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Organo-Group 15 derivatives of triosmium clusters containing naphthyl ligands

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Abstract

Reactions of the clusters $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_9$, **1**, and $Os_3(\mu\text{-}H)(\mu\text{-}\mathit{2}\text{-}OC_{10}H_7)(CO)_{10}$, **2**, with the group 15 ligands EPh_3 (E = P, As, Sb) generally afforded the mono- and, or disubstituted derivatives. These derivatives tend to decompose during chromatographic separations on silica gel; thus one of the decomposition products from the reaction of **1** with PPh_3 has been identified as $Os(H)_2(CO)_2(PPh_3)_2$, **3**. The molecular structures of **3**, as well as the derivatives $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_8(AsPh_3)$, **4**, $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_7(SbPh_3)_2$, **5c**, $Os_3(\mu\text{-}H)(\mu\text{-}\mathit{2}\text{-}OC_{10}H_7)(CO)_8(AsPh_3)_2$, **7b**, and $Os_3(\mu\text{-}H)(\mu\text{-}\mathit{2}\text{-}OC_{10}H_7)(CO)_8(SbPh_3)_2$, **7c**, have been determined by single crystal X-ray diffraction studies.

Keywords: Osmium; Naphthyl; Group 15 ligands

1. Introduction

We have been interested in whether cluster-bound substrates may exhibit unusual reactivity compared to the free ligands and hence be gainfully employed in organic transformations [1]. An interesting class of substrates are the aromatics; for instance, it has been shown that cluster-bound quinolines react with nucleophiles with a regiochemistry different from that of the free quinolines [2]. Similarly, cluster-bound phenylenes can undergo Friedel–Crafts reactions [3] and carbonylation [4]. The anchoring of naphthols onto a triosmium cluster has been reported earlier by Deeming and coworkers [5] and recently re-investigated by us [6]. Our ultimate intent was to examine the effect of the cluster on the chemistry of the naphthols. Part of the investigation involved derivatisation of the naphthyl clusters with group 15 ligands, which would allow for modification of the stereoelectronic properties of the cluster. We would like to report here our attempts at this with the group 15 ligands EPh_3 (E = P, As and Sb) on the clusters $Os_3(\mu\text{-}H)_2(\mu_3\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_9$, **1**, and $Os_3(\mu\text{-}H)(\mu\text{-}\mathit{2}\text{-}OC_{10}H_7)(CO)_{10}$, **2**.

2. Results and discussion

Substitution reactions involving PPh_3 occurred with great ease, while chemical activation with TMNO was required with $SbPh_3$ and $AsPh_3$. The reaction of **1** with PPh_3 gave an orange solid (**A**) that decomposed during attempts at chromatographic separation. One of the decomposition products was the mononuclear complex *trans*-$Os(H)_2(CO)_2(PPh_3)_2$, **3** [7]. This has been characterised by a single crystal X-ray crystallographic study; the ORTEP diagram is shown in Fig. 1, together with selected bond parameters. The structural and spectroscopic data are in accord with this being a typical dihydride species [8].

The reaction of **1** with $AsPh_3$ or $SbPh_3$ permitted the isolation of the disubstituted derivatives, viz., $Os_3(\mu\text{-}H)_2(\mu\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_7(AsPh_3)_2$, **5b**, and $Os_3(\mu\text{-}H)_2(\mu\text{-}\mathit{1}\text{-}OC_{10}H_6)(CO)_7(SbPh_3)_2$, **5c**, respectively. In the case of $AsPh_3$, the monosubstituted derivative $Os_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}\mathit{1}\text{-}OC_{10}H_6)(AsPh_3)$, **4b**, was also isolated. Both **4b** and **5c** were characterised by single crystal X-ray crystallographic studies; the ORTEP diagrams and selected bond parameters are given in Figs. 2 and 3, respectively. The structural parameters for **4b** and **5c** are generally unremarkable, although it is interesting to note that

