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The Metallostibine $\text{Os}_2(\text{CO})_8(\mu\text{-SbPh})$: A Versatile Donor Precursor for Antimony-Containing Heterometallic Clusters

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Abstract: The metallostibine $\text{Os}_2(\text{CO})_8(\mu\text{-SbPh})$, **2**, acts as a good two-electron donor ligand, reacting readily with Group 8 metal carbonyls to give heterometallic clusters. Specifically, it undergoes ligand substitution reaction with $\text{Fe}_2(\text{CO})_9$, $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$, or $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ to afford $\text{Os}_2\text{Fe}(\text{CO})_{12}(\mu_3\text{-SbPh})$, **3**, $\text{Os}_5(\text{CO})_{19}(\mu_3\text{-SbPh})$, **4**, or $\text{Os}_7(\text{CO})_{26}(\mu_3\text{-SbPh})_2$, **5**, respectively, in moderate to high yields. An analogous reaction with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ afforded another spirocyclic cluster $\text{Os}_3\text{Ru}(\text{CO})_{14}(\mu\text{-PhCO})(\mu_4\text{-Sb})$, **9**. UV irradiation of **4** afforded the spirocyclic clusters $\text{Os}_5(\text{CO})_{18}(\mu, \eta^2\text{-PhCO})(\mu_4\text{-Sb})$, **6**, and $\text{Os}_5(\text{CO})_{18}(\mu, \eta^2\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_4\text{-Sb})$, **7**, while the raft-like cluster $\text{Os}_5(\text{CO})_{19}(\mu_3\text{-SbPh})$, **8**, was obtained when a methanolic solution was exposed to natural light; cluster **5** failed to react under similar conditions. All the new clusters have been characterized spectroscopically and crystallographically, and possible pathways for the formation of **6-9** proposed.

Keywords: Metalloligand, metallostibine, heteronuclear, heterometallic, transition metal carbonyl clusters

Introduction

Heterometallic clusters containing oxophilic main group metals such as Sb, Bi or Sn are of interest as single-source precursors for heterometallic nanoparticles with enhanced activity and selectivity in oxidation and hydrogenation reactions [1]. The

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most common way to introduce antimony, for example, is to use triorganostibines such as SbPh_3 but a disadvantage is that triorganostibines are generally rather weak ligands and hence can easily dissociate during calcinations [2]. One way around this, which have been examined with osmium- and ruthenium carbonyl clusters, is to use Sb-Cl , Sb-H , or Sb-Sb bond cleavage reactions with SbPh_2Cl , SbPh_2H or Sb_2Ph_4 [3]. These lead to products containing bridging SbPh_2 moieties, which should be more suited as precursors for antimony-containing metallic nanoparticles.

We recently reported the synthesis of the metallostibine $\text{Os}_2(\text{CO})_8(\mu\text{-SbPh})$, **2**, which exhibits strong donor strength comparable to that of alkylphosphines. It is also less sterically hindered compared to, for example, PPh_3 [4]. It should thus be a versatile precursor for the introduction of both Sb and Os atoms, via simple substitution of a CO or other two-electron ligands, in the construction of larger clusters. We report here our studies on its reactions with some of the heavier group 8 metal carbonyls.

Results and Discussion

The metallostibine **2** can be generated in a relatively pure form from the cluster $\text{Os}_3(\text{CO})_{11}(\mu_3\text{-SbPh})(\text{Cl})_2$, **1** [3b]. Isolation is generally not necessary and hence it can be generated *in-situ* and directly reacted with $\text{Fe}_2(\text{CO})_9$, $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$, or $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ to afford the clusters $\text{Os}_2\text{Fe}(\text{CO})_{12}(\mu_3\text{-SbPh})$, **3**, $\text{Os}_5(\text{CO})_{19}(\mu_3\text{-SbPh})$, **4**, or $\text{Os}_7(\text{CO})_{26}(\mu_3\text{-SbPh})_2$, **5**, respectively (Scheme 1).

The products are relatively air-stable and can be purified by thin layer chromatography. They have been characterised spectroscopically and by single-crystal X-ray diffraction studies, although the crystal of **5** exhibited severe disorder, including of the metal core. ORTEP plots showing the molecular structures of **3** and **4**, together with selected bond parameters, are shown in Figures 1 and 2, respectively.

In cluster **3**, the Fe-CO bond *trans* to the metallostibine (**2**) is slightly shorter than the others (sum of Fe-C and C-O = 2.917(11) Å, *cf.*, 2.927(11)-2.935(13) Å for the others). This is similar to the situation in the complex (Ph₃Sb)Fe(CO)₄, in which the Fe-CO bond *trans* to SbPh₃ is significantly shorter than the others (2.904 Å vs 2.924-2.936 Å) [5], and is indicative that **2** has a stronger *trans* influence than SbPh₃ and comparable to that of CO and a bridging SbPh₂ [6]. Although the solid-state structure of **3** shows that the ligand **2** occupies an axial position in the coordination sphere of the Fe atom (labeled as *axial* isomer), fast equilibration in solution between the axial and equatorial isomers is expected for such trigonal bipyramidal structures. This is corroborated by the ¹³C{¹H} NMR spectrum, which shows one resonance for the CO ligand coordinated to Fe (~216 ppm) down to -80 °C (Figures S5-6), and the computed free energies which shows that the equatorial isomer lies 0.7 kJ/mol above the axial isomer (Figure S23).

In the Os₃(CO)₁₁ fragment of cluster **4**, the Os-Os bond *cis* to the metallostibine (**2**) is longer than the other two Os-Os bonds (Os3-Os5 = 2.9183(4) Å, *cf.*, 2.8527(3) and 2.8955(3) Å). This is consistent with previous observations that with the trinuclear clusters, a Group 15 ligand lengthens the metal-metal bond *cis* to it [7]. The room temperature ¹³C{¹H} NMR spectrum of **4** showed only four peaks in the carbonyl region (Figure S8), probably due to ligand fluxionality as commonly observed for transition metal carbonyl clusters [8].

