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An exhibition of different coordination modes displayed by 2-vinylpyrazine and 2-vinylpyridine at triosmium centres

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TOC graphic

An Exhibition of Different Coordination Modes Displayed by 2-Vinylpyrazine and 2-Vinylpyridine at Triosmium Centres¹

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¹ This paper is dedicated to Prof. Richard D. Adams to honor the occasion of his 70th birthday.

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Abstract

The reactivity of 2-vinylpyrazine and 2-vinylpyridine at different triosmium clusters has been investigated. Room temperature reaction of 2-vinylpyrazine with formally unsaturated $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ or lightly-stabilized $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ leads to the formation of $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})]$ (**1**) through β -vinyl C—H bond activation. In contrast, direct reaction between $[\text{Os}_3(\text{CO})_{12}]$ and 2-vinylpyrazine at elevated temperatures affords $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_2\text{N}_2\text{CH=CH}_2)(\mu\text{-H})]$ (**2**) via aryl C—H bond activation. The metalated 2-vinylpyrazine ligand acts as a five-electron donor in **1**, but serves as a three electron donor in **2**. The high temperature reaction between 2-vinylpyrazine with the bis(diphenylphosphino)methane (dppm) substituted cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ furnishes $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**3**) and $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH}_2)(\mu_3\text{-C}_4\text{H}_3\text{N}_2\text{CH=C})(\mu\text{-dppm})]$ (**4**) through single and double β -vinyl C—H bond activation, respectively. The metalated 2-vinylpyrazine ligand acts as five- and six-electron donors in **4** and **5**, respectively. Cluster **5** also contains an intact 2-vinylpyrazine

ligand coordinating to an osmium like an olefin using the vinylic double bond thus serving as a two-electron donor. A similar reaction between $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ and 2-vinylpyridine affords the analogous $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_5\text{H}_4\text{NCH=CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**5**) and $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_5\text{H}_4\text{NCH=CH}_2)(\mu_3\text{-C}_5\text{H}_4\text{NCH=C})(\mu\text{-dppm})]$ (**6**). The solid-state molecular structures of **1-6** have been determined by single crystal X-ray diffraction analysis.

Keywords: Triosmium clusters; Carbonyls; 2-vinylpyrazine; 2-vinylpyridine; X-ray structures; β -vinyl C–H bond activation

1. Introduction

The chemistry of transition metals with 2-vinylpyridines has been widely investigated in recent years in order to develop new catalysts for selective olefinic C–H bond activation via cyclometallation which is an important process in catalysis and also in the synthesis of organometallic compounds [1-15]. Most of these studies have utilised mononuclear complexes in which chelation of 2-vinylpyridines occurs either through π -complexation of the alkene functionality or activation of a β -C–H alkenyl bond in addition to coordination of pyridinyl nitrogen [6-15]. In contrast, surprisingly little attention has been paid to related reactions of 2-vinylpyridines with polynuclear centres [16-22]. The first report of the reactivity of 2-vinylpyridine with polynuclear complexes was by Deeming and co-workers [16] who studied reactions with triosmium clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$. This led to formation of an open cyclometallated cluster $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-NC}_5\text{H}_4\text{CH=CH})]$, while a phosphine adduct $[\text{HOs}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})(\mu\text{-NC}_5\text{H}_4\text{CH=CH})]$ was isolated as the major product from an analogous reaction with $[\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu\text{-H})_2]$ [16]. In both products the metalated 2-vinylpyridine ligand acts as a 5-electron donor and bridges a diosmium centre (**A**) (see Chart), the third osmium atom supporting only carbonyls and the generated hydride. We later investigated related reactions of 2-vinylpyridine with triruthenium clusters $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ [22]. Here a different reactivity pattern was observed, the novel activation of both β -C–H bonds of the vinyl functionality occurring to yielded pentanuclear $[\text{Ru}_5(\text{CO})_{14}(\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-NC}_5\text{H}_4\text{CH=C})(\mu\text{-H})_2]$ and trinuclear $[\text{Ru}_3\text{Cl}(\text{CO})_5(\mu\text{-CO})(\mu_3\text{-NC}_5\text{H}_4\text{CH=C})(\mu\text{-dppm})(\mu\text{-H})]$ respectively [22]. Now the dimetalated ligand acts as a 6-electron donor and bridges three (**B**) and four (**C**) ruthenium atoms respectively.

Chart Binding modes of non-metallated, mono-metallated and dimetallated 2-vinylpyrazine (E = N) and 2-vinylpyridine (E = CH) ligands previously reported and detailed in this paper

In order to develop this chemistry we report herein related reactions of 2-vinylpyrazine with a range of triosmium clusters. A number of products have been isolated and structurally characterized from these reactions in which the 2-vinylpyrazine ligand displays five different coordination modes including the novel η^2 -heptacity using vinylic double bond (Chart **D**) and aromatic ring metalation (Chart **E**). The reactivity of 2-vinylpyridine has also been investigated further for comparison.

