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Bridging phenyl ligands. Unsaturated mercury-triosmium carbonyl cluster complexes containing bridging phenyl ligands

Richard D. Adams*, Zhongwen Luo, Yuen Onn Wong

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

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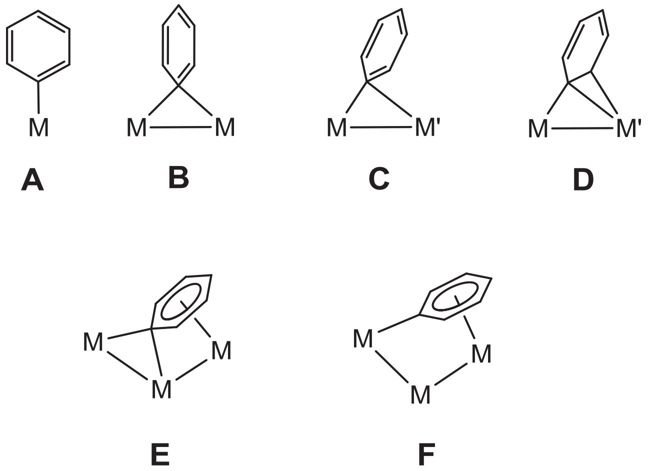
ABSTRACT

The gold phosphine group in the complex $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-AuPPh}_3)$, **1** can be replaced by mercury halide groups by reactions with mercury halides. The reaction of **1** with HgI_2 yielded the new compound $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-HgI})]_4$, **2** in 19% yield. The reaction of **1** with $HgCl_2$ yielded the new compound $Os_4(CO)_{13}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-Cl})_3$, **3** in 18% yield. When heated to reflux in cyclohexane solvent, compound **2** was converted into the compound $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-H})(\mu_3\text{-Hg})]_2Os(CO)_4$, **4** in 11% yield. All new compounds were characterized by single-crystal X-ray diffraction analyses. Compound **2** is a tetramer of the unit "$Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-HgI})$" that is held together by a cubane-like Hg_4I_4 core having D_2 symmetry. Each triosmium cluster is formally electronically unsaturated and contains one edge-bridging phenyl ligand. Compound **3** contains a $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-Hg})$ cluster, but in this case the Hg atom bridges to an additional $Os(CO)_3$ group via three bridging chloride ligands. Compound **4** contains two $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-H})(\mu_3\text{-Hg})$ clusters that are linked by a bridging $Os(CO)_4$ group. Each Os_3 cluster in **4** contains a triply bridging C_6H_4 benzyne ligand and one bridging hydrido ligand.

Introduction



The phenyl group typically coordinates to a single metal atom as a η^1-ligand serving as a single electron donor, **A** [1]. Over the years, a number of examples of polynuclear metal complexes containing bridging aryl ligands have been reported. Bridging ligands can coordinate as symmetrical η^1-ligands, **B** [2,3] or asymmetrical, η^1-semibridging ligands **C** [4] serving as one electron donors; as η^2-**D** ligands serving as three electron donors [5], or even as various $\sigma + \pi$ coordinated ligands μ-η^6-**E** or μ-η^6-**F** serving formally as 7-electron donors [6,7]. Still other coordination modes exist and it is likely that others will be found.

Recently, we reported a family of electronically unsaturated triosmium carbonyl ligands $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-Ar})(\mu\text{-AuPPh}_3)$, **1**, Aryl = phenyl = Ph, **1**, 2-naphthyl, 2-pyryl and 4-pyryl containing bridging aryl ligands of the type **B**.[8] Calculations showed that the bonding of the ring to the metal atoms included a significant amount π-electron donation from the ring to the metal atoms. When heated, these compounds eliminated CO and the edge-bridging aryl ligand was converted into a triply-bridging aryne ligand, e.g. eq. (1).

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* Corresponding author.
E-mail address: Adamsrd@mailbox.sc.edu (R.D. Adams).

