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Formation of $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)]^+$ (E = P, As) by Bromination: First Direct Evidence for the Bromonium Mechanism in Cluster Chemistry

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Summary: Bromination of the substituted triosmium clusters $Os_3(CO)_{10}(EPh_3)_2$ *(E = P, As) yielded the cluster cations* $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)]^+$*, which crystallized as the* $[Os(CO)_3Br_3]^-$ *salts. The osmate anions were the result of nucleophilic attack of* Br^- *on the cluster cations.*

Introduction

The mechanism by which triosmium clusters undergo halogenation reactions has been of recent interest. Essentially, the two major possibilities are via a radical mechanism[1] or a bromonium intermediate.[2] It has recently been shown that the reaction of Br^+ with the parent carbonyl cluster $Os_3(CO)_{12}$ gave the bromonium cluster $[Os_3(CO)_{12}(\mu\text{-}Br)]^+$, and it was also demonstrated that this cluster was not the intermediate involved in the direct bromination reaction.[3] In contrast, we have recently reported that the bromination of the substituted clusters $Os_3(CO)_{11}(EPh_3)$ (E = P, Sb) gave two isomeric products, $(Br)_2Os(CO)_3Os(CO)_4Os(CO)_4(EPh_3)$ and $(Br)(OC)_4OsOs(CO)_4Os(CO)_3(Br)(EPh_3)$ and suggested that the intermediate was a bromonium cluster with a terminal Br atom.[4]

We now report that the direct bromination of $Os_3(CO)_{10}(EPh_3)_2$ (E = P (**1a**), As (**1b**)) led, quite unexpectedly, to the isolation of stable bromonium cluster intermediates, $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]$ (**2**), thus providing the first direct evidence for the bromonium mechanism in the bromination of clusters.

Experimental Section

General Procedures. All reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were purified, dried, distilled, and kept under nitrogen prior to use. NMR spectra were recorded on a Bruker ACF300 300 MHz NMR spectrometer. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The clusters $Os_3(CO)_{10}(EPh_3)$ (E = P (**1a**), As (**1b**)) were prepared by the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with PPh_3 and $AsPh_3$, respectively;[5] all other reagents were from commercial sources and used as supplied.

Bromination of $Os_3(CO)_{10}(AsPh_3)_2$ (1b). To a solution of **1b** (190 mg, 0.130 mmol) in CH_2Cl_2 (30 mL), maintained in a −30 °C bath, was added Br_2 (1.7 mL of an 1/100 v/v solution in CH_2Cl_2, 0.29 mmol). The mixture was stirred for $^1/_2$ h and then concentrated to ~20 mL. Addition of hexane (~20 mL) resulted in precipitation of a yellow solid. Recrystallization from CH_2Br_2/hexane at −15 °C afforded yellow crystalline $[Os_3(CO)_{10}(AsPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]$ (**2b**; 118 mg, 45%). IR (ν(CO), CH_2Cl_2): 2121 (m), 2110 (w), 2087 (w), 2071 (m), 2039 (vs), 2017 (m) cm^{-1}. Anal. Calcd for $C_{49}H_{30}As_2Br_4O_{13}Os_4$: C, 28.61; H, 1.47. Found: C, 28.49; H, 1.67.

Table 1. Crystal and Refinement Data for $[Os_3(CO)_{10}(PPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]\cdot 2CH_2Br_2$ (2a) and $[Os_3(CO)_{10}(AsPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]\cdot 2CH_2Br_2$ (2b)

	2a	2b
formula	$C_{51}H_{34}Br_8O_{13}Os_4P_2$	$C_{51}H_{34}As_2Br_8O_{13}Os_4$
fw	2316.80	2404.70
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.7278(1)	12.8242(4)
b, Å	15.6244(1)	15.7024(5)
c, Å	17.7522(1)	17.9569(6)
α, deg	80.5383(2)	80.4290(8)
β, deg	70.7213(3)	70.6163(9)
γ, deg	72.7831(2)	72.7826(3)
V, Å^3	3174.28(4)	3248.9(2)
Z	2	2
D(calcd), g cm^{-3}	2.424	2.458
μ(Mo Kα), cm^{-1}	13.121	13.781
F(000)	2116	2188
cryst size, mm	0.35 × 0.17 × 0.10	0.30 × 0.10 × 0.08
θ range, deg	1.76−29.51	1.21−28.50
no. of rflns collected	26 849	16 864
no. of indep rflns	15 313	12 835
no. of data/restraints/params	15 313/46/728	12 835/6/708
goodness of fit on F^2	1.012	0.955
final R indices ($I > 2\sigma(I)$)	R1 = 0.0525	R1 = 0.0552
	wR2 = 0.1059	wR2 = 0.1206
R indices (all data)	R1 = 0.1036	R1 = 0.1112
	wR2 = 0.1304	wR2 = 0.1441
largest diff peak and hole, e Å^{-3}	1.646 and −2.053	1.722 and −2.059

