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Cluster build up with arsinidene ligands: synthesis and characterization of some RAs-bridged tri-, tetra- and penta-nuclear osmium carbonyl clusters *

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Abstract

Reaction of the labile cluster $Os_3(CO)_{11}(NCMe)$ (**1**) with primary arsines ($RAsH_2$; R = Ph, Me, H) yields the arsinidene compounds $H_2Os_2(CO)_{11}(\mu_3\text{-AsR})$ (**2a**: R = Ph; **2b**: R = Me; **2c**: R = H) in which the cluster framework consists of an $HOs(CO)_4$ and an $HOs_2(CO)_7$ unit linked together by a μ_3-AsR group. The ^1H NMR spectra of **2a**–**2c** reveal the presence of two isomers in each case. At elevated temperatures, **2a** can be transformed to the AsPh capped cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-AsPh})$ (**3**). Treatment of the phenyl derivative **2a** with Os sources such as $Os_3(CO)_{12}$, $H_2Os_2(CO)_{10}$, or $H_2Os(CO)_4$ gives, under thermolytic conditions, the tetranuclear cluster $(\mu\text{-H})_2Os_4(CO)_{12}(\mu_3\text{-AsPh})$ (**4**) and the pentanuclear cluster $Os_5(CO)_{15}(\mu_4\text{-AsPh})$ (**5**).

Introduction

Since the first report of a cluster compound containing a μ-ER group [1] (E = group 15 element), the study of this type of compound has become of importance in the chemistry of transition-metal carbonyl clusters [2–4]. Many derivatives with the capping μ-PR ligand, in particular, have been investigated in view of the ability of the PR clamp to hold the metal framework together during a reaction. In contrast to that well developed field, considerably less is known about the chemistry of the related μ-AsR bridged cluster compounds. In view of the key role μ-PR ligands can play in the construction of higher nuclearity osmium carbonyl clusters [3–6], it was also of interest to examine the utility of μ-AsR groups in similar build-up reactions. In this work we report the synthesis and characterization of osmium clusters with up to five metal atoms containing bridging μ-AsR ligands.

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday.

As synthetic precursors for the introduction of the arsinidene ligand, primary arsines ($RAsH_2$) have been used.

Results and discussion

The acetonitrile cluster $Os_3(CO)_{11}(NCMe)$ (**1**) (a proven starting material for the preparation of phosphinidene osmium clusters [3,6]) reacts with primary arsines ($RAsH_2$; R = Ph, Me, H) at ambient conditions to give products of the general formula $H_2Os_3(CO)_{11}AsR$ (**2a**–**2c**) in high yields.

$$\underset{(\mathbf{1})}{Os_3(CO)_{11}(NCMe)} + RAsH_2 \xrightarrow[\text{r.t.}]{CH_2Cl_2} H_2Os_3(CO)_{11}AsR$$

(**2a**: R = Ph,
2b: R = Me,
2c: R = H)

On the basis of a simple electron counting scheme combined with the spectroscopic data we suggest that two Os–Os bonds have been cleaved in the reaction. The ^1H NMR spectra of **2a**–**2c** show two signals in the region normally associated with terminally bound hydride ligands on osmium centres. Hence, the pale yellow compounds **2a**–**2c** can be formulated as "opened cluster", consisting of a dinuclear $HOs_2(CO)_7$ and a mononuclear $HOs(CO)_4$ unit held together by a μ_3-bridging RAs ligand. The ability of primary arsines to break As–Os bonds under mild conditions was observed previously in the reaction of $Os_3(CO)_{11}(NCMe)$ (**1**) and Me_2AsH to give $HOs_3(CO)_{11}(\mu\text{-}AsMe_2)$ [7]. The hydride on the $HOs(CO)_4$ spike can adopt a *cis* and a *trans* position with respect to the arsenic atom, resulting in formation of two isomers in an ca. 1/1 ratio (Fig. 1).

In the ^1H NMR spectrum (Table 1) of **2c** (R = H) the signals of each isomer can be assigned since the two H–As resonances exhibit a small and a large coupling to the hydride on the $HOs(CO)_4$ spike (Fig. 2), however the assignment to a structure (*cis* or *trans*) is not possible in this case. A structure containing a $H_2Os(CO)_3$ and a $Os_2(CO)_6$ fragment (two hydrides bonded to the same Os atom) can be ruled out on the basis of chemical shift differences and the multiplicity patterns.

