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The heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ — a high yield synthesis, isomerism and a triphenylphosphine derivative

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Abstract

A high-yielding alternative synthesis of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ has been developed. It is also demonstrated that the cluster exists as at least three isomers, which rapidly interconvert in solution. A triphenylphosphine derivative, $RuOs_3(\mu\text{-}H)_2(CO)_{12}(PPh_3)$, has also been prepared; this exists as two isomers, both of which have been characterised by single-crystal X-ray crystallographic studies. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Heteronuclear clusters are of interest as the presence of different transition-metal atoms in close proximity has the potential to effect novel reactions via synergistic interactions. One of the few almost complete families of heteronuclear clusters is that of the tetranuclear clusters of formulae $M'M_3(\mu\text{-}H)_2(CO)_{13}$, where M and M′ are different Group 8 elements [1]. These clusters have a relatively stable tetrahedral metal core. Although the chemistry of some members of the family, for example, $FeOs_3(\mu\text{-}H)_2(CO)_{13}$ [2], has been well investigated those of others is still rare; an example of the latter is $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**1**). It is well-known that in the iron triad, ruthenium and osmium are more similar chemically to each other than they are to iron; they have identical covalent radii too. Thus, the chemistry of this cluster should be interesting, for example, in revealing the relative importance of steric and electronic effects.

One of the underlying reasons for the paucity of studies into **1** is probably the lack of a high-yield synthetic route to it; the original preparation by the UV photolysis of $Ru_3(CO)_{12}$ with $Os_3(\mu\text{-}H)_2(CO)_{10}$ gave a ~ 30% yield of **1**, unconsumed $Ru_3(CO)_{12}$, and a number of side products such as $Ru_4(\mu\text{-}H)_2(CO)_{13}$ and $Os_4(\mu\text{-}H)_4(CO)_{12}$ [3]. Considering that the cost of osmium carbonyl is about five times that of ruthenium carbonyl, we had sought to develop a synthesis that was more efficient in the use of osmium carbonyl. We thought that since the above photochemical synthesis appeared to require the fragmentation of $Ru_3(CO)_{12}$ to produce the requisite $Ru(CO)_4$ fragment, we may improve the yield of the reaction by separating the photofragmentation of $Ru_3(CO)_{12}$ from the cluster formation step; such a strategy also has the possible advantage of a reduction in the amount of side-products generated from photodegradation of $Os_3(\mu\text{-}H)_2(CO)_{10}$ and **1**. Indeed, a similar strategy was attempted by Gates et al. using $Ru(CO)_5$ as the source of the $Ru(CO)_4$ fragment. However, the preparation of $Ru(CO)_5$ required high temperature (180°C) and pressure (100 atm of a 2:1 $CO\text{–}H_2$ mixture), and only resulted in a slightly improved yield (30–45% with respect to $Os_3(\mu\text{-}H)_2(CO)_{10}$) [4].

It has been shown that $Ru(CO)_4(C_2H_4)$ is a convenient synthetic equivalent for the $Ru(CO)_4$ synthon, and can be easily prepared from the photolysis of a solution of $Ru_3(CO)_{12}$ in the presence of ethene [5]. Indeed, Chen and Poe have shown that the photolysis need not be carried out with a UV lamp [6]. We have thus adopted the latter methodology and scaled it up. Using an excess of the $Ru(CO)_4(C_2H_4)$ so prepared, we

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were able to obtain a 72% yield (with respect to $Os_3(\mu-H)_2(CO)_{10}$) of **1**, with no sign of $Ru_4(\mu-H)_2(CO)_{13}$ and a little of $Os_4(\mu-H)_4(CO)_{12}$. Most of the latter were found to have been carried over from the synthesis of $Os_3(\mu-H)_2(CO)_{10}$; careful purification of the $Os_3(\mu-H)_2(CO)_{10}$ usually reduced its presence in crude samples of **1** to negligible levels that could be removed entirely by recrystallisation.

The X-ray structural study [2d] and ^1H-NMR spectrum [3,4] of **1** have been reported. The data were consistent with a structure in which the metal hydrides bridged two different Os–Os edges. Specifically, there was no report of any other isomers being present in solution. It therefore came as a surprise that the ^1H-NMR spectrum of our sample of **1** showed a broad signal at ca. − 21.2 ppm (in $CDCl_3$) at room temperature, and on lowering the temperature, it began to sharpen and additional resonances with much lower intensities began to appear at lower field (Fig. 1). Indeed, at 233 K, the resonance has sharpened to the extent that two tiny resonances flanking both sides of the main resonance was also observable. We have assigned these as satellites due to coupling with ^{187}Os ($^1J(^{187}Os-^1H) = 35.0$ Hz).

