Bromination of $Os_3(CO)_{11}(EPh_3)$ (E = P, Sb): Unexpected Formation of a Tandem Donor−Acceptor Metal Chain

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Summary: Bromination of the substituted triosmium clusters $Os_3(CO)_{11}(EPh_3)$ (E = P, Sb) yielded two trimetallic chain compounds, viz., $(Br)_2Os(CO)_3Os(CO)_4Os(CO)_4(EPh_3)$ and $(Br)(OC)_4OsOs(CO)_4Os(CO)_3(Br)(EPh_3)$. The former contains two donor−acceptor metal−metal bonds in tandem.

Introduction

An interesting class of compounds that has emerged from work in one of our laboratories are compounds that formally contain an unbridged donor−acceptor metal−metal bond.[1,2] Such compounds are still relatively uncommon, and even rarer still are those containing two such donor−acceptor metal−metal bonds in tandem.[2] Up until now, the synthetic route employed involved putting together a donor organometallic fragment and an acceptor organometallic fragment; these fragments are often not particularly accessible. We now report an unexpected reaction that leads to such tandem donor−acceptor metal chains which may be exploited as a simple route to this class of compounds.

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 300 MHz NMR spectrometer. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The clusters $Os_3(CO)_{11}(PPh_3)$ (**1a**) and $Os_3(CO)_{11}(SbPh_3)$ (**1b**) were prepared by the reaction of $Os_3(CO)_{11}(CH_3CN)$ with PPh_3 and $SbPh_3$, respectively;[3] all other reagents were from commercial sources and used as supplied.

Bromination of $Os_3(CO)_{11}(PPh_3)$ and $Os_3(CO)_{11}(SbPh_3)$. To a solution of $Os_3(CO)_{11}(PPh_3)$ (218 mg, 0.191 mmol) in dichloromethane (30 mL), maintained at −30 °C, was added a solution of bromine in dichloromethane (1.1 mL of a 1/100 (v/v) solution, 0.191 mmol). After stirring for 30 min, the solution was concentrated to ~20 mL and an equal volume of hexane added to precipitate yellow crystalline **2a**, which was collected by filtration (69.5 mg, 28%). Further concentration of the yellow filtrate followed by addition of hexane and cooling to −30 °C gave a pale yellow precipitate, which was recrystallized from CH_2Cl_2/hexane to give crystalline **3a** (109 mg, 44%). **2a**: IR (ν(CO), CH_2Cl_2) 2131 (vw), 2089 (m), 2075 (w), 2051 (sh), 2036 (vs), 2005 (m) cm^{-1}; $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) δ 185.67 (s, 4C), 180.84 (d, $^2J_{PC}$ = 4.3 Hz, 4C), 174.05 (s, 2C), 166.35 (s, 1C); $^{31}P\{^1H\}$ ($CDCl_3$) δ −6.94 (s). Anal. Calcd for $C_{29}H_{15}Br_2O_{11}Os_3P$: C, 26.78; H, 1.16; P, 2.38; Br, 12.28. Found: C, 26.50; H, 1.25; P, 2.61; Br, 12.36. **3a**: IR (ν(CO), CH_2Cl_2) 2134 (w), 2094 (w), 2053 (s), 2024 (vs), 2003 (w) cm^{-1}; $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) δ 186.30 (s, 4C), 185.39 (d, $^2J_{PC}$ = 5.6 Hz, 2C), 177.73 (s, 2C), 174.34 (d, $^2J_{PC}$ = 3.5 Hz, 1C), 169.60 (s, 1C), 160.79 (s, 1C); $^{31}P\{^1H\}$ δ −7.88 (s). Anal. Calcd for $C_{29}H_{15}Br_2O_{11}Os_3P$: C, 26.78; H, 1.16; P, 2.38. Found: C, 26.86; H, 1.31; P, 2.75.

The bromination reaction of $Os_3(CO)_{11}(SbPh_3)$ was carried out in a similar manner to give yellow **2b**, which was recrystallized from CH_2BrCl/hexane (130 mg, 45%), and pale yellow **3b** (98 mg, 34%). **2b**: IR (ν(CO), CH_2Cl_2) 2130 (vw), 2091 (m), 2078 (w), 2035 (vs), 2005 (m) cm^{-1}; $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) δ 184.98 (s, 4C), 179.86 (s, 4C), 173.90 (s, 2C), 166.20 (s, 1C). Anal. Calcd for $C_{29}H_{15}Br_2O_{11}Os_3Sb$: C, 25.03; H, 1.08. Found: C, 25.48; H, 1.24. **3b**: IR (ν(CO), CH_2Cl_2) 2135 (w), 2094 (w), 2053 (s), 2025 (vs), 2004 (w) cm^{-1}. Anal. Calcd for $C_{29}H_{15}Br_2O_{11}Os_3Sb$: C, 25.03; H, 1.08. Found: C, 24.96; H, 1.47.

