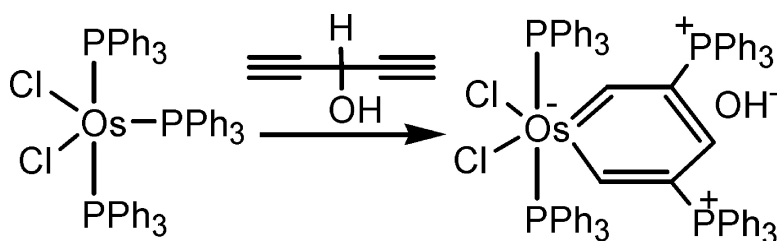


Osmabenzenes from the Reactions of $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ with $\text{OsX}(\text{PPh}_3)$ ($\text{X} = \text{Cl}, \text{Br}$)

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Osmabenzenes from the Reactions of $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ with $\text{OsX}_2(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}$)

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The chemistry of transition metal containing metallabenzenes¹ is attracting increasing attention both experimentally² and theoretically.³ Metallabenzenes are interesting because they can display aromatic properties and they can mediate organometallic reactions. The isolation and characterization of stable metallabenzenes represents one of the major issues of metallabenzene chemistry. The common strategies previously employed to construct stable metallabenzene rings include cyclization reactions of alkynes with metal-thiocarbonyl,^{2i,4} deprotonation of pentadienediyl iridium species (derived from the reactions of $\text{IrCl}(\text{PR}_3)_3$ with potassium 3,5-dimethylpentadienide),⁵ reactions of L_nMCl with lithiated 3-vinyl-1-cyclopropenes,^{2a,d,e,6} and oxidation of bicyclic iridium complexes derived from the coupling of alkynes.^{2b} During an investigation of the reactivity of $\text{OsCl}_2(\text{PPh}_3)_3$ with terminal alkynes,⁷ we found a new convenient route to prepare osmabenzenes starting from readily accessible $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$. The investigation led us to isolate the first phosphonium salts of metallabenzenes.

Treatment of $\text{OsCl}_2(\text{PPh}_3)_3$ (**1**) with $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ ⁹ in dichloromethane produced **2**, which can be isolated as a green solid in 44% yield (Scheme 1). Compound **2** has been characterized by solution NMR spectroscopic data and elemental analysis.¹⁰ The ³¹P{¹H} NMR spectrum in CD_2Cl_2 showed two singlets at 20.1 and -15.5 ppm assignable to CPh_3 and OsPPh_3 , respectively. The presence of the metallacycle is clearly indicated by the ¹H and ¹³C NMR data. In particular, the ¹H NMR spectrum in CD_2Cl_2 showed the characteristic OsCH signal at 23.13 ppm and the $\gamma\text{-CH}$ signal at 8.57 ppm; the ¹³C{¹H} NMR spectrum in CD_2Cl_2 showed the signals of OsCH , CPh_3 , and $\gamma\text{-CH}$ at 239.7, 112.7, and 160.5 ppm, respectively. The structure of **2** has been confirmed by X-ray diffraction. As shown in Figure 1, the complex contains an essentially planar six-membered metallacycle with two PPh_3 substituents. The maximum deviation from the least-squares plane through Os(1), C(1), C(2), C(3), C(4), and C(5) is 0.0754 Å for C(1). The Os–C(1) (1.946 (12) Å) and Os–C(5) (1.971 (12) Å) bond distances are shorter than the Os–CH distances in osmabenzenes $\text{Os}(\text{C}(\text{SMe})\text{CHCHC}(\text{X})\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{NO}_2$, 2.011(7) Å; $\text{X} = \text{Br}$, 2.039(9) Å).^{2j} The C–C bond distances of the metallacycle are longer than typical C=C double bonds and shorter than typical C–C single bonds. The NMR as well as the X-ray diffraction data indicate that the six-membered metallacycle of the complex cation of **2** has a delocalized structure with contribution from **2A**–**2D**. The similarity in P–C(phenyl) and P–C(metallabenzene) bond distances indicates that **2A** and **2B** are the dominant resonance structures.