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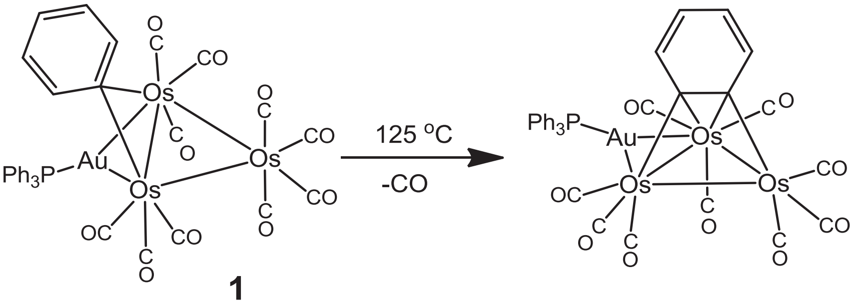

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(1)

In the present work, we have investigated the reactions of complex **1** with mercuric halides. In the reaction of **1** with HgI_2, it was found that the bridging Au(PPh_3) group was replaced by a bridging HgI group. The product of empirical formula "$Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}Ar)(\mu\text{-}HgI)$", then condensed by a self-assembly to form the tetramer, $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}Ar)(\mu\text{-}HgI)]_4$, **2**, in the solid state that is held together by formation of a rare cubane-shaped Hg_4I_4 core. The reaction of **1** with $HgCl_2$ yielded the compound $Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}Hg)(\mu\text{-}Cl)_3Os(CO)_3$, **3** which contains an unsaturated phenyl bridged Os_3 cluster. This is linked to an $Os(CO)_3$ group by a bridging $HgCl_3$ group. When heated compound **2** was converted to the new compound yellow $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]_2Os(CO)_4$, **4** which contains two $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]$ clusters with each having a triply bridging benzyne ligands. The two Os_3 clusters in **4** are linked by a bridging $Os(CO)_4$ group. The results of our studies of the synthesis and characterizations of compounds **2**–**4** are described in this report.

Experimental details

General data

Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Chromatographic separations were performed on Biobeads, S-X1 gel permeation beads 200–400 mesh, that were obtained from Bio-Rad Laboratories. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. $Os_3(CO)_{10}(\mu\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$, **1** was prepared according to the previously reported procedure [8a].

*Reaction of $Os_3(CO)_{10}(\mu_2\text{-}C_6H_5)(\boldsymbol{\mu}\text{-}AuPPh_3)$, **1** with HgI_2*

43.4 mg (0.0955 mmol) of HgI_2 was added to 84.0 mg (0.060 mmol) of $Os_3(CO)_{10}(\mu\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$ and dissolved in 30 mL of dichloromethane. The reaction was heated to reflux for 15 min. The solvent was removed *in vacuo*, and the dark green product was then isolated by chromatography on Bio-Beads by using a 4:1 hexane/methylene chloride solvent mixture for elution. 16.3 mg (19% yield) of dark green crystals of $[Os_3(CO)_{10}(\mu\text{-}C_6H_5)(\mu\text{-}HgI)]_4$, **2** were obtained following evaporation of the solvent. (Ph_3P)AuI is the major colorless coproduct in this reaction. It can be removed with difficulty by a series of fractional crystallizations. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2100(m), 2057(s), 2049(m), 2021(m), 2013(s), 1995(m), 1984(w). ^1H NMR (CD_2Cl_2, 25 °C, TMS, in ppm) $\delta = 8.95$ (d, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph), 8.76 (d, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph), 8.31 (t, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph), 7.15 (t, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph), 6.90 (t, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph). Mass Spec. EI/MS *m*/*z*: 2506 and 1256.

*Reaction of $Os_3(CO)_{10}(\boldsymbol{\mu}\text{-}C_6H_5)(\boldsymbol{\mu}\text{-}AuPPh_3)$, **1** with $HgCl_2$*

21.4 mg (0.078 mmol) of $HgCl_2$ was added to 56.0 mg (0.040 mmol) of **1** dissolved in 50 mL of dichloromethane. The reaction was heated to reflux for 15 min. The solvent was then removed *in vacuo*, and the product was isolated by fractional crystallization by using a hexane/methylene chloride solvent mixture to give 10.0 mg (18% yield) of dark green $Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}Hg)(\mu\text{-}Cl)_3Os(CO)_3$, **3**. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2130(m), 2101(m), 2072(w), 2061(s), 2053(m), 2048(m), 2032(w), 2020(m), 2012(s), 2000(m), 1987(w). ^1H NMR (CD_2Cl_2, 25 °C, TMS, in ppm) $\delta = 8.86$ (d, 1H, $^3J_{H\text{-}H} = 6$ Hz, Ph), 8.82 (d, 1H, $^3J_{H\text{-}}$

Table 1
Crystallographic data for compounds **2**, **3** and **4**.