2. Results and Discussion

2.1. Reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$: β -vinyl C–H bond activation

We first investigated reactions of 2-vinylpyrazine with triosmium clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$. In both cases a slow (24 h) reaction took place at room temperature to afford $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})]$ (**1**) in moderate yields (Scheme 1). The ^1H NMR spectrum of **1** shows six equally intense resonances; a high field singlet at δ –9.73 associated with a terminal hydride and five signals in the aromatic region, four doublets at δ 9.36 (J 7.0 Hz), 8.49 (J 1.5 Hz), 7.82 (J 3.5 Hz), 5.34 (J 7.0 Hz) and a doublet of doublets at δ 8.44 (J 3.5 Hz). This data is fully consistent with the oxidative-addition of one β -C–H bond of the vinyl moiety and nitrogen coordination akin to the behaviour noted by Deeming and co-workers for the analogous reactions with 2-vinylpyridine [16]. In order to confirm this, a single crystal X-ray diffraction study was

carried out, the results of which are summarised in Fig. 1 and its caption. The structure is virtually identical to that reported by Deeming for $[\text{HOS}_3(\text{CO})_{10}(\mu\text{-C}_5\text{H}_3\text{NCH=CH})]$ and $[\text{HOS}_3(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu\text{-C}_5\text{H}_3\text{NCH=CH})]$ [16]. The Os–Os–Os bond angle of $157.69(2)^\circ$ is close to that of $160.0(1)^\circ$ reported for the vinylpyridine analogue and the two osmium–osmium distances of 2.8954(7) (unbridged) and 2.8392(7) (bridged) Å are also very similar to those reported by Deeming. The metalated 2-vinylpyrazine ligand bridges the shorter osmium–osmium vector [Os(2)–Os(3)] using the vinylic carbons and one of the ring nitrogen atoms. It is bound to the terminal osmium of this edge through the β -vinyl carbon and nitrogen whilst coordinates with the central osmium through the vinylic double bond. The C(11)–C(12) distance of 1.428(10) Å are identical with that reported for $[\text{HOS}_3(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu\text{-C}_5\text{H}_3\text{NCH=CH})]$ [1.42(2) Å] [16]. The hydride ligand was located from a Fourier map and found to occupy an equatorial coordination site of Os(1). Considering the metalated 2-vinylpyrazine ligand is serving as a five-electron donor, cluster **1** formally has 50 CVE (cluster valence electron), consistent with the two formal osmium–osmium bonds observed in it.

2.2. Reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_{12}]$: aryl C–H bond activation

We next investigated the reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_{12}]$. As anticipated, no change occurred at room temperature and in order to facilitate a reaction the two were heated in toluene for 14 h. This led to isolation of a single low yield (8 %) product, namely $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_2\text{N}_2\text{CH=CH}_2)(\mu\text{-H})]$ (**2**) (Scheme 2). From the ^1H NMR spectrum it is apparent that the vinyl group remains intact as shown by three equal intensity resonances at δ 7.09 (dd, J 17.0, 11.0, 1H), 6.36 (dd, J 17.0, 2.5, 1H) and 5.66 (dd, J 11.0, 2.5, 1H), while C–H oxidative-addition is confirmed by the observation of a high field singlet at δ –14.61, the position of which is characteristic of a bridging hydride. In order to confirm metalation of the aromatic ring a single crystal X-ray diffraction study was carried out, the results of which are

summarised in Fig. 2 and its caption. The metalated ligand acts as a 3-electron donor ligand coordinating through nitrogen and carbon atoms. This mode of coordination is found upon addition of pyridines [16,24] and pyrazines [25,26] to $[\text{Os}_3(\text{CO})_{12}]$. The hydride ligand was not located crystallographically, but we suggest that it spans across the longest osmium-osmium edge $[\text{Os}(2)\text{--}\text{Os}(3)]$ which is also bridged by the metalated 2-vinylpyrazine ligand since the equatorial OC--Os--Os angles along this edge widened significantly $[\text{C}(6)\text{--}\text{Os}(2)\text{--}\text{Os}(3) 116.73(19)^\circ$ and $\text{C}(8)\text{--}\text{Os}(3)\text{--}\text{Os}(2) 118.68(18)^\circ]$ compared to those along the other osmium-osmium edges $[\text{C}(5)\text{--}\text{Os}(2)\text{--}\text{Os}(1) 84.85(17)^\circ$, $\text{C}(3)\text{--}\text{Os}(1)\text{--}\text{Os}(2) 99.43(19)^\circ$, $\text{C}(4)\text{--}\text{Os}(1)\text{--}\text{Os}(3) 98.33(18)^\circ$ and $\text{C}(9)\text{--}\text{Os}(3)\text{--}\text{Os}(1) 84.54(19)^\circ]$. As **2** is formed in only low yields it is not possible to rule out that the dominant C–H activation pathway results from addition of the vinyl moiety but this route does not form a product that is stable under the harsh reaction conditions.

