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Triruthenium clusters containing bridging dppm and capping sulfido and selenido ligands: X-ray structures of [Ru₃(CO)₅(μ₃-CO)(μ₃-Se)(μ-dppm)₂], [Ru₃(CO)₆(μ₃-CO)(μ₃-Se)(μ-dppm)(η¹-Ph₂PCH₂P(=O)Ph₂)] and [Ru₂(CO)₄(μ-SePh)₂(μ-dppm)]

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Abstract

The reaction of $[Ru_3(CO)_{10}(\mu-dppm)]$ (1) with dppmSe at 66 °C affords $[Ru_3(CO)_8(\mu-dppm)_2]$ (2), $[Ru_3(CO)_7(\mu_3-CO)(\mu_3-Se)(\mu-dppm)_2]$ (4) and $[Ru_3(CO)_6(\mu_3-CO)(\mu_3-Se)(\mu-dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (5) in 7%, 5%, 9% and 33% yields, respectively. A similar reaction between 1 with dppmS gives $[Ru_3(CO)_7(\mu_3-S)_2(\mu-dppm)]$ (6), $[Ru_3(CO)_7(\mu_3-CO)(\mu_3-S)(\mu-dppm)]$ (7) $[Ru_3(CO)_5(\mu_3-CO)(\mu_3-S)(\mu-dppm)_2]$ (8) and $[Ru_3(CO)_6(\mu_3-CO)(\mu_3-S)(\mu-dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (9) in 8%, 7%, 14% and 35% yields, respectively. Treatment of 1 with PhSeSePh at 66 °C affords the dinuclear compound $[Ru_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$ (10) in 14% yield. Thermolysis of 5 and 9 in refluxing toluene at 110 °C gives 4 and 8, respectively. The molecular structures of 4, 9 and 10 have been determined by single-crystal X-ray diffraction studies. The cores of the new clusters 4, 5, 8 and 9 consist of metal triangles capped by μ_3 -sulfur or selenium atoms with the bidentate ligand bridging in equatorial positions. In compounds 4 and 8, two bidentate dppm ligands bridge the Ru₃ triangle in such a way that each ligand bridges two ruthenium atoms and one Ru–Ru edge remains unbridged. Compounds 5 and 9 contain one bridging dppm ligand and one dangling dppm mono-oxide ligand Ph_2PCH_2P(=O)Ph_2 coordinated to the rear metal atom at an equatorial position. The molecular structure of 10 shows classical "sawhorse" structure with two bridging SePh ligands as well as the dppm ligand. © 2004 Elsevier B.V. All rights reserved.

Keywords: Triruthenium carbonyl clusters; Sulfido and selenido ligands; Bis(diphenylphosphino)methane mono-oxide; Crystal structures

1. Introduction

Transition metal carbonyl clusters containing chalcogenide elements (S, Se or Te) as bridging ligands have

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important chemical and structural significance, since they can be regarded as discrete molecular models of extended inorganic solids [1]. The presence of chalcogenido ligands often appears to be decisive in cluster aggregation reactions and in generating new coordination modes and geometries [2,3]. Presently, different synthetic routes are available for the preparation of sulfido

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or selenido transition-metal clusters, among these, those that involve the oxidative addition of tertiary phosphine chalcogenide compounds to zero-valent metal centers appear to be the most effective [4]. This method, takes advantage of the frailty of the $Ph_3P=E$ (E = S or Se) bond and has been successfully used by the Tiripicchio group to synthesize tertiary phosphine substituted iron and ruthenium clusters containing capping calcogenido ligands [5]. Adams et al. [6] have recently reported some manganese and mixed iron-manganese carbonyl clusters bearing triphenylphosphine and triply bridging selenido ligands from the reactions of Ph₃P=Se with [Mn₂(CO)₉(MeCN)] and [CpFeMn(CO)₇] while Braunstein et al. [7] have reported a series of mixed metal tri- and tetranuclear clusters containing capping selenido ligands from the reactions between $[(\mu-H)MCo_3]$ $(CO)_{12}$] (M = Fe or Ru) and phosphine selenides such as Ph₃PSe, Ph₂P(Se)CH₂PPh₂, (2-C₅H₄N)Ph₂PSe and $(2-C_4H_3S)Ph_2PSe.$

