Inorganica Chimica Acta 376 (2011) 170-174

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Chalcogenide-capped triruthenium clusters: X-ray structures of $[Ru_3(CO)_6(\mu_3-CO)\{P(C_4H_3S)_3\}(\mu-dppm)(\mu_3-O)]$ and $[(\mu-H)_2Ru_3(CO)_6\{P(C_4H_3S)_3\}(\mu-dppm)(\mu_3-S)]$

Md. Delwar H. Sikder^a, Shishir Ghosh^a, Shariff E. Kabir^{a,*}, Graeme Hogarth^b, Derek A. Tocher^b

^a Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh ^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK

ARTICLE INFO

Article history: Received 9 October 2010 Accepted 5 June 2011 Available online 16 June 2011

Keywords: Ruthenium cluster Carbonyls Oxygen-capped Sulfur-capped Bridging dppm Crystal structures

ABSTRACT

Treatment of $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppm)]$ (1) [dppm = bis(diphenylphosphino)methane] with molecular oxygen in benzene at 60 °C affords oxo-capped $[Ru_3(CO)_6(\mu_3-CO){P(C_4H_3S)_3}(\mu-dppm)-(\mu_3-O)]$ (2), while with elemental sulfur and selenium related chalcogenide-capped clusters $[Ru_3(CO)_6(\mu_3-CO){P(C_4H_3S)_3}(\mu-dppm)(\mu_3-E)]$ (3, E = S; 5, E = Se) and bis(chalcogenide) clusters $[Ru_3(CO)_6{P(C_4H_3S)_3}(\mu-dppm)(\mu_3-E)]$ (4, E = S; 6, E = Se) result. Reaction of 1 with H₂S in refluxing THF affords the previously reported $[(\mu-H)_2Ru_3(CO)_7(\mu-dppm)(\mu_3-S)]$ (7) together with the new sulfido-capped dihydride $[(\mu-H)_2Ru_3(CO)_6{P(C_4H_3S)_3}(\mu-dppm)(\mu_3-S)]$ (8). All new compounds have been characterized by spectroscopic data, and 2 and 8 by single-crystal X-ray diffraction analyses. Oxo-capped 2 consists of a triangular ruthenium framework capped on opposite sides by oxo and carbonyl groups, while 8 consists of a ruthenium triangle by a capping sulfido ligand and two inequivalent bridging hydride ligands.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide-containing transition metal clusters serve as discrete molecular models in furthering our understanding of extended inorganic solids [1] with the chalcogenide often playing a pivotal role in cluster aggregation reactions and displaying exotic coordination modes and geometries [2–19]. Their incorporation can be achieved in a variety of different ways, with the addition of tertiary phosphine chalcogenides (R₃P=E) [10-12,20-30] and diaryl dichalcogenides [13,31–36] to low-valent cluster centres providing particularly useful for the synthesis of sulfido- and seleno-containing materials. Both of these take advantage of the relative frailty of the R₃P=E and E-E bonds, and neither is generally applicable for the synthesis of related oxo-clusters. An attractive alternative is the addition of elemental chalcogen to transition metal clusters and while examples of such reactivity are known they remain relatively scarce [37,38]. Apart from the obvious atom-efficiency of this method, it also does not result in either concomitant phosphine incorporation or rely on secondary element-carbon bond cleavage events. This method also potentially allows the synthesis of low-valent metal-oxo clusters which are rare [39–47].

It has been known for some years now that the zero-valent triruthenium clusters $[Ru_3(CO)_8(\mu-dppm)_2]$ and $[Ru_3(CO)_6]$ $(\mu$ -dppm)₃] both react with molecular oxygen at elevated temperatures to afford oxo-capped $[Ru_3(CO)_5(\mu_3-CO)(\mu_3-O)(\mu-dppm)_2]$ [46] and $[Ru_3(CO)_3(\mu_3-CO)(\mu_3-O)(\mu-dppm)_3]$ [48] respectively. In contrast, while the mono(dppm) complex, [Ru₃(CO)₁₀(µ-dppm)], exhibits a rich and diverse chemistry [49] such a reaction does not occur presumably since the trinuclear centre is not electronrich enough to undergo oxidation. We have recently reported the synthesis of $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppm)]$ (1), formed in almost quantitative yield from the Me₃NO initiated reaction of [Ru₃- $(CO)_{10}(\mu$ -dppm)] with tri(2-thienyl)phosphine, and have begun to explore its reactivity. Thus, upon mild thermolysis in the presence of further Me₃NO it transforms smoothly into the thiophyne complex $[Ru_3(CO)_7(\mu-dppm)(\mu_3-\eta^2-C_4H_2S)(\mu-P(C_4H_3S)_2)]$ as a result of both carbon-hydrogen and carbon-phosphorus bond activation [50]. In light of the reactivity towards oxygen of dppm-substituted triruthenium clusters discussed above, we began to consider if 1 was electron-rich enough to undergo oxidation by molecular oxygen. In this note we report that this is indeed the case, and moreover show that it reacts smoothly with different group 16 elements to yield chalcogenide-capped clusters in good yields. To