Of the additional resonances observed at 233 K, the weakest in intensity was the resonance at − 20.04 ppm. The other two resonances, at − 20.17 and − 20.95 ppm, were of equal intensity. In order to confirm that these additional resonances were due to isomers and not impurities, we have carried out an EXSY experiment at 273 K (Fig. 2), which showed crosspeaks due to chemical exchange among all the resonances. A spin-saturation transfer experiment performed at 278 K showed that the resonance at − 20.04 ppm experienced a 4% drop in intensity, while the other two resonances experienced a 9% drop each (with respect to that for the main resonance at − 21.17 ppm set as 100%) on irradiation at the − 21.17 ppm resonance. These confirmed that the species giving rise to the resonances were undergoing chemical exchange and further, that the exchange process was stepwise. We believe that a consistent set of assignments and the exchange pathway is

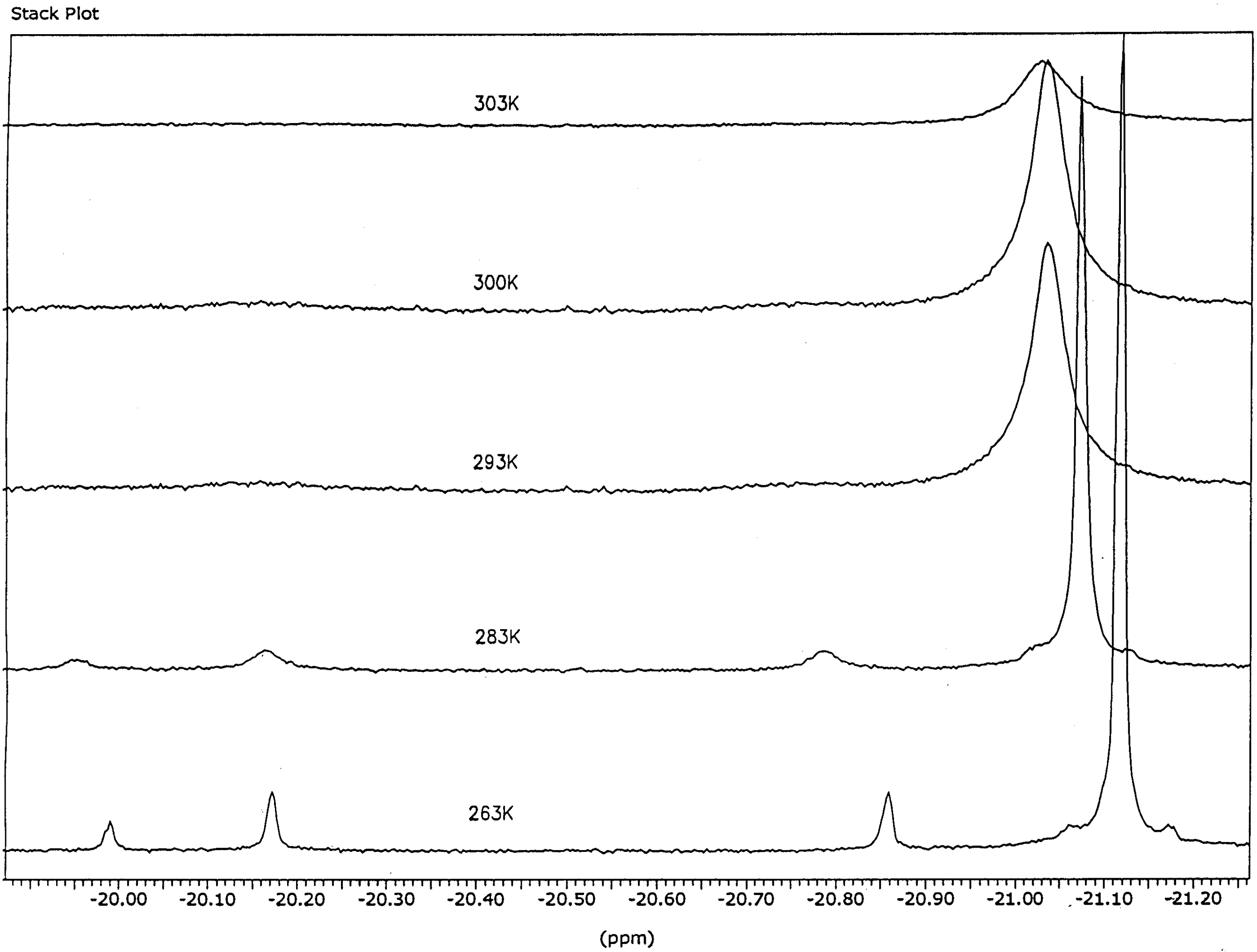

Fig. 1. VT ^1H-NMR overlay for **1**.