Bis(diphenylphosphino)methane (dppm) has been extensively used as a ligand and the chemistry of its dioxide (dppmO₂), disulfide (dppmS₂) and diselenide (dppmSe₂) and its monoxide (dppmO), monosulfide (dppmS) and monoselenide (dppmSe) is known [8]. It has been found that the reactions of [Fe₃(CO)₁₂] with the diselenides dppmSe₂, dppeSe₂ and dppfSe₂ produce the 50-electron, *nido*-clusters [Fe₃(CO)₇(μ_3 -Se)₂(μ -(Ph₂P)₂R)] (R = CH₂, dppm; R = (CH₂)₂, dppe; R = (C₅H₄)₂Fe, dppf) as the main products [9]. In some cases, these reactions lead to species not easily accessible by other routes. For example, dppmSe₂ reacts with [Ru₃(CO)₁₂] in refluxing toluene to give, in addition to the expected primary product [Ru₃(CO)₇(μ_3 -Se)₂(μ - dppm)], the cubane like cage cluster $[Ru_4(CO)_{10}(\mu_3 Se_{4}(\mu$ -dppm) [10]. Previously, we reported the synthesis and reactivity of the capping sulfido compound $[Os_3(CO)_7(\mu_3-S)_2(\mu-dppm)]$ from the reaction of $[Os_3(CO)_{10}(\mu$ -dppm)] with tetramethylthiourea [11] and the capping selenido compounds [Os₃(CO)₇(µ₃-Se)₂(µdppm)] and $[Os_3(CO)_7(\mu_3-CO)(\mu_3-Se)(\mu-dppm)]$ from the reaction between [Os₃(CO)₁₀(MeCN)₂] and dppmSe [12]. With the aim of synthesizing capping selenido and sulfido triruthenium compounds containing more than one edge bridging dppm ligand we have investigated the reaction of $[Ru_3(CO)_{10}(\mu-dppm)]$ (1) with dppmSe and dppmS and the results are described in the present paper. The proposed doubly edge bridged and chalcogenide capped clusters should exhibit exceptional thermal stability and could prove useful for cluster aggregation transformations.

2. Results and discussion

The reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (1) with dppmSe in refluxing THF gives two previously reported compounds $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ (2) and $[Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})]$ (3) in 7% and 5% yields, respectively, and two new compounds $[Ru_3(CO)_5(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})_2]$ (4) and $[Ru_3(CO)_6(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})_2]$ (4) and $[Ru_3(CO)_6(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})_2]$ (5) in 9% and 33% yields, respectively (Scheme 1). Compound 2 was reported from the reaction of $[Ru_3(CO)_{12}]$ with dppm [13] and 3 from the reaction of 1 with elemental selenium and was characterized by X-ray diffraction studies [14]. A similar reaction between 1 and dppmS in refluxing



Scheme 1.

THF yields two known clusters $[Ru_3(CO)_7(\mu_3-S)_2(\mu dppm)]$ (6) and $[Ru_3(CO)_7(\mu_3-CO)(\mu_3-S)(\mu dppm)]$ (7) in 8% and 7% yields and two new clusters $[Ru_3-(CO)_5(\mu_3-CO)(\mu_3-S)(\mu dppm)_2]$ (8) and $[Ru_3(CO)_6-(\mu_3-CO)(\mu_3-S)(\mu dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (9) (Scheme 1) in 14% and 35% yields, respectively. Both compounds 6 and 7 were also obtained from the reaction of 1 with tetramethylthiourea and were characterized by X-ray diffraction studies [14].

The compounds 4 and 8 have been characterized by elemental analysis, IR, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data together with single-crystal X-ray diffraction analysis for 4. The molecular structure of 4 is depicted in Fig. 1, crystal data are given in Table 1 and selected bond distances and angles are shown in Table 2. The molecule consists of a triangular cluster of three ruthenium atoms containing one triply bridging selenido ligand, two edge bridging dppm ligands, five terminal and one triply bridging carbonyl ligands. The complex displays a tetrahedral Ru₃Se core in which an almost equilateral triangle of ruthenium atoms (Ru(1)-Ru(3) = 2.838(3) Å, Ru(2)-Ru(3) = 2.816(3) Å and Ru(1)–Ru(2) = 2.837(3) Å) is symmetrically capped by the selenium atom (Ru(1)-Se(1) = 2.517(3) Å, Ru(3)-Se(1) = 2.481(3) Å and Ru(2)-Se(1) = 2.496(3) Å). In contrast, the triply bridging carbonyl group is bonded asymmetrically to the Ru₃ triangle with three distinctly different Ru–C distances (Ru(2)–C(28) = 2.19(2)) A, Ru(1)-C(28) = 2.07(2) Å and Ru(3)-C(28) = 2.26(2)A). The triply bridging carbonyl and selenido ligands lie on opposite faces of the Ru₃ triangle resulting in a trigonal bipyramidal geometry for the Ru₃(Se)(CO) core. The dppm supported Ru-Ru bond lengths are similar to the supported bond lengths in 2 (2.833(2) and 2.826(2) Å) but the unsupported bond distance is somewhat shorter than that in 2(2.858(2) Å) [15]. There are



Fig. 1. The solid-state structure of $[Ru_3(CO)_5(\mu_3-CO)(\mu_3-Se)(\mu_3-pm)_2]$ (4). Thermal ellipsoids are at the 50% probability level.

five terminal carbonyl groups, two each on Ru(2) and Ru(3) and one on Ru(1). The Ru–P bond distances in **4** (Ru(1)–P(1) = 2.382(6) Å, Ru(1)–P(4) = 2.284(6) Å, Ru(3)–P(3) = 2.363(6) Å and Ru(2)–P(2) = 2.302(6) Å) are comparable to the Ru–P distances in **2** [15] and **1** [13].

The spectroscopic data for **4** are in accord with the solid-state structure and the spectroscopic data for **8** indicate that it is a direct analog of **4** (Scheme 1). The ³¹P{¹H} NMR spectra of **4** and **8** contain two doublets (δ 29.5 (J = 57.3 Hz) and 27.8 (J = 57.3 Hz) for **4**; δ 29.2 (d, J = 57.3 Hz) and 27.3 (d, J = 57.3 Hz) for **8**), indicating two different types of phosphorus atoms in the molecule. In addition to the usual phenyl resonances in the aromatic region, the aliphatic region of the ¹H NMR spectra of **4** and **8** show two equal intensity multiplets (δ 4.12 and 3.65 for **4** and δ 3.87 and 3.59 for **8**) due to the methylene protons of the dppm ligands. The FAB mass spectra of **4** and **8** show the molecular ion peaks at m/z 1317 and 1270, respectively, and ions due to stepwise loss of five carbonyls groups.

