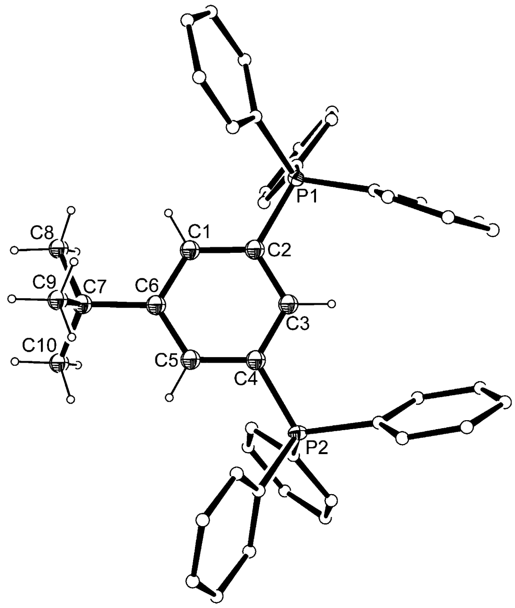


Figure 1. X-ray structure of **2** (ellipsoids at the 50 % probability level). The counter anion and some of the hydrogen atoms are omitted for clarity.

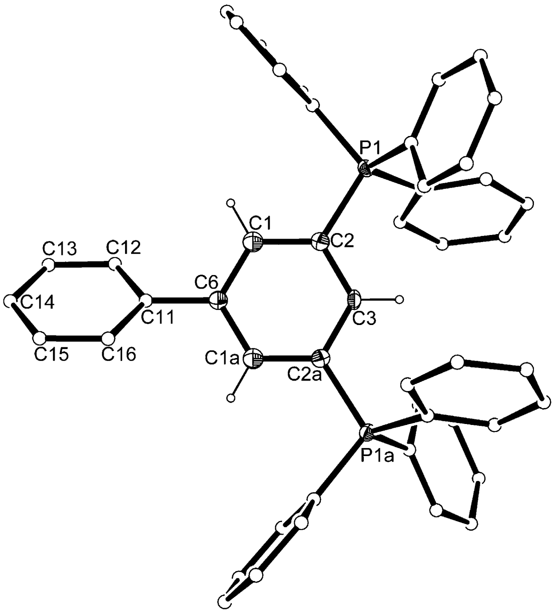


Figure 2. X-ray structure of **4** (ellipsoids at the 50 % probability level). The counter anion and some of the hydrogen atoms are omitted for clarity.

Both structures of the phosphonium derivatives **4** (Figure 2) and **5** (Figure 3) as well as the cluster $[Cu(PPh_3)Cl]_4$ (Figure S2 in the Supporting Information) have been confirmed by X-ray diffraction studies. The clusters $[Ag(PPh_3)Cl]_4$ (**3**) and $[Cu(PPh_3)Cl]_4$ (**6**) are known compounds, and were previously generated from reaction of silver chloride with triphenylphosphine[7] and reaction of copper chloride with triphenylphosphine,[8] respectively.

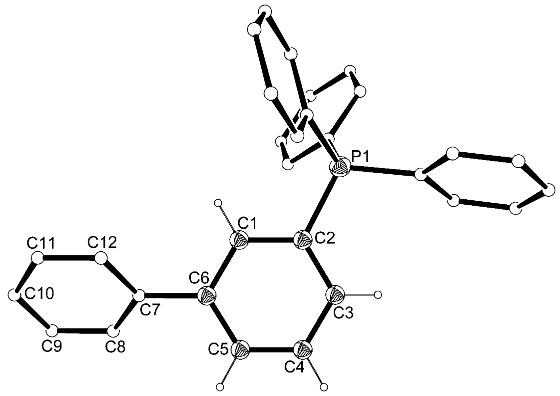
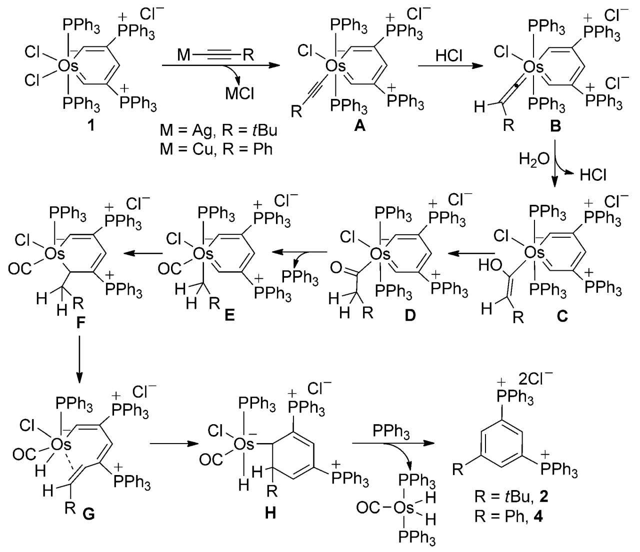