^{0020-1693/\$ -} see front matter \odot 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.06.012

complement this work we also report our studies on the reactivity of 1 towards H_2S .

2. Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. [Ru₃(CO)₉{P(C₄H₃S)₃}(μ -dppm)] (1) was prepared according to the published procedure [50]. Elemental selenium and sulfur were purchased from Strem Co., Ltd., and Aldrich Co., Ltd., respectively. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. The chemical shifts were referenced to residual solvent resonances or 85% H₃PO₄ in ¹H and ³¹P NMR spectra as appropriate. Elemental analyses were performed by Microanalytical Laboratories, University College London. Fast atom bombardment mass spectra were obtained on a JOEL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and Csl as calibrant.

2.1. Reaction of $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppm)]$ (1) with O_2

An oxygen saturated benzene solution (25 mL) of 1 (30 mg. 0.025 mmol) was heated at 60 °C for 2 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (3:2, v/v) developed two bands. The first band gave a trace amount of unreacted 1. The second band afforded $[Ru_3(CO)_6(\mu_3-CO)\{P(C_4H_3S)_3\}$ $(\mu$ -dppm) $(\mu_3$ -O)] (2) (11 mg, 38%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. Spectral data for **2**: Anal. Calc. for C₄₄H₃₁O₈P₃Ru₃S₃: C, 44.78; H, 2.65. Found: C, 45.08; H, 2.72%. IR (v_{CO}, CH₂Cl₂): 2030 s, 2005 vs, 1996 sh, 1962 s, 1670 br cm⁻¹. ¹H NMR (CDCI₃): δ 7.80 (m, 2H), 7.66 (m, 3H), 7.54 (m, 1H), 7.43 (m, 1H), 7.35 (m, 9H), 7.26 (m, 10H), 7.13 (m, 3H), 3.67 (m, 1H), 3.85 (m, 1H). ${}^{31}P{}^{1}H{}$ NMR (CDCI₃): δ 4.58 (s, 1P), 29.5 (s, 2P). MS (FAB): *m*/*z* 1179 (M⁺).

2.2. Reaction of 1 with elemental sulfur

A CH₂Cl₂ solution (20 mL) of 1 (30 mg, 0.025 mmol) and S₈ (2 mg, 0.062 mmol) was heated to reflux for 4 h. A similar chromatographic separation to that above developed three bands. The first band gave unreacted 1 (trace). The second and third bands afforded $[Ru_3(CO)_6(\mu_3-CO)\{P(C_4H_3S)_3\}(\mu-dppm)(\mu_3-S)]$ (3) (12 mg, 41%) as yellow crystals and $[Ru_3(CO)_6{P(C_4H_3S)_3}(\mu-dppm)]$ $(\mu_3-S)_2$ (4) (8 mg, 27%) as red crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. Spectral data for **3**: Anal. Calc. for C₄₄H₃₁O₇-P₃Ru₃S₄: C, 44.18; H, 2.61. Found: C, 44.52; H, 2.72%. IR (v_{co}, CH₂Cl₂): 2032 m, 2009 vs, 1996 s, 1953 br 1653 w cm⁻¹. ¹H NMR (CDCl₃): δ 7.64 (m, 3H), 7.53 (m, 7H), 7.35 (m, 6H), 7.17 (M, 9H), 7.06 (m, 4H), 3.90 (m, 1H), 3.46 (m, 1H). ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 29.0 (s, 2P), 15.2 (s, 1P). MS (FAB): *m*/*z* 1195 (M⁺). Spectral data for 4: Anal. Calc. for C₄₃H₃₁O₆P₃Ru₃S₅: C, 43.03; H, 2.60. Found: C, 43.51; H, 2.71%. IR (v_{CO}, CH₂Cl₂): 2071 w, 2022 m, 2001 vs, 1967 m, 1943 m cm⁻¹. ¹H NMR (CDCl₃): δ 7.72 (m, 4H), 7.65 (m, 2H) 7.59 (m, 6H), 7.49 (m, 2H), 7.40 (m, 4H), 7.19 (m, 9H), 7.11 (m, 2H), 3.0 (m, 2H). ³¹P{¹H} NMR (CDCl₃): δ 26,7 (s, 1P), 14.7 (s, 2P). MS (FAB): *m*/*z* 1201 (M⁺).