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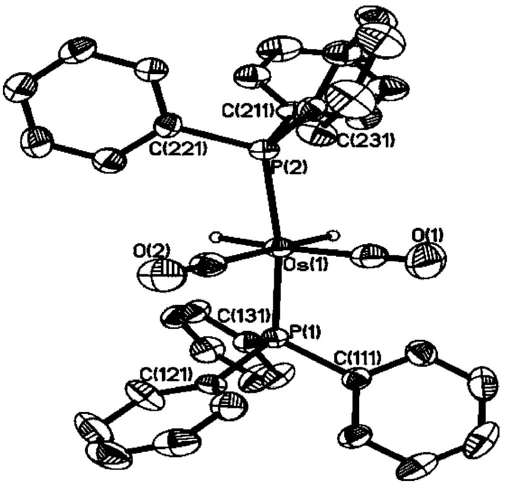


Fig. 1. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) and selected bond parameters for **3**. Os(1)–P(1) = 2.3621(11) Å; Os(1)–P(2) = 2.3541(11) Å; Os(1)–C(1) = 1.932(6) Å; Os(1)–C(2) = 1.923(5) Å; O(1)–C(1) = 1.138(6) Å; O(2)–C(2) = 1.148(6) Å; $\angle$P(1)Os(1)P(2) = 163.08(4)°; $\angle$C(1)Os(1)C(2) = 97.9(2)°.

both have an EPh_3 substitution at the unbridged osmium. This may suggest that the initial site of nucleophilic attack is at this osmium.

The reaction of **2** with PPh_3 afforded an orange solid (**B**) which was unstable on silica; the monosubstituted derivative $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_9(PPh_3)$, **6a**, identified on the basis of the similarity of its IR carbonyl stretch pattern with those for clusters of the type $Os_3(\mu\text{-}H)(\mu\text{-}OR)(CO)_9(L)$ (where R = H, alkyl and Ph; L = PPh_3 and $P(OMe)_3$) [9], was isolated from the supernatant. The magnitude of the $^2J_{PH}$ has been used to assess the position of substitution in similar phosphite-substituted alkoxy-bridged triosmium clusters [10]; the ^1H NMR spectrum of **6a** showed one set of doublet at −12.44 ppm ($^2J_{PH} = 6$ Hz), and given the steric bulk of the naphthyl, the phosphine probably occupied position C (Fig. 4).

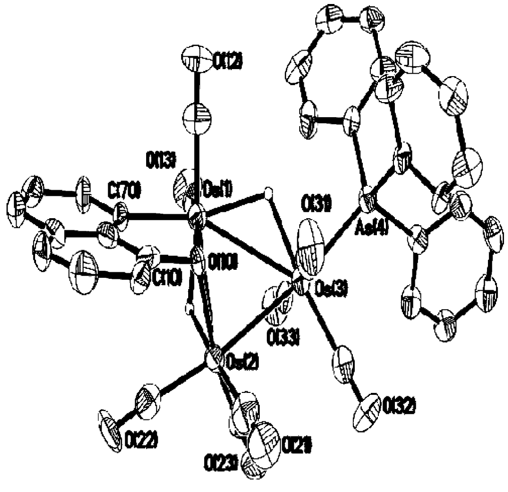


Fig. 2. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **4b**. Os(1)–Os(2) = 2.8109(7) Å; Os(1)–Os(3) = 3.0603(7) Å; Os(2)–Os(3) = 2.8251(7) Å; Os(1)–O(10) = 2.111(8) Å; Os(2)–O(10) = 2.138(8) Å; Os(1)–C(70) = 2.101(12) Å; Os(3)–As(4) = 2.4675(13) Å; $\angle$Os(1)Os(2)Os(3) = 65.775(17)°; $\angle$Os(2)Os(1)Os(3) = 57.335(16)°; $\angle$Os(1)Os(3)Os(2) = 56.890(15)°; $\angle$Os(1)O(10)Os(2) = 82.8(3)°.