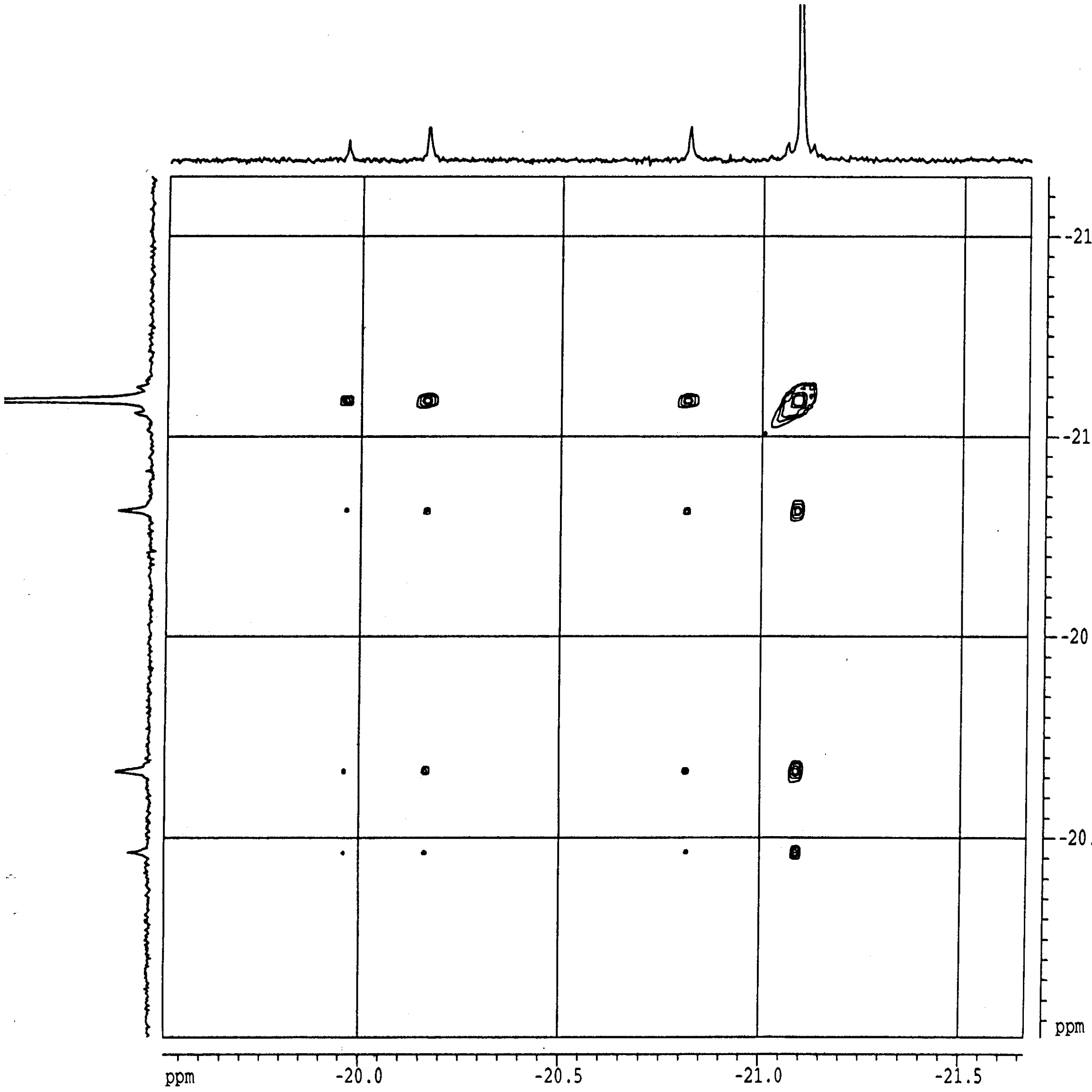

Fig. 2. EXSY spectrum (273 K) for **1**.