Compound	**2**	**3**	**4**
Empirical formula	$Os_{12}Hg_4I_4O_{40}C_{64}H_{20}$	$Os_4HgCl_3O_{13}C_{19}H_5$	$Os_7Hg_2O_{22}C_{34}H_{10}$
Formula weight	5021.56	1508.97	2503.00
Crystal system	Orthorhombic	Triclinic	Monoclinic
Lattice parameters			
a (Å)	12.3967(4)	9.1741(4)	29.1051(12)
b (Å)	29.9460(9)	10.0883(4)	10.9507(4)
c (Å)	28.1291(8)	16.2759(7)	14.7602(6)
α (deg)	90.0	82.851(1)	90.00
β (deg)	90.0	75.574(1)	97.999(1)
γ (deg)	90.0	89.921(1)	90.00
V ($Å^3$)	10442.4(6)	1446.83(11)	4658.6(3)
Space group	*Ccca* (#68)	P^{-}-1 (#2)	*C*2/c (#15)
Z value	4	2	4
ρ_{calc} (g/cm^3)	3.19	3.46	3.57
μ (Mo Kα) (mm^{-1})	21.6	23.12	25.65
Temperature (K)	294(2)	294(2)	294(2)
$2\Theta_{max}$ (°)	49.40	50.06	50.04
No. Obs. ($I > 2\sigma(I)$)	4157	4328	3657
No. Parameters	281	361	297
Goodness of fit (GOF)	1.112	1.079	1.075
Max. shift in cycle	0.013	0.001	0.025
Residuals[a]: R1; wR2	0.0347; 0.1004	0.0287; 0.0616	0.0389; 0.1094
Absorption Correction, Max/min	Multi-scan 1.00/0.503	Multi-scan 1.00/0.66	Multi-scan 1.00/0.39
Largest peak in Final Diff. Map ($e^-/Å^3$)	1.947	1.151	3.484

[a] $R1 = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $wR2 = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$; $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data}-n_{vari})]^{1/2}$.

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$_{\text{H}} = 6$ Hz, Ph), 8.30 (t, 1H, $^3J_{\text{H-H}} = 6$ Hz, Ph), 7.11 (t, 1H, $^3J_{\text{H-H}} = 6$ Hz, Ph), 6.87 (t, 1H, $^3J_{\text{H-H}} = 6$ Hz, Ph). Mass Spec. EI/MS *m*/*z*: 1510.

Transformation of **2** *into* $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]_2Os(CO)_4$, **4**

14.2 mg (0.0058 mmol) of **2** was dissolved in cyclohexane. The solution was heated to reflux for 70 min. The solvent was then removed *in vacuo*. 1.5 mg (11% yield) of yellow $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]_2Os(CO)_4$, **4** was isolated by TLC on silica gel by using a hexane/methylene chloride solvent mixture (4/1, v/v). Spectral data for **4**: IR ν_{CO} (cm^{-1} in hexane): 2101(w), 2087(w), 2080(m), 2070(s), 2052(s), 2024(w), 2017(m), 2012(w), 1996(m), 1989(m). ^{1}H NMR (CD_2Cl_2, 25 °C, TMS, in ppm) $\delta = 7.93$ (d, 1H, $^3J_{\text{H-H}} = 6$ Hz, C_6H_4), 7.92 (d, 1H, $^3J_{\text{H-H}} = 6$ Hz, C_6H_4), 6.88 (d, 1H, $^3J_{\text{H-H}} = 6$ Hz, C_6H_4), 6.87 (d, 1H, $^3J_{\text{H-H}} = 6$ Hz, C_6H_4), -21.05 (s, 1H, hydride); Mass Spec. EI/MS *m*/*z*: 2504.