Reaction of **2** with PMe_3 produced osmabenzene **3** (Scheme 1), which is closely related to Roper's osmabenzenes $\text{Os}(\text{C}(\text{SMe})\text{CHCHC}(\text{X})\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$.^{2i,j,4} The structure of **3** has also been

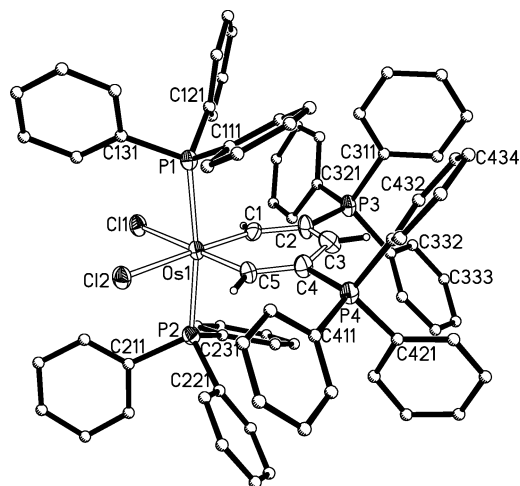
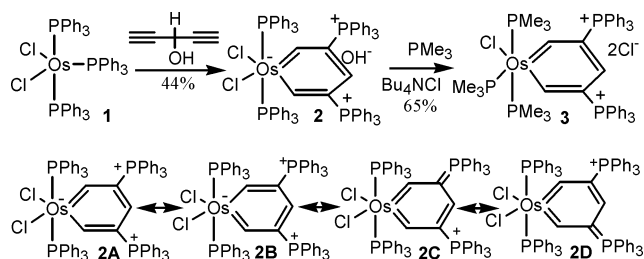


Figure 1. Molecular structure for the complex cation of **2**. The hydrogens of phenyls are omitted for clarity. Selected bond distances (Å): Os–Cl, 1.946(12); C1–C2, 1.398(15); C2–C3, 1.373(16); C3–C4, 1.448(17); C4–C5, 1.363(15); C5–Os, 1.971(12).

Scheme 1



confirmed by X-ray diffraction (Figure 2). As expected, slight short–long bond alternations were observed for the Os–C and C–C distances of the metallacycle. The solid-state structure is fully supported by the solution NMR spectroscopic data.

A plausible mechanism for the formation of the cationic complex **2** from the reaction of $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ with **1** is proposed in Scheme 2. Complex **1** can initially react with $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ to give intermediate **A**, which can react with PPh_3 to give **4**. **4** may then react with additional PPh_3 present in solution to give intermediate **B**, which loses an OH^- from the γ -carbon to give compound **2**. Addition reactions of phosphines to coordinated alkynes are known reactions.¹¹ The dissociation of OH^- from **B** is interesting and can be related to the formation of allenylidene complexes $\text{L}_n\text{M}=\text{C}=\text{C}=\text{CR}_2$ from the reactions of L_nM with $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_2$.¹²

One of the intermediates, complex **4**, has been isolated as a yellow solid from the reaction of **1** with $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ carried out in THF. The structure of **4** can be readily assigned on

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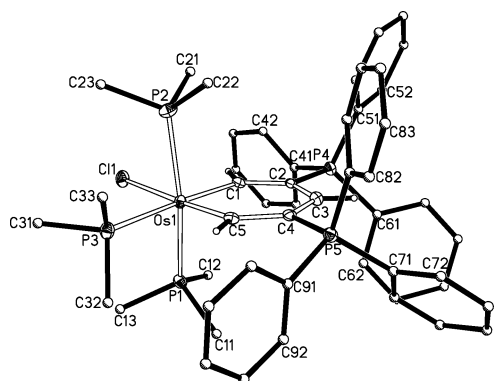
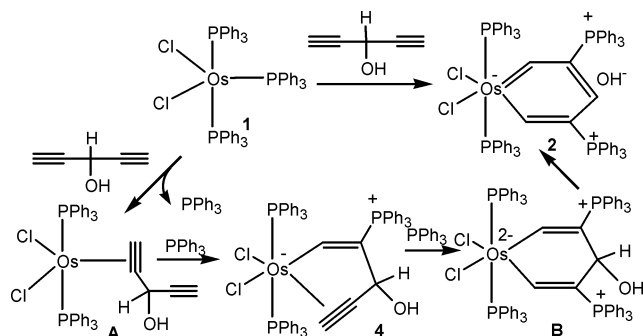