2.3. Reactions of 2-vinylpyrazine and 2-vinylpyridine with $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$: double β -vinyl C–H bond activation

Since the direct reaction between $[\text{Os}_3(\text{CO})_{12}]$ and 2-vinylpyrazine at elevated temperatures did not lead to the isolation of product(s) formed by the addition of vinyl moiety, we next examined the reaction of 2-vinylpyrazine with dppm-substituted cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$. It is well-established that incorporation of dppm stabilizes the trimetallic core with respect to degradation under forcing reaction conditions [23]. Thus heating a xylene solution of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ and 2-vinylpyrazine at 139 °C for 2 h led to the isolation of two products formed by the addition of vinyl moiety, namely $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**3**) (15%) and $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH}_2)(\mu_3\text{-C}_4\text{H}_3\text{N}_2\text{CH=C})(\mu\text{-dppm})]$ (**4**) (24%), in moderate yield (combined) (Scheme 3). Cluster **3** is formed by single β -vinyl C–H bond activation in which the metalated vinylpyrazine ligand acts as a 5-electron donor coordinating through nitrogen and

olefinic carbon atoms, while the metalated ligand acts as a 6-electron donor in **4** as a result of double β -vinyl C–H bond activation. Cluster **4** also contains a second 2-vinylpyrazine ligand coordinating to an osmium like an olefin using only the vinylic carbons thereby acting as a 2-electron donor ligand. Since the reaction of 2-vinylpyridine with $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ has not been reported in literature, we also carried out a similar reaction with 2-vinylpyridine which led to the formation of analogous products $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_5\text{H}_4\text{NCH=CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**5**) (15%) and $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_5\text{H}_4\text{NCH=CH}_2)(\mu_3\text{-C}_5\text{H}_4\text{NCH=C})(\mu\text{-dppm})]$ (**6**) (30%) (Scheme 3). The yield of these reactions did not show any significant change when excess (3 equivalents with respect to the parent cluster) 2-vinylpyrazine or 2-vinylpyridine was used.

Single crystal X-ray diffraction analysis has been carried out for all these clusters as the spectroscopic data provide too little information about their structures. The solid-state molecular structures of **3** and **5** are depicted in Figs. 3 and 5 with the captions containing selected bond distances and angles. Both contain an open triosmium core with an Os–Os–Os angle of $155.91(2)^\circ$ (for **3**) or $159.80(2)^\circ$ (for **5**) and two formal osmium-osmium bonds; one bridged by the metalated 2-vinylpyrazine or 2-vinylpyridine ligand and the other by a metalated-dppm ligand, the former edge is ca. $0.05 \text{ \AA}$ shorter than the latter. Both also contain eight terminal carbonyl ligands; three are bound to each terminal osmiums while the central osmium is bound by two. The coordination mode of the 2-vinyl ligands in both clusters are similar to that observed in **1**, i.e. they bridge an osmium-osmium edge through the vinylic carbons using σ, π -vinyl coordination mode while also coordinate to the terminal osmium of the same edge using the ring nitrogen. In both, the metalated dppm ligand spans the second osmium-osmium edge using both phosphorus atoms and one of the phenyl rings. A phenyl ring on the phosphorus which is bound to central osmium is bonded to the terminal osmium of this edge through an ortho C–H bond activation occurred during the reaction. The

solution spectroscopic data of **3** and **5** are not very informative but show that the solid-state structures persist in solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of both exhibit two doublets due to the phosphorus nuclei of the metalated dppm ligand as expected.

The solid-state molecular structures of **4** and **6** are shown in Figs. 4 and 6, selected bond distances and angles are listed in the captions. Both clusters contain a triangle of osmium atoms at the core with three different osmium-osmium edges. Six terminal carbonyls that are equally distributed to the osmium atoms, a dppm, a metalated 2-vinylpyrazine/pyridine and an intact 2-vinylpyrazine/pyridine ligands complete the coordination sphere of these clusters. In both, the dppm is acting in bridging capacity by spanning the shortest osmium-osmium edge, whilst the metalated 2-vinylpyrazine/pyridine ligand caps one face of the metal triangle by coordinating to all three osmium atoms as a result of double β -vinyl C–H bond activation. The metalated 2-vinylpyrazine/pyridine ligand bridges the longest osmium-osmium edge through the β -vinyl carbon while coordinates to the third osmium using the vinylic double bond. In addition, (one of) the ring nitrogen is also bound to an osmium which is coordinated by the intact 2-vinylpyrazine/pyridine ligand. In both clusters, this intact 2-vinylpyrazine/pyridine ligand is coordinated to a single osmium through the vinylic double bond like an olefin with the heterocyclic ring lying almost perpendicular to the metallic plane. Again the ^1H NMR spectra of both clusters are not very informative, while their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit two doublets for the phosphorus atoms of the dppm ligand.