Crystallographic analyses

Dark green single crystals of **2** and **3** suitable for X-ray diffraction analyses were obtained by slow evaporation of the solvent at room temperature from solutions of the pure compound in hexane solvent. Orange single crystals of **4** were obtained by slow evaporation of solvent from a solution in hexane solvent at 5 °C. The data crystals were glued onto the end of thin glass fibers. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [9]. Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and were refined by full-matrix least-squares on F^2 by using the SHELXTL software package [10]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compound **2** crystallized in the orthorhombic crystal system. The space group *Ccca* was indicated by the systematic absences in the data and confirmed by the successful solution and refinement of the structure. The crystal structure of **2** contains a significant void of 426 Å^3. The void appeared to contain a highly disordered hexane molecule that was cocrystallized from the crystallization solvent. Our efforts to devise and refine a suitable disorder model were unsuccessful and the void was ignored in the final refinements. Compound **3** crystallized in the triclinic crystal system. The space group *P*-1 was confirmed by the successful solution and refinement of the structure. Compound **4** crystallized in the monoclinic crystal system. The space group *C*2/*c* was indicated by the systematic absences in the data and confirmed by the successful solution and refinement of the structure. The Os – H distances in **4** were refined with distance contraints of 1.80 Å.

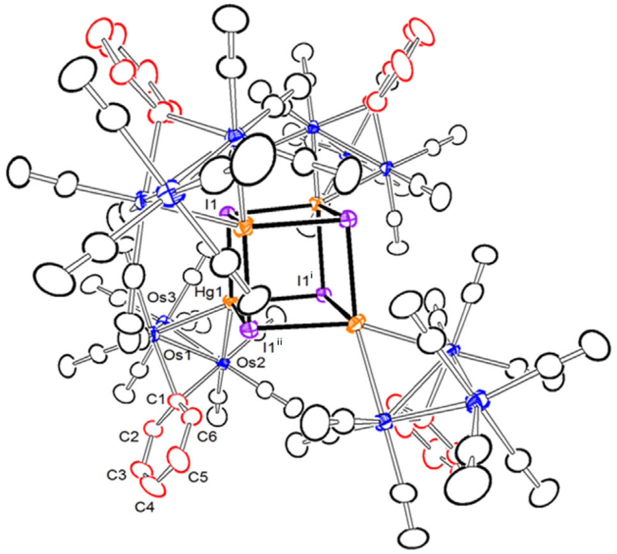

Fig. 1. An ORTEP diagram of the molecular structure of $[Os_3(CO)_{10}HgI(\mu\text{-}Ph)]_4$, **2** showing 20% thermal ellipsoid probabilities. Hg is orange, I is purple, Os is blue and the carbon atoms of the phenyl rings are colored red. Selected interatomic bond distances (Å) and angles (°) are as follow: Os(1) – Os(2) = 2.8205(6) Å, Os(1) – Os(3) = 2.8761(6), Os(2) – Os(3) = 2.8748(7), Os(1) – C(1) = 2.309(12), Os(2) – C(1) = 2.285(12) Å, Os(1) – Hg(1) = 2.7930(6) Å, Os(2) – Hg(1) = 2.7978(7), Hg(1) – I(1) = 2.9112(8) Å, Hg(1) – I(1^{i}) = 2.9645(8), Hg(1) – I(1^{ii}) = 3.524(1); Os(2) – Os(1) – Os(3) = 60.607(16), Os(1) – Hg(1) – Os(2) = 60.596(15), I(1) – Hg(1) – I(1^{i}) = 87.29(2), Hg(1) – I(1) – Hg(1^{i}) = 91.11(2), Os(1) – C(1) – Os(2) = 75.8(4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Results and discussion