2.3. Reaction of 1 with Se

A THF solution (50 mL) of **1** (30 mg, 0.025 mmol) and selenium powder (4 mg, 0.051 mmol) was heated to reflux for 1 h. A similar work up and chromatographic separation described as above

developed three bands. The first band was unreacted 1 (trace) while the second and third bands afforded $[Ru_3(CO)_6(\mu_3 -$ CO {P(C₄H₃S)₃ {(μ -dppm)(μ ₃-Se)] (**5**) (8 mg, 26%) as yellow crystals and $[Ru_3(CO)_6{P(C_4H_3S)_3}(\mu-dppm)(\mu_3-Se)_2]$ (6) (10 mg, 31%) as orange crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. Spectral data for 5: Anal. Calc. for C₄₄H₃₁O₇P₃Ru₃S₃Se: C, 42.52; H, 2.51. Found: C, 42.96; H, 2.59%. IR (v_{CO}, CH₂Cl₂): 2030 m, 2007 vs, 1994 s, 1959 m, 1652 br cm⁻¹, ¹H NMR (CDCl₃): δ 7.65–7.63 (m, 3H), 7.54 (m, 7H) 7.37 (m, 6H), 7.20-7.03 (m, 13H), 419 (m, 1H), 3.43 (m, 1H), ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 29.4 (s, 2P), 13.2 (s, 1P); MS (FAB): m/z 1243 (M⁺). Spectral data for **6**: Anal. Calc. for C43H31O6P3Ru3S3Se2: C, 39.91; H, 2.41. Found: C, 40.241; H, 2.48%. IR (v_{CO} , CH₂Cl₂): 2069 s, 2022 vs, 1999 m, 1972 v cm⁻¹, ¹H NMR (CDCl₃): δ 7.74 (m, 6H), 7.59 (m, 8H) 7.50 (m, 1H), 7.40 (m, 2H), 7.17 (m, 10H), 7.12 (m, 2H), 4.20 (m, 1H), 3.53 (m, 1H). ³¹P{¹H} NMR (CDCl₃): δ 26.6 (s, 1P), -3.0 (s, 2P). MS (FAB): m/z1295.

2.4. Reaction of **1** with H_2S

H₂S gas was bubbled through a THF solution (25 mL) of **1** (40 mg, 0.033 mmol) for 2 min and the resulting solution was refluxed for 2 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (3:2, v/v) developed two bands. The faster moving band gave $[(\mu-H)_2Ru_3(CO)_7(\mu-dppm)(\mu_3-S)]$ (**7**) (9 mg, 28%) and the slower moving band afforded $[(\mu-H)_2Ru_3(CO)_6[P(C_4H_3S)_3]$ (μ -dppm)(μ_3 -S)] (**8**) (12 mg, 31%) as orange crystals from hexane/

Table 1

Crystallographic data and structure refinement for 2 and 8.

