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

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ⓢ Supporting Information

ABSTRACT: The reaction of $Os_3(CO)_{10}(NCMe)_2$ (**1**) with $C_6H_5Au(PPh_3)$ has yielded the complex $Os_3(CO)_{10}(\mu,\eta^1\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$ (**2**), which contains an bridging η^1-phenyl ligand and a $Au(PPh_3)$ 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 $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}AuPPh_3)(\mu\text{-}H)$ (**3**), which contains a triply bridging benzyne ligand by a CH cleavage on the bridging phenyl ring. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $(1\text{-}C_{10}H_7)Au(PPh_3)$ $(1\text{-}C_{10}H_7 = 1\text{-naphthyl})$ yielded the complex $Os_3(CO)_{10}(\mu\text{-}2\text{-}C_{10}H_7)(\mu\text{-}AuPPh_3)$ (**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 η^1-2-naphthyl ligand and a bridging $Au(PPh_3)$ group and is electronically unsaturated overall. The pink isomer **4b** contains a bridging η^2-2-naphthyl ligand and a bridging $Au(PPh_3)$ group and is electronically saturated. The pink isomer is found in hexane solution and was converted to the complex $Os_3(CO)_9(\mu_3\text{-}C_{10}H_6)(\mu\text{-}AuPPh_3)(\mu\text{-}H)$ (**5**) when heated to reflux in octane (125 °C) for 30 min. Compound **5** contains a triply bridging 1,2-naphthyne ligand.
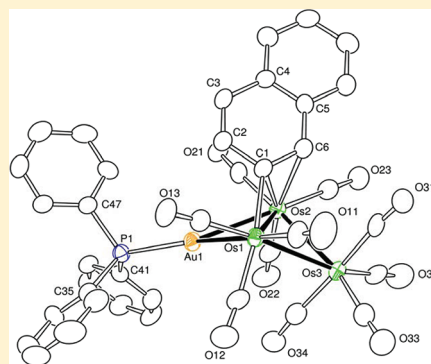
Years ago Johnson and Lewis showed that the triosmium carbonyl complex $Os_3(CO)_{10}(NCMe)_2$ (**1**) reacts with arenes to yield the complexes $Os_3(CO)_{10}(\mu_3\text{-}C_6H_2R^1R^2)(\mu\text{-}H)_2$ (R^1, R^2: H, H; H, Me; H, Pr^n; H, CHCHPh; H, Cl; Me, Me), which contain triply bridging aryne ligands.[1] Over the years, a variety of triosmium and triruthenium aryne complexes have also been obtained from the reactions of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with aryl-substituted phosphines,[2,3] arsines,[3] stibines,[4] thioethers,[5] etc. at elevated temperatures. To date, very little has actually been established with regard to the mechanism(s) of the formation of the aryne ligands in these reactions. Presumably, they begin with the loss of a ligand(s) from the cluster, which is followed by a series of two CH cleavages from the arene or a cleavage of an aryl group from an aryl-substituted group V or VI donor and a cleavage of one CH bond from the aryl ligand. Hartwig et al. have investigated the transformation of a σ-phenyl ligand into an η^2-benzyne ligand in a mononuclear ruthenium complex.[6] Johnson et al. showed that the triply bridging $\eta^6\text{-}C_6H_6$ ligand in the complex $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$ was converted into a benzyne ligand in the complex $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)_2$ under irradiation.[7]

Herein we report the first examples of the formation of triply bridging arynes directly from bridging aryl ligands in stable unsaturated triosmium complexes generated from reactions of $Os_3(CO)_{10}(NCMe)_2$ with the gold complexes $ArylAu(PPh_3)$ (Aryl = phenyl, naphthyl ($C_{10}H_7$)). The compound $C_6H_5Au(PPh_3)$[8] can be regarded as a close relative of C_6H_6 itself; the $Au(PPh_3)$ is isolobal with H and also contains one odd electron for bonding to the carbon atom of the C_6H_5 group.[9] Compound **1** reacts with $C_6H_5Au(PPh_3)$ in CH_2Cl_2 at 40 °C