The behaviour of the arsines $RAsH_2$ towards the acetonitrile complex $Os_3(CO)_{11}(NCMe)$ (**1**) is remarkably different from that of the related phosphines RPH_2. The phosphines give in the first step the substitution products $Os_3(CO)_{11}PRH_2$ which can be isolated and transformed by heat [8,9] or base (for R = H [11]) into the phosphido-bridged clusters $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PRH)$. In the case of the arsines $RAsH_2$, the primary product "$Os_3(CO)_{11}AsRH_2$" (R = Ph) has

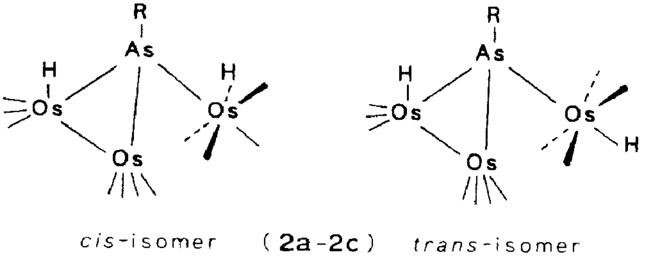


Fig. 1. Suggested structures for the two isomers of $H_2Os_3(CO)_{11}(\mu_3\text{-}AsR)$ (**2a**–**2c**).

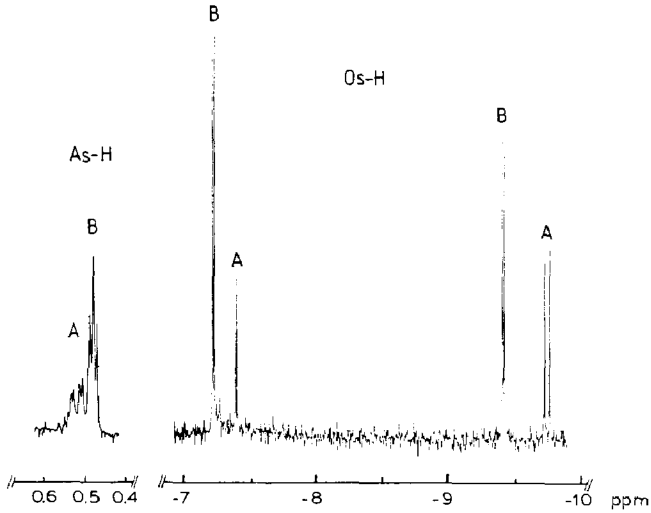


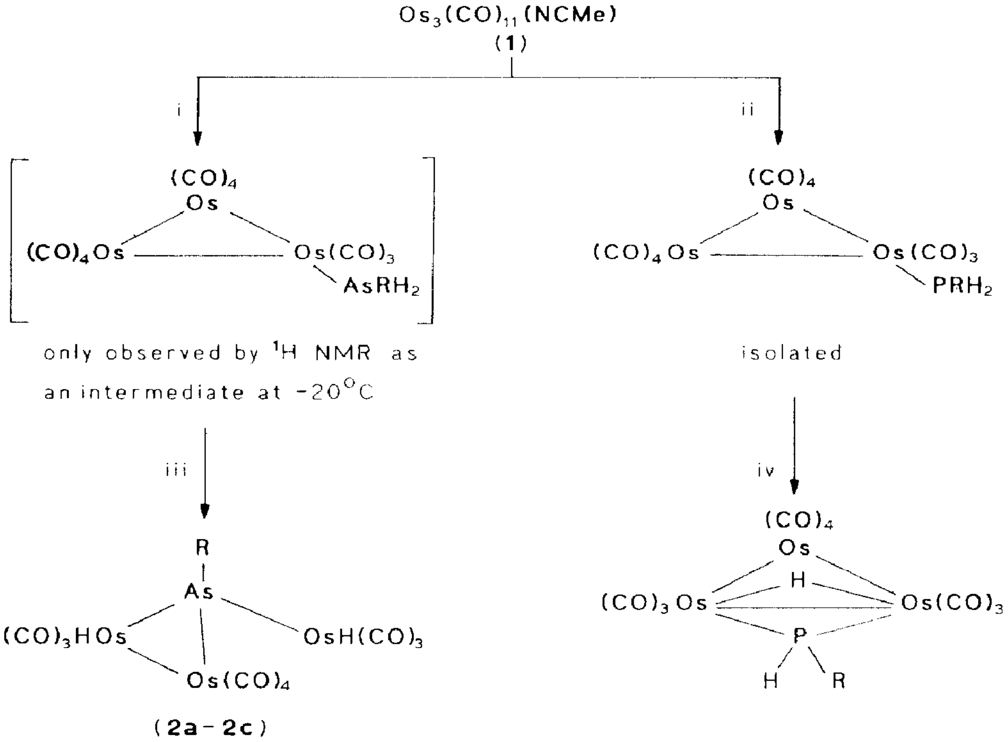
Fig. 2. ^1H NMR spectrum of **2c** showing the presence of two isomers **A** and **B**.

only been observed by ^1H NMR spectroscopy as a transient species at low temperatures (δ 1.56 ppm for the As-hydrogens). At room temperature, and on exposure to light, the mono-substitution products react rapidly to give the opened clusters $H_2Os_3(CO)_{11}(\mu_3\text{-AsR})$ (**2a**–**2c**) described above (Scheme 1).