The reaction of $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}Ph)(\mu\text{-}AuPPh_3)$, **1** with HgI_2 yielded the new compound $[Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}HgI)]_4$, **2** in 19% yield. $(Ph_3P)AuI$ is the major colorless coproduct in this reaction. Compound **2** was characterized by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **2** is shown in Fig. 1. Compound **2** is a tetramer of $Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}HgI)$ that is held together by a cubane-like Hg_4I_4 core having D_2 symmetry. There are three independent Hg – I bond distances: Hg(1) – I(1) = 2.9112(8) Å, Hg(1) – I(1^{i}) = 2.9645(8) Å and Hg(1) – I(1^{ii}) = 3.524(1) Å. Although transition metal halide cubanes are commonly found among the copper halide family of complexes, they are rare among the Group IIB family of compounds [11]. In fact, there has been only one previous structural verification of a complex containing an Hg_4I_4 cubane core. That was for the complex anion $[Hg_8I_{20}]^{4-}$ [12]. The Hg – I distance in the cubane core of this ion is 3.026(9) Å. Compound **2** contains four symmetry equivalent $Os_3(CO)_{10}(\mu\text{-}Ph)$ clusters. Each of which is linked to the cubane core via one bridging Hg atom. Each triosmium cluster in **2** contains ten linear carbonyl ligands and one edge-bridging phenyl ligand. The latter which is analogous to the bridging phenyl ligand in **1** serves as a 1-electron donor, **B**. Viewed as an uncharged fragment the HgI group also serves as a 1-electron donor and therefore each Os_3 cluster formally has only 46 valence electrons instead of the expected 48 and is electronically unsaturated like compound **1** [8a]. The unsaturation lies on the region of the bridging phenyl ligand and the Os(1) – Os(2) bond, 2.8205(6) Å is significantly shorter than the Os(1) – Os(3) = 2.8761(6) Å and Os(2) – Os(3) = 2.8748(7) Å bonds. The analogous short bond in **1** is significantly shorter, 2.7521(6) Å, than that in **2**. The two independent Os – Hg bond distances, Os(1) – Hg(1) = 2.7930(6) Å, Os(2) – Hg(1) = 2.7978(7) Å, are slightly shorter than those found to the bridging mercury atom in the compound $[Os_3(CO)_{10}(\mu\text{-}Cl)]_2(\mu_4\text{-}Hg)$, 2.822(1) Å – 2.859(1) Å [13]. The Os – C distances to the bridging phenyl ligand are nearly equivalent, Os(1) – C(1) = 2.309(12) Å and Os(2) – C(1) = 2.285(12) Å.

The bridging phenyl ligand in **1** was observed to undergo a dynamical 2-fold rotation of the ring perpendicular to the Os – Os bond on the ^{1}H NMR timescale at elevated temperatures [8b]. Unfortunately, compound **2** is readily transformed thermally into another product, see below, when heated so a traditional temperature-dependent dynamic NMR investigation of **2** was not possible. However, a 2D EXSY spectrum of **2** did show cross peaks confirming the existence of exchange between the protons on the ring carbons C(2) with C(6) and C(3) with C(5), see Fig. 2. This spin transfer is best explained by a 2-fold rotational process similar to that found in **1**.

An electron impact mass spectrum of **2** did not show the parent ion. The highest mass ions were attributed to the monomeric and dimeric fragments of the empirical formula $[Os_3(CO)_{10}HgI(\mu\text{-}Ph)]$. Evidently, the cubane cluster is split under the forcing conditions of the mass spectrometer to yield the monomeric and dimeric fragments.