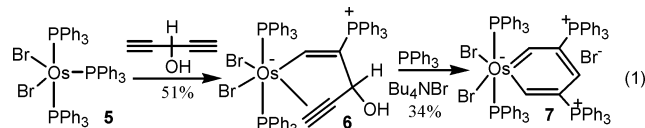
Figure 2. Molecular structure for the complex cation of **3**. The hydrogens of phenyls and methyls are omitted for clarity. Selected bond distances (Å): Os–Cl, 1.995(3); C1–C2, 1.383(5); C2–C3, 1.426(5); C3–C4, 1.382(5); C4–C5, 1.429(5); C5–Os, 1.920(4).

Scheme 2



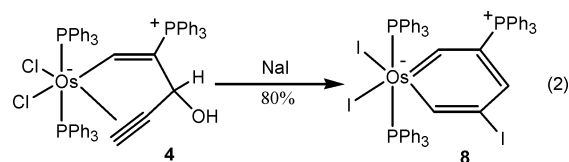
the basis of its analytical and spectroscopic data. The ^1H NMR spectrum (in CD_2Cl_2) showed OsCH , CHOH , and $\text{C}\equiv\text{CH}$ signals at 12.93, 5.39, and 3.75 ppm, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 , 246 K) showed five signals of the $\text{HC}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}\equiv\text{CH}$ chain at 206.5 (OsCH), 111.2 (CPPh_3), 85.0 ($\text{C}=\text{CH}$), 78.6 ($\text{C}\equiv\text{CH}$), and 77.8 (CHOH) ppm. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2), the signals of CPPh_3 appeared at 9.8 ppm and the signals of OsPPh_3 appeared at -6.9 and -7.9 ppm. Observation of two signals of OsPPh_3 is expected because of the presence of the $\text{CH}(\text{OH})\text{C}\equiv\text{CH}$ group.

The production of **2** from **4** has been confirmed experimentally. Thus, treatment of **4** with PPh_3 quickly produced **2** in good yield. Similar chemistry was also observed starting from $\text{OsBr}_2(\text{PPh}_3)_2$ (**5**). Thus treatment of **5** with $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$ in THF produced complex **6**, which reacted with PPh_3 to give **7** after metathesis with Bu_4NBr (eq 1). Complexes **6** and **7** presumably



have the same structures as **4** and **2** respectively as judged on the basis of the spectroscopic data. The new osmabenzene **2**, **3**, and **7** appear to be air stable in both solid state and in solution for at least a week.

Preliminary study shows that other nucleophiles can also react with **4** to give osmabenzene. For example, treatment of **4** with NaI in CH_2Cl_2 produced a brown solid. On the basis of spectroscopic data, the major species of the solid can be formulated as the iodo-osmabenzene **8** (eq 2). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in



CD_2Cl_2 showed a CPPh_3 signal at 18.8 and the OsPPh_3 signal at -27.3 ppm. The chemical shift of the CPPh_3 is similar to those of complex **2**, indicating that the PPh_3 groups are in a similar environment. The ^1H NMR spectrum in CD_2Cl_2 showed two OsCH signals at 20.1 (OsCHCl) and 19.0 (OsCHCPPh_3) ppm and the OsCHClCH signal at 8.10 ppm. In the ^{13}C NMR spectrum, the five carbon signals of the $\text{HCC}(\text{PPh}_3)\text{CHClCH}$ chain were observed at 248.2 (OsCHCl), 220.9 (OsCHCPPh_3), 152.6 (OsCHClCH), 112.9 (OsCHCPPh_3), and 98.3 (OsCHCl) ppm.

In summary, we found a very convenient route for the preparation of osmabenzene starting from readily accessible $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$. The reactions involve nucleophilic attack of coordinated alkynes by nucleophiles such as PPh_3 and I^- , followed by dissociation of OH^- at γ -carbon. The isolation of osmabenzene **2**, **7**, and **8** is interesting because it demonstrates that metallabenzene, like benzene, can also form phosphonium salts. We are in the process of extending the chemistry to prepare other metallabenzene and studying the chemistry of our new osmabenzene.

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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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