The synthetic potential of the spike clusters $H_2Os_3(CO)_{11}(\mu_3\text{-AsR})$ (**2a**–**2c**) for the build up of higher nuclearity osmium clusters has been investigated for the phenyl derivative **2a** because of its ready formation and relative thermal stability. Thermolysis of $H_2Os_3(CO)_{11}(\mu_3\text{-AsPh})$ (**2a**) in boiling toluene leads to the loss of two CO ligands and to recombination of the cluster framework to give the trinuclear arsinidene capped compound, $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-AsPh})$ (**3**), in good yields (Scheme 2). A singlet in the ^1H NMR spectrum at -21.42 ppm indicates that the two hydrides adopt structurally equivalent bridging positions on two Os–Os edges. Spectroscopic data (Table 1) are similar to those for the related phosphinidene cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-PPh})$ [8] and for the Ru/As cluster $(\mu\text{-H})_2Ru_3(CO)_9(\mu\text{-AsPh})$ [9], which suggests a structural similarity to these species. Heating of the μ_3-AsH complex **2c** under similar conditions resulted solely in decomposition. All attempts to close up the cluster **2a** by a deprotonation–protonation sequence or by irradiation have been unsuccessful.

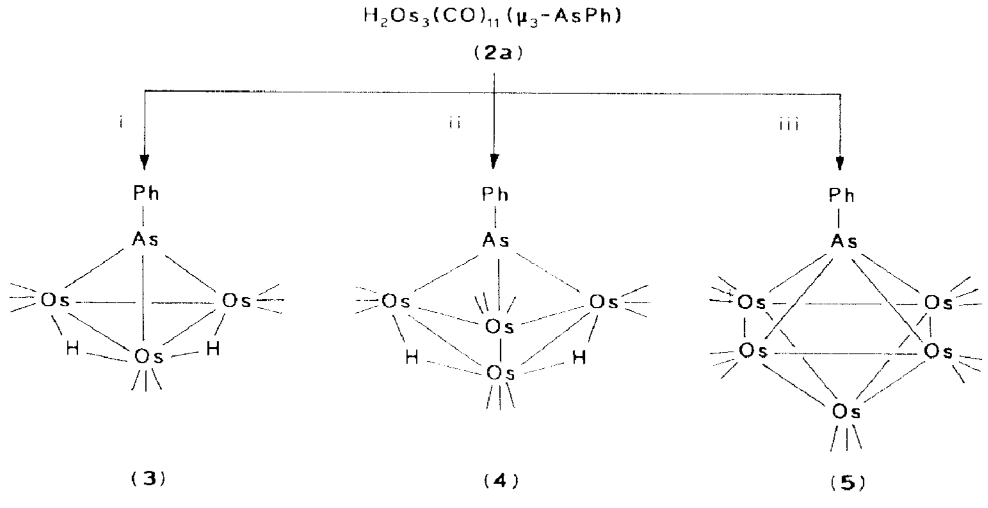
In refluxing toluene and in the presence of osmium sources such as $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ or $H_2Os(CO)_4$, **2a** is converted into the yellow tetranuclear osmium cluster $(\mu\text{-H})_2Os_4(CO)_{12}(\mu_3\text{-AsPh})$ (**4**) (Scheme 2). The pentanuclear cluster $Os_5(CO)_{15}(\mu_4\text{-AsPh})$ (**5**) is also formed in the reaction with $H_2Os_3(CO)_{10}$, or with $Os_3(CO)_{12}$ in refluxing octane (125°C). Complexes **4** and **5** have been identified by their spectroscopic similarities to known compounds.