The compounds 5 and 9 have been characterized by elemental analysis, IR, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data together with single-crystal X-ray diffraction analysis for 9. The molecular structure of 9 is shown in Fig. 2, crystal data are given in Table 1 and selected bond distances and angles are given in Table 3. The molecule consists of a triangular cluster of three ruthenium atoms containing one triply bridging sulfido ligand, one bridging dppm ligand, one η^1 -coordinated dppm mono-oxide (Ph₂PCH₂P(=O)Ph₂) ligand, one triply bridging and six terminal carbonyl ligands. The two metal-metal bonds, Ru(1)-Ru(2) = 2.8201(10)Å and Ru(2)–Ru(3) = 2.8108(9) Å are essentially equal in length and slightly longer than the third bond, Ru(1)-Ru(3) = 2.7892(10) Å. All three metal-metal bonds are shorter than those found in 1 (2.8341(1), 2.841(1) and 2.860(1) Å) [13]. The compound 9 contains a triply bridging sulfido ligand on one triangular face and a triply bridging carbonyl ligand on the other. The geometry of the Ru₃S core in which an isosceles triangle of ruthenium atoms is almost symmetrically caped by the S atom (Ru(1)-S(1) = 2.3606(17) Å, Ru(3)-S(1) = 2.3636(15) Å and Ru(2)-S(1) = 2.3536(15) Å) can be described as tetrahedral. In contrast the triply bridging carbonyl ligand is bonded asymmetrically to the Ru₃ triangle (Ru(2)–C(16) = 2.121(5) Å, Ru(3)– C(16) = 2.202(5) Å and Ru(1)-C(16) = 2.198(5) Å). The three Ru-P bond distances in 9 are different (Ru(2)-P(1) = 2.3521(14) Å, Ru(2)-P(2) = 2.3255(15) Åand Ru(3)-P(3) = 2.3522(14) Å). An intriguing structural feature of 9 is the presence of an unusual dangling η^{1} -Ph₂PCH₂P(=O)Ph₂ ligand. We believe that the dppm mono-oxide ligand is formed by in situ oxidation of one of the PPh₂ groups of the dppm ligand. The source of oxygen may be moisture in the solvent

Table 1 Crystal data for compounds **4**, **9** and **10**

Compounds	4	9	10
Empirical formula	$C_{56}H_{44}O_6P_4Ru_3Se$	C57H44O8P4Ru3SCH2Cl2	$C_{41}H_{32}O_4P_2Ru_2 Se_2$
Formula weight	1318.96	1401.07	1010.67
<i>T</i> (K)	293(2)	293(2)	293(2)
λ	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	14.397(2)	10.342(3)	11.324(1)
b (Å)	14.444(2)	13.695(3)	18.567(2)
<i>c</i> (Å)	15.946(3)	21.274(4)	20.460(3)
α (°)	79.15(1)	72.48(2)	110.24(1)
β (°)	67.65(1)	81.13(2)	99.10(1)
γ (°)	77.80(1)	89.81(3)	92.34(1)
$V(\text{\AA}^3)$	2976.2(8)	2835.9(12)	3964.1(8)
Ζ	2	2	4
$D_{\text{calc}} (\text{mg/m}^3)$	1.472	1.641	1.693
Absorption coefficient (mm ⁻¹)	1.514	1.086	2.719
<i>F</i> (000)	1308	1400	1984
Crystal size (mm ³)	$0.2 \times 0.1 \times 0.1$	$0.4 \times 0.3 \times 0.2$	$0.5 \times 0.4 \times 0.1$
Theta range for data collection (°)	2.13-17.50	2.03-22.50	2.06-19.99
Index ranges	$-10 \leqslant h \leqslant -11$,	$-1 \leqslant h \leqslant 11$,	$-1 \leqslant h \leqslant 9$,
	$-11 \leqslant k \leqslant 12,$	$-14 \leqslant k \leqslant 14,$	$-16 \leqslant k \leqslant 16$,
	$0 \leq l \leq 13$	$-22 \leqslant l \leqslant 22$	$-19 \leqslant l \leqslant 19$
Reflections collected	3650	8362	8327
Independent reflections (R_{int})	3650 (0.0401)	6910 (0.0323)	6858 (0.0218)
Completeness (%) (to theta (°))	96.6 (17.50)	93.2 (22.50)	92.7 (19.99)
Absorption correction	None	None	None
Data/restraints/parameters	3650/0/561	6910/0/685	6858/0/919
Goodness-of-fit on F^2	1.278	1.076	1.100
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0719, wR_2 = 0.2142$	$R_1 = 0.0363, wR_2 = 0.0856$	$R_1 = 0.0458, wR_2 = 0.1148$
R indices (all data)	$R_1 = 0.0925, wR_2 = 0.2318$	$R_1 = 0.0491, wR_2 = 0.0916$	$R_1 = 0.0557, wR_2 = 0.1211$
Largest difference peak and hole (e $Å^{-3}$)	1.892 and -0.671	0.844 and -0.619	1.860 and -1.145

(THF). Each of the ruthenium atoms contains two linear terminal carbonyl ligands. The cluster **9** is a 48-electron system, as expected for an electron precise trinuclear metal cluster containing three metal-metal bonds. To the best of our knowledge compound **9** represents the first example of a triruthenium cluster containing a bridging dppm and a dangling oxygenated dppm (Ph₂PCH₂P(=O)Ph₂) ligands.