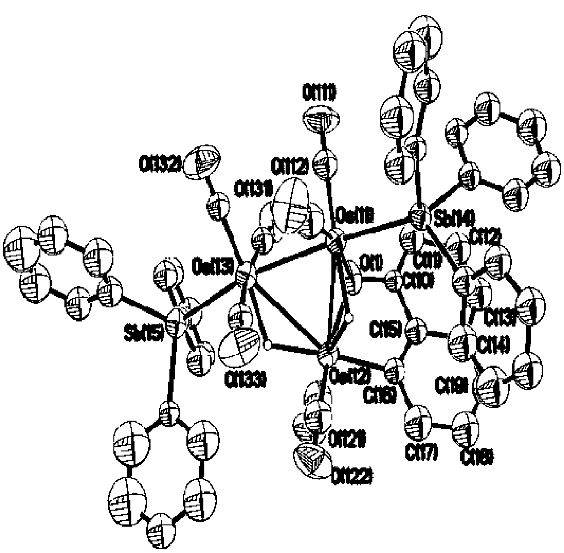


Fig. 3. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for molecule A of **5c**. Os(11)–Os(12) = 2.8420(13) Å; Os(11)–Os(13) = 2.8255(13) Å; Os(12)–Os(13) = 3.0616(13) Å; Os(11)–O(1) = 2.188(14) Å; Os(12)–O(1) = 2.125(17) Å; Os(12)–C(16) = 2.06(2) Å; Os(11)–Sb(14) = 2.6420(17) Å; Os(13)–Sb(15) = 2.6123(18) Å; $\angle$Os(11)Os(12)Os(13) = 57.04(3)°; $\angle$Os(12)Os(11)Os(13) = 65.39(3)°; $\angle$Os(11)Os(13)Os(12) = 57.56(3)°; $\angle$Os(11)O(1)Os(12) = 82.4(5)°.

The reaction of **2** with $AsPh_3$ gave the disubstituted derivative $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_8(AsPh_3)_2$, **7b**, and another cluster **C**. The latter has a mass spectrum that suggests the formulation $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_9(AsPh_3)$, but its IR spectrum is very different from that of **6a**. On the other hand, the reaction with $SbPh_3$ gave three major products which were identified as the substituted derivatives $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_9(SbPh_3)$, **6c**, $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_8(SbPh_3)_2$, **7c**, and the cluster $Os_3(CO)_{10}(SbPh_3)_2$, **8**. The structures of **7b** and **7c** have been confirmed by single crystal X-ray crystallographic studies; the ORTEP diagram for **7b** is shown in Fig. 5 and selected bond parameters for **7b** and **7c** are tabulated in Table 1. In contrast to **5c**, these clusters have disubstitution by the EPh_3 ligands at the two naphthyl-bridged osmiums; this is probably attributable to steric effects of the naphthyl ring in **5c**. As may

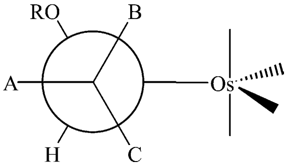


Fig. 4. Possible substitution positions at an alkoxy-bridged osmium; Newman projection along the bridged Os–Os bond.

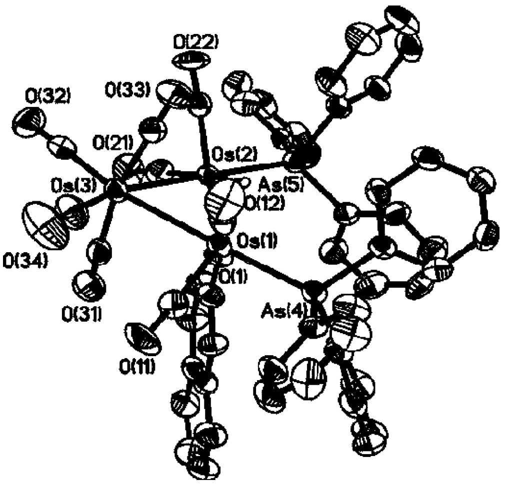


Fig. 5. ORTEP diagram (organic hydrogens omitted, 50% probability thermal ellipsoids) for **7b**.

be expected, a comparison between the structural parameters of **7b** and **7c** shows that there are some differences in the bond parameters associated with the triosmium core which may be attributed to the different stereoelectronic properties of arsine versus stibine.