Scheme 1. Reactions of **2** with $\text{Fe}_2(\text{CO})_9$ or $\text{Os}_3(\text{CO})_{12-n}(\text{CH}_3\text{CN})_n$ ($n = 1, 2$).

Although there was severe disorder in the crystal of **5**, the metal core was unambiguously revealed to have a *trans-trans* configuration of the two metallostibine ligands about an $\text{Os}_3(\text{CO})_{10}$ unit (Figure S1). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of **5** are not well resolved, and suggests that it probably exists as a dynamic equilibrium of *trans-trans* and *trans-cis* isomers (with respect to the Os-Os bond in between the two metallostibine units), as is typical of triosmium clusters of the general formula $\text{Os}_3(\text{CO})_{10}\text{L}_2$ [9]. A computational study shows that the *trans-trans* isomer lies 2.3 kJ/mol above the *trans-cis* isomer in free energy (Figure S23).

Figure 1. ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)–Os(2) = 2.9477(3); Os(1)–Sb(3) = 2.6770(4); Os(2)–Sb(3) = 2.6722(4); Sb(3)–Fe(4) = 2.5264(8); Os(2)–Sb(3)–Os(1) = 66.879(10); Fe(4)–Sb(3)–Os(2) = 128.33(2); Fe(4)–Sb(3)–Os(1) = 122.41(2).

Figure 2. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Os2 = 2.9616(3), Os2–Sb1 = 2.6907(5), Os1–Sb1 = 2.6942(5), Os3–Sb1 = 2.6241(4), Os3–Os5 = 2.9183(4), Os3–Os4 = 2.8527(3), Os4–Os5 = 2.8955(3), Os1–Sb1–Os2 = 66.731(12), Os1–Sb1–Os3 = 126.797(17), Os2–Sb1–Os3 = 129.035(17), Os1–Sb1–C111 = 105.11(15), Os2–Sb1–C111 = 111.49(15), Os3–Sb1–C111 = 110.19(15).

Scheme 2. Reaction of **2-Bi** with $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$. Adapted from reference [10].

The isolation and characterisation of cluster **4** is interesting as it is reminiscent of the chemistry reported for the bismuth analogue of **2**, *viz.*, $\text{Os}_2(\text{CO})_8(\mu\text{-BiPh})$, **2-Bi**, which was obtained in 5% yield from the reaction of $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ with BiPh_3 . The reaction of **2-Bi** with $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ in refluxing hexane was reported to give the spirocyclic clusters $\text{Os}_5(\text{CO})_{19}(\text{Ph})(\mu_4\text{-Bi})$, **6'-Bi**, and $\text{Os}_5(\text{CO})_{18}(\mu\text{-H})(\mu, \eta^2\text{-C}_6\text{H}_4)(\mu_4\text{-Bi})$, **7-Bi**. These two clusters most probably originated from an initial substitution product $\text{Os}_2(\text{CO})_8(\mu_3\text{-BiPh})\text{Os}_3(\text{CO})_{11}$, **4-Bi**, an analogue of **4** which was not isolated, via oxidative addition of the Bi-Ph bond across the adjacent Os-Os bond

(Scheme 2) [10]. The Sb-C bond in **2** is relative weak (compared to P-C and As-C bonds) and hence may be expected to cleave similarly; the cleavage of phenyl rings from stibine ligands such as SbPh₃ or SbPhCl₂ under mild conditions has been observed with some rhenium and osmium carbonyl clusters [3b,11]. While **4** was stable in refluxing 1,2-dichloroethane (DCE) or acetone, UV irradiation of a toluene solution gave two spirocyclic clusters Os₅(CO)₁₈(μ,η²-PhCO)(μ₄-Sb), **6**, and Os₅(CO)₁₈(μ-H)(μ,η²-C₆H₄)(μ₄-Sb), **7** (Scheme 3). The latter is the antimony analogue of **7-Bi**, while the former is a close analogue of **6'-Bi**. Such spirocyclic clusters, containing a μ₄-Sb moiety, are relatively rare [12].

Interestingly, this photochemical reaction of **4** was found to be solvent-dependent; in methanol, under the same conditions, neither **6** nor **7** were obtained; only several unidentified products obtained in trace amounts (Scheme 3). Exposure of the methanol solution to natural light over several days without stirring, however, afforded the raft-like cluster Os₅(CO)₁₉(μ₃-SbPh), **8**, as a red crystalline solid formed at the bottom of reaction vessel. Cluster **8** is stable but poorly soluble in most of the organic solvents. Both the methanol and natural (visible) light irradiation were essential for this conversion as standing the solution in the dark, or similar irradiation of a solution in a less polar solvent such as DCM, gave no product **8** (other than for a small amount of **6**) even after a prolonged period (~1 month). The photochemical behaviour of **4** may be rationalised in terms of an initial photoproduct **A** which may then undergo a binuclear oxidation addition across either an Os-Sb bond (pathway a), or the Sb-C(Ph) bond (pathway b). Pathway “a” leads directly to **8**, while pathway “b” leads to the unobserved **6'**, which corresponds to **6'-Bi** in the bismuth system (Scheme 2). From **6'**, a CO migratory insertion to **B** followed by O-coordination and migration of the carbonyl ligands (via a merry-go-round) would lead to **6**, while decarbonylation followed by

orthometallation would give **7**. Cluster **6** was obtained as the major product, indicating that the former pathway was more favourable. This is consistent with the need for CO loss in the formation of **7**, and also with observation for the bismuth system that **6'-Bi** converted to **7-Bi** under UV irradiation. The determinants for the two pathways are not entirely clear although the solvent must play a part (methanol favours pathway “a” while toluene favours pathway “b”); the effect of solvent on photochemistry is known [13].

