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

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ABSTRACT

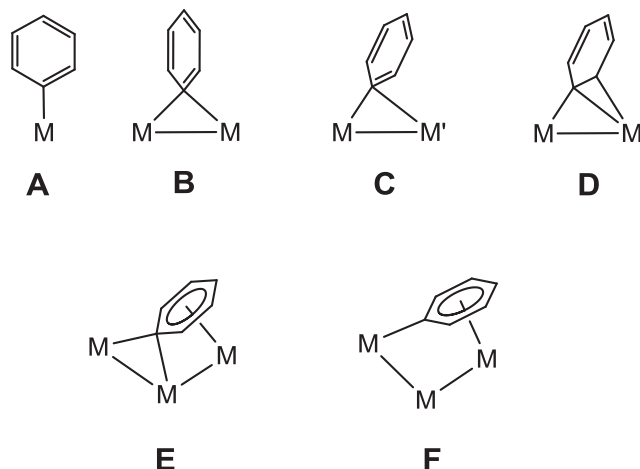
The gold phosphine group in the complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-AuPPh}_3)$, **1** can be replaced by mercury halide groups by reactions with mercury halides. The reaction of **1** with HgI_2 yielded the new compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-HgI})]_4$, **2** in 19% yield. The reaction of **1** with HgCl_2 yielded the new compound $\text{Os}_4(\text{CO})_{13}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-Cl})_3$, **3** in 18% yield. When heated to reflux in cyclohexane solvent, compound **2** was converted into the compound $[\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_3\text{-Hg})]_2\text{Os}(\text{CO})_4$, **4** in 11% yield. All new compounds were characterized by single-crystal X-ray diffraction analyses. Compound **2** is a tetramer of the unit “ $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-HgI})$ ” 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 $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ph})(\mu\text{-Hg})$ cluster, but in this case the Hg atom bridges to an additional $\text{Os}(\text{CO})_3$ group via three bridging chloride ligands. Compound **4** contains two $\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_3\text{-Hg})$ clusters that are linked by a bridging $\text{Os}(\text{CO})_4$ group. Each Os_3 cluster in **4** contains a triply bridging C_6H_4 benzyne ligand and one bridging hydrido ligand.

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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 $\mu\text{-}\eta^6$ -**E** or $\mu\text{-}\eta^6$ -**F** serving formally as 7-electron donors [6,7]. Still other coordination modes exist and it is likely that others will be found.

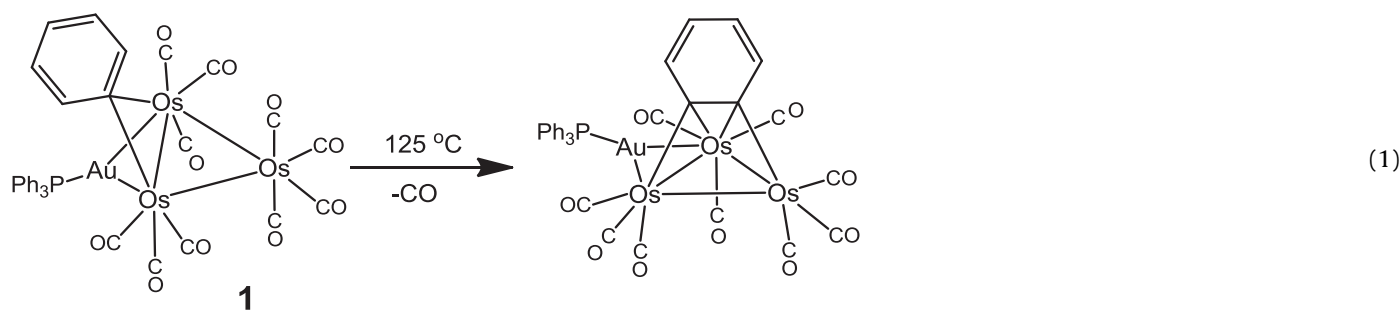
Recently, we reported a family of electronically unsaturated triosmium carbonyl ligands $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ar})(\mu\text{-AuPPh}_3)$, **1**, Aryl = phenyl = Ph, **1**, 2-naphthyl, 2-pyryl and 4-pyryl containing bridging aryl ligands of the type **B**.⁸ Calculations showed 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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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 $\text{Au}(\text{PPh}_3)$ group was replaced by a bridging HgI group. The product of empirical formula “ $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ar})(\mu\text{-HgI})$ ”, then condensed by a self-assembly to form the tetramer, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-Ar})(\mu\text{-HgI})]_4$, **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 $\text{Os}_3(\text{CO})_{10}(\mu\text{-Ph})(\mu\text{-Hg})(\mu\text{-Cl})_3\text{Os}(\text{CO})_3$, **3** which contains an unsaturated phenyl bridged Os_3 cluster. This is linked to an $\text{Os}(\text{CO})_3$ group by a bridging HgCl_3 group. When heated compound **2** was converted to the new compound yellow $[\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_3\text{-Hg})]_2\text{Os}(\text{CO})_4$, **4** which contains two $[\text{Os}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_3\text{-Hg})]$ clusters with each having a triply bridging benzyne ligands. The two Os_3 clusters in **4** are linked by a bridging $\text{Os}(\text{CO})_4$ 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. $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_5)(\mu\text{-AuPPh}_3)$, **1** was prepared according to the previously reported procedure [8a].