by elimination of the two NCMe ligands and an oxidative addition of the Au−C bond of the $C_6H_5Au(PPh_3)$ to the $Os_3(CO)_{10}$ group to give the complex $Os_3(CO)_{10}(\mu\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$ (**2**) in 47% yield. The structure of **2** was established crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 1. The molecule contains a triangular cluster of three osmium atoms with a η^1-bridging phenyl ligand and a bridging $AuPPh_3$ group across the Os1−Os2 bond. The bond distances to the carbon atom C(1) of the bridging phenyl group, Os1−C1 = 2.191(13) Å and Os2−C1 = 2.236(11) Å, are shorter (on the average) than those found in two previously reported triosmium cluster complexes containing bridging phenyl ligands: $Os_3(CO)_8(\mu_3\text{-}Se_2)(\mu\text{-}Ph)(\mu\text{-}PhC=O)$[10] (2.24(2) and 2.51(2) Å) and $Os_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}Ph)(\mu\text{-}PhC_6H_4)$[2a] (2.19 and 2.39 Å). The doubly bridged Os1−Os2 bond in **2** is significantly shorter (2.7521(6) Å) than the two other Os−Os bonds (Os1−Os3 = 2.8785(5) Å, Os2−Os3 = 2.8746(5) Å) in **2**. Assuming that the phenyl ligand and the Au(PPh_3) group are both 1-electron donors, then compound **2** contains a total of 46 electrons at the metal atoms and the cluster is formally unsaturated. Compound **2** is electronically similar to the 46-electron triosmium cluster complexes $Os_3(CO)_{10}(\mu\text{-}H)_2$,[11] $Os_3(CO)_{10}(\mu\text{-}AuPEt_3)_2$,[12] and $Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}H)$,[13] whose doubly bridged Os−Os bonds (2.683(1),[11b] 2.684(1),[12] and 2.699(1) Å,[13] respectively) are also significantly shorter than the unbridged Os−Os bonds.
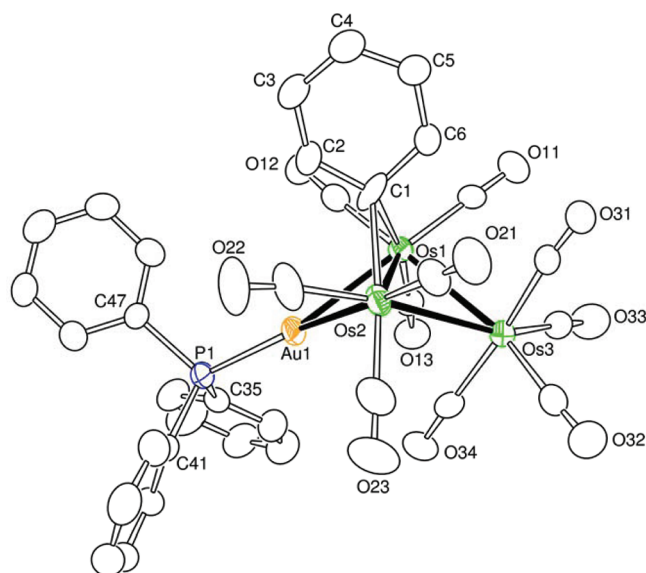
**Figure 1.** ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu$-$C_6H_5)(\mu$-AuPPh$_3$) (**2**), with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): Os1−Os2 = 2.7521(6), Os1−Os3 = 2.8785(5), Os2−Os3 = 2.8746(5), Os1−C1 = 2.191(13), Au1−Os1 = 2.7621(5), Au1−Os2 = 2.7668(5), Os2−C1 = 2.236(11); Os1−C1−Os2 = 76.9(4).