ORTEP plots showing the molecular structures of **6-8**, together with selected bond parameters, are given in Figures 3-5, respectively. The four-membered Os₃Sb ring in **6** is puckered because of the μ, η^2 -O=CPh ligand; the dihedral angle between the Os1Os2Os3 and Os1Sb6Os3 planes is 58.4°. At 286 ppm, the ¹³C resonance for this ligand is very far downfield of typical terminal CO ligands (166-185 ppm); two weak IR absorptions at 1450 and 1417 cm⁻¹ have been tentatively assigned to a ring vibration and a $\nu(\text{C=O})$ stretch, respectively, by comparison with literature values, [14,18a] and through a computational study. The four-membered ring in **7** has, in contrast, a mean deviation from planarity of ~0.17 Å; the presence of a bridging hydride is indicated by a singlet at -19.29 ppm in its ¹H NMR spectrum (Figure S15) and, as is well documented [15], the hydrido-bridged bond is significantly elongated (Os1-Os2 = 3.1358(3) Å vs Os2-Os3 = 2.9638(3) Å and Os4-Os5 = 2.9479(3) Å).

There are two crystallographically independent molecules, with similar bond metrics, observed in the crystal of **8**. The novel metal core may be viewed as comprising an Os₅ chain capped by the μ_3 -SbPh moiety at the two terminal and the middle Os atoms. The five Os atoms are almost coplanar, with a mean deviation of 0.031 Å from planarity, and the μ_3 -SbPh ligand lies 0.78 Å above this plane. Compared to the spirocyclic-Sb atom in **6** and **7**, it is much closer to a regular tetrahedron in **8** as a consequence of the

reduced ring strain for the four-membered metal rings. There is close contact between an ortho-H atom of the phenyl ring and an axial carbonyl O atom of an adjacent Os(CO)₃ moiety, with an H...O distance of ~2.52 Å (Figure S2), but a Hirshfeld surface analysis suggests that this is probably due to close intermolecular contacts which pushed that axial CO ligand inwards, i.e., crystal packing forces (Figure S3).

Scheme 3. Proposed reaction pathways to clusters **6**, **7** and **8**.

Figure 3. ORTEP plot of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Os2 = 2.8824(3), Os2–Os3 = 2.9449(3), Os3–Sb6 = 2.6894(5), Os1–Sb6 = 2.6910(4), Os5–Sb6 = 2.6907(4), Os5–Os4 = 2.9366(3), Os4–Sb6 = 2.7195(4), Os3–C34 = 2.120(6), Os1–O14 = 2.129(4), C34–O14 = 1.256(7), Os1–Sb6–Os3 = 87.638(13), Os4–Sb6–Os5 = 65.746(11), Sb6–Os3–Os2 = 80.694(12), Sb6–Os1–Os2 = 81.826(11), Os3–Os2–Os1 = 79.468(9).

Figure 4. ORTEP plot of **7**. Thermal ellipsoids are drawn at the 50% probability level. Organic hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Os2 = 3.1358(3), Os2–Os3 = 2.9638(3), Os3–Sb6 = 2.7403(4), Os1–Sb6 = 2.7217(4), Os5–Sb6 = 2.6925(4), Os5–Os4 = 2.9479(3), Os4–Sb6 = 2.7267(4), Os2–C24 = 2.137(7), Os1–C25 = 2.140(6), C24–C25 = 1.410(8), C25–C26 = 1.411(10), C26–C27 = 1.366(10), C27–C28 = 1.386(11), C28–C29 = 1.370(11), C24–C29 = 1.398(8), Os1–Sb6–Os3 = 103.923(14), Os4–Sb6–Os5 = 65.904(11), Sb6–Os3–Os2 = 83.045(11), Sb6–Os1–Os2 = 80.170(10), Os3–Os2–Os1 = 89.660(8).

Figure 5. ORTEP plot of one of two crystallographically independent molecules of **8**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Os2 = 3.0152(3), Os2–Sb1 = 2.7330(4), Os5–Sb1 = 2.7322(4), Os4–Os5 = 2.9988(3), Os3–Os4 = 2.9737(3), Os1–Os3 = 2.9565(3), Os3–Sb1 = 2.6588(4), Os2–Sb1–Os3 = 105.885(13), Os5–Sb1–Os3 = 106.100(12), Os2–Sb1–Os5 = 124.303(13), Os2–Sb1–C111 = 100.96(12), Os3–Sb1–C111 = 121.13(13), Os5–Sb1–C111 = 99.84(13), Sb1–Os2–Os1 = 76.987(9), Os2–Os1–Os3 = 92.199(8), Os1–Os3–Sb1 = 79.145(9), Sb1–Os3–Os4 = 79.299(9), Os3–Os4–Os5 = 92.339(7), Os4–Os5–Sb1 = 77.731(9).

The interesting photochemistry of **4** prompted us to attempt the synthesis of its ruthenium analogue, *viz.*, $\text{Os}_2\text{Ru}_3(\text{CO})_{19}(\mu_3\text{-SbPh})$, **4-Ru**, via the reaction of **2** with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ [16]. In a number of attempts under varying conditions, unreacted $\text{Ru}_3(\text{CO})_{12}$ was recovered from most of these reactions, but we also managed to isolate and identify two new clusters, *viz.*, $\text{Os}_2\text{Ru}_3(\text{CO})_{18}(\mu, \eta^2\text{-PhCO})(\mu_4\text{-Sb})$, **6-Ru**, and $\text{Os}_3\text{Ru}(\text{CO})_{14}(\mu\text{-PhCO})(\mu_4\text{-Sb})$, **9** (Scheme 4). Cluster **6-Ru** is the ruthenium analogue of **6** (their IR and ^1H NMR spectra show similar patterns (Figures S13, S20 and S22), and the chemical formulation is also supported by the MS spectrum (Figure S21). Although it could be isolated by TLC on silica, a DCM solution gradually decomposed at room temperature to $\text{Ru}_3(\text{CO})_{12}$ and other unidentified species; cluster **9** was not among them, indicating that **6-Ru** was not the precursor to **9**.

