Synthesis and Characterization of an Air-Stable *p*-Osmaphenol

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*Summary: The synthesis and characterization of an air-stable
p-osmaphenol and some related complexes are presented.*

Since the first examples of stable metallabenzenes (in 1982)[1] were reported, as a novel family of organometallics that are consistent with the presence of an aromatic ring system,[2] metallabenzenes have been of great interest due to their delocalized π-bonding, corresponding aromatic properties,[3] and anticipated physical properties such as NLO behavior.[4] Various metallabenzenes and related complexes have been reported recently.[5–8] However, metallaphenols, which would seem to be an important series of metallabenzene derivants, are still very

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Scheme 1. Synthesis of Osmaphenol 5
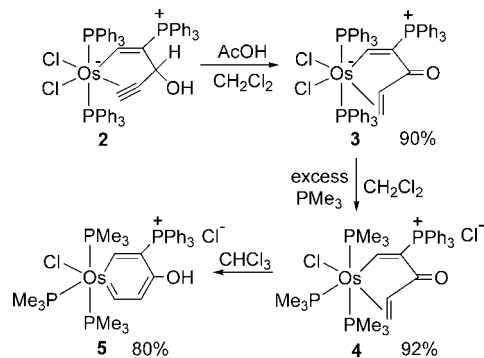
rare. The *o*-iridaphenols[6i] reported previously by Bleeke et al. in 1997 and an *o*-osmaphenol[5a] reported by Jia et al. very recently are the rare stable metallaphenol examples. The *o*-ruthenaphenoxide reported in 1995 could be detected by NMR at −78 °C but is unstable at −30 °C.[9] Metallaphenoxides and metallanaphthalene oxides of Ru, Fe, and Re have been proposed as transient intermediates.[10] Roper's *o*-osmathiophenol complex is an additional structurally related example, which was characterized by IR.[1] In this paper, we report a typical air-stable osmaphenol bearing a hydroxyl on the para carbon of the metal atom prepared from a relatively convenient method under mild conditions.

In our recent work we have developed a convenient route to prepare some stable metallabenzenes from the readily accessible HC≡CCH(OH)C≡CH (**1**).[5e,7d,e] In the course of our synthesis of the osmabenzene [Os(CHC(PPh₃)CHC(PPh₃)CH)Cl₂-(PPh₃)₂]OH, the key intermediate OsCl₂(CH=C(PPh₃)-CH(OH)C≡CH)(PPh₃)₂ (**2**) has been isolated successfully.[5e] The intermediate **2**, which can be stored as a solid under nitrogen but is unstable in solution at room temperature, can undergo some interesting reactions and evolve to the *p*-osmaphenol here.

Treatment of a suspension of **2** in dichloromethane with acetic acid for about 4 h led to the precipitation of a red solid with poor solubility, which could be isolated in 90% yield and was identified to be **3** (Scheme 1).

Figure 1 shows the structure of a single crystal of complex **3** determined by X-ray diffraction.[11] In the structure, Os(1), C(1), C(2), C(3), and C(4) are almost coplanar, which is reflected by the deviation (0.028 Å) from the rms planes of the best fit, while C(5) deviates out of the ring, together with C(4), constituting a terminal alkene double bond coordinated to the metal center. The dihedral angle between the five-membered ring and the

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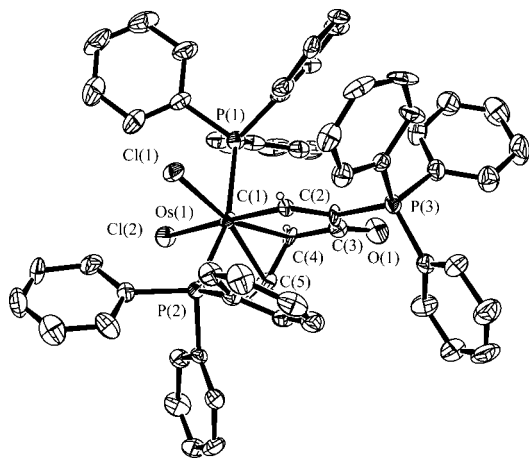
Figure 1. Molecular structure for the complex **3** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)−C(1) = 1.988(7), Os(1)−C(5) = 2.143(7), Os(1)−C(4) = 2.160(7), O(1)−C(3) = 1.239(10), C(1)−C(2) = 1.369(11), C(2)−C(3) = 1.482(12), C(3)−C(4) = 1.465(11), C(4)−C(5) = 1.435(12); C(1)−Os(1)−C(5) = 90.7(3), C(1)−Os(1)−C(4) = 79.0(3), C(4)−Os(1)−C(5) = 39.0(3), C(1)−C(2)−C(3) = 114.8(7), C(2)−C(3)−C(4) = 113.2(7), C(3)−C(4)−C(5) = 114.3(7), O(1)−C(3)−C(4) = 122.5(8), O(1)−C(3)−C(2) = 124.3(8).