Compound	2	8
Empirical formula	C46H31O9P3Ru3S3	C43H33O6P3Ru3S4
Formula weight	1220.01	1170.05
T (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	ΡĪ	PĪ
Unit cell dimensions		
a (Å)	11.3825(9)	11.042(2)
b (Å)	14.186(1)	12.908(2)
<i>c</i> (Å)	14.318(1)	17.152(3)
α (°)	88.066(1)	80.547(3)
β (°)	74.783(1)	82.825(3)
γ (°)	88.059(1)	70.538(3)
$V(Å^3)$	2228.9(3)	2267.2(7)
Ζ	2	2
ho (g cm ⁻³)	1.818	1.714
$\mu (\mathrm{mm}^{-1})$	1.309	1.322
F(000)	1208	1160
Crystal size (mm ³)	$\textbf{0.48} \times \textbf{0.36} \times \textbf{0.10}$	$0.46 \times 0.42 \times 0.08$
θ (°)	2.32-28.30	1.21-28.30
Index ranges	$-14 \leqslant h \geqslant 14$	$-14 \leqslant h \geqslant 14$
	$-18\leqslant k\geqslant 18$	$-16 \leqslant k \geqslant 17$
	$-18 \leqslant l \geqslant 18$	$-22 \leqslant l \geqslant 22$
Reflections collected	19 079	19 260
Independent reflections (R _{int})	10 145 (0.0301)	10 295 (0.0275)
Refinement method	full-matrix least-	full-matrix least-
	squares on F ²	squares on F ²
Max. and min. transmission	0.8802 and 0.5723	0.9016 and 0.5814
Data/restraints/	10 145/0/533	10 295/0/524
parameters		, ,
Goodness-of-fit on F^2	1.072	1.065
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0477$,	$R_1 = 0.0395$,
	$wR_2 = 0.1366$	$wR_2 = 0.1225$
R indices (all data)	$R_1 = 0.0536$,	$R_1 = 0.0439$,
· · · ·	$wR_2 = 0.1444$	$wR_2 = 0.1307$
Largest diff. peak and hole (e $Å^{-3}$)	2.850 and -1.906	1.647 and -1.524

CH₂Cl₂ at 4 °C. Spectral data for **8**: *Anal.* Calc. for C₄₃H₃₃O₆P₃Ru₃S₄: C, 44.14; H, 2.84. Found: C, 44.68; H, 2.97%. IR (ν_{CO} , CH₂Cl₂): 2041 m, 2012 vs, 1982 m, 1949 s cm⁻¹. ¹H NMR (CDCl₃): δ 7.59–7.12 (m, 29H), 3.79 (m, 1H), 3.29 (m, 1H), -17.30 (br s, 2H). ³¹P{¹H} NMR (CDCl₃): δ 22.0 (br s, 2P), -5.3 (br s, 1P). MS (FAB): *m/z* 1171.

2.5. X-ray structure determination of compounds 2 and 8

Single crystals of **2** and **8** suitable for diffraction analysis were grown by slow diffusion of hexane into a dichloromethane solution at 4 °C. All geometric and crystallographic data for **2** and **8** were collected at 150 °C on a Bruker SMART APEX CCD diffractometer using Mo K α radiation (λ = 0.71073). Data reduction and integration was carried out with SAINT + and absorption corrections were applied using the program sADABS [51]. Structures were solved by direct methods and developed using alternating cycles of leastsquares refinement and difference-Fourier synthesis. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions and their thermal parameters linked to those of the atoms to which they were attached (ridging model). The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [52]. Final difference maps did not show any residual electron density of stereochemical significance. The details of the data collection and structure refinement are given in Table 1.

3. Results and discussion

3.1. Reaction of $[Ru_3(CO)_9(\mu-dppm){P(C_4H_3S)_3}]$ (1) with chalcogenides

Heating a benzene solution of $[Ru_3(CO)_9(\mu-dppm){P(C_4H_3S)_3}]$ (1) with molecular oxygen resulted in the isolation of $[Ru_3(CO)_6{P(C_4H_3S)_3}(\mu_3-CO)(\mu-dppm)(\mu_3-O)]$ (2) in 38% yield after work-up. A similar reaction of 1 with elemental sulfur at 40 °C afforded two new compounds; $[Ru_3(CO)_6(\mu_3-CO){P(C_4H_3S)_3}]$ $(\mu$ -dppm)(μ_3 -S)] (**3**) (41%) and $[Ru_3(CO)_6\{P(C_4H_3S)_3\}(\mu$ -dppm) $(\mu_3$ -S)_2] (**4**) (27%), while the selenium homologues $[Ru_3(CO)_6$ $(\mu_3$ -CO){ $P(C_4H_3S)_3$ }(μ -dppm)(μ_3 -Se)] (**5**) $[Ru_3(CO)_6\{P(C_4H_3S)_3\}(\mu$ -dppm)(μ_3 -Se)_2] (**6**) were obtained in 26% and 31% yields respectively from the reaction of **1** with elemental selenium at 66 °C (Scheme 1). All new compounds have been characterized by elemental analysis, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data. In addition, the solid-state structure of **2** has been determined by single crystal X-ray diffraction study.