that given below (Fig. 3). The assignments were based on: (i) what was believed to be the hydride positions in the major isomer (I) obtained from the X-ray structural study, (ii) the assumption that the effect of the carbonyl ligands (terminal and bridging) on the molecular symmetry could be disregarded, and (iii) the chemical shift for a metal hydride bridging an Os–Os edge would lie in a higher field than that bridging an Os–Ru edge [7]. We have not been able to unambiguously assign a structure to isomer (II); although the absence of coupling between the resonances at −20.17 and −20.95 ppm, down to 218 K, may appear to indicate that the corresponding hydrides did not share a common heavy atom, the absence of $^1H-^1H$ coupling is also observed in the phosphine-substituted derivative **2b** (see later), which has non-equivalent hydrides sharing a common heavy atom. Furthermore, all homo- and heteronuclear $M_4(\mu\text{-}H)_2(CO)_{13}$ clusters known to date have hydrides sharing a common heavy atom [8]. Thus, we prefer the structure (IIa) for isomer (II). From integration, the

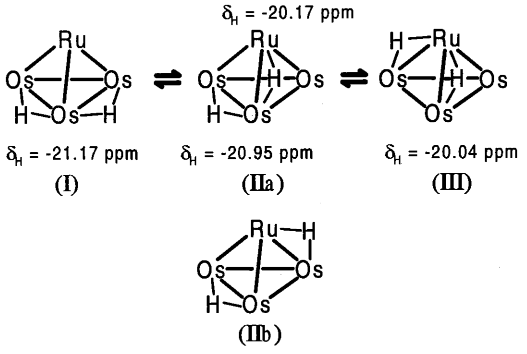

Fig. 3. Isomers and ^1H-NMR assignments (233 K) for **1**.

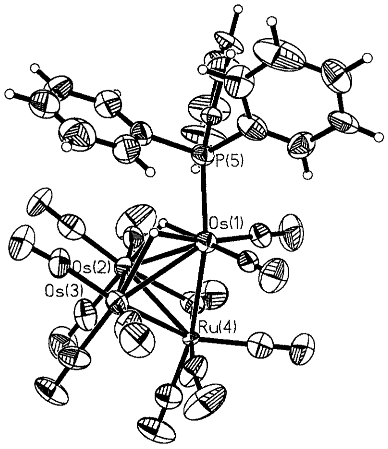

Fig. 4. ORTEP plot (50% probability thermal ellipsoids) for **2a**. Os(1)–Os(2) = 2.9714(8), Os(1)–Os(3) = 2.9371(7), Os(1)–Ru(4) = 2.8104(10), Os(2)–Os(3) = 2.8281(7), Os(2)–Ru(4) = 2.8059(10), Os(3)–Ru(4) = 2.8200(10), Os(1)–P(5) = 2.352(3) Å.

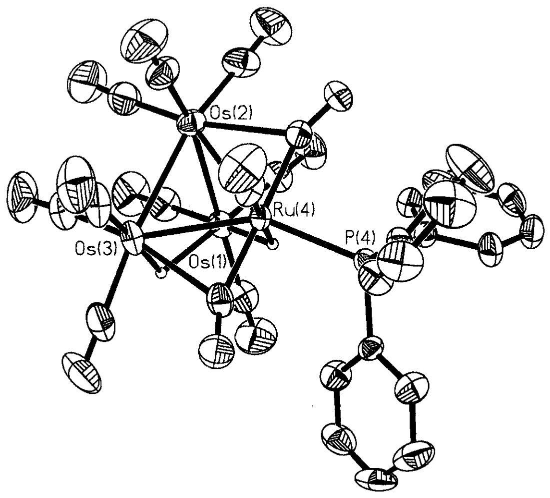

Fig. 5. ORTEP plot (50% probability thermal ellipsoids) for **2b**. Os(1)–Os(2) = 2.8150(4), Os(1)–Os(3) = 2.9327(4), Os(1)–Ru(4) = 2.9905(5), Os(2)–Os(3) = 2.8384(4), Os(2)–Ru(4) = 2.7974(5), Os(3)–Ru(4) = 2.8053(5), Ru(4)–P(4) = 2.3904(15) Å.

isomeric distribution obtained was 88:10:2 for isomers I:II:III, respectively.