3. Conclusions

The reactions of 2-vinylpyrazine and 2-vinylpyridine with a range of triosmium clusters have been investigated. Unsaturated $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ or lightly stabilized $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ which are more reactive than the parent $[\text{Os}_3(\text{CO})_{12}]$ slowly reacts with 2-vinylpyrazine to afford **1** via β -vinyl C–H bond activation of the ligand. The metalated ligand acts as a five-electron donor by bridging an osmium-osmium edge of this open cluster using vinylic carbons and a ring nitrogen. In contrast, $[\text{Os}_3(\text{CO})_{12}]$ reacts with 2-vinylpyrazine only at elevated temperatures lead to the formation of **2** through an aryl C–H bond activation of the ligand. In **2**, the metalated ligand bridges an osmium-osmium edge using a nitrogen and carbon of the heterocyclic ring and donates three electrons to the cluster core. No products due to addition of vinyl moiety were isolated from this reaction which we suggest is due to

the instability of such products at elevated temperatures. Consequently, the reaction of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ with 2-vinylpyrazine was investigated which took place in boiling xylene (139 °C) and resulted in the isolation of two products formed by addition of vinyl moiety. Cluster **3** was formed through single β -vinyl C–H bond activation and the coordination mode of the metalated ligand is akin to that observed in **1**, whereas formation of **4** required double β -vinyl C–H bond activation. The metalated ligand is serving as a six-electron donor in **4** by capping a face of the cluster using vinylic carbons and a ring nitrogen. Cluster **4** also contains an intact 2-vinylpyrazine ligand which is bound to an osmium like an olefin using the vinylic double bond thereby acting as a two-electron donor. A similar reaction with 2-vinylpyridine furnishes **5** and **6** which are structural analogues of **3** and **4** respectively. To the best of our knowledge, the η^2 coordination mode using vinylic double bond as shown by 2-vinylpyrazine and 2-vinylpyridine in the present study is unprecedented. This study also shows that both 2-vinylpyrazine and 2-vinylpyridine parallel their reactivity at triosmium surfaces.

4. Experimental Section

4.1. General methods and materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagent-grade solvents were dried using appropriate drying agents and distilled by standard methods prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer or IR (WMSRC). NMR spectra were recorded on Bruker DPX 400 or Varian Inova 500 instruments. Elemental analyses were performed by Microanalytical Laboratories, UCL. $[\text{Os}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{12}]$ were purchased from Strem Chemicals Inc. and used without further purification. 2-Vinylpyrazine and 2-vinylpyridine were purchased from Acros Organics and used as received. Clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ [27], $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ [28] and $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ [29] were prepared according to literature methods.

4.2. Reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ or $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$

To a CH_2Cl_2 solution (30 mL) of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ (50 mg, 0.059 mmol) was added 2-vinylpyrazine (13 mg, 0.122 mmol) and the mixture was stirred at room temperature for 1 d. Volatiles were removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3 v/v) gave three bands, the third and major band of which afforded $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})]$ (**1**) (30 mg, 53%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. The contents of the other two bands were too small for complete characterization. Similarly, a benzene solution (20 mL) of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (50 mg, 0.054 mmol) and 2-vinylpyrazine (11 mg, 0.104 mmol) was stirred at room temperature for 1 d. A similar work up and chromatographic separation as described above gave **1** (24 mg, 47%). Spectral data for **1**: Anal. Calcd for $\text{C}_{16}\text{H}_6\text{N}_2\text{O}_{10}\text{Os}_3$: C, 20.08; H, 0.63; N, 2.93. Found: C, 20.31; H, 0.66; N, 2.99%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2113 m, 2074 vs, 2048 m, 2020 vs, 2003 sh, 1986 m, 1966 sh cm^{-1} . ^1H NMR (CDCl_3): δ 9.36 (d, J 7.0, 1H), 8.49 (d, J 1.5, 1H), 8.44 (dd, J 3.5, 1.5, 1H), 7.82 (d, J 3.5, 1H), 5.34 (d, J 7.0, 1H), –9.73 (s, 1H).

4.3. Reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_{12}]$

A toluene solution (25 mL) of $[\text{Os}_3(\text{CO})_{12}]$ (100 mg, 0.110 mmol) and 2-vinylpyrazine (12 mg, 0.113 mmol) was heated to reflux for 14 h. Volatiles were removed under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (2:3, v/v) developed one major and several minor bands. The major band gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_2\text{N}_2\text{CH=CH}_2)(\mu\text{-H})]$ (**2**) (8 mg, 8%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. Characterizing data for **2**: Anal. Calcd for $\text{C}_{16}\text{H}_6\text{N}_2\text{O}_{10}\text{Os}_3$: C, 20.08; H, 0.63; N, 2.93. Found: C, 20.27; H, 0.68; N, 3.01%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2106 m, 2066 vs, 2055 vs, 2023 vs, 2010 vs, 1991 s, 1972 sh cm^{-1} . ^1H NMR (CDCl_3): δ 7.98 (d, J 3.0, 1H), 7.85 (d, J 3.0, 1H), 7.09 (dd, J 17.0, 11.0, 1H), 6.36 (dd, J 17.0, 2.5, 1H), 5.66 (dd, J 11.0, 2.5, 1H), –14.61 (s, 1H).