The crystallographic study on **9** showed unambiguously that it had the formulation depicted as **9-A** in Scheme 4, i.e., the $\mu, \eta^2\text{-O=CPh}$ ligand bridges an Os-Ru bond, with the O atom coordinated to the sole Ru atom. The crystal exhibited racemic twinning, and there were two crystallographically independent molecules with similar bond metrics; the ORTEP diagram of one of them, together with selected bond parameters, is given in Figure 6. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** showed three sets of resonances, including three at very low field which were ascribable to the benzoyl moiety. This suggested that **9** was a mixture of three compounds. A variable temperature ^1H NMR experiment did not show evidence of exchange, thus precluding the possibility of isomers in equilibrium (Figure S19). The mass spectrum showed two sets of molecular and fragmentation peaks (Figure S21); one corresponding to **9-A**, *viz.*, $\text{Os}_3\text{Ru}(\text{CO})_{14}(\mu\text{-PhCO})(\mu_4\text{-Sb})$, and another to the formulation $\text{Os}_2\text{Ru}_2(\text{CO})_{14}(\mu\text{-PhCO})(\mu_4\text{-Sb})$; there was no evidence for a formulation

$\text{Os}_4(\text{CO})_{14}(\mu\text{-PhCO})(\mu\text{-Sb})$. These data are consistent with the presence of three different clusters, **9-A**, **9-B** and **9-C**, in which the first two are isomers, and the solid-state structure is that of **9-A**. The product **9** crystallized out from a DCM/ether as uniform, light-orange plates, and repeated crystallographic analyses on randomly selected crystals only gave **9-A**. Repeated attempts at separating the mixture were also unsuccessful. Although a number of osmium-antimony [3,6,12,17], and a handful of ruthenium-antimony [18], clusters have been reported, **9-A** is the first example of an osmium-ruthenium mixed metal cluster containing antimony.

We propose that the initial product from the reaction of **2** with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ is **4-Ru**, which quickly undergoes migratory insertion and rearrangement to **6-Ru** in an analogous manner to the OsBi and OsSb systems described above, or decomposes/fragments into a reactive species which reacts with **2** to form **9** (Scheme 4). That **4-Ru** is unstable is consistent with the known chemistry of osmium and ruthenium carbonyl clusters; the latter is more prone to fragmentation, especially under photo-irradiation, due to the weaker Ru-Ru bond and lower transition energy [19]. Mono-stibine substituted triruthenium clusters are also more susceptible to intramolecular rearrangement *via* Ru-Ru bond cleavage, as exemplified by the ready conversion of $\text{Ru}_3(\text{CO})_{11}(\text{SbPh}_3)$ to $\text{Ru}_3(\text{CO})_{10}(\mu\text{-PhCO})(\mu\text{-SbPh}_2)$ at room temperature [18a], in contrast to the osmium analogue $\text{Os}_3(\text{CO})_{11}(\text{SbPh}_3)$ which is stable even at elevated temperatures [20]. It is envisaged that stable heterotrimetallic clusters may be obtained by the reaction of **2** with, for example, diphosphine-substituted triruthenium carbonyl clusters such as $\text{Ru}_3(\text{CO})_{10}(\text{dppe})$; bidentate ligands have been shown to significantly decrease the tendency for Ru-Ru bond cleavage [19,21].

Figure 6. ORTEP plot of one of two crystallographically independent molecules of **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os1A–Os2A = 2.9718(9), Os2A–Sb5A = 2.6720(10), Os1A–Sb5A = 2.6652(10), Os3A–Sb5A = 2.6355(9), Ru4A–Sb5A = 2.6160(13), Os3A–Ru4A = 2.8243(11), Os3A–C34A = 2.102(13), C34A–O44A = 1.304(14), Ru4A–O44A = 2.142(9), Os2A–Sb5A–Os1A = 67.67(3), Os3A–Sb5A–Ru4A = 65.07(3), Os1A–Os2A–Sb5A = 56.06(2), Sb5A–Os3A–Ru4A = 57.13(3).

Scheme 4. Reaction of **2** with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$.

Concluding remarks

We have shown that the strongly electron-donating metallostibine **2** is a good synthon for the preparation of multimetallic clusters, exemplified by its reaction with the Group 8 transition metal carbonyls. Cleavage of the relatively weak $\text{Sb}-\text{C}(\text{Ph})$ bond also led to novel intramolecular transformations into spirocyclic clusters. It is clear that this chemistry of **2** may be extended to other transition metals or main group metals. We have also shown that the apparently disparate chemistry of the bismuth and ruthenium analogues may be understood in terms of the chemistry of the antimony-osmium clusters.

Experimental

General procedures. All reactions were carried out under an argon atmosphere with standard Schlenk techniques. Reagent grade solvents were dried over the appropriate drying agents and were freshly distilled prior to use. The clusters **1**, $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$,

$\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ and $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$, were prepared as described in the literatures [4,22]. TLC separations were carried out on $20 \times 20 \text{ cm}^2$ plates coated with silica gel 60 F254 from Merck. NMR spectra were recorded on a 400 MHz NMR spectrometer at room temperature unless otherwise specified. All ^1H and ^{13}C chemical shifts were referenced to the residual proton and ^{13}C resonances of the deuterated solvent used. Mass spectra were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were carried out in-house. A standard UVP Pen-Ray lamp (Mercury UV Lamp, model 11SC-1, nominal output power = 4.9 W) was used for the UV irradiation of **4**.