The observation of isomers in **1** has not been noticed in the earlier studies on **1** nor in the more intensively studied $FeRu_3(\mu\text{-}H)_2(CO)_{13}$ and $FeOs_3(\mu\text{-}H)_2(CO)_{13}$, which have the same structures [7,9]. Although the low abundance of isomers II and III precluded ^{13}C-NMR analysis, if we assume that the distribution of ligands in the three isomers are maintained then isomer III, for example, would be expected to have bridging (or more likely, semibridging) carbonyls along two Os–Os edges. This would be in agreement with the observation that bridging carbonyls occur less frequently with third row transition metals.

With this high-yield synthesis of **1**, we have embarked on an investigation into its chemistry. Thus, its reaction with PPh_3 in the presence of TMNO resulted in both mono- and disubstituted phosphine derivatives, viz., $RuOs_3(\mu\text{-}H)_2(CO)_{13-n}(PPh_3)_n$ ($n = 1, 2$). We have found that these derivatives existed as mixtures of isomers, in a similar manner to the corresponding $FeRu_3(\mu\text{-}H)_2(CO)_{13-n}(PR_3)_n$ clusters [10]. The monosubstituted derivative, $RuOs_3(\mu\text{-}H)_2(CO)_{12}(PPh_3)$, was found to exist as two isomers. We were able to isolate crystals of both isomers and subject them to crystallographic analysis (Figs. 4 and 5).

The two isomers corresponded to substitution of the phosphine ligand at an osmium (**2a**) or the ruthenium atom (**2b**); the structure of **2a** exhibited disorder about the unsubstituted Os_2Ru basal plane (amounting to about a 21% Os occupancy at the Ru atom site). The two isomers also differed in two other gross structural aspects: (a) isomer **2a** has both hydrides bridging Os–Os edges, while **2b** has a hydride bridging an Os–Os edge and another bridging an Os–Ru edge; the hydrides were located in low angle ($\theta < 30°$) difference maps and their locations were supported by the ^{1}H-NMR data and potential energy calculations [11]. (b) Isomer **2a** appears to have one bridging CO while **2b** has two. This may be due to the increased electron density donated by the phosphine ligand onto the ruthenium in **2b**; ruthenium is less able than osmium to accept additional electron density.

Samples of crystals of **2a** or **2b** separated by hand exhibited the same IR spectrum in solution, indicating that an equilibrium mixture of the isomers was established rapidly. The ^{31}P-NMR spectrum showed two resonances, at 33.60 and 49.39 ppm, assigned to **2a** and **2b**, respectively, in a $\approx 1{:}2$ intensity ratio. The ^{1}H-NMR spectrum at 253 K showed a doublet at -19.51 ppm, which was assigned to **2a**, and a singlet at -19.74 and a doublet at -21.29 ppm, which were assigned to **2b**; the couplings were confirmed by selective decoupling, and the correlation between the ^{1}H and ^{31}P resonances were established via a ^{31}P, ^{1}H HMBC experiment. The assignment of the signals to the isomers were made on the assumption that in solution at 253 K, the relative positions of the metal hydrides persisted, while the bridging carbonyls were probably in rapid exchange with some of the terminal carbonyls so that, for example, **2a** has a plane of symmetry through Ru(4), Os(1) and P(5).

2. Experimental

All reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried, distilled, and kept under nitrogen prior to use. Routine NMR spectra were recorded on a Bruker ACF300 NMR spectrometer while the spin-saturation transfer, HMBC and EXSY experiments were carried out on an AMX500 spectrometer. The EXSY spectrum was collected over 2048 data points in the F2 dimension with 256 increments of 16 scans; a mixing time of 500 ms was used. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The cluster $\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}$ was prepared according to the literature method [12]; all other reagents were from commercial sources and used as supplied.

2.1. Preparation of ***1***

The mononuclear ruthenium compound, $\mathrm{Ru(CO)_4(C_2H_4)}$, was prepared by the irradiation of a suspension of $\mathrm{Ru_3(CO)_{12}}$ in hexane under an atmosphere of $\mathrm{C_2H_4}$. Typically, 30 mg (47 μmol) of $\mathrm{Ru_3(CO)_{12}}$ was placed with hexane (60 ml) into a 100-ml round-bottomed flask fitted with a Teflon valve. After three freeze–pump–thaw cycles, ethene gas at $\sim$20 psi was introduced at ambient temperature. The mixture was then irradiated by a 60 W Phillips reflector lamp, while being cooled in an ice-water bath, until the solution became colourless (from 40 min to 2 h). This solution was then poured into a 100-ml Schlenk vessel containing $\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}$ (37 mg, 43 μmol). The mixture was stirred under a nitrogen atmosphere for 1.5 h, whereupon the colour changed to orange. Removal of the solvent and volatiles in vacuo and column chromatographic separation of the residue, with hexane as eluant, gave a small amount of unconsumed $\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}$ as a yellow band (identified by IR spectroscopy), followed by a red–orange band of **1** (68 mg, 72%). Found: C, 15.27; H, 0.04. Calc. for $\mathrm{C_{13}H_2O_{13}Os_3Ru}$: C, 15.04; H, 0.19%. ν(CO, hexane): 2081s, 2066s, 2056s, 2028m, 2023m, 2017ms cm^{-1}.