The ^{1}H NMR spectrum of **7b** showed two singlet metal hydride resonances at -10.28 and -10.43 ppm, in a relative intensity ratio of 6:5, suggesting that there are two geometrical isomers. The solid-state structure is that in which the two $AsPh_3$ ligands are in position A (Fig. 4), and hence presumably the other isomer may have one or both ligands in the sterically more favourable position C. In contrast, the ^{1}H NMR spectrum of **7c** showed five singlets in the metal hydride region; the two metal hydride resonances at -10.06 and -10.90 ppm may be attributed to two geometrical isomers, in analogy to **7b**. Additional resonances observed at -14.02, -14.38 and -22.37 ppm may be attributed to decomposition products of **7c** on silica during TLC separation; this sensitivity may also account for the isolation of cluster **8** among the products (Table 2).

Our results are summarised in Scheme 1. Thus, we have shown that nucleophilic substitution reactions of the naphthyl clusters appear to be more complicated than was expected; in many cases, the initial reaction product(s) obtained decomposed during chromatographic separation.

Table 1
Selected bond lengths (Å) and angles (°) for **7b** and **7c**

Bond parameter	**7b**	**7c**
Os(1)–Os(2)	2.8605(5)	2.8693(4)
Os(1)–Os(3)	2.8224(6)	2.8003(3)
Os(2)–Os(3)	2.8112(6)	2.8046(4)
Os(1)–O(1)	2.131(7)	2.129(5)
Os(2)–O(1)	2.123(6)	2.123(4)
Os(1)–As(4)/Sb(1)	2.5055(11)	2.6531(5)
Os(2)–As(5)/Sb(2)	2.4932(11)	2.6454(6)
∠Os(2)Os(1)Os(3)	59.292(14)	59.282(9)
∠Os(1)Os(2)Os(3)	59.680(14)	59.135(9)
∠Os(1)Os(3)Os(2)	61.029(14)	61.584(10)
∠Os(1)O(1)Os(2)	84.5(2)	84.87(16)

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. NMR spectra were recorded at ambient temperature on a Bruker ACF-300 FT-NMR spectrometer in $CDCl_3$ unless otherwise stated. IR spectra were recorded as hexane solutions, unless otherwise stated. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. All reagents were from commercial sources and used as supplied. Preparation of the clusters $(\mu\text{-H})_2(\mu_3\text{-}\mathit{1}\text{-OC}_{10}H_6)(CO)_9$, **1**, and $Os_3(\mu\text{-H})(\mu\text{-}\mathit{2}\text{-OC}_{10}H_7)(CO)_{10}$, **2**, has been reported elsewhere [5].

3.2. Reaction of *1* with PPh_3

Triphenylphosphine (48.3 mg, 167 μmol) was added to a solution of **1** (35.9 mg, 37.8 μmol) in hexane (7.5 ml). The mixture was allowed to stir at room temperature for about 4 d. The colour of the solution turned from yellow to orange, accompanied by precipitation of an orange solid. The orange precipitate (**A**) was separated by decantation. (Yield = 23 mg. ν_{CO}/cm^{-1}: 2094w, 2075w, 2032m, 2016s, 2004vs, 1962m, 1939m, 1883m.) On column chromatographic separation of this solid, it decomposed to give $Os(H)_2(CO)_2(PPh_3)_2$, **3**, as a pale yellow solid.

3: ν_{CO}/cm^{-1}: 2020s, 1990vs; ν_{OsH}/cm^{-1}: 1926m, 1871s; ^{1}H NMR δ 7.5–7.0 (m, 30H, *Ph*), -7.83 (t, 2H, Os*H*, $^2J_{PH} = 22.68$ Hz) (lit.:[7e] ν_{CO}/cm^{-1}: 2020s, 1990vs; ν_{OsH}/cm^{-1}: 1926m, 1871s; ^{1}H NMR τ 17.08 ($^2J_{PH} = 22.75$ Hz)); $^{31}P\{^1H\}$NMR δ 18.02s.