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
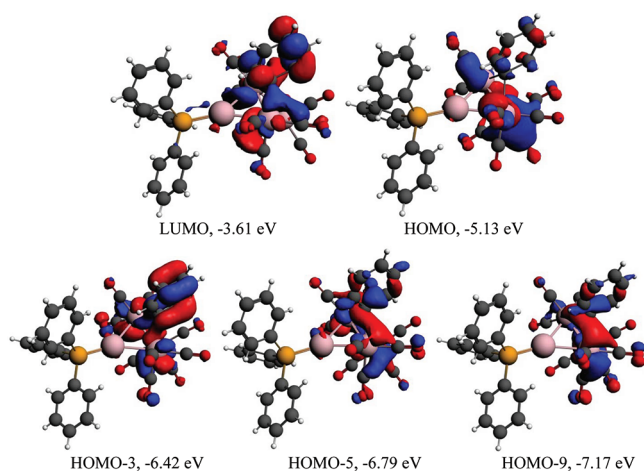
Figure 2. Contour diagrams of the LUMO, HOMO, HOMO-3, HOMO-5, and HOMO-9 with calculated energies showing the bonding of the η^1-bridging phenyl ligand to the osmium atoms in **2**.

eV (see Figure 2) there is a strong absorption at λ 632 nm (ε = 560 M$^{-1}\cdot$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 $Os_3(CO)_9(\mu_3$-$C_6H_4)(\mu$-AuPPh$_3$)(μ-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 $Os_3(CO)_9(\mu_3$-
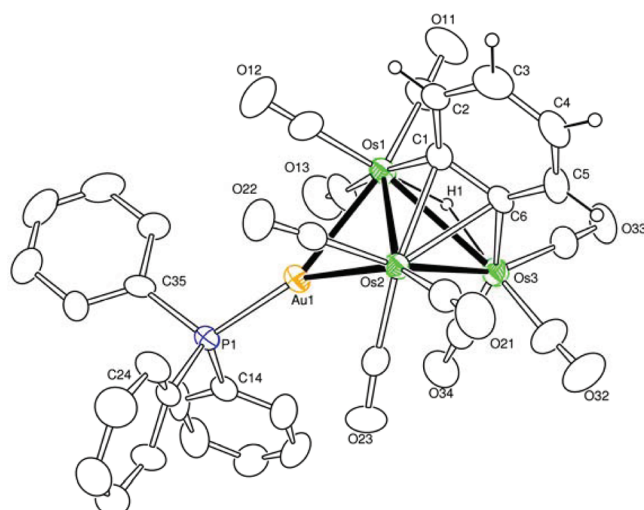
Figure 3. ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu_3$-$C_6H_4)(\mu$-AuPPh$_3$)(μ-H) (**3**), with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.8902(6), Os1−Os3 =3.0229(7), Os2−Os3 = 2.7560(6), Au1−Os1 =2.7507(6), Au1−Os2 = 2.8131(6), Os1−C1 = 2.085(10), Os3−C6 = 2.097(10), Os2−C1 = 2.285(10), Os2−C6 = 2.374(10), Os1−H1 = 1.69(9), Os3−H1 = 1.99(9), C1−C6 = 1.429(14).