Reaction of 2 with $\text{Fe}_2(\text{CO})_9$. Cluster **1** (30 mg, 26 μmol) was dissolved in dry THF (10 ml) followed by addition of neutral $\gamma\text{-Al}_2\text{O}_3$ (0.6 g). The mixture was stirred at room temperature for 20 min, followed by *in-situ* addition of $\text{Fe}_2(\text{CO})_9$ (10 mg, 27 μmol). The reaction mixture was further stirred at room temperature for 30 min. The $\gamma\text{-Al}_2\text{O}_3$ was then filtered off and the solvent pumped off; the residue was separated by TLC on silica with DCM/hexane (2:3, v/v) as the eluent to give one orange separable band, which was identified as $\text{Os}_2\text{Fe}(\text{CO})_{12}(\mu\text{-SbPh})$, **3** (R_f = 0.44; yield = 11 mg, 44% based on **1**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2133w, 2096m, 2053s, 2035s cm^{-1} . ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.29-7.32 (m, 3H, Ph-*H*), 7.47-7.50 (d, 2H, $J_{\text{H,H}}$ = 8 Hz, Ph-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): $\delta(\text{Os-CO})$ 170.3, 170.9, 174.3, 174.7; $\delta(\text{Ph-C})$ 129.3, 129.9, 132.3, 135.9; $\delta(\text{Fe-CO})$ 215.6. Anal. Calcd for $\text{C}_{18}\text{H}_5\text{O}_{12}\text{FeOs}_2\text{Sb}$: C 22.26, H 0.52. Found: C 21.81, H 0.91. ESI- MS^+ (m/z): 973 $[\text{M}]^+$, 861 $[\text{M}-4\text{CO}]^+$, 823 $[\text{M}-6\text{CO}+\text{H}_2\text{O}]^+$.

Reaction of 2 with $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$. Cluster **1** (80 mg, 70 μmol) was dissolved in dry THF (25 ml) followed by addition of neutral $\gamma\text{-Al}_2\text{O}_3$ (1.6 g). The mixture was stirred at room temperature for 20 min. Then the THF solvent was removed in *vacuo* and dry DCM

(25 ml) was added. To the yellow suspension, maintained at 0 °C, was added Os₃(CO)₁₁(CH₃CN) (69 mg, 75 μmol), and the reaction mixture was further stirred at 0 °C for 24 h, leading to a bright and light orange suspension. The γ-Al₂O₃ was then filtered off and the solvent pumped off; the residue was separated by TLC on silica with DCM/hexane (1:1, v/v) as the eluent to give three bands.

Band 1, light yellow, minor product, was identified as Os₃(CO)₁₂ (*R_f* = 0.80; yield = 4.0 mg).

Band 2, orange, major product, was identified as Os₅(CO)₁₉(μ₃-SbPh), **4** (*R_f* = 0.65; yield = 102 mg, 87% based on **1**). IR (CH₂Cl₂): ν(CO) 2133m, 2100s, 2095s, 2078w, 2054s, 2041w, 2017s, 1984w cm⁻¹. ¹H NMR (C₆D₆, 400 MHz): δ 7.34(d, 2H, *J_{H,H}* = 8 Hz, Ph-*H*), 6.94 (t, 2H, *J_{H,H}* = 8 Hz, Ph-*H*), 6.84 (t, 1H, *J_{H,H}* = 8 Hz, Ph-*H*). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ(CO, not fully observed probably due to the merry-go-round fluxionality) 174.3, 174.1, 170.4, 169.8; δ(Ph-C) 135.4, 129.6, 129.3, 128.7. Anal. Calcd for C₂₅H₅O₁₉Os₅Sb: C 17.85, H 0.30. Found: C 17.82, H 1.06. ESI-MS⁺ (*m/z*): 1683 [M+H]⁺, 1577 [M-Ph-CO+H]⁺.

Band 3, dark orange/red, minor product, was identified as Os₇(CO)₂₆(μ₃-SbPh)₂, **5** (*R_f* = 0.45; yield = 4.0 mg, 5% based on **1**). IR (CH₂Cl₂): ν(CO) 2132sh, 2126m, 2092s, 2075w, 2051vs, 2036w, 2022w, 2009w, 1959w cm⁻¹. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.36-7.43 (m, 4H, Ph-*H*), 7.16-7.26 (m, 6H, Ph-*H*). ¹H NMR (CDCl₃, 400 MHz): δ 7.33-7.39 (m, 4H, Ph-*H*), 7.23 (t, 4H, Ph-*H*), 7.15 (t, 2H, Ph-*H*). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, not fully observed due to the isomerization in solution): δ(CO) 192.9, 179.7, 175.1, 174.6, 171.4, 171.1, 170.5; δ(Ph-C) 135.9, 135.8, 129.3, 129.0, 128.4, 128.3. Anal. Calcd for C₃₈H₁₀O₂₆Os₇Sb₂: C 18.57, H 0.41. Found: C 18.93, H 1.03. ESI-MS⁺ (*m/z*): 2458 [M+H]⁺.

Reaction of 2 with Os₃(CO)₁₀(CH₃CN)₂. Cluster **1** (80 mg, 70 μmol) was dissolved in dry THF (25 ml) followed by addition of neutral γ-Al₂O₃ (1.6 g). The mixture was stirred at room temperature for 20 min. Then the THF solvent was removed in vacuo and dry DCM (25 ml) was added. To the yellow suspension, Os₃(CO)₁₀(CH₃CN)₂ (36 mg, 38 μmol) was added at room temperature and the reaction mixture was further stirred at room temperature for 36 h, leading to a red suspension. The γ-Al₂O₃ was then filtered off and the solvent pumped off; the residue was separated by TLC on silica with DCM/hexane (1:1, v/v) as the eluent to give two bands.

Band 1, light yellow, minor product, was identified as Os₃(CO)₁₂ (*R_f* = 0.80; yield = 3.0 mg).

Band 2, dark orange/red, minor product, was identified as Os₇(CO)₂₆(μ₃-SbPh)₂, **5** (*R_f* = 0.45; yield = 63 mg, 78% based on **1**).

Conversion of 4 to 6 and 7 under UV-light irradiation. Cluster **4** (22 mg, 13 μmol) was dissolved in dry toluene (40 ml) and four cycles of freeze-pump-thaw were performed. The resulting bright orange solution was irradiated by UV light (>300 nm) for 60 h, leading to a yellow solution. Then the solvent was removed by rotary evaporator and the residue separated by TLC on silica with DCM/hexane (1:1, v/v) as the eluent to give four separable bands.

Band 1, light yellow, was identified as trace amount of Os₃(CO)₁₂ (*R_f* = 0.90).