3.3. Reaction of *1* with $AsPh_3$

$AsPh_3$ (41.0 mg, 134 μmol) was added to a solution of **1** (125 mg, 131 μmol) in dichloromethane (6 ml), followed by trimethylamine-N-oxide dihydrate (20.0 mg, 180 μmol). Upon stirring, the reaction mixture turned from yellow to orange. After one hour of stirring, the solvent was removed in vacuo. TLC separation of the residue with 1:1 (v/v) dichloromethane/hexane as eluant afforded two major yellow bands which were characterised as $Os_3(\mu\text{-H})_2(\mu\text{-}\mathit{1}\text{-OC}_{10}H_6)(CO)_8(AsPh_3)$, **4b** ($R_f = 0.61$, 26.8 mg, 17%) and $Os_3(\mu\text{-H})_2(\mu\text{-}\mathit{1}\text{-OC}_{10}H_6)(CO)_7(AsPh_3)_2$, **5b** ($R_f = 0.39$, 16.4 mg, 8%).

Table 2
Crystal data for **3**, **4b**, **5c**, **7b**, and **7c**

Compound	**6**	**7b**	**8c**	**10b**	**10c**
Empirical formula	$C_{38}H_{32}O_2OsP_2$	$C_{36}H_{23}AsO_9Os_3$	$C_{53}H_{38}O_8Os_3Sb_2$	$C_{54}H_{38}As_2O_9Os_3.CH_2Cl_2$	$C_{54}H_{38}O_9Os_3Sb_2.CH_2Cl_2$
Formula weight	772.78	1245.06	1616.93	1636.21	1687.41
Temperature (K)	293(2)	223(2)	223(2)	223(2)	173(2)
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	*Pbca*	$P2_1/c$	*Cc*	$P\bar{1}$	$P\bar{1}$
a (Å)	17.9212(1)	13.876	39.6392(2)	12.1754(1)	13.1401(1)
b (Å)	18.2188(1)	18.3063(2)	22.5392(3)	13.4516(1)	14.6401(1)
c (Å)	19.7090(2)	15.0157(2)	23.5202(3)	18.7162(1)	14.7908(2)
α (°)	90	90	90	102.981(1)	93.692(1)
β (°)	90	110.560(1)	105.499(1)	94.822(1)	97.837(1)
γ (°)	90	90	90	115.845(1)	105.685(1)
Volume (Å^3)	6435.04(8)	3571.45(6)	20249.6(4)	2629.69(3)	2698.46(5)
No. of reflections to determine cell parameters	6309	8192	8192	8004	6330
Z	8	4	16	2	2
Density (calculated) (g/cm^3)	1.595	2.316	2.122	2.066	2.077
Absorption coefficient (mm^{-1})	4.095	11.619	8.607	8.636	8.128
F(000)	3056	2288	12000	1540	1570
Crystal size (mm^3)	0.19 × 0.18 × 0.06	0.38 × 0.32 × 0.30	0.32 × 0.26 × 0.18	0.18 × 0.10 × 0.08	0.20 × 0.10 × 0.08
Theta range for data collection (°)	2.07–29.25	2.05–29.36	2.02–29.34	1.76–29.35	1.63–29.37
Reflections collected	41803	27661	155213	19664	23023
Independent reflections	8176 [$R_{int} = 0.0644$]	8850 [$R_{int} = 0.1183$]	44564 [$R_{int} = 0.1062$]	12341 [$R_{int} = 0.0463$]	12876 [$R_{int} = 0.0410$]
Maximum and minimum transmission	0.745880 and 0.534168	0.111081 and 0.056763	0.210958 and 0.101915	0.526897 and 0.332783	0.563893 and 0.356326
Data/restraints/parameters	8176/0/426	8850/0/442	44564/26/1026	12341/0/643	12876/1/643
Goodness-of-fit on F^2	1.079	0.992	1.026	1.032	1.002
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0409$ $wR_2 = 0.0624$	$R_1 = 0.0572$ $wR_2 = 0.1664$	$R_1 = 0.0789$ $wR_2 = 0.1590$	$R_1 = 0.0576$ $wR_2 = 0.0997$	$R_1 = 0.0410$ $wR_2 = 0.0840$
R indices (all data)	$R_1 = 0.0818$ $wR_2 = 0.0746$	$R_1 = 0.0790$ $wR_2 = 0.1821$	$R_1 = 0.1474$ $wR_2 = 0.1963$	$R_1 = 0.1133$ $wR_2 = 0.1217$	$R_1 = 0.0678$ $wR_2 = 0.0944$
Largest diff. peak and hole (e Å^{-3})	0.565 and −0.766	4.213 and −4.555	3.555 and −3.142	1.880 and −1.528	1.952 and −2.156
Absolute structure parameter			−0.026(7)		