The molecular structure of **2** is depicted in Fig. 1 and selected bond distances and angles are listed in the caption. The structure consists of a triangular ruthenium framework symmetrically capped with a triply bridging oxo-ligand on one face [Ru–O(8) 2.051(3)–2.057(3) Å] and a triply bridging carbonyl ligand on the opposite face [Ru-C(7) 2.148(4)-2.173(5) Å], a bridging dppm, a terminally coordinated tri(2-thienvl)phosphine ligand and six terminal carbonyl groups. Cluster **2** is structurally similar to that of compound $[Ru_3(CO)_5(\mu_3-CO)(\mu-dpam)_2(\mu_3-O)]$ the related {dpam = bis(diphenylarsino)methane} which was obtained from the reaction of $[Ru_3(CO)_8(\mu-dpam)_2]$ with molecular oxygen [48]. Ruthenium-ruthenium distances [Ru-Ru 2.7069(5)-2.7462(5)Å] are significantly shorter than those in 1 [Ru-Ru 2.8523(3)-2.8938(3)Å], but comparable to those in $[Ru_3(CO)_5(\mu_3-CO)]$ $(\mu-dpam)_2(\mu_3-O)$ [Ru-Ru 2.670(2)–2.750(2)Å] [48], consistent with some level of oxidation of the ruthenium atoms. The dppm ligand occupies equatorial sites and Ru-P bond distances involving the bridging dppm in 2 [Ru-P 2.337(1) and 2.345(1) Å] are comparable to those in [Ru₃(CO)₁₀(µ-dppm)] [2.322(2) and 2.334(2)Å] [53]. The terminally coordinated tri(2-thienyl)phosphine ligand is equatorially bonded to Ru(3). The Ru-P bond distance involving the terminal monophosphine ligand [Ru(3)-P(3) 2.327(1)Å] is comparable to those found in $[Ru_3(CO)_6(\mu_3-CO)(PPh_3)(\mu-dppm)]$ (μ_3-S)] [2.353(13)Å] [11]. Considering oxygen as a four-electron donor, cluster 2 contains 48 cve, as expected for an electron precise trinuclear cluster containing three metal-metal bonds [54]. There are few reported examples of triruthenium carbonyl clusters containing triply bridging oxo ligand [46,48,49].



Scheme 1.



Fig. 1. Molecular structure of $[Ru_3(CO)_6(\mu_3-CO)\{P(C_4H_3S)_3\}(\mu-dppm)(\mu_3-O)]$ (2) with thermal ellipsoids drawn at the 50% probability level. Ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7365(5), Ru(1)–Ru(3) 2.7462(5), Ru(2)–Ru(3) 2.7069(5), Ru(1)–P(1) 2.3368(12), Ru(2)–P(2) 2.3445(12), Ru(3)–P(3) 2.3266(12), Ru(1)–O(8) 2.051(3), Ru(2)–O(8) 2.057(3), Ru(3)–O(8) 2.054(3), Ru(1)–C(7) 2.148(4), Ru(2)–C(7) 2.156(5), Ru(3)–C(7) 2.173(5), Ru(2)–Ru(1)–Ru(3) 59.17(1), Ru(3)–Ru(2)–Ru(1) 60.59(1), Ru(2)–Ru (3)–Ru(1)–O(8)–Ru(2) 83.6(1), Ru(1)–O(8)–Ru(3) 84.0(1), Ru (3)–O(8)–Ru(2) 82.4(1), Ru(1)–C(7)–Ru(2) 79.0(2), Ru(1)–C(7)–Ru(3) 78.9(2), Ru(2)–C(7)–Ru(3) 77.4(2), P(3)–Ru(3)–Ru(1) 98.97(3).