$C_6H_4)(\mu$-H)$_2$ except for the presence of the bridging AuPPh$_3$ in the place of one of the bridging hydride ligands.[1] The benzyne C−C bond distance C1−C2 = 1.429(14) Å is typical of those of other benzyne ligands.[2−5] 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 naphthyne ligands; therefore, for comparison, we also investigated the reaction of **1** with 1-NpAu(PPh$_3$)[15] (1-Np = 1-naphthyl = 1-C$_{10}$H$_7$). The reaction of 1-NpAu(PPh$_3$) with **1** provided a product having the formula $Os_3(CO)_{10}$(2-Np)(μ-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 η^1-2-Np ligand that bridges the AuPPh$_3$-bridged Os−Os bond (Os1−C1 = 2.313(11) Å and Os2−C1 = 2.332(11) Å). The plane of the C$_{10}$ ring is virtually perpendicular (86.1(2)°) to the plane of the Os$_3$ 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 AuPPh$_3$ 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
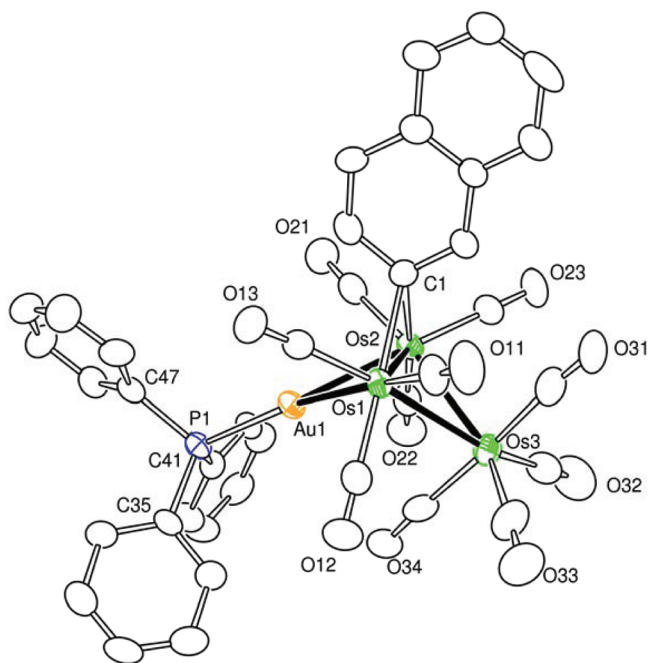
Figure 4. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu$-2-Np$)(\mu$-AuPPh$_3$) (**4a**) obtained from the green crystals, with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.7484(6), Os1−Os3 = 2.8745(6), Os2−Os3 = 2.8668(6), Au1−Os1 = 2.7424(6), Au1−Os2 = 2.7772(6), Os1−C1 = 2.313(11), Os2−C1 = 2.332(11).
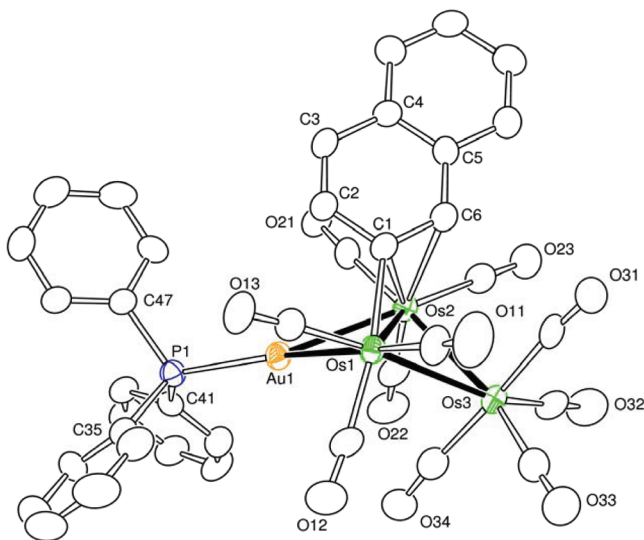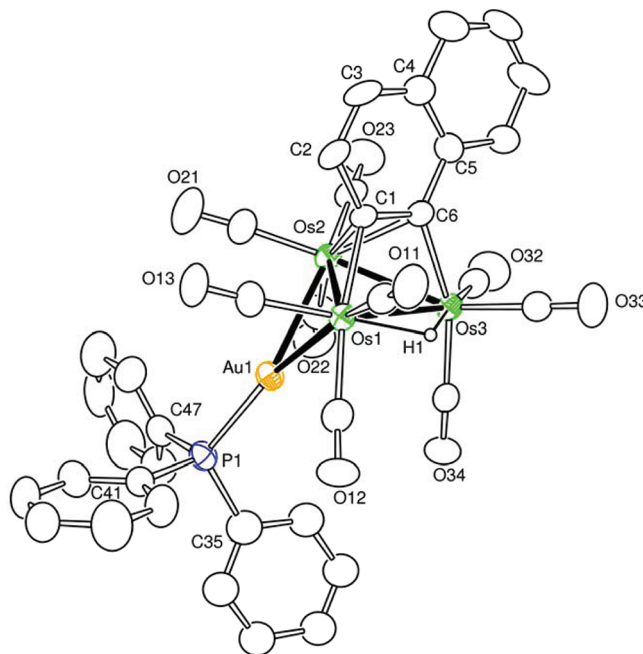