The spectroscopic data for **9** are consistent with its solid state structure and are very similar to the spectroscopic data for **5** (Scheme 1). Both the solution and the solid state IR spectra of **5** and **9** are superimposable, indicating that they are isostructural. The ³¹P{¹H} NMR spectra of **5** and **9** contain three sets of signals, one integrating for 2 phosphorus atoms and two each integrating for one phosphorus atom, indicating the presence of three different types of phosphorus atoms in the molecule. The doublets at δ 25.4 and 41.2 (J = 28.6 Hz) for **5** and δ 28.5 and 41.2 (J = 28.6 Hz) for **5** and δ 37.0 for **9** are due to the equivalent phosphorus atoms of the bridging dppm ligands. In addition to

the usual phenyl resonances, the ¹H NMR spectra of **5** and **9** show triplets integrating for two protons and two multiplets each integrating for one proton (4.19 (m), 3.99 (t) and 3.50 (m) for **5**; 4.20 (m), 3.98 (t) and 3.59 (m) for **9**). The multiplets are due to the methylene protons of the dppm mono-oxide ligand and the triplets are due to the methylene protons of the methylene protons of the bridging dppm ligands. The FAB mass spectra of **5** and **9** show the molecular ion peaks at m/z 1362 and 1315, respectively, and ions due to the sequential loss of seven carbonyl ligands.

The formation of the dppm mono-oxide ligand is most interesting in that it is apparently associated with the activation of the P–S and P–Se bonds by the cluster. This is evidenced by the facts that no related compounds are observed in the reactions of dppm with $Ru_3(CO)_{12}$ and that the dppmS and dppmSe ligands are stable towards hydrolysis under the reaction conditions associated with the formation of **5** and **9**. Thus, one can visualize a reaction pathway whereby initial coordination of phosphorus is followed by activation of the P–S or P–Se bond by the cluster and then by nucleophilic attack by trace water at the activated bonds. This Table 2

Selected bond distances (Å) and angles (°) for $[Ru_3(CO)_5(\mu_3\text{-}CO)(\mu_3\text{-}Se)(\mu\text{-}dppm)_2]$ (4)

Bond distances			
Ru(1)–C(28)	2.07(2)	P(2)-Ru(2)	2.302(6)
Ru(1)–P(4)	2.284(6)	O(28)–C(28)	1.19(2)
Ru(1) - P(1)	2.382(6)	C(28)–Ru(2)	2.19(2)
Ru(1)-Se(1)	2.517(3)	C(28)–Ru(3)	2.26(2)
Ru(1)-Ru(2)	2.837(3)	Ru(2)–Se(1)	2.496(3)
Ru(1)-Ru(3)	2.838(3)	Ru(2)-Ru(3)	2.816(3)
P(3)–Ru(3)	2.363(6)	Ru(3)–Se(1)	2.481(3)
Bond angles			
C(28)-Ru(1)-P(4)	117.4(6)	P(2)-Ru(2)-Se(1)	96.24(16)
C(28)-Ru(1)-P(1)	134.8(6)	C(28)-Ru(2)-Ru(3)	51.8(6)
P(4)-Ru(1)-P(1)	107.3(2)	P(2)-Ru(2)-Ru(3)	144.69(17)
C(28)-Ru(1)-Se(1)	92.3(7)	Se(1)-Ru(2)-Ru(3)	55.29(7)
P(4)-Ru(1)-Se(1)	97.03(17)	C(28)-Ru(2)-Ru(1)	46.4(6)
P(1)-Ru(1)-Se(1)	87.93(16)	P(2)-Ru(2)-Ru(1)	87.25(17)
C(28)–Ru(1)–Ru(2)	50.1(6)	Se(1)-Ru(2)-Ru(1)	55.89(7)
P(4)-Ru(1)-Ru(2)	143.36(17)	Ru(3)-Ru(2)-Ru(1)	60.26(6)
P(1)-Ru(1)-Ru(2)	96.00(16)	C(28)-Ru(3)-P(3)	133.6(6)
Se(1)-Ru(1)-Ru(2)	55.20(7)	C(28)-Ru(3)-Se(1)	88.8(6)
C(28)-Ru(1)-Ru(3)	52.0(6)	P(3)-Ru(3)-Se(1)	85.98(16)
P(4)-Ru(1)-Ru(3)	85.51(16)	C(28)-Ru(3)-Ru(2)	49.7(6)
P(1)-Ru(1)-Ru(3)	142.23(17)	P(3)-Ru(3)-Ru(2)	141.32(17)
Se(1)-Ru(1)-Ru(3)	54.82(7)	Se(1)-Ru(3)-Ru(2)	55.80(7)
Ru(2)-Ru(1)-Ru(3)	59.51(6)	C(28)–Ru(3)–Ru(1)	46.1(6)
P(2)–C(13)–P(1)	112.2(12)	P(3)-Ru(3)-Ru(1)	95.24(16)
P(3)-C(43)-P(4)	109.9(11)	Se(1)-Ru(3)-Ru(1)	56.01(7)
O(28)–C(28)–Ru(1)	133.8(17)	Ru(2)-Ru(3)-Ru(1)	60.23(6)
O(28)–C(28)–Ru(2)	129.9(16)	Ru(3)-Se(1)-Ru(2)	68.91(8)
Ru(1)–C(28)–Ru(2)	83.5(9)	Ru(3)-Se(1)- $Ru(1)$	69.17(8)
O(28)–C(28)–Ru(3)	129.5(16)	Ru(2)-Se(1)-Ru(1)	68.91(8)
Ru(1)–C(28)–Ru(3)	81.9(9)	C(28)–Ru(2)–P(2)	115.9(6)
Ru(2)–C(28)–Ru(3)	78.5(8)	C(28)-Ru(2)-Se(1)	89.9(6)