Band 2, yellow, major product, was identified as Os₅(CO)₁₈(μ, η²-PhCO)(μ₄-Sb), **6** (*R_f* = 0.85; yield = 7.0 mg, 47% based on consumed **4**). IR (CH₂Cl₂): ν(CO) 2126m, 2088s, 2057vs, 2042sh, 2031sh, 2005s, 1972w cm⁻¹. IR (ATR): ν(CO) 2126m, 2085s, 2048s, 2035s, 1993s, 1966s; ν(Ph ring) 1450w; ν(C=O) 1417w cm⁻¹. ¹H NMR (CDCl₃, 400 MHz):

δ 7.78 (d, 1H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*), 7.54 (t, 1H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*), 7.43 (t, 2H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): $\delta(\text{PhCO})$ 286.1; $\delta(\text{CO})$ 184.4, 182.5, 181.7, 181.3, 179.4, 179.1, 176.9, 176.0, 175.9, 175.4, 175.2, 174.9, 174.7, 174.2, 172.8, 170.5, 170.4, 166.8; $\delta(\text{Ph-C})$ 155.4, 132.4, 128.6, 128.3. Anal. Calcd for $\text{C}_{25}\text{H}_5\text{O}_{19}\text{Os}_5\text{Sb}$: C 17.85, H 0.30. Found: C 17.53, H 0.74. ESI- MS^+ (m/z): 1654 $[\text{M-CO}]^+$, 1644 $[\text{M-2CO+H}_2\text{O}]^+$, 1616 $[\text{M-3CO+H}_2\text{O}]^+$.

Band 3, light yellow, minor product, was identified as $\text{Os}_5(\text{CO})_{18}(\mu, \eta^2\text{-C}_6\text{H}_4)(\mu\text{-H})(\mu_4\text{-Sb})$, **7** ($R_f = 0.78$; yield = 2.5 mg, 17% based on consumed **4**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2129m, 2096s, 2088vs, 2080s, 2056sh, 2044s, 2033sh, 2021sh, 2006w, 1986w cm^{-1} . ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.51 (d, 1H, Ph-*H*), 7.30 (d, 1H, $J_{\text{H,H}} = 4$ Hz, Ph-*H*), 6.98 (t, 1H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*), 6.85 (t, 1H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*). Anal. Calcd for $\text{C}_{24}\text{H}_5\text{O}_{18}\text{Os}_5\text{Sb}$: C 17.43, H 0.30. Found: C 17.27, H 1.18. ESI- MS^+ (m/z): 1657 $[\text{M+H}]^+$, 1493 $[\text{M-Ph-3CO+H}]^+$.

Band 4, orange, was identified as unreacted **4** ($R_f = 0.75$; 7.0 mg).

Below B4 are several thin (light orange to light purple) bands which are not well separated with each other and thus directly discarded.

Conversion of 4 to 8 in MeOH. Cluster **4** (20 mg, 12 μmol) was dissolved in normal MeOH (60 ml) in a 100 ml RBF and the RBF was sealed with glass stopper. The resulting light orange solution was left in fumehood under ambient conditions for 15 days. Some red crystalline product was formed on the bottom, which was collected by filtration and washed with mixed solution DCM/Hex (1:1, v/v, 1 ml) twice. The red crystalline was identified as $\text{Os}_5(\text{CO})_{19}(\mu_3\text{-SbPh})$, **8** (6.0 mg). The washing solution was combined with the very light

yellow supernatant; the solvent was pumped off and the residue separated by TLC on silica with DCM/hexane (1:1, v/v) as the eluent to three bands.

Band 1, light yellow, was identified as $\text{Os}_5(\text{CO})_{18}(\mu, \eta^2\text{-PhCO})(\mu_4\text{-Sb})$, **6** ($R_f = 0.85$; yield = 3.0 mg, 21% based on consumed **4**).

Band 2, light orange, was identified as $\text{Os}_5(\text{CO})_{19}(\mu_3\text{-SbPh})$, **8** ($R_f = 0.78$; yield = 2.0 mg).

Overall yield = 8.0 mg (57% based on consumed **4**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2125w, 2098s, 2078vs, 2042vs, 2020w, 2008w, 1986sh, 1950w, 1936w cm^{-1} . ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.40 (m, 1H, Ph-*H*), 7.26-7.28 (m, 4H, Ph-*H*). Anal. Calcd for $\text{C}_{25}\text{H}_5\text{O}_{19}\text{Os}_5\text{Sb}$: C 17.85, H 0.30. Found: C 17.33, H 0.73. ESI- MS^+ (m/z): 1683 $[\text{M}+\text{H}]^+$, 1577 $[\text{M}-\text{Ph}-\text{CO}+\text{H}]^+$.

Band 3, orange, was identified as unreacted **4** ($R_f = 0.75$; yield = 6.0 mg).

Reaction of 2 with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$. Cluster **1** (60 mg, 52 μmol) was dissolved in dry THF (15 ml) followed by addition of neutral $\gamma\text{-Al}_2\text{O}_3$ (1.2 g). The mixture was stirred at room temperature for 20 min. Then the $\gamma\text{-Al}_2\text{O}_3$ was filtered off and washed with THF (5 ml). The washing solution and the filtrate were combined and the solvent was removed in vacuo, leading to yellow crystalline but a little oily product **2**. Compound **2** was redissolved in dry DCM (3.0 ml). The solution of **2** was then dropwise added to $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ (35 mg, 54 μmol) solution in dry DCM/ CH_3CN (10/2 ml) within 2 min at $-40\text{ }^\circ\text{C}$. The low temperature bath was then removed and the resulting orange solution was allowed to naturally warmed to room temperature. The color gradually became red and further dark red from orange during the reaction. After 24 h, the solvents were removed by rotary evaporator and the black residue was first purified by TLC on silica with DCM/hexane (1:1, v/v) as the eluent to give large amount of $\text{Ru}_3(\text{CO})_{12}$ (Band 1, $R_f = 0.90$; unweighed) and several other bands ($R_f = 0.85\text{-}0.50$), which were not well separated

with each other and contaminated with small amount of $\text{Ru}_3(\text{CO})_{12}$. The product mixture, from the latter several bands, were repurified by TLC on silica with DCM/hexane (2:3, v/v) as the eluent to give six bands.