three-membered ring made up of C(4), C(5), and Os(1) is 104.8°. The geometry of the Os center can be viewed as a distorted octahedron with two PPh_3 ligands at the axial positions. The two chlorides, the vinyl carbon (C(1)), and the olefin double bond (C(4)=C(5)) are located at the equatorial coordination sites. The C(3)−O(1) distance of 1.233(4) Å is typical of a normal carbon−oxygen double bond, which is very close to that in the analogous complex[12] ((1,2,5-η)-2,4-dimethylpenta-1,3-dien-5-oyl)Ir(PMe$_3$)$_3$ (1.235(8) Å) reported by Bleeke.[6i] The bond distance between C(4) and C(5) is 1.435 Å, which is longer than typical C=C double bonds (∼1.35 Å) and shorter than typical C−C single bonds (∼1.55 Å), consistent with the value of a coordinated olefin.

A possible mechanism for the conversion of **2** to **3** under acidic conditions is shown in Scheme 2. The isomerization process may be initiated by protonation of the coordinated terminal alkyne to give intermediate **A**, which undergoes β-H elimination to give **B**. Keto–enol tautomerization of **B** to **C** followed by dissociation of the protic hydride ligand and subsequent coordination of the terminal double bond to the metal center produces **3**.

Treatment of **3** with excess PMe$_3$ in dichloromethane afforded complex **4** in 92% isolated yield. The structure of **4** has also been confirmed by X-ray diffraction (Figure 2).[13] In comparison with **3**, complex **4** has a similar structure, except the PPh$_3$ and one of the chloride ligands were substituted by PMe$_3$ ligands to give the cationic structure.

Although compound **4** is more stable than **2** and can be crystallized from solution, it slowly isomerizes in chloroform

Scheme 2. Possible Mechanism for the Conversion of 2 to 3
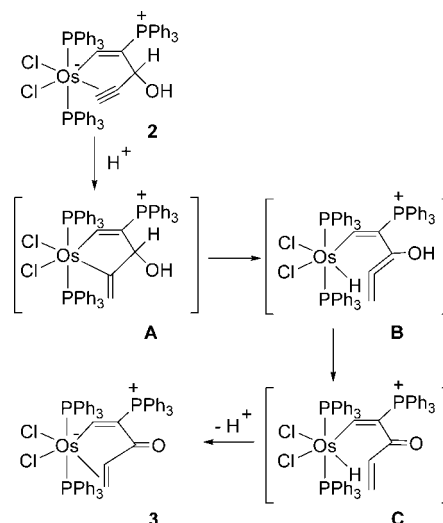
solution to the interesting *p*-osmaphenol **5**. A plausible mechanism for the formation of **5** is proposed in Scheme 3, which may involve an electronic tautomerization of **4** to give intermediate **D** and subsequent intermolecular deprotonation at the α-carbon. After a slow but mild process, *p*-osmaphenol **5** can be produced in high yield.