process must also be associated with the formation of capping sulfur and selenium clusters under relatively mild conditions relative to the reaction of elemental sulfur or selenium with related clusters.



Fig. 2. The solid-state structure of $[Ru_3(CO)_6(\mu_3-CO)(\mu_3-S)(\mu-dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (9). Thermal ellipsoids are at the 50% probability level.

Bond distances			
Ru(1)–C(16)	2.198(5)	Ru(2)-S(1)	2.3536(15)
Ru(1) - P(1)	2.3521(14)	Ru(2)-Ru(3)	2.8108(9)
Ru(1)-S(1)	2.3606(17)	Ru(3)–C(16)	2.202(5)
Ru(1)-Ru(3)	2.7892(10)	Ru(3) - P(3)	2.3522(14)
Ru(1)-Ru(2)	2.8201(10)	Ru(3)-S(1)	2.3636(15)
Ru(2)–C(16)	2.121(5)	P(4)-O(3)	1.484(4)
Ru(2)–P(2)	2.3255(15)	O(16)–C(16)	1.190(6)
Bond angles			
C(16)-Ru(1)-P(1)	131.89(13)	C(16)-Ru(3)-S(1)	87.61(14)
C(16)-Ru(1)-S(1)	87.78(15)	P(3)-Ru(3)-S(1)	169.47(5)
P(1)-Ru(1)-S(1)	91.97(6)	C(16)-Ru(3)-Ru(1)	50.60(13)
C(16)-Ru(1)-Ru(3)	50.73(13)	P(3)-Ru(3)-Ru(1)	116.34(4)
P(1)-Ru(1)-Ru(3)	145.18(4)	S(1)-Ru(3)-Ru(1)	53.76(4)
S(1)-Ru(1)-Ru(3)	53.86(4)	C(16)-Ru(3)-Ru(2)	48.21(13)
C(16)-Ru(1)-Ru(2)	48.07(14)	P(3)-Ru(3)-Ru(2)	120.48(4)
P(1)-Ru(1)-Ru(2)	95.69(4)	S(1)-Ru(3)-Ru(2)	53.26(4)
S(1)-Ru(1)-Ru(2)	53.15(4)	Ru(1)-Ru(3)-Ru(2)	60.47(3)
Ru(3)-Ru(1)-Ru(2)	60.14(2)	Ru(2)-S(1)-Ru(1)	73.48(5)
C(16)-Ru(2)-P(2)	118.99(14)	Ru(2)-S(1)-Ru(3)	73.15(5)
C(16)-Ru(2)-S(1)	89.79(14)	Ru(1)-S(1)-Ru(3)	72.37(5)
P(2)-Ru(2)-S(1)	98.73(5)	P(2)-C(1)-P(1)	111.5(3)
C(16)-Ru(2)-Ru(3)	50.72(14)	P(3)-C(40)-P(4)	126.3(3)
P(2)-Ru(2)-Ru(3)	145.70(4)	O(3)-P(4)-C(40)	117.0(3)
S(1)-Ru(2)-Ru(3)	53.59(4)	C(58)–C(53)–P(4)	124.4(5)
C(16)-Ru(2)-Ru(1)	50.44(13)	O(16)-C(16)-Ru(2)	132.1(4)
P(2)-Ru(2)-Ru(1)	88.55(4)	O(16)-C(16)-Ru(1)	131.3(4)
S(1)-Ru(2)-Ru(1)	53.37(4)	Ru(2)–C(16)–Ru(1)	81.49(18)
Ru(3)-Ru(2)-Ru(1)	59.38(3)	O(16)-C(16)-Ru(3)	132.0(4)
C(16)-Ru(3)-P(3)	82.48(14)	Ru(2)-C(16)-Ru(3)	81.07(19)
Ru(1)-C(16)-Ru(3)	78.67(17)		