4b: ν_{CO}/cm^{-1}: 2096s, 2066m, 2055m, 2029s, 2014vs, 2010sh, 1990w, 1979w, 1973w, 1957m, 1948w; MS (FAB): 1246 (calculated for M$^+$, 1246).

5b: ν_{CO}/cm^{-1}: 2080w, 2023s, 2004vs, 1985w, 1945s. ^{1}H NMR δ 7.4–6.9 (m, aromatic), −9.82 (s, 1H, Os*H*Os), −13.71 (s, 1H, Os*H*Os). MS (FAB): 1523 (calculated for M$^+$, 1524).

A similar reaction with $SbPh_3$ (41.0 mg, 11.6 μmol), **1** (24.4 mg, 25.7 μmol) and trimethylamine-N-oxide dihydrate (6.2 mg, 56 μmol) gave one major band upon TLC separation, which was characterised as $Os_3(\mu\text{-}H)_2(\mu\text{-}1\text{-}OC_{10}H_6)(CO)_7(SbPh_3)_2$, **5c** ($R_f = 0.49$, 6.2 mg, 25%).

5c: ν_{CO}/cm^{-1}: 2078w, 2024s, 2005vs, 1949s, 1946s. ^{1}H NMR δ 7.8–6.1 (m, aromatic), −9.91 (s, 1H, Os*H*Os) and −14.32 (s, 1H, Os*H*Os). *Anal.* (Found) C, 39.81; H, 2.80. Calc. for $C_{53}H_{38}O_8Os_3Sb_2$: C, 39.33; H, 2.35.