The reaction of **1** with $HgCl_2$ yielded the new compound $Os_4(CO)_{13}(\mu\text{-}Ph)(\mu\text{-}Cl)_3$, **3** in 18% yield. Compound **3** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **3** is shown in Fig. 3. Compound **3** contains a $Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}Hg)$ cluster similar that of **2**, but in this case the Hg atom bridges to an additional $Os(CO)_3$ group via three bridging chloride ligands. The Os − Os bond distances in **3** are similar to those in **2**, Os(1) - Os(2) = 2.8275(6) Å, Os(1) − Os(3) = 2.8676(6) Å, Os(2) − Os(3) = 2.8685(6) Å and the Os(1) − Os(2) bond that is bridged by the phenyl ligand is again significantly shorter than the other two. The Os − C bonds to the bridging phenyl ligand, Os(1) − C(1) = 2.343(12) Å, Os(2) − C(1) = 2.302(12) Å, are very similar to those in **1** and **2**. The Os − Hg distances in **3**, Os(1) − Hg(1) = 2.7522(6) Å, Os(2) − Hg(1) = 2.7620(6) Å, are slightly shorter than those in **2**. The coordination geometry of the mercury atom can be described as a distorted square pyramid with Os(1), Os(2), Cl(1) and Cl(2) forming the square base and Cl(3) in the apical position. The Hg − Cl distance to the apical Cl, Cl(3) is significantly longer, Hg(1) − Cl(3) = 2.983(3) Å than those to the basal Cl ligands, Hg(1) − Cl(1) = 2.797(3) Å, Hg(1) − Cl(2) = 2.637(3) Å. Osmium Os(4) must have been derived from a fragment of an original triosmium cluster and was captured by the Hg-bridged $PhOs_3$ group found in **3**. The nature of the fragmentation process was not established in this study. Os(4) contains three linear terminal carbonyl ligands in a *fac* arrangement. Each of the three chloro ligands are coordinated to Os(4): Os(4) − Cl(1) = 2.404(3), Os(4) − Cl(2) = 2.432(3) Å, Os(4) − Cl(3) = 2.404(3) Å, to give a pseudo-octahedral geometry. 2D EXSY H NMR spectra of the phenyl protons in **3** indicate the phenyl is also dynamically active as found in compounds **1** and **2**, see Supplementary Material.

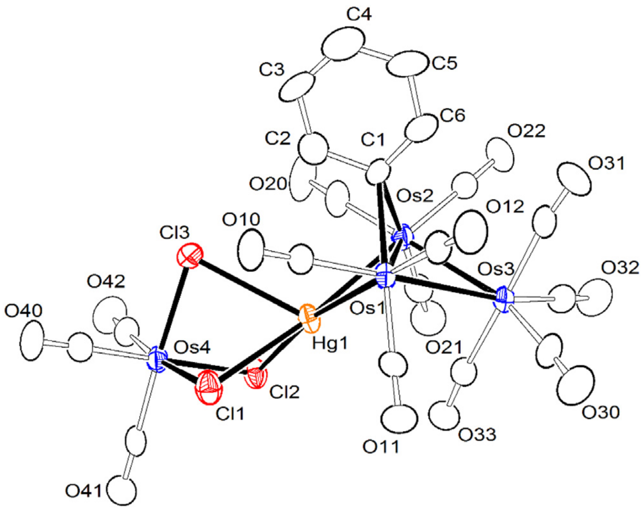

Fig. 3. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu\text{-}Ph)(\mu\text{-}Hg)(\mu\text{-}Cl)_3Os(CO)_3$, **3** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follow: Os(1) − Os(2) = 2.8275(6), Os(1) − Os(3) = 2.8676(6), Os(2) − Os(3) = 2.8685(6), Os(1) − C(1) = 2.343(12), Os(2) − C(1) = 2.302(12), Os(1) − Hg(1) = 2.7522(6), Os(2) − Hg(1) = 2.7620(6), Hg(1) − Cl(1) = 2.797(3) Å, Hg(1) − Cl(2) = 2.637(3) Å, Hg(1) − Cl(3) = 2.983(3) Å, Os(4) − Cl(1) = 2.404(3), Os(4) − Cl(2) = 2.432(3) Å, Os(4) − Cl(3) = 2.404(3), Os(1) − Hg(1) − Os(2) = 61.698(16), Os(2) − Os(1) − Os(3) = 60.482(15), Os(1) − C(1) − Os(2) = 75.0(3).