Crystal Structure Determination of 2b and 3a. The crystals were mounted on a quartz fiber (**2b**) or in a glass capillary (**3a**). Crystal data and structure refinement details are given in Table 1. The data were measured on a Siemens SMART diffractometer equipped with a CCD detector, using Mo Kα radiation (λ = 0.710 73 Å) at 298 K. The data were corrected for absorption effects with SADABS (Sheldrick, G. M. 1996). The final unit cell parameters were obtained by least squares on 8192 strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs (Siemens Energy & Automation Inc., Madison, WI). The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The phenyl hydrogens were placed in calculated positions. All non-hydrogen atoms were given anisotropic displacement parameters in the final refinement. Refinements were on $\sum[w(F_o^2 - F_c^2)^2]$. Atomic coordinates are given in the Supporting Information; selected bond lengths and angles are listed in Table 2.

Results and Discussion

Recent work into the initial products of the halogenation of $Os_3(CO)_{12}$ has shown that the reactions are quite

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[3] (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (b) Leong, W. K. M.Sc. Thesis, National University of Singapore, 1992.

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Table 1. Crystal and Refinement Data for $(Br)_2Os(CO)_3Os(CO)_4Os(CO)_4(SbPh_3)$ (2b) and $(Br)(OC)_4OsOs(CO)_4Os(CO)_3(Br)(PPh_3)$ (3a)

compound	**2b**	**3a**
formula	$C_{29}H_{15}Br_2O_{11}Os_3Sb$	$C_{29}H_{15}Br_2O_{11}Os_3P$
fw	1391.58	1300.80
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	16.9111(2)	17.1075(4)
b, Å	9.4115(1)	11.3436(3)
c, Å	23.6748(1)	17.7078(3)
β, deg	109.355(1)	101.691(1)
vol., Å^3	3555.09(6)	3365.10(13)
Z	4	4
D(calc), g cm^{-3}	2.600	2.568
μ(Mo Kα), cm^{-1}	13.470	13.778
F(000)	2504	2360
cryst size, mm × mm × mm	0.25 × 0.38 × 0.38	0.15 × 0.20 × 0.25
θ range, deg	1.30−28.96	1.51−28.02
reflns no. of colld	24 741	18 706
no. of indep reflns	8507	7188
data/restraints/params	8507/0/416	7188/8/425
goodness-of-fit on F^2	0.989	1.068
final R indices [$I > 2\sigma(I)$]	R1 = 0.0417, wR2 = 0.0830	R1 = 0.0454, wR2 = 0.0913
R indices (all data)	R1 = 0.0826, wR2 = 0.0973	R1 = 0.0900, wR2 = 0.1117
ext coeff	0.00064(4)	
largest diff. peak and hole, e Å^{-3}	1.425 and −1.540	1.884 and −1.360

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b and 3a

	2b	**3a**
Bond Lengths		
Os(1)−Os(2)	2.8882(5)	2.9139(6)
Os(2)−Os(3)	2.9308(5)	2.9373(5)
Os(3)−E(4)	2.6303(6)	2.388(3)
Os(1)−Br(1)	2.5886(12)	2.575(2)
Os(1)−Br(2)	2.5806(11)	
Os(3)−Br(3)		2.587(2)
Bond Angles		
Os(1)−Os(2)−Os(3)	175.12(2)	177.08(2)
Os(2)−Os(3)−E(4)	176.10(2)	175.97(7)

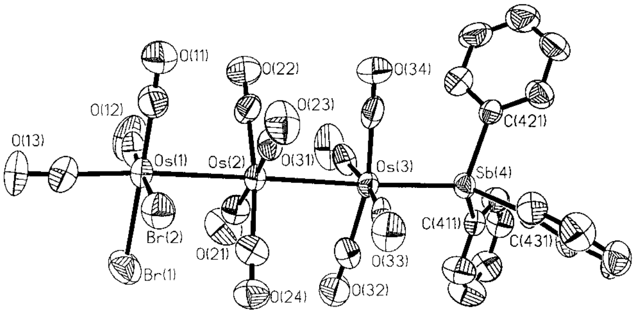

Figure 1. ORTEP diagram of the molecular structure of **2b**.

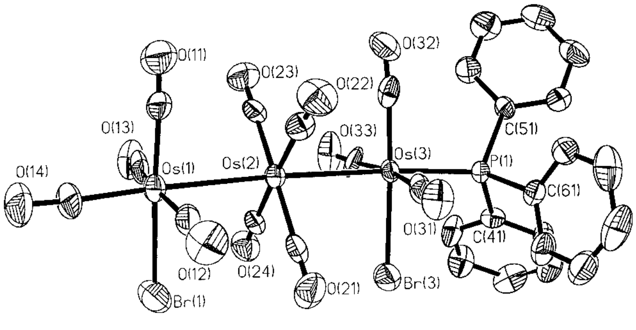

Figure 2. ORTEP diagram of the molecular structure of **3a**.

complicated.[4,5] In particular, the bromonium adduct of $Os_3(CO)_{12}$, $[Os_3(CO)_{12}Br]^+$, was synthesized and its structure established by X-ray crystallography as the $\{B[C_6H_3(CF_3)_2]_4\}^-$ salt. It was also demonstrated that this adduct was not the intermediate in the reaction of $Os_3(CO)_{12}$ with Br_2.[5] To gain more insight into the bromination process, the analogous bromination reaction with the substituted triosmium cluster $Os_3(CO)_{11}(PPh_3)$ (**1a**) was investigated. It was believed that the presence of the PPh_3 ligand would help direct the bromination and also provide a convenient NMR probe to follow the course of the reaction.