2.2. Reaction of ***1*** *with* PPh_3

A solution of **1** (46 mg, 44 μmol) and $\mathrm{PPh_3}$ (12 mg, 44 μmol) in $\mathrm{CH_2Cl_2}$ (90 ml) was placed in a three-necked round-bottomed flask and deoxygenated by passing through nitrogen. A solution of trimethylamine *N*-oxide dihydrate (48 mg, 43 μmol) in acetonitrile (50 ml) was similarly deoxygenated and then introduced dropwise into the solution of **1** via a pressure-equalising dropping funnel over 1.5 h. The solution was stirred for a further 3 h, and was then filtered through a short silica column. Removal of the solvent by rotary evaporation followed by chromatographic separation on silica gel yielded unconsumed **1** (6 mg, 12%), a red–orange band of $\mathrm{RuOs_3(\mu\text{-}H)_2(CO)_{12}(PPh_3)}$ (**2**, 25 mg, 43%) and another red–orange band of $\mathrm{RuOs_3(\mu\text{-}H)_2(CO)_{11}(PPh_3)_2}$ (**3**, 5 mg, 9%).

Analytical data for **2**. Found: C, 28.47; H, 1.66; P, 2.11. Calc. for $\mathrm{C_{30}H_{17}O_{12}Os_3PRu}$: C, 28.32; H, 1.34; P, 2.44%. ν(CO, hexane): 2094mw, 2064m, 2054vs, 2039m, 2027m, 2010mw, 1995mw, 1981w, 1970w cm^{-1}; δ_P (295 K, $\mathrm{CDCl_3}$) 33.60s (**2a**), 49.39s (**2b**); δ_H (253 K, $\mathrm{CDCl_3}$) -19.51 (d, $^2J_\mathrm{PH} = 7.4$ Hz, **2a**), -19.74 (s, OsHOs, **2b**), -21.29 (d, $^2J_\mathrm{PH} = 9.1$ Hz, OsHRu, **2a**).

Analytical data for **3**. Found: C, 38.66; H, 2.42. Calc. for $\mathrm{C_{47}H_{32}O_{11}Os_3P_2Ru}$: C, 37.48; H, 2.13%. ν(CO, hexane): 2076m, 2041s, 2017m, 2001mw, 1982w, 1973w cm^{-1}.

Crystal data for **2a**: $\mathrm{C_{30}H_{17}O_{12}Os_3PRu}$, $M_\mathrm{w} = 1272.08$, monoclinic, space group $P2_1/c$, $a = 12.8692(5)$, $b = 15.3942(6)$, $c = 17.7316(7)$ Å, $\beta = 107.029(1)°$; $U = 3358.8(2)$ Å^3; $Z = 4$; $\rho_\mathrm{calc.} = 2.516$ Mg m^{-3}; μ(Mo–K$_\alpha$) = 11.861 mm^{-1}, $T = 295$ K, 25 588 reflections collected, 8356 unique reflections, final $R = 13.04\%$, $wR = 12.60\%$ for all data, 433 parameters and seven restraints.

Crystal data for **2b**: $\mathrm{C_{30}H_{17}O_{12}Os_3PRu}$, $M_\mathrm{w} = 1272.08$, triclinic, space group $P\bar{1}$, $a = 10.1555(1)$, $b = 12.7303(1)$, $c = 13.4129(2)$ Å, $\alpha = 90.001(1)$, $\beta = 91.628(1)$, $\gamma = 102.758(1)°$; $U = 1690.52(3)$ Å^3; $Z = 2$; $\rho_\mathrm{calc.} = 2.499$ Mg m^{-3}; μ(Mo–K$_\alpha$) = 11.783 mm^{-1}, $T = 295$ K, 15 104 reflections collected, 8178 unique reflections, final $R = 5.80\%$, $wR = 7.20\%$ for all data and 432 parameters.

3. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 140542 and 140541. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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