4.4. Reaction of 2-vinylpyrazine with $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$

A xylene solution (25 mL) of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ (30 mg, 0.025 mmol) and 2-vinylpyrazine (3 mg, 0.028 mmol) was heated to reflux for 2 h. Volatiles were removed by rotary evaporation under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 gave three bands. The first afforded $[\text{Os}_3(\text{CO})_8(\mu\text{-$

$\text{C}_4\text{H}_3\text{N}_2\text{CH}=\text{CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}\}$ (**3**) (5 mg, 15%) as orange crystals, while the third gave $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{CH}=\text{CH}_2)(\mu_3\text{-C}_4\text{H}_3\text{N}_2\text{CH}=\text{C})(\mu\text{-dppm})]$ (**4**) (8 mg, 24%) as red crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C . The content of the second band was too small for characterization. Characterizing data for **3**: Anal. Calcd for $\text{C}_{39}\text{H}_{26}\text{N}_2\text{O}_8\text{Os}_3\text{P}_2$: C, 36.50; H, 2.05; N, 2.18. Found: C, 36.82; H, 2.12; N, 2.23%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2067 s, 2047 s, 2017 m, 1990 vs, 1979 sh, 1963 s, 1950 m, 1939 w, 1912 w cm^{-1} . ^1H NMR (CDCl_3): δ 8.21 (m, 1H), 7.95 (m, 3H), 7.73 (m, 4H), 7.57 (m, 3H), 7.42 (m, 3H), 6.97 (m, 2H), 6.86 (m, 4H), 6.58 (m, 1H), 6.25 (m, 2H), 4.71 (m, 1H), 4.27 (m, 1H), 3.56 (m, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -13.1 (d, J 65, 1P), -22.2 (d, J 65, 1P). Characterizing data for **4**: Anal. Calcd for $\text{C}_{43}\text{H}_{32}\text{N}_4\text{O}_6\text{Os}_3\text{P}_2$: C, 38.73; H, 2.42; N, 4.20. Found: C, 38.97; H, 2.46; N, 4.26. IR ($\nu(\text{CO})$, CH_2Cl_2): 2012 vs, 1976 s, 1959 m, 1933 m, 1910 m cm^{-1} . ^1H NMR (CDCl_3): 8.94 (d, J 1.5, 1H), 8.30 (dd, J 3.5, 1.0, 1H), 8.02 (m, 2H), 7.91 (d, J 4.0, 1H), 7.83 (d, J 2.5, 1H), 7.53-7.31 (m, 15H), 7.20 (m, 1H), 7.05 (m, 2H), 6.86 (m, 2H), 5.55 (dd, J 27.0, 13.0, 1H), 4.15 (d, J 7.0, 1H), 3.89 (dd, J 13.0, 8.5, 1H), 3.50 (dd, J 27.0, 13.0 Hz, 1H), 2.93 (dd, J 10.5, 4.0, 1H), 2.84 (dd, J 10.5, 4.0, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.7 (d, J 34, 1P), -3.1 (d, J 34, 1P).

4.6. Reaction of 2-vinylpyridine with $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$

To a xylene solution (25 mL) of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-dppm})]$ (30 mg, 0.025 mmol) was added 2-vinylpyridine (3 mg, 0.029 mmol) and the reaction mixture was heated to reflux for 1 h. Volatiles were removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (1:1 v/v) gave four bands. The first afforded $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_5\text{H}_4\text{NCH}=\text{CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}\}$ (**5**) (5 mg, 15%) as yellow crystals, while the fourth gave $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_5\text{H}_4\text{NCH}=\text{CH}_2)(\mu_3\text{-C}_5\text{H}_4\text{NCH}=\text{C})(\mu\text{-dppm})]$ (**6**) (10 mg, 30%) as red crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C . The contents of the other two bands were too small for characterization. Characterizing data for **5**: Anal. Calcd for $\text{C}_{40}\text{H}_{27}\text{NO}_8\text{Os}_3\text{P}_2$: C, 37.47; H, 2.13; N, 1.09. Found: C, 37.65; H, 2.18; N, 1.15%. IR ($\nu(\text{CO})$, CH_2Cl_2): 2067 m, 2044 m, 2018 m, 1992 vs, 1958 vs, 1921 m, 1963 s, 1882 w cm^{-1} . ^1H NMR (CDCl_3): δ 9.10 (d, J 5.6, 1H), 8.31 (m, 1H), 7.97 (m, 1H), 7.68 (m, 2H), 7.54 (m, 1H), 7.34 (m, 3H), 7.20 (m, 2H), 7.13 (m, 6H), 6.98 (m, 1H), 6.75 (m, 3H), 6.25 (m, 2H), 5.61 (d, J 8.0, 1H), 4.31 (d, J 8.0, 1H), 3.63 (m, 1H), 2.98 (m, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -5.6 (d, J 73, 1P), -35.9 (d, J 73, 1P). Characterizing data for **6**: Anal. Calcd for $\text{C}_{45}\text{H}_{34}\text{N}_2\text{O}_6\text{Os}_3\text{P}_2$: C, 40.59; H, 2.58; N, 2.10. Found: C, 40.76; H, 2.64; N, 2.15%. IR

($\nu(\text{CO})$, CH_2Cl_2): 2030 m, 2006 vs, 1970 s, 1953 sh, 1926 m, 1904 m cm^{-1} . ^1H NMR (CDCl_3): δ 8.42 (d, J 8.0, 1H), 8.02 (m, 2H), 7.63 (m, 2H), 7.55 (m, 2H), 7.48-7.29 (m, 13H), 7.15 (m, 1H), 7.02 (m, 2H), 6.90 (m, 2H), 6.60 (m, 2H), 6.54 (m, 2H), 6.01 (d, J 8.0, 1H), 5.64 (dd, J 27.2, 13.2, 1H), 4.36 (d, J 8.0, 1H), 4.00 (t, J 9.2, 1H), 3.48 (dd, J 27.2, 13.2, 1H), 2.81 (m, 1H), 2.31 (m, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.1 (d, J 36, 1P), -3.5 (d, J 36, 1P).