Bromination of $Os_3(CO)_{10}(PPh_3)_2$ (1a). An analogous reaction with **1a** (80 mg, 0.058 mmol) afforded yellow crystalline $[Os_3(CO)_{10}(PPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]$ (**2a**; 40.7 mg, 36%). IR (ν(CO), CH_2Cl_2): 2120 (m), 2111 (w), 2086 (w), 2069 (m), 2039 (vs), 2017 (m) cm^{-1}. $^{31}P\{^1H\}$ ($CDCl_3$): δ −5.86 (s). Anal. Calcd for $C_{49}H_{30}Br_4O_{13}Os_4P_2$: C, 29.88; H, 1.52. Found: C, 29.57; H, 1.13.

Crystal Structure Determination of 2a and 2b. The crystals, grown by slow cooling of a CH_2Br_2/hexane solution, were sealed in glass capillaries with a small amount of the supernatant. Crystal data and structure refinement details are given in Table 1. The intensities were measured on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ = 0.710 73 Å) at 295 K. The data were

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a and 2b

	2a	2b
Bond Lengths		
Os(1)···Os(2)	4.038(5)	4.027(7)
Os(1)−Os(3)	2.9770(5)	2.9647(7)
Os(2)−Os(3)	2.9736(5)	2.9605(7)
Os(1)−E(1)	2.407(2)	2.5097(14)
Os(2)−E(2)	2.392(2)	2.5009(14)
Os(1)−Br(1)	2.5896(10)	2.5960(14)
Os(2)−Br(1)	2.5970(10)	2.6002(14)
Bond Angles		
Os(1)−Os(3)−Os(2)	85.479(13)	85.63(2)
Os(1)−Br(1)−Os(2)	102.27(3)	101.61(5)
E(1)−Os(1)−Br(1)	88.49(6)	87.91(4)
E(2)−Os(2)−Br(1)	92.10(7)	90.12(5)

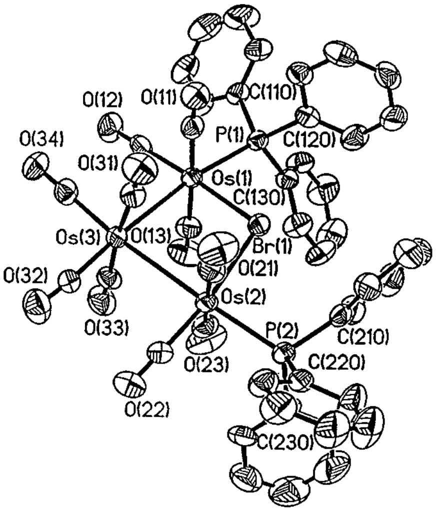


Figure 1. ORTEP diagram of the molecular structure of the cluster cation in **2a**.

corrected for absorption effects with SADABS (G. M. Sheldrick, 1996). The final unit cell parameters were obtained by least squares on 8192 (for **2a**) or 7015 (for **2b**) strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs (Siemens Energy & Automation Inc., Madison, WI). The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Two molecules of solvent of crystallization (CH_2Br_2) in the asymmetric unit were found, one of which was disordered. Details on the modeling of the disorder are given in the Supporting Information. All the hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were given anisotropic displacement parameters in the final refinement. Refinements were on $\Sigma[w(F_o^2 - F_c^2)^2]$. Atomic coordinates are given in the Supporting Information; selected bond lengths and angles are listed in Table 2.

Results and Discussion

When bromine was added to a dichloromethane solution of the disubstituted triosmium clusters $Os_3(CO)_{10}(EPh_3)_2$ (E = P (**1a**), As (**1b**)), the initial yellow mixture faded to a pale yellow, from which the clusters $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3]$ (**2**) could be isolated. Compounds **2a** and **2b** are isomorphic and isostructural, and they are only the third examples of structurally characterized halonium ions of carbonyl clusters. The X-ray crystal structure of the cluster cation in **2a** (Figure 1) shows that the osmium−osmium edge carrying the two group 15 substituents has been cleaved (Os(1)···Os(2) distances of 4.038(5) and 4.027(7) Å for **2a** and **2b**, respectively) to form an open bromonium-bridged compound. Their structures are similar to that of the earlier reported $[Os_3(CO)_{12}(\mu\text{-}Br)]^+$, and they may thus be viewed as group 15 substituted derivatives of the latter cluster cation.[3]