Figure 5. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu_3$-η^2-2-Np$)(\mu$-AuPPh$_3$) (**4b**), with thermal ellipsoids given at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å): Os1−Os2 = 2.8538(6), Os1−Os3 = 2.8997(6), Os2−Os3 = 2.8899(7), Au1−Os1 = 2.7573(6), Au1−Os2 = 2.8146(6), Os1−C1 = 2.174(11), Os2−C1 = 2.369(10), Os2−C6 = 2.544(10), C1−C6 = 1.380(14).

contains a σ,π-coordinated η^2-2-Np ligand that bridges the AuPPh$_3$-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

planar C_{10} ring is not perpendicular to the Os$_3$ triangle but is 49.27(0.27)° from the Os$_3$ 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 AuPPh$_3$ group serves as a 1-electron donor; thus, the osmium atoms in the pink isomer **4b** contain a total of 48 electrons. The triosmium 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 = 3009 cm^{-1} M^{-1}),[14] 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 **4** was heated to reflux in octane solvent, it was decarbonylated and transformed into the naphthyne compound $Os_3(CO)_9(\mu_3$-1,2-η^2-$C_{10}H_6)(\mu$-AuPPh$_3)(\mu$-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 naphthyne C−C bond distance (C1−C6 = 1.435(16) Å) is similar in length to that


Figure 6. ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu_3$-1,2-η^2-$C_{10}H_6)(\mu$-AuPPh$_3)(\mu$-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 = 2.8950(6), Os1−Os3 = 2.9882(7), Os2−Os3 = 2.7494(6), Os1−C1 = 2.123(11), Os2−C1 = 2.298(11), Os2−C6 = 2.370(12), Os1−Au1 = 2.7395(7), Os2−Au1 = 2.7923(7), Os3−C6 = 2.085(12), Au1−P1 = 2.284(3), C1−C6 = 1.435(16).

found in the benzyne ligand in **3**. The Au- and H-bridged bonds (Os1−Os2 = 2.8950(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 η^1-bridging aryl ligands into η^2-triply bridging aryne ligands. It seems plausible that other complexes containing triply bridging aryne ligands may be formed via unobserved intermediates containing η^1-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
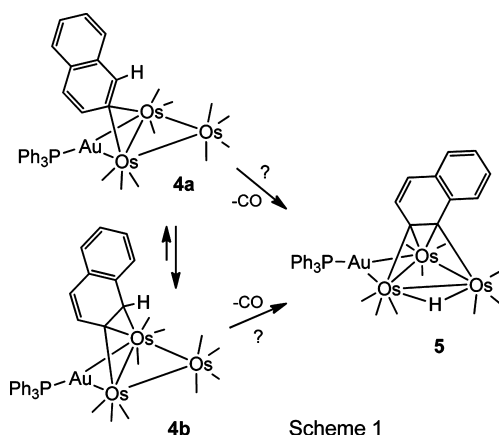
■ ASSOCIATED CONTENT

S 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.

■ ACKNOWLEDGMENTS

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(17) A triply bridging diaminonaphthyl ligand having a η^2-C,C coordination was observed in the compound $Os_3(CO)_9[\mu_3\text{-}1,8\text{-}(NH_2)_2C_{10}H_5](\mu\text{-H})$; see: Cabeza, J. A.; Nöth, H.; de Jesus Rosales-Hoz, M.; Sanchez-Cabrera, G. *Eur. J. Inorg. Chem.* **2000**, 2327−2332.

(18) ^{1}H NMR and ^{31}P NMR spectra of solutions of **4** in toluene-d_8 solvent at room temperature and at −80 °C indicate the presence of only one isomer, and on the basis of color, it is the pink isomer **4b**.