4.7. X-ray structure determinations

Single crystals of **1-6** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at 4 °C. All geometric and crystallographic data were collected at 150(2) K on a Bruker SMART APEX CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) [30]. Data reduction and integration were carried out with SAINT+ [31] and absorption corrections were applied using the program SADABS [32]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 [33,34]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in the calculated positions and their thermal parameters were linked to those of the atoms to which they were attached (riding model). The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [34]. Details of the data collection and structure refinement are given in Table 1. For **1** the hydride was located and refined in a fixed position. For **6** the CH_2Cl_2 solvent is disordered over two sites (sharing the chlorides) and there are some large ghost peaks near to the osmium atoms.

Supplementary Data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data centre. CCDC 1530484-1530489 contain supplementary crystallographic data for **1-6** respectively. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.ac.uk>).

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Table 1 Crystallographic data and structure refinement details for compounds 1-6

Compound	1	2	3	4	5	6
Empirical formula	C ₁₆ H ₆ N ₂ O ₁₀ Os ₃	C ₁₆ H ₆ N ₂ O ₁₀ Os ₃	C ₃₉ H ₂₆ N ₂ O ₈ Os ₃ P ₂	C ₄₄ H ₃₄ Cl ₂ N ₄ O ₆ Os ₃ P ₂	C ₄₀ H ₃₁ NO ₁₀ Os ₃ P ₂	C ₄₅ H ₃₄ N ₂ O ₆ Os ₃ P ₂
Formula weight (Å)	956.83	956.83	1283.16	1418.19	1318.20	1331.28
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	C ₂ /c	P 2 ₁ /c	P 2 ₁ 2 ₁ 2 ₁	P 2 ₁ /n	P-1	P 2 ₁ /n
Unit cell dimensions						
<i>a</i> (Å)	18.584(5)	9.1102(10)	8.9894(17)	12.6453(11)	9.1586(17)	11.2688(14)
<i>b</i> (Å)	16.295(4)	14.2913(15)	18.969(4)	18.8102(16)	12.700(2)	19.041(2)
<i>c</i> (Å)	14.195(4)	15.6436(17)	22.575(4)	18.7492(16)	17.726(3)	20.358(3)
α (°)	90	90	90	90	80.000(3)	90
β (°)	111.095(4)	94.499(2)	90	93.4680(10)	83.826(3)	94.946(2)
γ (°)	90	90	90	90	71.746(3)	90
Volume (Å ³)	4010.4(17)	2030.5(4)	3849.4(12)	4451.5(7)	1925.2(6)	4352.0(9)
Z	8	4	4	4	2	4
Density (calculated) (Mg/m ³)	3.169	3.130	2.214	2.116	2.274	2.032
Absorption coefficient (mm ⁻¹)	19.021	18.784	10.015	8.786	10.019	8.860
F(000)	3392	1696	2384	2664	1232	2496
Crystal size (mm)	0.22 × 0.14 × 0.06	0.20 × 0.10 × 0.08	0.10 × 0.06 × 0.03	0.20 × 0.13 × 0.08	0.12 × 0.04 × 0.03	0.20 × 0.13 × 0.10
θ Range for data collection (°)	2.57 to 28.30	2.85 to 28.28	2.44 to 28.31	2.18 to 28.27	2.21 to 28.27	2.28 to 28.29
Index ranges	-23 ≤ <i>h</i> ≤ 24, -20 ≤ <i>k</i> ≤ 20, -18 ≤ <i>l</i> ≤ 18	-11 ≤ <i>h</i> ≤ 11, -18 ≤ <i>k</i> ≤ 18, -20 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11, -25 ≤ <i>k</i> ≤ 25, -30 ≤ <i>l</i> ≤ 29	-16 ≤ <i>h</i> ≤ 16, -25 ≤ <i>k</i> ≤ 24, -24 ≤ <i>l</i> ≤ 23	-12 ≤ <i>h</i> ≤ 11, -16 ≤ <i>k</i> ≤ 16, -22 ≤ <i>l</i> ≤ 23	-14 ≤ <i>h</i> ≤ 14, -24 ≤ <i>k</i> ≤ 25, -25 ≤ <i>l</i> ≤ 27
Reflections collected	14775	16394	32433	36234	15897	35734
Independent reflections	4531 [<i>R</i> _{int} = 0.0591]	4710 [<i>R</i> _{int} = 0.0476]	8904 [<i>R</i> _{int} = 0.1096]	10361 [<i>R</i> _{int} = 0.0507]	8406 [<i>R</i> _{int} = 0.0525]	10132 [<i>R</i> _{int} = 0.0708]
Max. and min. transmission	0.3949 and 0.1025	0.3149 and 0.1171	0.7532 and 0.4341	0.5400 and 0.2725	0.7531 and 0.3794	0.4711 and 0.2703
Data / restraints / parameters	4531 / 0 / 284	4710 / 0 / 280	8904 / 0 / 472	10361 / 0 / 539	8406 / 0 / 495	10132 / 0 / 523
Goodness-of-fit on <i>F</i> ²	1.000	1.035	0.639	1.063	0.866	0.943
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0368, <i>wR</i> ₂ = 0.0762	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0659	<i>R</i> ₁ = 0.0395, <i>wR</i> ₂ = 0.0737	<i>R</i> ₁ = 0.0706, <i>wR</i> ₂ = 0.1668	<i>R</i> ₁ = 0.0462, <i>wR</i> ₂ = 0.0916	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.00858
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.0812	<i>R</i> ₁ = 0.0369, <i>wR</i> ₂ = 0.0679	<i>R</i> ₁ = 0.0643, <i>wR</i> ₂ = 0.0816	<i>R</i> ₁ = 0.0859, <i>wR</i> ₂ = 0.1743	<i>R</i> ₁ = 0.0860, <i>wR</i> ₂ = 0.1020	<i>R</i> ₁ = 0.0738, <i>wR</i> ₂ = 0.0957
Largest diff. peak and hole (e. Å ⁻³)	3.415 and -2.735	1.788 and -3.361	1.675 and -1.655	10.456 and -2.723	2.342 and -3.121	3.704 and -1.896