The structure of **5** has also been established by X-ray diffraction[14] as depicted in Figure 3. Complex **5** is a typical metallabenzene derivant. It contains a perfectly coplanar six-membered ring, which is reflected by the small mean rms deviation (0.023 Å) from the least-squares plane through the seven atoms C(1), C(2), C(3), C(4), C(5), O(1), and Os(1). The carbon−carbon distances in the central ring are approximately equivalent to each other. This structural feature indicates that the metallacycle has a delocalized π-electron system. A hydroxyl group para to the osmium atom can be established by the C−O bond length of 1.353(7) Å, which is close to those reported for the *o*-iridaphenol (1.331(20) Å)[6i] and the *o*-osmaphenol (1.370(10) Å).[5a] The ^{13}C NMR signal at 171.2 ppm (attributed to *C*OH) also supports the existence of a carbon−oxygen single bond. (In organic phenol, the signal can be observed at 155 ppm;[15] the downfield chemical shift of **5** is due to the phosphonium group on C(2) and the metal center.) The room-temperature ^{31}P NMR and ^{1}H NMR spectra are also consistent with X-ray diffraction. In the ^{31}P NMR (in CDCl$_3$) spectrum, a signal attributed to the phosphonium group on the ring was observed at 21.2 ppm (dt, $^4J(PP)$ = 31.6, 2.4 Hz), while two sets of signals attributed to Os*P*Me$_3$ were found at −41.1 ppm (dd, $^2J(PP)$ = 27.9 Hz, $^4J(PP)$ = 2.4 Hz) and −47.2 ppm (dt, $^2J(PP)$ = 27.9 Hz, $^4J(PP)$ = 31.6 Hz). Especially, the coupling constants of the latter ($^2J(PP) < {}^4J(PP)$) indicate that there is a stronger interaction between the phosphonium group and the trimeth-

(11) Crystallographic data for **3**: Mo Kα (λ = 0.710 73 Å) radiation at 223(2) K, monoclinic, space group $P2_1$, a = 11.438(2) Å, b = 20.166(4) Å, c = 14.170(3) Å, α = 90°, β = 113.80°, γ = 90°, V = 2990.4(11) Å^3, Z = 2, 10 333 reflections measured, 9867 unique reflections (R_{int} = 0.0354), which were used in all calculations, R1 (I > 2$\sigma(I)$) = 0.0479, wR2 (all data) = 0.1238. CCDC-635739 contains the supplementary crystallographic data for this complex.

(12) Other complexes analogous to **3**: (a) Hughes, R. P.; Trujillo, H. A.; Egan, J. W., Jr.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 2261. (b) Hughes, R. P.; Trujillo, H. A.; Egan, J. W., Jr.; Rheingold, A. L. *Organometallics* **1999**, *18*, 2766. (c) Hughes, R. P.; Trujillo, H. A.; Gauri, A. J. *Organometallics* **1995**, *14*, 4319.

(13) Crystallographic data for **4**: Mo Kα (λ = 0.710 73 Å) radiation at 100(2) K, monoclinic, space group $P2_1/n$, a = 19.161(2) Å, b = 9.914(1) Å, c = 26.300(2) Å, α = 90°, β = 105.754(1)°, γ = 90°, V = 4808.2(7) Å^3, Z = 4, 9400 reflections measured, 7073 unique reflections (R_{int} = 0.0472), which were used in all calculations, R1 (I > 2$\sigma(I)$) = 0.0298, wR2 (all data) = 0.0527. CCDC-635740 contains the supplementary crystallographic data for this complex.

(14) Crystallographic data for **5**: Mo Kα (λ = 0.710 73 Å) radiation at 100(2) K, orthorhombic, space group *Pbca*, a = 16.122(2) Å, b = 17.089(2) Å, c = 32.257(4) Å, α = 90°, β = 90°, γ = 90°, V = 8887.3(18) Å^3, Z = 8, 7734 reflections measured, 5399 unique reflections (R_{int} = 0.0923), which were used in all calculations, R1 (I > 2$\sigma(I)$) = 0.0424, wR2 (all data) = 0.0816. CCDC-635741 contains the supplementary crystallographic data for this complex.