We have recently reported [16] that the reaction of $[Os_3(CO)_{10}(\mu$ -dppm)] with PhSeSePh at 110 °C affords the dinuclear compound $[Os_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$, three 50 electron, isomeric compounds with the formula [Os₃(CO)₈(µ-SePh)₂(µ-dppm)] and two benzyne compounds $[Os_3(CO)_8(\mu-SePh)_2(\mu-\eta^2-C_6H_4)(\mu-dppm)]$ and $[Os_3(CO)_6(\mu-CO)(\mu_3-Se)_2(\mu-\eta^2-C_6H_4)(\mu-dppm)].$ Following this observation we decided to investigate the reaction of 1 with PhSeSePh, with the intent of synthesizing the different isomers of $[Ru_3(CO)_8(\mu-SePh)_2($ dppm)] and to establish whether starting from the more reactive 1 (compared to $[Os_3(CO)_{10}(\mu-dppm)]$) influences the course of the reaction. In contrast to the above observation, the reaction of 1 with PhSeSePh in refluxing THF at 66 °C gives only the dinuclear compound $[Ru_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$ (10) in 14% yield (Scheme 2) along with some other very minor, uncharacterized products.

Compound 10 has been characterized by IR, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data together with single-crystal X-ray diffraction study. The molecular structure of 10 is depicted in Fig. 3, crystal data are given Table 1, selected bond distances and angles are shown in Table 4. There are two molecules in

Table 3 Selected bond distances and angles for $[Ru_3(CO)_6(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3-S)(\mu_3-CO)(\mu_3-S)(\mu_3$

Table 4





Fig. 3. The solid-state structure of $[Ru_2(CO)_4(\mu$ -SePh)_2(μ -dppm)] (10). Thermal ellipsoids are at the 50% probability level.

the unit cell which have the same overall geometry but differ mainly in the lengths of the Ru–Se bonds, probably due to crystal packing effects. The molecule consists of a ruthenium-ruthenium back-bone, ligated terminally by four carbonyl ligands adopting the Ru₂(CO)₄ classical 'sawhorse' arrangement and bridged by two phenylselenido ligands as well as a dppm ligand. The phenylselenido and the dppm ligands are transoid to each other and the selenido ligands are perpendicular each other to the Ru-Ru vector. The P–C–P angle of the short-bite dppm ligand $\{P(1)-C(1)-P(2) = 116.4(4)^{\circ}\}$ is very similar to that found for the dinuclear dppm substituted complexes $[Ru_2(CO)_4(\mu-SCH_2CH_2CH_2S)(\mu-dppm)]$ (114.4(2)°) [17] and $[Os_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$ (114.0(10)°) [16]. The interesting feature of the molecular structure 10 is short Ru-Ru distance. The Ru(1)-Ru(2) distance of 2.6929(11) A is significantly shorter than the corresponding Ru–Ru distances (2.8564(10) Å) in the parent compound 1 [13] but are comparable to the corresponding distances found for the other related diruthenium complexes such as, $[Ru_2 (CO)_6(\mu-SCH_2CH_2S)] (2.679(8) \text{ Å})$ [18], $[Ru_2(CO)_4(\mu-SC_6H_4S)(PPh_3)_2]$ (2.677(5) Å) [19] and $[Ru_2(CO)_6(\mu-SC_6H_4S)]$ (2.650(2) Å) [20]. This rela-

Selected bond distances (Å) and angles (°) for $[Ru_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$ (10)					
Bond distances					
Ru(3) - P(4)	2.317(3)	Ru(4)-Se(3)	2.5180(12)		
Ru(3)-Se(4)	2.5284(12)	Ru(4)-Se(4)	2.5190(12)		
Ru(3)-Se(3)	2.5468(12)	Ru(1) - P(2)	2.311(2)		
Ru(3)-Ru(4)	2.7001(10)	Ru(1)-Se(1)	2.5217(12)		
Ru(2) - P(1)	2.314(2)	Ru(1)–Se(2)	25253(12)		
Ru(2)–Se(1)	2.5150(13)	Se(3)-C(58)	1.941(9)		
Ru(2)–Se(2)	2.5155(12)	Se(4)–C(64)	1.927(10)		
Ru(2)-Ru(1)	2.6929(11)	Se(2)–C(17)	1.950(11)		
Ru(4) - P(3)	2.328(2)	Se(1)–C(23)	1.929(9)		
Bond angles					
P(4)-Ru(3)-Se(4)	151.07(7)	P(3)-Ru(4)-Ru(3)	94.77(6)		
P(4)-Ru(3)-Se(3)	92.76(7)	Se(3)-Ru(4)-Ru(3)	58.30(3)		
Se(4) - Ru(3) - Se(3)	77.23(4)	Se(4)-Ru(4)-Ru(3)	57.83(3)		
P(4)-Ru(3)-Ru(4)	94.17(6)	P(2)-Ru(1)-Se(1)	85.94(7)		
Se(4) - Ru(3) - Ru(4)	57.49(3)	P(2)-Ru(1)-Se(2)	151.71(7)		
Se(3)-Ru(3)-Ru(4)	57.27(3)	Se(1)-Ru(1)-Se(2)	77.75(4)		
P(1)-Ru(2)-Se(1)	89.88(7)	P(2)-Ru(1)-Ru(2)	94.21(6)		
P(1)-Ru(2)-Se(2)	154.79(7)	Se(1)-Ru(1)-Ru(2)	57.56(3)		
Se(1)-Ru(2)-Se(2)	78.05(4)	Se(2)-Ru(1)-Ru(2)	57.53(3)		
P(1)-Ru(2)-Ru(1)	96.95(6)	Ru(4)-Se(3)- $Ru(3)$	64.43(3)		
Se(1)-Ru(2)-Ru(1)	57.80(3)	Ru(4)-Se(4)- $Ru(3)$	64.68(3)		
Se(2)-Ru(2)-Ru(1)	57.89(3)	Ru(2)-Se(2)-Ru(1)	64.58(3)		
P(3)-Ru(4)-Se(3)	88.60(7)	Ru(2)-Se(1)- $Ru(1)$	64.64(3)		
P(3)-Ru(4)-Se(4)	152.58(7)	P(4)–C(43)–P(3)	113.9(5)		
Se(3)-Ru(4)-Se(4)	77.93(4)	P(2)-C(1)-P(1)	116.4(4)		