Fig. 1 Molecular structure of $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH})]$ (**1**) showing 50% probability thermal ellipsoids. Hydrogen atoms except the hydride are omitted for clarity. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: Os(1)–Os(2) 2.8954(7), Os(2)–Os(3) 2.8392(7), Os(3)–N(1) 2.121(6), Os(3)–C(11) 2.055(7), Os(2)–C(11) 2.209(7), Os(2)–C(12) 2.330(7), C(11)–C(12) 1.428(10), Os(1)–Os(2)–Os(3) 157.688(15), N(1)–Os(3)–Os(2) 83.29(16), N(1)–Os(3)–C(8) 92.4(3), N(1)–Os(3)–C(10) 169.3(3), C(11)–Os(3)–Os(2) 50.62(19), C(11)–Os(2)–Os(3) 45.97(19), C(11)–Os(2)–C(12) 36.6(3), N(1)–Os(3)–C(11) 78.9(3).

Fig. 2 Molecular structure of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_4\text{H}_2\text{N}_2\text{CH=CH}_2)(\mu\text{-H})]$ (**2**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: Os(1)–Os(2) 2.8563(4), Os(1)–Os(3) 2.8813(4), Os(2)–Os(3) 2.9179(4), Os(2)–N(1) 2.112(5), Os(3)–C(11) 2.138(6), C(15)–C(16) 1.319(9), Os(1)–Os(2)–Os(3) 59.855(10), Os(2)–Os(1)–Os(3) 61.135(8), Os(1)–Os(3)–Os(2) 59.010(9), N(1)–Os(2)–Os(3) 68.29(14), N(1)–Os(2)–Os(1) 89.26(13), N(1)–Os(2)–C(5) 93.7(2), N(1)–Os(2)–C(7) 177.0(2), C(11)–Os(3)–Os(2) 68.57(15), C(11)–Os(3)–Os(1) 89.19(15), C(11)–Os(3)–C(9) 94.4(3), C(11)–Os(3)–C(10) 171.2(2).

Fig. 3 Molecular structure of $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_4\text{H}_3\text{N}_2\text{CH}=\text{CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**3**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: Os(1)–Os(2) 2.9072(7), Os(2)–Os(3) 2.8503(7), Os(1)–P(1) 2.404(3), Os(2)–P(2) 2.359(2), Os(3)–N(1) 2.123(8), Os(1)–C(15) 2.175(10), Os(3)–C(9) 2.087(10), Os(2)–C(9) 2.142(9), Os(2)–C(10) 2.290(9), C(9)–C(10) 1.419(14), Os(1)–Os(2)–Os(3) 155.91(2), N(1)–Os(3)–Os(2) 82.7(2), N(1)–Os(3)–C(8) 93.2(4), N(1)–Os(3)–C(7) 171.4(4), C(9)–Os(3)–Os(2) 48.4(3), C(9)–Os(2)–Os(3) 46.8(3), Os(3)–C(9)–Os(2) 84.7(4), C(9)–Os(2)–C(10) 37.2(4), P(2)–Os(2)–Os(3) 124.97(7), P(2)–Os(2)–Os(1) 75.67(7), P(1)–Os(1)–Os(2) 90.93(6), C(15)–Os(1)–Os(2) 88.2(3), C(15)–Os(1)–P(1) 84.4(3), C(15)–Os(1)–C(2) 172.0(4).