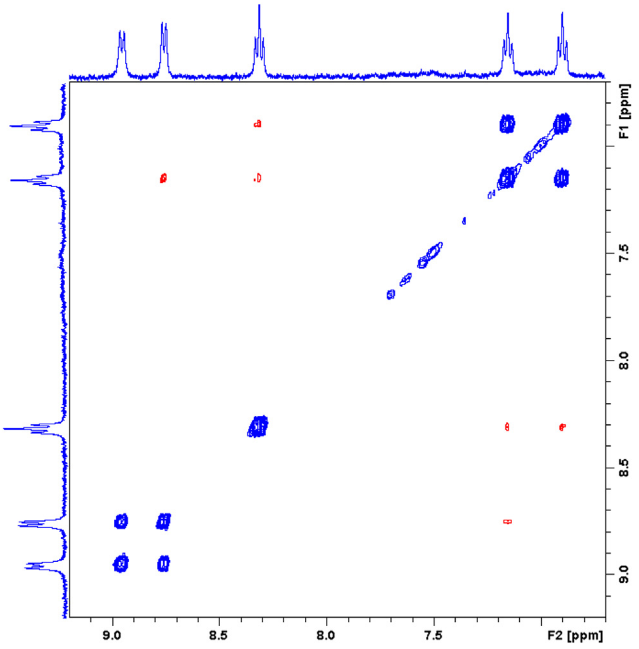

Fig. 2. A 2D EXSY H NMR spectrum of compound **2** (using 800 ms mixing time) for the resonances of the protons on phenyl ring carbon atoms C(2) and C(6) at 8.94 ppm and 8.76 ppm, and C(3) and C(5) at 7.15 ppm and 6.90 ppm. EXSY cross peaks are colored blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The bonding in **3** can be viewed as a combination of a 46-electron, positively charged $Os_3(CO)_{10}(\mu{-}\eta^1{-}Ph)(\mu\text{-}HgCl)$ fragment linked to a negatively charged 16-electron $[Os(CO)_3Cl_2]^-$ fragment. The latter would achieve an 18-electron configuration when two electrons are donated to it from the Cl ligand on the Hg atom in the Os_3 fragment.

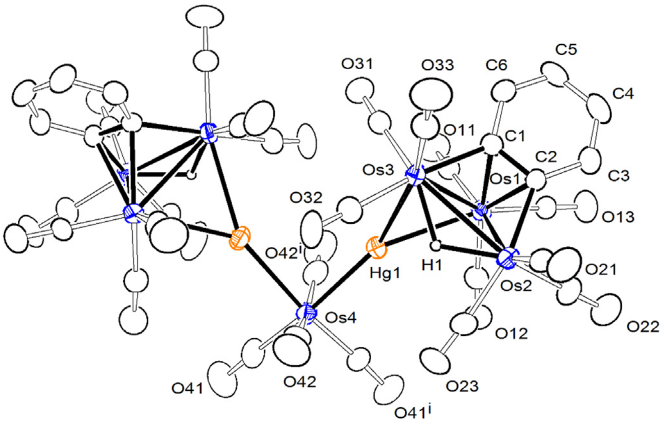

Fig. 4. An ORTEP drawing of the molecular structure of $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]_2Os(CO)_4$, **4** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follow: Os(1) − Os(2) = 2.7633(7), Os(1) − Os(3) = 2.8981(7), Os(2) − Os(3) = 3.0214(7), Os(1) − Hg(1) = 2.8575(7), Os(3) − Hg(1) = 2.8178(7), Os(4) − Hg(1) = 2.6837(8), Hg(1)···Hg(1′) = 3.549(1), Os(1) − C(1) = 2.287(11), Os(1) − C(2) = 2.402(12), Os(2) − C(2) = 2.101(12), Os(3) − C(1) = 2.121(12), Os(2) − H(1) = 1.78(2), Os(3) − H(1) = 1.79(2); Hg(1) − Os(4) - Hg(1′) = 82.78(3).