Spectroscopic data are in accord with the solid-state structure. The FAB mass spectrum shows a molecular ion peak at m/z 1179 consistent with its formulation and further ions corresponding to the successive loss of seven carbonyl ligands. The pattern of the IR is similar to that reported for $[Ru_3(CO)_6(\mu_3-CO)(PPh_3)]$ $(\mu$ -dppm) $(\mu_3$ -S)], synthesized from the reaction of **1** with Ph₃P=S [11]. In agreement with the presence of the triply bridging CO, the spectrum shows a characteristic low energy absorption band at 1670 cm⁻¹. The ³¹P{¹H}NMR spectrum shows two singlets at δ 4.6 and 29.5 in a 1:2 ratio. The broad singlet at δ 4.6 is assigned to the phosphorus atom of the tri(2-thienyl)phosphine ligand, while the singlet at δ 29.5 is attributed to the ³¹P nuclei of the bridging dppm ligand which are equivalent in solution due to the rapid movement of the tri(2-thienyl)phosphine between two equatorial positions at Ru(3) within the NMR timescale. IR spectra of **3** and 5 are very similar to that of structurally characterized [Ru₃ $(CO)_6(\mu_3-CO)(PPh_3)(\mu-dppm)(\mu_3-S)$ [11] and **2**. The ³¹P{¹H} NMR spectra of both displays two singlets in 1:2 ratio similar to that of [Ru₃(CO)₆(µ₃-CO)(PPh₃)(µ-dppm)(µ₃-S)] [11]. Their mass spectra exhibit parent molecular ions at m/z 1195 (for **3**) and m/z1243 (for 5) and further ions due to successive loss of seven carbonyl groups which are consistent with our proposed formulation. We performed an X-ray crystallographic analysis for 5 and partially determined its molecular structure (Supporting material) [55]. There are some serious absorption problems and disorder associated with the structure which precludes discussion of the structural details. However, the structure gives sufficient information about the geometry of the cluster and the orientation of the ligands on the cluster surface which shows that it is grossly similar to **2**.

Formation of **4** and **6** presumably occurs *via* secondary addition of chalcogens to **3** and **5** respectively, although we have not shown this in independent experiments. They were characterized by comparing their spectroscopic data with those of their PPh₃ analogues $[Ru_3(CO)_6(PPh_3)(\mu$ -dppm)(μ_3 -S)₂] and $[Ru_3(CO)_6(PPh_3)(\mu$ dppm)(μ_3 -Se)₂] which were structurally characterized by our group [11]. The carbonyl region of their IR spectra is very similar to those of their corresponding triphenylphosphine analogues which suggest they are isostructural. The ${}^{31}P{}^{1}H{}$ NMR spectra of both show two resonances in 1:2 ratio, while the mass spectrum shows parent molecular ions [*m*/*z* 1201 for **4** and *m*/*z* 1295 for **6**] together with ions due to stepwise loss of six carbonyl groups which are consistent with our proposed structure.

The reactivity of $[Ru_3(CO)_9(\mu-dppm){P(C_4H_3S)_3}]$ (1) towards group 16 elements differs somewhat from that of $[Ru_3(CO)_{10}$ (μ -dppm)] which does not react with dioxygen or elemental sulfur. Presumably the triruthenium centre is not electron-rich enough to undergo a formal two-electron oxidation. The decacarbonyl complex does react with elemental selenium at elevated temperatures but simple addition products akin to **5–6** are not major products; rather a mixture results which includes $[(\mu-H)_2Ru_3(CO)_7$ (μ -dppm)(μ_3 -Se)], $[Ru_3(CO)_6(\mu-CO){\mu-PhPCH_2Ph}(C_6H_4)](\mu_3-Se)]$ and $[Ru_4(CO)_8(\mu-dppm)(\mu_3-Se)_2]$ [56]. Thus the role of the tri(thienyl)phosphine appears to be to both activate the cluster towards chalcogen addition, while also serving to maintain the cluster integrity.