Band 1, light yellow, was identified as $\text{Ru}_3(\text{CO})_{12}$ ($R_f = 0.80$; yield = 6.0 mg).

Band 2, light orange, was identified as $\text{Ru}_5(\text{CO})_{18}(\mu, \eta^2\text{-PhCO})(\mu_4\text{-Sb})$, **6-Ru** ($R_f = 0.63$; yield = 2.5 mg, 3.9% based on **1**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2123m, 2085s, 2056vs, 2041sh, 2006s, 1969w cm^{-1} . ^1H NMR (*d*-acetone, 400 MHz): δ 7.75-7.83 (m, 2H, Ph-*H*), 7.56-7.60 (m, 1H, Ph-*H*), 7.48-7.52 (t, 2H, $J_{\text{H,H}} = 8$ Hz, Ph-*H*). Anal. Calcd for $\text{C}_{25}\text{H}_5\text{O}_{19}\text{Os}_2\text{Ru}_3\text{Sb}$: C 21.22, H 0.36. Found: C 20.93, H 1.14. ESI- MS^+ (m/z): 1323 $[\text{M-Ph-2CO}+\text{CH}_3\text{CN}]^+$, 1179 $[\text{M-Ph-7CO}+2\text{H}_2\text{O}]^+$, 1020 $[\text{M-Ph-12CO}+\text{H}_2\text{O}]^+$.

Band 3, orange, was identified as $\text{Os}_3\text{Ru}(\text{CO})_{14}(\mu\text{-PhCO})(\mu_4\text{-Sb})$, **9** ($R_f = 0.55$; 8.5 mg, 19% based on **1**). IR (CH_2Cl_2): $\nu(\text{CO})$ 2126m, 2088s, 2061sh, 2050vs, 2031sh, 2011w, 1994w, 1983w, 1956w cm^{-1} . IR (ATR): $\nu(\text{CO})$ 2125m, 2087s, 2028s, 1981s, 1952sh; $\nu(\text{Ph ring})$ 1455w; $\nu(\text{C=O})$ 1429w cm^{-1} . ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.42-7.57 (m, 3H, Ph-*H*), 7.24-7.38 (m, 2H, Ph-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): $\delta(\text{PhCO})$ 283.7, 262.7, 262.5; $\delta(\text{CO})$ 201.6, 201.4, 201.2, 201.1, 199.5, 199.3, 198.1, 197.1, 196.8, 194.6, 194.4, 194.3, 194.1, 192.9, 191.8, 188.4, 188.3, 188.0, 187.9, 185.9, 183.5, 183.3, 182.7, 182.5, 181.3, 181.3, 178.4, 177.1, 176.6, 176.5, 176.3, 175.3, 175.1, 175.0, 174.8, 172.7, 172.6, 172.2, 170.7, 170.4, 170.3, 168.8; $\delta(\text{Ph-C})$ 149.3, 149.2, 147.9, 135.4, 132.9, 132.8, 132.6, 128.7, 128.3, 127.6, 127.5, 127.0. Anal. Calcd for $\text{C}_{21}\text{H}_5\text{O}_{15}\text{Os}_3\text{RuSb}$ (**9-A/9-B**): C 19.54, H 0.3; Anal. Calcd for $\text{C}_{21}\text{H}_5\text{O}_{15}\text{Os}_2\text{Ru}_2\text{Sb}$ (**9-C**): C 20.99, H 0.42. Found for **9**: C 20.82, H 0.69. ESI- MS^+ (m/z): **9-A/9-B**: 1415 $[\text{M}+3\text{CH}_3\text{CN}]^+$, 1305 $[\text{M-CO}+\text{CH}_3\text{CN}]^+$, 1248 $[\text{M-}$

$3\text{CO}+\text{CH}_3\text{CN}]^+$; **9-C**: 1175 $[\text{M}-\text{CO}]^+$, 1118 $[\text{M}-3\text{CO}]^+$, 1035 $[\text{M}-6\text{CO}]^+$, 1042 $[\text{M}-7\text{CO}+2\text{H}_2\text{O}]^+$.

Band 4, light red, was not structurally identified ($R_f = 0.50$; < 1.0 mg). IR (CH_2Cl_2): $\nu(\text{CO})$ 2127sh, 2118m, 2087s, 2050vs, 2034sh, 2014w cm^{-1} .

Band 5, light brown, was not structurally identified ($R_f = 0.47$; < 1.0 mg). IR (CH_2Cl_2): $\nu(\text{CO})$ 2127m, 2117sh, 2089s, 2063vs, 2049vs, 2018w, 1999w cm^{-1} .

Band 6, yellow, was not structurally identified ($R_f = 0.35$; < 1.0 mg). IR (CH_2Cl_2): $\nu(\text{CO})$ 2131m, 2094s, 2050vs, 2031m, 2014sh, 1989w cm^{-1} .

Crystallographic studies. All diffraction-quality crystals were obtained by slow evaporation of solutions as follows: **3** (red, diethyl ether); **4**, **7** and **8** (yellow, DCM/hex, 1:1, v/v); **5** (dark-red, toluene solution); **6** (yellow, toluene/THF/ether, 1:5:10, v/v/v); **9** (orange-yellow, DCM/ether, 1:2, v/v). X-ray diffraction intensity data were collected using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) on either (a) a SuperNova (dual source) Agilent diffractometer, and the data processed and corrected for absorption effects with CrysAlisPro (clusters **4** and **8**) [23], or (b) a Bruker Kappa diffractometer equipped with a CCD detector running on the SMART suite of programs [24], and the data processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS [25]. A disordered solvate was observed in **6** which was modelled as comprising a toluene and two orientations of a THF, with fixed occupancies (0.3, 0.4 and 0.3, respectively) and geometry restraints. The crystal of **9** was refined as a near-racemic twin. All structural solutions and refinements were performed with the SHELXTL suite of programs [26]. All non-hydrogen atoms were refined with

anisotropic thermal parameters in the final models. Crystal and refinement data are summarized in Tables 1 and 2.