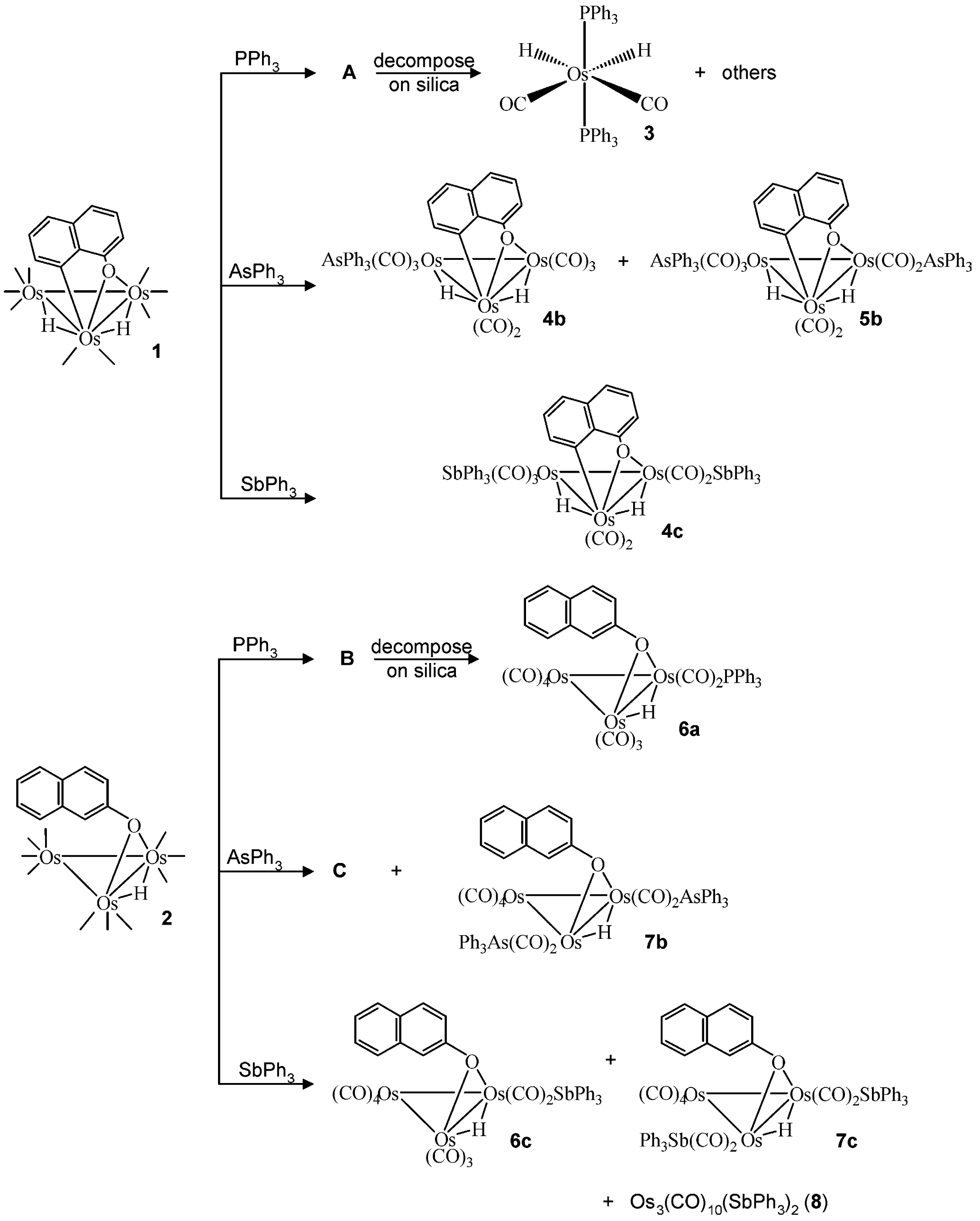
3.4. Reaction of 2 with PPh_3

PPh_3 (54.2 mg, 206 μmol) was added to a solution of **2** (44.9 mg, 46.4 μmol) in hexane (6 ml). The mixture was allowed to stir at room temperature for 2d. The colour of the reaction mixture turned from yellow to orange and upon further stirring an orange solid precipitated. The orange precipitate (**B**) was separated by decantation. (Yield = 24.2 mg. ν_{CO}/cm^{-1}: 2113w, 2082sh, 2070sh, 2063br,vs, 2011br,vs, 1999br,vs.) An attempt at chromatographic separation led to decomposition. The supernatant was subjected to TLC separation with 1:9 (v/v) dichloromethane/hexane as eluant to afford $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_7)(CO)_9(PPh_3)$, **6a** ($R_f = 0.34$, 5.1 mg, 11%) as the major product.

6a: ν_{CO}/cm^{-1}: 2095m, 2054s, 2017vs, 2010vs, 1990w, 1978m, 1972m, 1952m; ^{1}H NMR δ 7.5–7.4 (m, 22H, aromatic), −12.44 (d, 1H, Os*H*Os, $^2J_{PH} = 6$ Hz); $^{31}P\{^1H\}$ NMR δ 19.53s. MS (FAB): 1200 (calculated for [M–CO]$^+$, 1202).

3.5. Reaction of 2 with $AsPh_3$

$AsPh_3$ (26.1 mg, 85.3 μmol) was added to a solution of **2** (84.3 mg, 87.0 μmol) in dichloromethane (8 ml). The mixture was allowed to stir at room temperature for about 1 h to ensure dissolution before the addition of trimethylamine-N-oxide dihydrate (20.0 mg, 180 μmol).