tively shortened Ru–Ru bond, in comparison to that observed in parent compound 1 is presumably due to the "pincer" effect exerted by the bridging phenylselenido ligands. Considering the μ -SePh as a three electron donor ligand, the molecule is a normal 34-electron species with each ruthenium atom in a distorted octahedral environment determined by the other ruthenium atom, the bridging phenylselenido groups and three appropriate two-electron donor ligands.

The infrared spectrum of 10 in the carbonyl stretching region in CH₂Cl₂ exhibits absorption bands at 2002s, 1979vs and 1940s cm⁻¹. The ¹H NMR spectrum of 10 shows signals at δ 7.39 (m), 4.41 (dt) and 3.88 (dt) with a relative intensity of 30:1:1. The doublet of triplets at δ 4.41 and 3.88 are due to the methylene protons of the dppm ligand. The multiplet centered at δ 7.39 has been assigned to the phenyl protons of both the dppm and SePh ligands. The ${}^{31}P{}^{1}H{}$ NMR spectrum shows a singlet at δ 24.2, which indicates that the two ³¹P nuclei of the dppm ligand are in an equivalent environment. The mass spectrum of 10 shows a molecular ion peak at m/z 1010 which is consistent with the proposed molecular formula [Ru₂] $(CO)_4(\mu$ -SePh)₂(μ -dppm)]. Thus, the spectroscopic data of 10 are consistent with the solid-state structure. As is generally the case, fragmentation of the starting trinuclear cluster is less pronounced with osmium than with ruthenium where formation of several selenido

trinuclear clusters is observed. Also, the osmium analog of 10 exists as two isomers in solution which differ by the relative disposition of the phenyl groups on the selenium whereas only one isomer of 10 is observed in solution.

3. Experimental

All the reactions were routinely performed under a nitrogen atmosphere using standard Schlenk techniques although no special precautions were taken to exclude air during work-up. Reagent grade solvents were dried and distilled prior to use by standard methods (CH₂Cl₂ over CaH₂ and THF from sodium benzophenone). Infrared spectra were recorded on a Shimadzu FT-IR 8101 spectrophotometer. ¹H and ³¹P{¹H} NMR spectra were recorded on a Varian Unity Plus 400 and a Bruker DPX 400 spectrometers. Chemical shifts for the ³¹P{¹H} NMR spectra were recorded on Varian Mat 312 mass spectrometer. The starting cluster [Ru₃(CO)₁₀(µ-dppm)] (1) [21] and the ligands dppmS and dppmSe [22] were prepared by the literature procedures.

3.1. Reaction of 1 with dppmSe

A THF solution (35 mL) of 1 (0.200 g, 0.210 mmol) and dppmSe (0.192 g, 0.415 mmol) was heated to reflux under N2 for 2 h. The solvent was removed under reduced pressure and the residue was dissolved in a minimal amount of CH₂Cl₂ and separated by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (3:2, v/v) developed four bands. The first band and the second bands gave the known compounds $[Ru_3(CO)_8(\mu-dppm)_2]$ (2) (0.020 g, 7%) and $[Ru_3(CO)_7(\mu_3-CO)(\mu_3-Se)(\mu-dppm)]$ (3) (0.010 g, 5%). The third band yielded [Ru₃] $(CO)_5(\mu_3-CO)(\mu_3-Se)(\mu-dppm)_2$ (4) (0.025 g, 9%) as yellow crystals after recrystallization from CH₂Cl₂/hexane at 4 °C (Anal. Calc. for C₅₆H₄₄O₆P₄Ru₃Se: C, 51.01; H, 3.37. Found: C, 50.98; H, 3.33%). IR (vCO, CH₂Cl₂): 2017 vs, 1986 s, 1958 vs cm⁻¹; IR (vCO, KBr): 1647 w cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.18 (m, 40H), 4.11 (m, 2H), 3.65 (m, 2H); ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂): δ 29.5 (d, 2P, J = 57.3 Hz) 27.9 (d, 2P, J = 57.3 Hz); mass spectrum: m/z 1317. The fourth band gave [Ru₃(CO)₆ $(\mu_3-CO)(\mu_3-Se)(\mu-dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (5) (0.090 g, 33%) as yellow crystals from CH₂Cl₂/hexane at 4 °C (Anal. Calc. for C₅₇H₄₄O₈P₄Ru₃Se: C, 50.22; H, 3.26. Found: C, 50.45; H, 3.15%). IR (vCO, CH₂Cl₂): 2029 s, 2008 vs, 1992 vs, 1958 s cm⁻¹; IR (vCO, KBr): 1624 w cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.26 (m, 40H), 4.19 (m, 1H), 3.99 (m, 2H), 3.50 (m, 1H); ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂): δ 41.2 (d, 1P, J = 28.6 Hz), 28.3 (s, 2P), 25.4 (d, 1P, J = 28.6 Hz); mass spectrum: m/z 1362.