Computational studies. DFT calculations were performed with the Gaussian 09W suite of programs [27], utilizing Becke's three-parameter hybrid function and Lee–Yang–Parr's gradient-corrected correlation function (B3LYP) [28]. The LanL2DZ (Los Alamos effective core potential double- ζ) basis set, together with d- or f-type polarization functions for the Os or Sb atoms, respectively, is employed [29], while the 6-311+G(2d, p) or 6-31G(d, p) basis set is used for the remaining atoms in **3** and **5**, respectively. Spin-restricted calculations were used for geometry optimization. Harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. Hirshfeld surface analysis was carried out using CrystalExplorer 17 [30].

Supporting Information

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1584288-92 and 1584734. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk). Table of crystal and refinement data, and ORTEP plot of **5**; NMR, MS and IR spectra of all the new structures; Hirshfeld surface analysis plot for **8**; coordinates and free energies for the computed structures **3** and **5**.

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Table 1. Crystallographic data for compounds **3**, **4** and **6**.

Compound	3	4	6
Empirical formula	C ₁₈ H ₅ FeO ₁₂ Os ₂ Sb	C ₂₅ H ₅ O ₁₉ Os ₅ Sb	C ₂₅ H ₅ O ₁₉ Os ₅ Sb· 0.3C ₇ H ₈ ·0.7C ₄ H ₈ O
Formula weight	971.22	1682.04	1760.15
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c
<i>a</i> (Å)	11.4457(4)	12.2069(3)	16.9783(4)
<i>b</i> (Å)	14.9956(5)	19.4858(4)	18.6699(4)
<i>c</i> (Å)	13.3964(5)	15.2445(3)	12.6168(3)
α (deg)	90	90	90
β (deg)	94.7537(15)	111.614(3)	108.5524(9)
γ (deg)	90	90	90
<i>V</i> (Å ³)	2291.38(14)	3371.10(12)	3791.48(15)
<i>Z</i>	4	4	4
ρ_{calc} (g/cm ³)	2.815	3.314	3.084
μ (Mo K α) (mm ⁻¹)	12.902	19.641	17.472
<i>F</i> (000)	1752	2952	3124
Crystal size, mm ³	0.06 × 0.10 × 0.12	0.16 × 0.10 × 0.10	0.03 × 0.11 × 0.22
θ_{max} (°)	33.44	26.37	28.30
Reflections collected	36786	18655	63085
Independent reflections	8878 [<i>R</i> (int) = 0.0738]	6875 [<i>R</i> (int) = 0.0347]	9404 [<i>R</i> (int) = 0.0623]
Max. and min. transmission	0.5120 and 0.3070	0.2441 and 0.1452	0.6310 and 0.1180
Data/parameters	8878/307	6875/451	9404/596
Goodness of fit on <i>F</i> ²	1.082	0.986	1.051
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0375 w <i>R</i> 2 = 0.0834	<i>R</i> 1 = 0.0249 w <i>R</i> 2 = 0.0454	<i>R</i> 1 = 0.0275 w <i>R</i> 2 = 0.0618
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0543 w <i>R</i> 2 = 0.0915	<i>R</i> 1 = 0.0323 w <i>R</i> 2 = 0.0485	<i>R</i> 1 = 0.0374 w <i>R</i> 2 = 0.0682
Largest diff. peak and hole (e ⁻ Å ⁻³)	2.417 and -3.962	1.157 and -1.408	1.725 and -1.664

Table 2. Crystallographic data for compounds **7**, **8** and **9**.

Compound	7	8	9
Empirical formula	C ₂₄ H ₄ O ₁₈ Os ₅ Sb	C ₂₅ H ₅ O ₁₉ Os ₅ Sb	C ₂₁ H ₅ O ₁₅ Os ₃ RuSb
Formula weight	1653.02	1682.04	1290.67
Temperature (K)	253(2)	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ 2 ₁ 2
<i>a</i> (Å)	9.5985(2)	24.7075(6)	14.9727(17)
<i>b</i> (Å)	21.2399(3)	15.5036(3)	30.066(6)
<i>c</i> (Å)	15.8939(3)	16.8634(3)	12.6111(16)
α (deg)	90	90	90
β (deg)	93.9943(8)	96.0901(19)	90
γ (deg)	90	90	90
<i>V</i> (Å ³)	3232.44(10)	6423.2(2)	5677.1(15)
<i>Z</i>	4	8	8
ρ_{calc} (g/cm ³)	3.397	3.479	3.020
μ (Mo K α) (mm ⁻¹)	20.478	20.616	14.908
<i>F</i> (000)	2892	5904	4592
Crystal size, mm ³	0.12 × 0.09 × 0.07	0.14 × 0.08 × 0.08	0.06 × 0.28 × 0.35
θ_{max} (°)	25.24	26.37	30.96
Reflections collected	49638	39694	110837
Independent reflections	15606 [<i>R</i> (int) = 0.0300]	13114 [<i>R</i> (int) = 0.0300]	17975 [<i>R</i> (int) = 0.0526]
Max. and min. transmission	0.0140 and 0.0029	0.2893 and 0.1604	0.4890 and 0.0770
Data/parameters	15606/433	13114/901	17975/740
Goodness of fit on <i>F</i> ²	1.042	1.001	1.056
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0377 <i>wR</i> 2 = 0.0926	<i>R</i> 1 = 0.0216 <i>wR</i> 2 = 0.0389	<i>R</i> 1 = 0.0412 <i>wR</i> 2 = 0.1130
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0594 <i>wR</i> 2 = 0.1049	<i>R</i> 1 = 0.0306 <i>wR</i> 2 = 0.0420	<i>R</i> 1 = 0.0444 <i>wR</i> 2 = 0.1153
Largest diff. peak and hole (e·Å ⁻³)	3.897 and -1.168	1.261 and -1.348	4.301 and -3.935

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