Reaction of $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-C}_6\text{H}_5)(\mu\text{-AuPPh}_3)$, **1** with HgI_2

43.4 mg (0.0955 mmol) of HgI_2 was added to 84.0 mg (0.060 mmol) of $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_5)(\mu\text{-AuPPh}_3)$ 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 $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_5)(\mu\text{-HgI})]_4$, **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) δ = 8.95 (d, 1H, $^3J_{\text{H-H}}$ = 6 Hz, Ph), 8.76 (d, 1H, $^3J_{\text{H-H}}$

= 6 Hz, Ph), 8.31 (t, 1H, $^3J_{\text{H-H}}$ = 6 Hz, Ph), 7.15 (t, 1H, $^3J_{\text{H-H}}$ = 6 Hz, Ph), 6.90 (t, 1H, $^3J_{\text{H-H}}$ = 6 Hz, Ph). Mass Spec. EI/MS m/z : 2506 and 1256.

Reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_5)(\mu\text{-AuPPh}_3)$, **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 $\text{Os}_3(\text{CO})_{10}(\mu\text{-Ph})(\mu\text{-Hg})(\mu\text{-Cl})_3\text{Os}(\text{CO})_3$, **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) δ = 8.86 (d, 1H, $^3J_{\text{H-H}}$ = 6 Hz, Ph), 8.82 (d, 1H, $^3J_{\text{H-H}}$

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

Compound	2	3	4
Empirical formula	$\text{Os}_{12}\text{Hg}_4\text{I}_4\text{O}_{40}\text{C}_{64}\text{H}_{20}$	$\text{Os}_4\text{HgCl}_3\text{O}_{13}\text{C}_{19}\text{H}_5$	$\text{Os}_7\text{Hg}_2\text{O}_{22}\text{C}_{34}\text{H}_{10}$
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)	$P\bar{1}$ (#2)	C2/c (#15)
Z value	4	2	4
ρ_{calc} (g/cm^3)	3.19	3.46	3.57
μ (Mo K α) (mm^{-1})	21.6	23.12	25.65
Temperature (K)	294(2)	294(2)	294(2)
$2\theta_{\text{max}}$ (°)	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 :	0.0347; 0.1004	0.0287; 0.0616	0.0389; 0.1094
R1; wR2			
Absorption Correction	Multi-scan	Multi-scan	Multi-scan
Max/min	1.00/0.503	1.00/0.66	1.00/0.39
Largest peak in Final Diff. Map ($\text{e}^-/\text{Å}^3$)	1.947	1.151	3.484

^a $R1 = \sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; $wR2 = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} wF_{\text{obs}}^2]^{1/2}$; $w = 1/(\sigma^2(F_{\text{obs}}))$; $\text{GOF} = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vars}})]^{1/2}$.

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