Synthesis and Transformations of Triosmium Carbonyl Cluster Complexes Containing Bridging Aryl Ligands

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Supporting Information

ABSTRACT: The reaction of Os3(CO)10(NCMe)2 (1) with C6H5Au(PPh3) has yielded the complex Os3(CO)10(μ-η2-C6H5)(μ-AuPPh3) (2), which contains a bridging η2-phenyl ligand and a Au(PPh3) group that bridges the same unsaturated Os−Os bond in the 46-electron cluster complex. When it was heated to reflux in an octane solution (125 °C), compound 2 was decarbonylated and converted to the complex Os3(CO)9(μ-η2-C6H4)(μ-AuPPh3)(μ-H) (3), which contains a triply bridging benzene ligand by a CH cleavage on the bridging phenyl ring. The reaction of Os3(CO)10(NCMe)2 with (1-C10H7)Au(PPh3) (1-C10H7 = 1-naphthyl) yielded the complex Os3(CO)9(μ-2-2'-C10H6)(μ-AuPPh3) (4), which exists as two isomeric forms in the solid state. A 1,2-hydrogen shift in the naphthyl ligand occurred in the formation of 4. The green isomer 4a is structurally similar to 2 and contains a bridging η2-2-naphthyl ligand and a bridging Au(PPh3) group and is electronically unsaturated overall. The pink isomer 4b contains a bridging η2-2-naphthyl ligand and a bridging Au(PPh3) group and is electronically saturated. The pink isomer is found in hexane solution and was converted to the complex Os3(CO)9(μ-2-2'-C6H4)(μ-AuPPh3)(μ-H) (5) when heated to reflux in octane (125 °C) for 30 min. Compound 5 contains a triply bridging 1,2-naphthylene ligand.

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The unsaturation in 2 results in delocalized bonding across the Os(1), Os(2), and C(1) atoms. The nature of this delocalized bonding can be seen in the DFT calculated molecular orbitals HOMO-3, HOMO-5, and HOMO-9 of 2, which are shown in Figure 2.14 As a result of a small HOMO/LUMO gap of 1.52 eV (see Figure 2) there is a strong absorption at \( \lambda \approx 632 \text{ nm} \) (\( e = 560 \text{ M}^{-1} \text{cm}^{-1} \)) in the visible region of the spectrum, which is responsible for the bright green color of the complex.14

When a solution of 2 was heated to reflux in octane solvent, it was decarbonylated and transformed into the benzyne compound Os₃(CO)₉(\( \mu - \text{C}_{10} \text{H}_7 \))\( (\mu - \text{AuPPh}_3) \)(\( \mu - \text{H} \)) (3) in 94% yield. Compound 3 was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 3. The structure of 3 is similar to that of Os₃(CO)₉(\( \mu - \text{C}_{10} \text{H}_7 \))\( (\mu - \text{AuPPh}_3) \)(\( \mu - \text{H} \)).

C₆H₄)(\( \mu - \text{H} \))₂ except for the presence of the bridging AuPPh₃ in the place of one of the bridging hydride ligands.² Compound 3 was formed by the loss of a CO ligand from the Os(CO)₄ group and the activation of one of the ortho-positioned CH bonds in the bridging phenyl ligand in 2. It is an electronically saturated 48-electron complex.

There have been no previous reports of naphthylene ligands; therefore, for comparison, we also investigated the reaction of 1 with 1-NpAu(PPh₃)₁₅ (1-Np = 1-naphthyl = 1-C₁₀H₇). The reaction of 1-NpAu(PPh₃) with 1 provided a product having the formula Os₃(CO)₉(2-Np)(\( \mu - \text{AuPPh}_3) \) (4) in 58% yield. Unlike 2, the color of 4 is pink in solution. Interestingly, however, crystals grown from hexane solutions at room temperature are green and are similar in color to those of 2, but crystals of 4 grown from hexane at –25 °C are pink, like the solutions. The molecular structures of 4 in both crystal modifications were established crystallographically. The structure found in the green crystals will be called 4a and the isomeric structure found in the pink crystals will be called 4b.

An ORTEP diagram of the molecular structure of 4a is shown in Figure 4. The structure of 4a is similar to that of 2 except that it contains an \( \eta^2 \)-2-Np ligand that bridges the AuPPh₃-bridged Os–Os bond (Os₁–C₁ = 2.313(11) Å and Os₂–C₁ = 2.332(11) Å). The plane of the C₁₀ ring is virtually perpendicular to the plane of the Os₃ triangle. A 1,2-hydrogen shift in the naphthyl ligand must have occurred in the formation of 4a. If the 2-Np ligand and the AuPPh₃ group both serve as 1-electron donors, then the cluster of 4a contains 46 electrons and is unsaturated just like 2. Accordingly, the Os₁–Os₂ bond is short (2.7484(6) Å) compared to the other Os–Os bonds (Os₁–Os₃ = 2.8745(6) Å, Os₂–Os₃ = 2.8668(6) Å).