Compound **4** shows a parent ion in the mass spectrum at *m/e* 1258 corresponding to the fragment $[H_2Os_4(CO)_{12}(AsPh)]^+$. The IR and the ^1H NMR spectra of **4** are similar to the structurally characterized cluster $(\mu\text{-H})_2Os_4(CO)_{12}(\mu_4\text{-PPh})$ [4]. This suggests that **4** has an analogous structure to the phosphinidene compound, and hence that the osmium atoms adopt a butterfly arrangement, with the arsinidene ligand bridging an open triangular face of one "hinge" atom and the two



Scheme 1. Comparison of the reactivity of arsines and phosphines of the type (E = P, As) towards $Os_3(CO)_{11}(NCMe)$. i = $RAsH_2$, −20 °C; ii = RPH_2, r.t.; iii = r.t., light; iv = ΔT.

"wingtip" osmium atoms (Scheme 2). The hydride ligands must be bridging between second hinge Os and the wingtip Os atoms, giving rise to the observed singlet in the ^1H NMR spectrum (Table 1). Electron counting rules suggest the presence of five metal–metal bonds, consistent with the proposed structure.



Scheme 2. Synthesis of tri-, tetra- and penta-nuclear Os clusters from $H_2Os_3(CO)_{11}(\mu_3\text{-}AsPh)$ (**2a**). i = toluene, 110 °C; ii = $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ or $(CO)_4$, toluene, 110 °C; iii = $Os_3(CO)_{12}$, n-octane, 125 °C or $H_2Os_3(CO)_{10}$, toluene, 110 °C.

Table 1

Spectroscopic data for new compounds

	IR (hexane; cm^{-1})	^1H NMR ($CDCl_3$, ppm)
$H_2Os_3(CO)_{11}(\mu_3\text{-AsPh})$ (**2a**)	2142w, 2105m, 2987m, 2062vs, 2055s, 2051s, 2030s, 2026s, 2020sh, 2006w, 1994ms, 1971m, 1945m(br)	6.8–7.5(m) −7.23(s), −7.34(s) −8.87(s), −9.16(s)
$H_2Os_3(CO)_{11}(\mu_3\text{-AsMe})$ (**2b**)	2144w, 2101m, 2086sh, 2083m, 2064s, 2054s, 2025vs, 2019s, 1997m, 1972m, 1925vw(br)	2.65(s), 2.48(s) −7.20(s), −7.22(s) −9.20(s), −9.66(s)
$H_2Os_3(CO)_{11}(\mu_3\text{-AsH})$ (**2c**)	2149w, 2105m, 2988m(br), 2069s, 2054s, 2029vs, 2022m, 1999ms, 1975m	0.54(dd)(*J* 8.3/3.0 Hz) 0.48(dd)(*J* 3.6 Hz) −7.21(d)(*J* 3.5 Hz) −7.39(d) (*J* 2.9 Hz) −9.42(d)(*J* 3.6 Hz) −9.75(d)(*J* 8.4 Hz)
$(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-AsPh})$ (**3**)	2104w, 2077vs, 2050vs, 2030ms, 2026sh, 2010s, 1994m, 1980w,	7.4–7.9(m) −21.42(s)
$(\mu\text{-H})_2Os_4(CO)_{12}(\mu_3\text{-AsPh})$ (**4**)	2104w, 2977s, 2031vs, 2027sh, 2018m, 2010s, 1994m, 1980w	7.4–7.5(m) −18.45(s)
$Os_5(CO)_{15}(\mu_3\text{-AsPh})$ (**5**)	2102w, 2060vs, 2035s, 1994w	

The application of these rules to cluster **5** indicates that it must involve an $Os_5(\mu_4\text{-As})$ octahedron. Infrared and mass spectroscopic data imply that **5** is probably structurally similar to the related phosphinidene clusters $Os_5(CO)_{15}(\mu_4\text{-PPh})$ [6] and $Os_5(CO)_{15}(\mu_4\text{-POMe})$ [11]. Therefore, the probable structure for **5** is that of an octahedron consisting of five $Os(CO)_3$ vertices, with the sixth vertex being a μ_4-AsPh ligand.

Experimental

All reactions were carried out under dry nitrogen by standard Schlenk techniques. The solvents were distilled under N_2 from appropriate drying agents. Thin layer chromatography of product mixtures was performed in air on plates coated with silica (Merck Kieselgel 60, 70–230 mesh). ^1H NMR data were recorded on Bruker WM 250 or AM 400 instruments at r.t. in $CDCl_3$ with the solvent as lock and reference (7.24 ppm). Infrared spectra were recorded on a Perkin–Elmer 983 instrument between 2200 and 1600 cm^{-1}. Mass spectra were recorded on a AE1 MS12 spectrometer (70 eV ionising potential; reference: tris(perfluoroheptyl)-s-triazine). The starting materials $Os_3(CO)_{11}(NCMe)$ [12], $Os_3(CO)_{10}(NCMe)_2$ [12], $H_2Os_3(CO)_{10}$ [13], $H_2Os(CO)_4$ [14], $MeAsH_2$ [15], $PhAsH_2$ [16] and AsH_3 [17] were prepared by published methods. The gases AsH_3 and $MeAsH_2$ were handled in a conventional vacuum line fitted with Teflon taps.