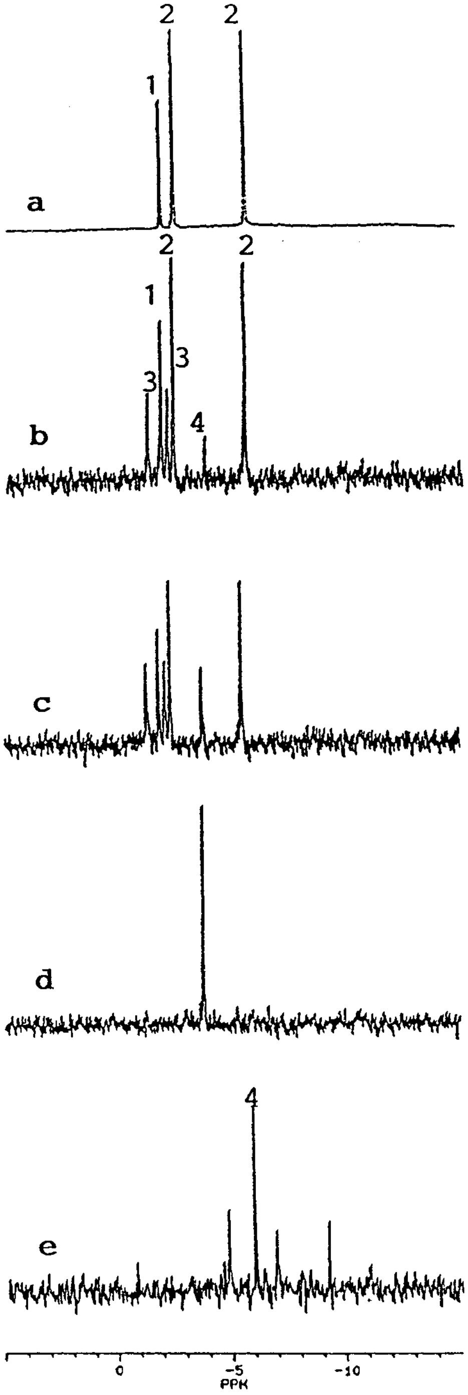


Figure 2. $^{31}P\{^1H\}$ NMR spectra at −80 °C of (a) $Os_3(CO)_{10}(PPh_3)_2$, (b) $Os_3(CO)_{10}(PPh_3)_2 + Br_2$ (0.3 equiv) at −50 °C, (c) $Os_3(CO)_{10}(PPh_3)_2 + Br_2$ (0.5 equiv) at −50 °C, (d) $Os_3(CO)_{10}(PPh_3)_2 + Br_2$ (1.0 equiv) at −50 °C, and (e) $[Os_3(CO)_{10}(EPh_3)_2(\mu\text{-}Br)][Os(CO)_3Br_3] + [Et_4N]Br$ (1.0 equiv) at room temperature (peak 1, *trans,trans*-**1a**; peak 2, *cis,trans*-**1a**; peak 3, *cis,trans*-**2a**; peak 4, *cis,cis*-**2a**).

We have followed the course of formation of **2a** by both $^{31}P\{^1H\}$ NMR and IR spectroscopy (Figures 2 and 3, respectively). Data obtained at or near room temperature suggested that the initial product was the bro-

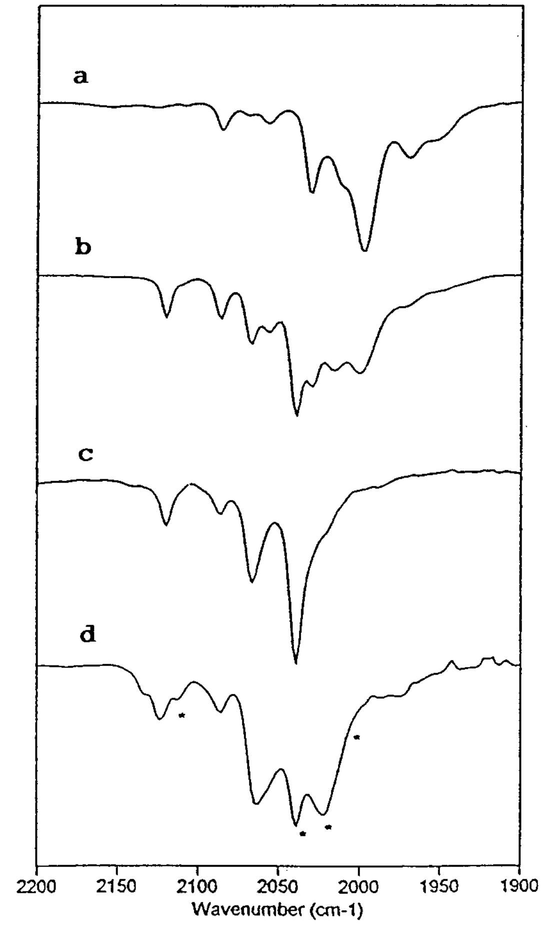
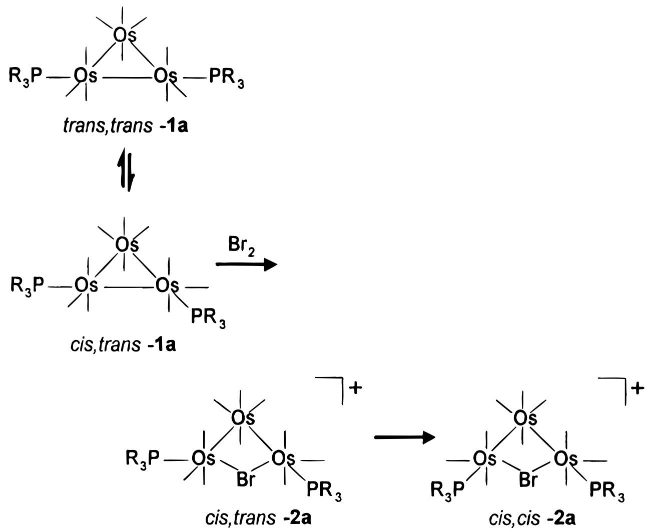