Scheme 1.

The colour of the reaction mixture turned from yellow to orange. After 1 h of stirring, the solvent was removed in vacuo. TLC separation of the residue with dichloromethane/hexane (1:1, v/v) as eluant afforded two major products, viz., $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_6)(CO)_8(AsPh_3)_2$, **7b** ($R_f = 0.53$, 21.5 mg, 26%) as a dark orange crystalline solid, and a yellow powder (**C**) which has been tentatively formulated as $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_6)(CO)_9(AsPh_3)$ ($R_f = 0.47$, 8.1 mg, 10%).

C: ν_{CO}/cm^{-1}: 2080s, 2071m, 2059w, 2031w, 2019sh, 2008vs, 2003s,sh, 1970m, 1939s. MS (FAB): 1244 (calculated for for M^+, 1246).

7b: ν_{CO}/cm^{-1}: 2084m, 2073w, 2031w, 2008vs, 1972w, 1961w, 1942m; ^1H NMR δ 7.9–7.0 (m, 37H, aromatic), −10.28 (s, 1H, Os*H*Os). MS (FAB): 1523 (calculated for M^+, 1523).

A similar reaction with $SbPh_3$ (111.4 mg, 31.6 μmol), **2** (44.9 mg, 4.51 μmol) and trimethylamine-N-oxide dihydrate (6.2 mg, 56 μmol) gave, after TLC separation (dichloromethane/hexane, 3:7, v/v), three major products, *viz.*, $Os_3(\mu\text{-}H)(\mu\text{-}2\text{-}OC_{10}H_6)(CO)_9(SbPh_3)$, **6c** ($R_f = 0.62, = 9.1$ mg, 20%) as a bright yellow solid, the known cluster $Os_3(CO)_{10}(SbPh_3)_2$, **8** ($R_f = 0.49$, 6.9 mg, 15%) as a yellow crystalline solid, and $Os_3(\mu\text{-}H)$

(μ-2-$OC_{10}H_6$)$(CO)_8(SbPh_3)_2$, **7c** (R_f = 0.45, 6.2 mg, 14%) as an orange crystalline solid.

6c: ν_{CO}/cm^{-1}: 2098w, 2059s, 2020vs, 2016sh, 1997w, 1986w, 1980w, 1949w. ^{1}H NMR δ 7.7–6.4 (m, aromatic), −11.23 (s, 1H, Os*H*Os). MS (FAB): 1320 (calculated for M$^+$, 1320).

7c: ν_{CO}/cm^{-1}: 2086w, 2076m, 2033w, 2003vs, 1987m, 1966w, 1950w, 1930w. ^{1}H NMR δ 7.6–6.3 (m, aromatic), −10.06 (s, 1H, Os*H*Os). MS (FAB): 1617 (calculated for [M–CO]$^+$, 1618).

8: ν_{CO}/cm^{-1}: 2087w, 2033m, 2017m, 2005vs, 1973w, 1961w, 1949w. MS (FAB): 1556 (calculated for M$^+$, 1558).

3.6. Crystal structure determinations

Crystals were grown by slow cooling from dichloromethane/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, with the SMART suite of programs [11]. Data were corrected for Lorentz and polarisation effects with SAINT [12], and for absorption effects with SADABS [13]. The final unit cell parameters were obtained by least squares on a number of strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs [14].

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic H atoms were generally placed in calculated positions and given isotropic thermal parameters at 1.5 times that of the C atoms to which they are attached. The metal hydride positions were either located by low angle difference maps (**3**, **4b**, **7b** and **7c**) and their positions refined but with the isotropic thermal parameters fixed, or were placed in calculated positions with XHYDEX (**5c**) [15]. All non-hydrogen atoms were given anisotropic thermal parameters in the final models, except for 8c, in which the carbon atoms were also given isotropic thermal parameters, and vibration restraints were placed on all Os–C–O bonds.

There was a dichloromethane solvent molecule found in **5c**, modelled as being present with an occupancy factor of 0.5.

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