Figure 3. X-ray structure of **5** (ellipsoids at the 50 % probability level). The counter anion and some of the hydrogen atoms are omitted for clarity.



Scheme 2. Proposed mechanism for reaction of the osmabenzene **1** with transition-metal acetylides.

Attempts to trap related intermediates or osmium complexes from the reactions failed. Here, we propose a putative mechanism (Scheme 2) to account for the transformations of the osmabenzene **1** to the tetraphenylphosphonium salts **2** or **4**. As shown in Scheme 2, reaction of the osmabenzene **1** with a silver/copper acetylide may initially generate the alkynyl intermediate **A**. Transformations of alkynyl complexes to alkyl–carbonyl complexes in the presence of water molecules are well-established processes.[9] In this context, it should be further mentioned that Chin and Lee[9d] have experimentally verified the relevant steps for the transformation of an alkynyl ligand to an acyl ligand. These steps include protonation of an alkynyl ligand leading to a vinylidene ligand and subsequent OH^- attack at the C_α atom of the resulting vinylidene. Thus, **A** can evolve into the vinylidene intermediate **B** by protonation at the C_β atom of the alkynyl ligand with traces of HCl (which acts as a catalyst) in the solvent chloroform. Intermediate **B** can then rearrange to the acyl **D**, via **C**. Acyl decarbonylation generates **E**, which may undergo migration of the alkyl ligand in **E** from the metal center to the C_α atom to afford **F**. Intermediate **F** may further undergo β-H elimination to generate the η^2-alkenyl-coordinated osmium complex **G**. Finally, a 6-*endo-trig* cyclization in **G** yields the intermediate **H**, which can easily convert to the tetraphenylphosphonium salt **2** or **4** and an osmium dihydride complex.

The proposed reaction mechanism is supported by further experimental observations. As indicated by in situ NMR spectroscopy, only a trace amount of **2** (or **4** and **5**) was observed within one week when the reactions of **1** with $t\text{BuC}\equiv\text{CAg}$ (or $\text{PhC}\equiv\text{CCu}$) were carried out in dichloromethane pretreated with calcium hydride (to remove water and acid). Compound **5** is likely derived from the P–C bond cleavage of **4**, as suggested by the signal of $Ph_3P{=}O$ in the in situ NMR spectra. Furthermore, we attempted to trap related intermediates or the hydride complexes from the reaction by addition of excess PPh_3. Monitoring of the reaction in presence of additional PPh_3 by $^{31}P\{^1H\}$ NMR spectroscopy only revealed the formation of the clusters **3** as the major product with a small amount of the phosphonium salt **2**. However, the crude mixture of the reaction shown in Equation (1) gives a strong band at 1916.87 cm^{-1} in the IR spectrum, which is assignable to a osmium carbonyl complex[10] and provides good evidence for the presence of a carbonyl ligand.

Tetraphenylphosphonium salts are versatile compounds, which have gained increasing importance in various fields of chemistry ranging from organic synthesis and material science. In the literature, typical methods for preparation of tetraphenylphosphonium salts are palladium- or nickel-catalyzed reactions of aryl halides or triflates.[11] In the metal-free methods, quaternization of phosphines is normally employed, which requires high temperature and/or harsh reaction conditions,[12] except for the quaternization of phosphines with arynes generated from (*o*-trimethylsilyl) aryl triflates.[13] To the best of our knowledge, there are no other reported examples of tetraphenylphosphonium salts containing two phosphonium substituents on the same benzene ring yet.

In conclusion, we here present the reactions of osmabenzene with silver/copper acetylide, which produced the new interesting tetraphenylphosphonium salts.

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