An ORTEP diagram of the molecular structure of 4b is shown in Figure 5. This structure is an isomer of 4a, and it
Os1 = 2.7424(6), Au1 C1 = 2.332(11). 2-Np = 2.7573(6), Au1 C6 = 2.369(10), Os2 = 2.7484(6), Os1 to both osmium atoms (Os1 Os2 bond distance is slightly longer.16,17 As a result, the plane of the bond. Naphthyl atom C(1) is bonded to Os(2) (Os2 C1 = 2.123(11), Os2−C6 = 2.544(10) Å), although the distance is slightly longer.16,17 As a result, the plane of the planar C10 ring is not perpendicular to the Os3 triangle but is 49.27(0.27)° from the Os3 plane. The C1−C6 distance is 1.380(14) Å. In this molecule the 2-Np ligand serves as a 3-electron donor and the AuPPh3 group serves as a 1-electron donor; thus, the osmium atoms in the pink isomer 4b contain a total of 48 electrons. The trisodium cluster in 4b is electronically saturated, and as a result, there are no unusually short Os−Os bonds. The doubly bridged Os1−Os2 bond (2.8538(6) Å) is nearly as long as the other two Os−Os bonds (Os1−Os3 = 2.8997(6) Å, Os2−Os3 = 2.8899(7) Å). As a result, the HOMO/LUMO gap in 4b is larger than that in 2 and the absorption in the visible spectrum lies at higher energy (λ = 518 nm, ε = 300 cm−1 M−1)13 which accounts for its pink color. Compound 4b must obviously convert to 4a when crystals are grown at room temperature. Conversely, when the green crystals of 4a are dissolved in hexane, the solutions are pink, indicating a facile and apparently complete transformation from 4a back to 4b. We have not yet obtained any spectroscopic evidence for the presence of significant amounts of isomer 4a in solutions at room temperature and at low temperature.18 Further investigations of the 4a−4b transformation are in progress.

When a solution of 4a was heated to reflux in octane solvent, it was decarbonylated and transformed into the naphthyl compound Os3(CO)9(μ-1,2-η2-C10H6)(μ-AuPPh3)(μ-H) (5) in 63% yield. Compound 5 was also characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 6. The structure of 5 is similar to that of 3. Compound 5 contains the first example of an unsubstituted triply bridging naphthyne ligand. The naphthyl C−C bond distance (C1−C6 = 1.435(16) Å) is similar in length to that contains a σπ-coordinated η2-2-Np ligand that bridges the AuPPh3-bridged Os−Os bond. Naphthyl atom C(1) is bonded to both osmium atoms (Os1−C1 = 2.313(11) Å and Os2−C1 = 2.332(11) Å). Interestingly, naphthyl atom C(6) is also bonded to Os(2) (Os2−C6 = 2.544(10) Å), although the distance is slightly longer.16,17 As a result, the plane of the

![Figure 4](image-url) ORTEP diagram of the molecular structure of Os3(CO)9(μ-2-Np)(μ-AuPPh3) (4a) obtained from the green crystals, with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.7484(6), Os1−Os3 = 2.332(11), Os2−Os3 = 2.369(10), Au1−Os1 = 2.7573(6), Au1−Os2 = 2.8146(6), Os1−C1 = 2.123(11), Os2−C1 = 2.544(10), C1−C6 = 1.380(14).

![Figure 5](image-url) ORTEP diagram of the molecular structure of Os3(CO)9(μ-1,2-η2-C10H6)(μ-AuPPh3)(μ-H) (4b), with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.7484(6), Os1−Os3 = 2.7573(6), Os2−Os3 = 2.332(11), Au1−Os1 = 2.7573(6), Au1−Os2 = 2.8146(6), Os1−C1 = 2.174(11), Os2−C1 = 2.332(11), Os3 = 2.8997(6), Os2 = 2.8899(7), Au1 = 2.7923(7), Os3−C6 = 2.085(12), Au1−P1 = 2.284(3), C1−C6 = 1.435(16).

![Figure 6](image-url) ORTEP diagram of the molecular structure of Os3(CO)9(μ-1,2-η2-C10H6)(μ-AuPPh3)(μ-H) (5), with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.8538(6), Os1−Os3 = 2.8899(7), Os2−Os3 = 2.8997(6), Au1−Os1 = 2.8745(6), Au1−Os2 = 2.7772(6), Os1−C1 = 2.313(11), Os2−C1 = 2.298(11), Os2 = 2.370(12), Os3−C6 = 2.085(12), Au1−P1 = 2.284(3), C1−C6 = 1.435(16).
found in the benzene ligand in 3. The Au- and H-bridged bonds (Os1–Os2 = 2.895(6) Å, Os1–Os3 = 2.9882(7) Å) are longer than the remaining Os–Os bond (Os2–Os3 = 2.7494(6) Å). The naphthyne ligand in 5 is a 4-electron donor, and the metal atoms thus contain a total of 48 electrons and are electronically saturated.

This work has demonstrated the multicenter conversion of η1-bridging aryl ligands into η4-triply bridging arylene ligands. It seems plausible that other complexes containing triply bridging arylene ligands may be formed via unobserved intermediates containing η2-bridging aryl ligands. The existence of two isomeric forms of the bridging naphthyl ligand and their facile interconversion in compound 4 is intriguing and raises the possibility of two slightly different pathways, via 4a or 4b, for the formation of the triply bridging naphthyne ligand in 5 (see Scheme 1). Efforts to try to distinguish between these two pathways by computational methods are in progress.

**Scheme 1**

![Scheme 1](image)

**ASSOCIATED CONTENT**

* Supporting Information  
Text, figures, tables, and CIF files giving details of the synthesis and characterizations of compounds 2–5, computational analyses for 2, and data for each of the structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes  
The authors declare no competing financial interest.

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