3.2. Reaction of 1 with dppmS

A similar reaction to that above of 1 (0.200 g, 0.210 g)mmol) with dppmS (0.192 g, 0.415 mmol) followed by similar chromatographic separation developed four bands. The first and second bands afforded the previously reported compounds [Ru₃(CO)₇(µ₃-S)₂(µ-dppm)] (6) (0.017 g, 8%) and $[Ru_3(CO)_7(\mu_3-CO)(\mu_3-S)(\mu-dppm)]$ (7) (0.015 g, 7%). The third band yielded $[Ru_3(CO)_5(\mu_3 CO(\mu_3-S)(\mu-dppm)_2$ (8) (0.036 g, 14%) as yellow crystals after recrystallization from CH₂Cl₂/hexane at 4 °C (Anal. Calc. for C₅₆H₄₄O₆P₄Ru₃S: C, 55.19; H, 3.64. Found: C, 54.90; H, 3.38%). IR (vCO, CH₂Cl₂): 2017 vs, 1987 s, 1958 vs cm⁻¹; IR (vCO, KBr): 1647 w cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.11 (m, 40H), 3.87 (m, 2H), 3.59 (m, 2H); ${}^{31}P{}^{1}H$ } NMR (CD₂Cl₂): δ 29.2 (d, 2P, J = 57.3 Hz) 27.3 (d, 2P, J = 57.3 Hz); mass spectrum: m/z 1270. The fourth band gave [Ru₃(CO)₆ $(\mu_3-CO)(\mu_3-S)(\mu-dppm)(\eta^1-Ph_2PCH_2P(=O)Ph_2)]$ (9). CH₂Cl₂ (0.102 g, 35%) as yellow crystals from CH₂Cl₂/hexane at 4 °C (Anal. Calc. for C₅₈Cl₂H₄₆O₈P₄ Ru₃S: C, 49.72; H, 3.32. Found: C, 49.98; H, 3.51%). IR (vCO, CH_2Cl_2) : 2029 s, 2009 vs, 1992 vs, 1958 s cm⁻¹; IR (vCO, KBr): 1626 w cm⁻¹; ¹H NMR (CD₂Cl₂): δ 7.26 (m, 40H), 4.20 (m, 1H), 3.98 (m, 2H), 3.59 (m, 1H); ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂): δ 41.4 (d, 1P, J = 28.6 Hz) 37.0 (s, 2P) 28.5 (d, 1P, J = 28.6 Hz); mass spectrum: *m*/*z* 1315.

3.3. Reaction of 1 with PhSeSePh

A solution of 1 (0.200 g, 0.210 mmol) and PhSeSePh (0.129 g, 0.414 mmol) in THF (35 ml) was heated to reflux for 1h. The solvent was removed under reduced pressure and the residue was dissolved in a minimal amout of CH₂Cl₂ and separated by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (7:3, v/v) developed one major and three very minor bands. The major band afforded $[Ru_2(CO)_4(\mu-SePh)_2(\mu-dppm)]$ (10) (0.030 g, 14%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ (Anal. Calc. for C₄₀H₃₀O₄P₂Ru₂ Se₂: C, 48.20; H, 3.04. Found: C, 48.38; H, 3.24%). IR (vCO, CH_2Cl_2): 2002 s, 1979 vs, 1940 s, cm^{-1} ; ¹H NMR (CD₂Cl₂): δ 7.39 (m, 30H), 4.41 (m, 1H), 3.88 (m, 1H); ³¹P{¹H} NMR (CD₂Cl₂): δ 24.2 (s); mass spectrum: *m*/ z 1010. The minor bands were too small for complete characterization.

3.4. Conversion of 5 to 4

A toluene solution (15 ml) of **5** (0.010 g, 0.007 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ developed a single band which afforded **5** (0.004 g, 41%).

3.5. Conversion of 9 to 8

A similar thermolysis to that above of a heptane solution of **9** (0.015 g, 0.011 mmol) followed by similar chromatographic separation gave 8 (0.006 g, 43%).

3.6. X-ray structure determinations

Crystals of 4, 9 and 10 for X-ray examination were obtained from saturated solutions of each in hexane/ dichloromethane solvent at -20 °C. Crystallographic data for 4, 9 and 10 were collected at 296 K, using Bruker P4 diffractometer with Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Data collection and processing were carried out using XSCANS [23]. The unit cells were indexed on low angle reflections and refined from 25 reflections in a range of 12-13°. The structures were solved by direct methods (SHELXS-97) [24] and refined on F^2 by full-matrix lest-squares (SHELXL-97) [25], utilized as incorporated in the WINGX [26] program package using all unique data. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent atom. Selected bond lengths and angles for 4, 9 and 10 are given in Tables 2-4, respectively. Crystallographic and other experimental data are summarized in Table 1.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos.: 238219 for compound **4**, 238220 for compound **9** and 238221 for compound **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (fax: +44 1336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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