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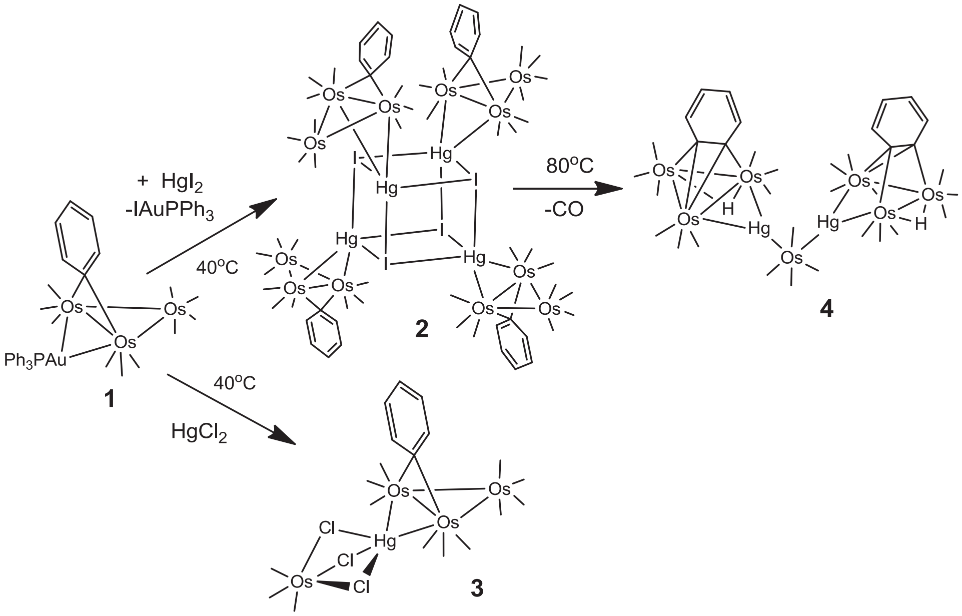

Scheme 1.

In earlier studies, it was shown that when compound **1** is heated to reflux in octane solvent, the compound is decarbonylated and the bridging phenyl ligand in **1** is converted into a bridging benzyne ligand and a hydride ligand by cleavage of the CH bond on one of the ortho-positioned carbon atoms [8a]. Similarly, when heated to reflux in cyclohexane solvent, compound **2** was converted to the new compound $[Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)]_2Os(CO)_4$, **4** in 11% yield. Compound **4** was characterized by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **4** is shown in Fig. 4. Compound **4** contains two $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}H)(\mu_3\text{-}Hg)$ clusters that are linked by a bridging $Os(CO)_4$ group. The $Os(CO)_4$ group must have originated by a fragmentation of some of the triosmium clusters present in the reaction solution. In the solid state, compound **4** lies on a 2-fold rotational symmetry axis that passes through the Os atom of the $Os(CO)_4$ group, so the two Os_3 clusters are symmetry equivalent. Each Os_3 cluster contains a triply bridging C_6H_4 "benzyne" ligand, nine linear terminal carbonyl ligands (three on each osmium atom) and one bridging hydrido ligand, ^1H NMR $\delta = -21.05$ ppm. As expected, the hydrido ligand was found to bridge the longest Os – Os bond [14]. The Os – Hg distances to the bridging mercury atom which is formally uncharged in **4** are longer, Os(1) – Hg(1) = 2.8575(7) Å, Os(3) – Hg(1) = 2.8178(7) Å, than those in **2**, but are similar to those in the compound $[Os_3(CO)_{10}(\mu\text{-}Cl)]_2(\mu_4\text{-}Hg)Os(CO)_4$ [13]. However, the Os – Hg distances to the unique osmium atom Os(4), Os(4) – Hg(1) = 2.6837(8) Å is significantly shorter. The shortness may be due to reduced steric interactions about the Os(4) – Hg(1) bond. The Hg(1) – Hg(1') distance of 3.549(1) Å in **4** is too long for any significant direct Hg–Hg bonding interaction. The benzyne ligands in **4** serve as a four electron donors, so each triosmium cluster contains a total 48 valence electrons. There is no formal unsaturation in these Os_3 clusters and each osmium atom formally achieves an 18 electron configuration.

Summary and conclusions

A summary of the results of this study are shown in Scheme 1. It has been shown in this work that the mercury halides HgI_2 and $HgCl_2$ can replace the $Au(PPh_3)$ group in the compound **1** to yield the unsaturated osmium carbonyl cluster complexes **2** and **3** containing η^1-bridging phenyl ligands. The HgI grouping in **2** has adopted an unusual cubane – like Hg_4I_4 assembly in the solid state. Compound **2** eliminates a CO ligand when heated and one of the ortho-positioned CH bonds on the bridging phenyl ligand is cleaved to form a bridging hydride ligand and a triply-bridging benzyne ligand.

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Appendix A. Supplementary material

CCDC 1007477–1007479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.08.009.

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