Preparation of $H_2Os_3(CO)_{11}(\mu_3$-AsR) (2a: R = Ph; 2b: R = Me; 2c: R = H)

In a typical reaction, 46 mg (0.05 mmol) of $Os_3(CO)_{11}$(NCMe) (**1**) was dissolved in 25 ml of dichloromethane and an excess of the arsine (ca. 2–3 equiv.) was added with vigorous stirring ($MeAsH_2$ and AsH_3 were condensed into the reaction vessel at liquid nitrogen temperatures). After 2–3 hours the IR spectrum of the solution showed the reaction to be complete, and the solvent and the excess of arsine were removed in vacuo. The residue was dissolved in 2 ml of CH_2Cl_2 and chromatographed on TLC plates with a CH_2Cl_2/hexane (3/7) mixture as eluant. The faint yellow, almost colourless, main band ($R_f = 0.59$ (**2a**), 0.45 (**2b**), 0.64 (**2c**)) could be identified only with the aid of an UV lamp (Yield: **2a**: 39 mg, 76%; **2b**: 34 mg, 71%; **2c**: 34 mg, 70%; pale yellow, only moderately air stable crystals). M^+: m/z 1038 (**2a**), m/z 976 (**2b**), m/z 962 (**2c**).

Preparation of $(\mu$-H$)_2Os_3(CO)_9(\mu_3$-AsPh) (3)

A solution of 40–50 mg (0.04–0.05 mmol) of **2a** was obtained by dissolving in 25 ml of toluene the crude product from the synthesis of **2a** (see above). After 5 h reflux at 110 °C the toluene was removed in vacuo and the residue purified bt TLC (CH_2Cl_2/hexane (3.5/6.5) as eluant). The light yellow main band ($R_f = 0.6$) was found to be compound **3** (overall yield, referred to $Os_3(CO)_{11}$(NCMe) (**1**): 29 mg, 60%; pale yellow, air stable crystals; Anal.: found C, 18,53; H, 0.63. $C_{15}H_7AsO_9O_5$ calcd.: C, 18.44, H, 0.72%). M^+: m/z 982.

Preparation of $(\mu$-H$)_2Os_4(CO)_{12}(\mu_3$-AsPh) (4)

Complex **2a** was prepared as above from 46 mg (0.05 mmol) of $Os_3(CO)_{11}$(NCMe) (**1**). After removal of the solvent from the reaction mixture, the crude product **2a** was dissolved in 25 ml of toluene. An equivalent amount of $Os_3(CO)_{12}$ (45 mg; 0.05 mmol), $H_2Os_3(CO)_{10}$ (43 mg; 0.05 mmol) or $H_2Os(CO)_4$ (4 ml of a solution in heptane containing ca. 6 mmol/l) was added, and the mixture was refluxed for 8 h. The toluene was then removed in vacuo and the residue purified by TLC (CH_2Cl_2/hexane (3/7) as eluant). The cluster **4** was isolated from an intense yellow band ($R_f = 0.61$) (overall yield, referred to **1**: 16 mg for $Os_3(CO)_{12}$; 20 mg for $H_2Os_3(CO)_{10}$; 25 mg for $H_2Os(CO)_4$; 25–40%; yellow, air stable crystals). M^+: m/z 1258.

Preparation of $Os_5(CO)_{15}(\mu_4$-AsPh) (5)

Again **2a** was used without further purification.

(a) A solution of 40–50 mg (0.04–0.05 mmol) of **2a** and 43 mg (0.05 mmol) of $H_2Os_3(CO)_{10}$ in 25 ml of toluene was refluxed for 8 h. The solution was then evaporated to dryness and the cluster **5** isolated by TLC (CH_2Cl_2/hexane (3/7) as eluant) as a dark red band ($R_f = 0.57$) (overall yield, referred to **1**: 15 mg; 20%; dark red, air stable crystals). M^+: m/z 1532.

(b) A solution of 40–50 mg (0.04–0.05 mmol) of **2a** and 45 mg (0.05 mmol) of $Os_3(CO)_{12}$ in 25 ml of n-octane was kept at 125 °C for 12 h. After removal of the solvent in vacuo, **5** was isolated as described in (a) (overall yield, referred to **1**: 11 mg; 15%).

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