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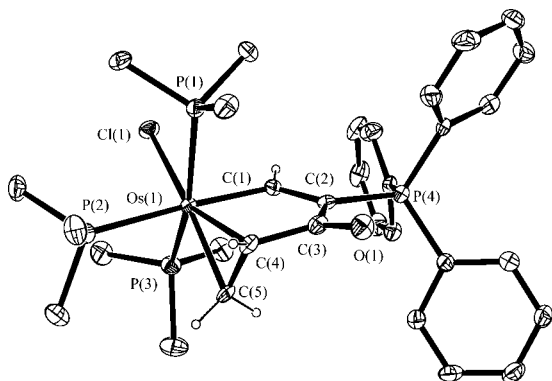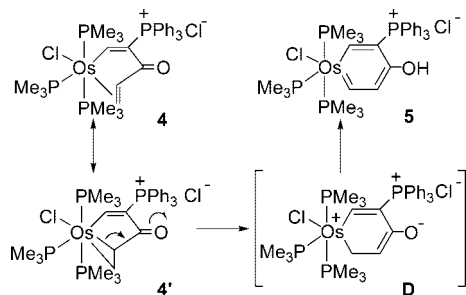
Figure 2. Molecular structure for the complex cation of **4** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)−C(1) = 2.019(4), Os(1)−C(5) = 2.143(3), Os(1)−C(4) = 2.153(3), O(1)−C(3) = 1.233(4), C(1)−C(2) = 1.376(5), C(2)−C(3) = 1.460(5), C(3)−C(4) = 1.497(5), C(4)−C(5) = 1.421(5); C(1)−Os-(1)−C(5) = 87.1(2), C(1)−Os(1)−C(4) = 78.1(1), C(4)−Os(1)−C(5) = 38.6 (1), C(1)−C(2)−C(3) = 114.0(3), C(2)−C(3)−C(4) = 112.8(3), C(3)−C(4)−C(5) = 115.9(3), O(1)−C(3)−C(4) = 123.5(3), O(1)−C(3)−C(2) = 123.7(4).

Figure 3. Molecular structure for the complex cation of **5** (50% probability). Some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)−C(1) = 2.032(5), Os(1)−C(5) = 1.918(6), O(1)−C(3) = 1.349(6), C(1)−C(2) = 1.388(8), C(2)−C(3) = 1.443(7), C(3)−C(4) = 1.377(8), C(4)−C(5) = 1.385(8); C(1)−Os(1)−C(5) = 87.3(2), Os(1)−C-(1)−C(2) = 130.0(4), C(1)−C(2)−C(3) = 121.9(5), C(2)−C(3)−C(4) = 123.5(5), C(3)−C(4)−C(5) = 124.6(5), C(4)−C(5)−Os(1) = 132.4(4).

Scheme 3. Proposed Mechanism for the Isomerization of 4 to 5

ylphosphine group which is opposite to the phosphonium group on the ring. In the ^{1}H NMR (in CDCl$_3$) spectrum, the four hydrogen signals on the central ring appeared at 16.5 (dd, OsC*H*CH), 13.3 (d, OsC*H*C(PPh$_3$)), 12.2 (s, CO*H*), and 8.4 ppm (dd, OsCHC*H*), respectively, consistent with the effect of the delocalized π-electronic system. The chemical shift of the proton opposite to the phosphonium group is significantly downfield compared with that at the ortho position, which also shows the effect of the delocalized π-electronic system.

In comparison with many other metallabenzenes and organic phenols, **5** is an air-stable complex (both in the solid state and in solution). The solution remains almost unchanged under air for over 1 week. To the best of our knowledge, **5** is the first
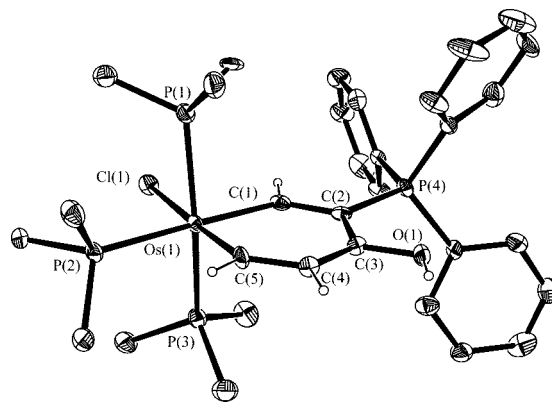
well-characterized *p*-osmaphenol. We have succeeded in preparing it under mild conditions via a comparatively convenient method. In comparison with the previously reported *o*-iradaphenol and *o*-osmaphenol, it is an extension of a metallaphenol with a different location of the hydroxyl group, on the carbon para to the metal atom. In addition, its stability should permit further study on the chemical and physical properties. Detailed mechanisms of these reactions and other chemical reactions or transformations as well as the optical and electrical properties of these interesting complexes are under investigation.

Supporting Information Available: Text giving experimental details, characterization data, and NMR spectra for all isolated compounds and CIF files giving X-ray data for **3−5**. This material is available free of charge via the Internet at http://pubs.acs.org.