Fig. 4 Molecular structure of $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_4\text{H}_3\text{N}_2\text{CH=CH}_2)(\mu_3\text{-C}_4\text{H}_3\text{N}_2\text{CH=C})(\mu\text{-dppm})]$ (**4**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: Os(1)–Os(2) 2.7683(7), Os(2)–Os(3) 2.9060(7), Os(1)–Os(3) 2.8070(7), Os(1)–P(1) 2.303(3), Os(2)–P(2) 2.279(3), Os(3)–N(1) 2.140(10), Os(3)–C(13) 2.171(15), Os(3)–C(14) 2.197(15), Os(3)–C(7) 2.099(12), Os(2)–C(7) 1.983(11), Os(1)–C(7) 2.171(11), Os(1)–C(8) 2.343(12), C(7)–C(8) 1.414(16), C(13)–C(14) 1.44(2), Os(1)–Os(2)–Os(3) 59.239(17), Os(1)–Os(3)–Os(2) 57.937(17), Os(2)–Os(1)–Os(3) 62.824(18), N(1)–Os(3)–Os(2) 120.3(3), N(1)–Os(3)–Os(1) 82.0(3), N(1)–Os(3)–C(14) 89.7(5), C(7)–Os(3)–Os(2) 43.0(3), C(7)–Os(2)–Os(3) 46.2(4), C(7)–Os(3)–Os(1) 50.0(3), C(7)–Os(1)–Os(3) 47.8(3), C(7)–Os(1)–Os(2) 45.4(3), C(7)–Os(2)–Os(1) 51.2(3), Os(3)–C(7)–Os(2) 90.8(5), Os(3)–C(7)–Os(1) 82.2(4), Os(1)–C(7)–Os(2) 83.5(4), C(7)–Os(1)–C(8) 36.2(4), C(13)–Os(3)–C(14) 38.4(6), N(1)–Os(3)–C(7) 77.6(4).

Fig. 5 Molecular structure of $[\text{Os}_3(\text{CO})_8(\mu\text{-C}_5\text{H}_4\text{NCH=CH})\{\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4\}]$ (**5**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Os(1)–Os(2) 2.8923(7), Os(2)–Os(3) 2.8402(8), Os(1)–P(1) 2.404(2), Os(2)–P(2) 2.359(2), Os(3)–N(1) 2.133(9), Os(1)–C(16) 2.181(10), Os(3)–C(9) 2.069(10), Os(2)–C(9) 2.168(10), Os(2)–C(10) 2.285(10), C(9)–C(10) 1.415(13), Os(1)–Os(2)–Os(3) 159.80(2), N(1)–Os(3)–Os(2) 83.4(2), N(1)–Os(3)–C(8) 171.6(4), N(1)–Os(3)–C(7) 93.9(5), C(9)–Os(3)–Os(2) 49.4(3), C(9)–Os(2)–Os(3) 46.4(3), Os(3)–C(9)–Os(2) 84.2(4), C(9)–Os(2)–C(10) 36.9(3), P(2)–Os(2)–Os(3) 120.02(6), P(2)–Os(2)–Os(1) 75.86(6), P(1)–Os(1)–Os(2) 90.21(6), C(16)–Os(1)–Os(2) 88.0(3), C(16)–Os(1)–P(1) 84.4(2), C(16)–Os(1)–C(2) 174.2(4).

Fig. 6 Molecular structure of $[\text{Os}_3(\text{CO})_6(\eta^2\text{-C}_5\text{H}_4\text{NCH=CH}_2)(\mu_3\text{-C}_5\text{H}_4\text{NCH=C})(\mu\text{-dppm})]$ (**6**) showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [$\text{\AA}$] and angles [$^\circ$]: Os(1)–Os(2) 2.7863(5), Os(2)–Os(3) 2.8023(5), Os(1)–Os(3) 2.9286(5), Os(1)–P(1) 2.2755(19), Os(2)–P(2) 2.3002(18), Os(3)–N(1) 2.158(6), Os(3)–C(14) 2.174(8), Os(3)–C(15) 2.199(8), Os(3)–C(7) 2.089(7), Os(2)–C(7) 2.149(7), Os(1)–C(7) 1.965(7), Os(2)–C(8) 2.352(8), C(7)–C(8) 1.426(10), C(14)–C(15) 1.430(13), Os(1)–Os(2)–Os(3) 63.206(11), Os(1)–Os(3)–Os(2) 58.131(12), Os(2)–Os(1)–Os(3) 58.663(11), N(1)–Os(3)–Os(2) 82.44(16), N(1)–Os(3)–Os(1) 119.80(18), N(1)–Os(3)–C(15) 90.8(3), C(7)–Os(3)–Os(2) 49.55(19), C(7)–Os(2)–Os(3) 47.68(19), C(7)–Os(3)–Os(1) 42.1(2), C(7)–Os(1)–Os(3) 45.4(2), C(7)–Os(1)–Os(2) 50.2(2), C(7)–Os(2)–Os(1) 44.7(2), Os(3)–C(7)–Os(2) 82.8(3), Os(3)–C(7)–Os(1) 92.5(3), Os(1)–C(7)–Os(2) 85.1(3), C(7)–Os(2)–C(8) 36.6(3), C(14)–Os(3)–C(15) 38.2(3), N(1)–Os(3)–C(7) 77.8(3).

Highlights for review

- Coordination of 2-vinylpyrazine to triosmium centre
- C-H activation of either ring or β -C-H groups
- Crystal structures of closed and open triosmium clusters