Figure 3. IR spectra (2200−1900 cm^{-1} region) of (a) $Os_3(CO)_{10}(PPh_3)_2$, (b) $Os_3(CO)_{10}(PPh_3)_2$ + Br_2 (0.5 equiv), (c) $Os_3(CO)_{10}(PPh_3)_2$ + Br_2 (1.0 equiv), and (d) $Os_3(CO)_{10}(PPh_3)_2$ + Br_2 (3.0 equiv) after stirring for 3 h. The asterisks indicate the absorption band positions expected for *fac*-[$Os(CO)_3Br_3$]$^-$.[6]

monium cluster cation [$Os_3(CO)_{10}(PPh_3)_2(Br)$]$^+$, but monitoring of the reaction at −50 °C by $^{31}P\{^1H\}$ NMR spectroscopy (at −80 °C) indicated the formation of another species prior to the formation of **2a**. The situation was complicated by the presence of isomers in **1a**;[7] three signals were observed in its $^{31}P\{^1H\}$ NMR spectrum taken at −80 °C—a resonance at −1.91 ppm (peak 1 in Figure 2) assigned to the isomer in which the two PPh_3 ligands are *trans* to the Os−Os edge carrying the two phosphines (*trans,trans*-**1**), and two resonances of equal intensities at −2.50 and −5.64 ppm (peaks 2 in Figure 2) assigned to the isomer in which the PPh_3 ligands are *cis* and *trans* to this Os−Os edge (*cis,trans*-**1a**). The $^{31}P\{^1H\}$ NMR spectra, however, clearly showed that bromination of **1a** at ca. −50 °C gave rise initially to three new signals; the two with the same intensities (peaks 3 in Figure 2) later collapsed while the third signal (peak 4 in Figure 2), corresponding to the bromonium cluster cation, grew. One explanation for this observation is that outlined in Scheme 1; i.e., there is an isomerization step involved in the formation of **2a**. This is consistent with the fact that, in **2a**, the two phosphine ligands are *cis* to the bromine, while in neither of the two isomers of **1a** are the phosphines arranged in that relative stereochemistry.

Scheme 1. Plausible Pathway for the Bromination of 1a



We were able to verify that **2a** did not react directly with bromine, but it reacted fairly rapidly with Et_4NBr at room temperature to give a similar mixture of products as in the reaction of **1** with excess Br_2. Interestingly, the spectroscopic evidence showed that the expected initial product from this reaction, the trimetallic chain compound $Os_3(CO)_{10}(PPh_3)_2Br_2$ obtained by Angelici et al. from the reaction of $Os_3(CO)_{12}Br_2$ with PPh_3,[1] was not formed. Instead, it appears that the attack of Br^- on the cationic bromonium cluster led to rapid cluster fragmentation.

As mentioned earlier, it has been demonstrated that the bromination of $Os_3(CO)_{12}$ did not proceed via the bromonium cluster [$Os_3(CO)_{12}(\mu$-$Br)$]$^+$, which was isolated from the reaction of $Os_3(CO)_{12}$ with Br^+,[3] while the bromination of $Os_3(CO)_{11}(PPh_3)$ gave products which suggested a bromonium cluster intermediate, the structure of which has not been confirmed.[4] The isolation and characterization of the compounds **2** here therefore constitute the first direct verification for the bromonium mechanism in the bromination of clusters. Bromine attacks, in a very specific manner, the most electron-rich osmium−osmium bond, similar to what occurs in alkenes.[8]

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Supporting Information Available: Text giving details about the X-ray experiments and refinement and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **2a** and **2b** (27 pages). Ordering information is given on any current masthead page.

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