The reaction of a bromine solution in dichloromethane with **1a** at −30 °C was almost instantaneous, forming a pale yellow solution from which $(Br)_2Os(CO)_3Os(CO)_4Os(CO)_4(PPh_3)$ (**2a**) and $(Br)(OC)_4OsOs(CO)_4Os(CO)_3(Br)(PPh_3)$ (**3a**) were isolated. Both compounds have been characterized spectroscopically and analytically. Cluster **3a** was also characterized by a single-crystal X-ray structural study (Figure 1). We were unable to obtain a satisfactory single-crystal structural study on **2a**, but we did manage to do so for the stibine analogue **2b** (Figure 2).

Compounds **2** and **3** are unique pairs of isomers; isomers **3** are structurally similar to the $Os_3(CO)_{10}(PR_3)_2(Br)_2$ chains reported earlier by Angelici et al.[6] Isomers **2** contain two donor−acceptor metal−metal bonds in tandem, and **2a** and **2b** are the only homonuclear examples yet reported. In the earlier reports on this class of compounds, it was noted that the metal−metal bond lengths were longer than comparable nondative bonds in closed polyhedra of metal atoms but in the usual range for linear metallic chains.[2] This is also found in **2b** and **3a** (Table 2), except that in **2b** the Os(1)−Os(2) length is somewhat short (2.8882(5) Å), being closer to the average Os−Os bond length in $Os_3(CO)_{12}$ of 2.877 Å.[7]

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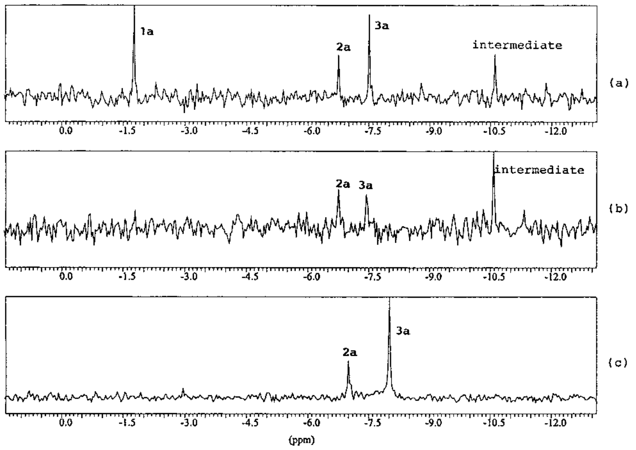
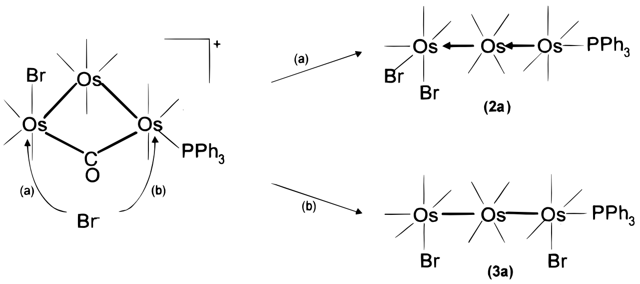


Figure 3. $^{31}P\{^1H\}$ NMR spectrum at −20 °C of (a) $Os_3(CO)_{11}(PPh_3) + Br_2$ (2:1 equiv), (b) $Os_3(CO)_{11}(PPh_3) + Br_2$ (1:1 equiv), and (c) after warming b to room temperature.

Compound **3a** was the product expected, a priori, from attack of the Os−Os bond cis to the phosphine ligand, which is the longest and also the most electron-rich Os−Os bond.[8] The formation of **2a** was thus unexpected. In an attempt to garner more information on the reaction mechanism, a low-temperature (−20 °C) $^{31}P\{^1H\}$ NMR study of the reaction (Figure 3) was carried out. The spectra clearly showed the initial formation of an intermediate species, which on warming to room temperature collapsed quickly into a mixture of **2a** and **3a**. This demonstrated the presence of a common intermediate for **2a** and **3a** and that the formation of **3a** was the preferred reaction pathway from the intermediate. A plausible structure for the intermediate and the possible modes of subsequent attack are shown in Scheme 1. In such an intermediate, the positive charge would likely be more localized at the osmium atom carrying the phosphine, hence leading to more favorable formation of **3a**. When the mixture obtained immediately after removal of solvent and excess bromine (at ca. 0 °C) was allowed to react with a large excess of [PPN]Cl, two products were obtained. These gave spectroscopic properties expected for the bromochloro analogues of **2a** and **3a**, although we were unable to obtain satisfactory C/H/N analyses. We have also not been able to determine the actual stereochemistry with respect to the positions of the Br and Cl atoms in these products, but their formation is sufficient indication that the intermediate species is cationic.

Scheme 1



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Supporting Information Available: Text giving full experimental details and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2b** and **3a** (14 pages). Ordering information is given on any current masthead page.

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