3.2. Reaction of $[Ru_3(CO)_9(\mu-dppm)\{P(C_4H_3S)_3\}]$ (1) with H_2S

In order to complement the reactivity of **1** towards chalcogens we have also studied its reaction with H₂S. In refluxing THF this led to the isolation of two sulfur capped triruthenium compounds; the known $[(\mu-H)_2Ru_3(CO)_7(\mu-dppm)(\mu_3-S)]$ (7) and a phosphinesubstituted analogue $[(\mu-H)_2Ru_3(CO)_6[P(C_4H_3S)_3](\mu-dppm)(\mu_3-S)]$ (8) in 28% and 31% yields, respectively (Scheme 1). The former also results from the reaction of $[Ru_3(CO)_{10}(\mu-dppm)]$ with H₂S [57]. Cluster 8 has been characterized by a combination of IR, ¹H and ³¹P{¹H} NMR, single-crystal X-ray diffraction and elemental analysis. The molecular structure is shown in Fig. 2 and selected bond distances and angles are listed in the caption. The molecule consists of a triangular ruthenium framework involving three distinct metal-metal bonds; [Ru(1)-Ru(2) 2.8597(6), Ru(1)-Ru(3) 2.9185(6) and Ru(2)-Ru(3) 2.7413(5) Å]. The sulfur atom caps one face quite symmetrically [Ru-S 2.364(1)-2.381(1)Å], bond lengths being similar to those found in 7. Hydrides were not located crystallographically but are believed to span across the Ru(1)-Ru(2) and Ru(1)-Ru(3) edges in the solid state since these two edges are significantly longer than the Ru(2)-Ru(3) edge [58]. The high-field region of the ¹H NMR spectrum is not informative as it shows a broad singlet at δ –17.30 which implies that



Fig. 2. Molecular structure of $[(\mu-H)_2Ru_3(CO)_6[P(C_4H_3S)_3](\mu-dppm)(\mu_3-S)]$ (**8**) with thermal ellipsoids drawn at the 50% probability level. Ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.8597(6), Ru(1)–Ru(3) 2.9185(6), Ru(2)–Ru(3) 2.7413(5), Ru(1)–P(1) 2.336(1), Ru(2)–P(2) 2.329(1), Ru(3)–P(3) 2.323(1), Ru(1)–S(1) 2.381(1), Ru(2)–S(1) 2.369(1), Ru(3)–S(1) 2.364(1), Ru(2)–Ru(1)–Ru(3) 56.63(1), Ru(3)–Ru(2)–Ru(1) 62.77(1), Ru(2)–Ru(3)–Ru(1) 60.60(2), Ru(3)–S(1)–Ru(2) 70.79(3), Ru(3)–S(1)–Ru(1) 75.91(3), Ru(2)–S(1)–Ru(1) 74.04(3), P(3)–Ru(1) 104.21(3).

hydride ligands are fluxional in solution. A similar situation was encountered for **7**, VT-¹H NMR spectra revealing the rapid exchange of the hydrides between the non-diphosphine bridged ruthenium-ruthenium edges on the NMR timescale [57]. The Ru-P bond distances involving the terminal phosphine [Ru(3)–P(3) 2.323(1) Å] and the bridging dppm [Ru(1)–P(1) 2.336(1) and Ru(2)–P(2) 2.329(1) Å] are very similar to those found in **1**. Compound **8** is structurally similar to that of **7** except in place of one carbonyl there is a terminal tri(2-thienyl)phosphine ligand on remote ruthenium atom, Ru(3). The FAB mass spectrum of compound **8** exhibit a parent molecular ion at m/z 1171 and other ions due to stepwise loss of six carbonyl groups which are also consistent with the solid state structure.

4. Conclusions

Introduction of the tri(thienyl)phosphine ligand onto [Ru₃ $(CO)_{10}(\mu$ -dppm)] leads to an increase in electron-density at the triruthenium centre thus facilitating reactions with group 16 elements in order to form chalogenide-capped clusters, [Ru₃ $(CO)_{6}(\mu_{3}-CO)\{P(C_{4}H_{3}S)_{3}\}(\mu-dppm)(\mu_{3}-E)\}$ (E = O, S, Se). Given the known propensity of both of the phosphine ligands in [Ru₃ $(CO)_9[P(C_4H_3S)_3](\mu$ -dppm)] (1) to undergo secondary transformations resulting from both carbon-hydrogen and carbonphosphorus bond activation it is slightly surprising that no such rearrangements were observed during these studies. This suggests that chalcogen reduction is relatively rapid and once the capping chalcogenide is in place then no further rearrangements occur. This may be due to the removal of electron density from the cluster core, which in turn deactivates the system towards further oxidative-addition, or as a result of the removal of required vacant coordination sites with the introduction of capping ligands. It is not yet clear whether it is the introduction of the tri(thienyl)phosphine which specifically leads to such behavior or whether related phosphine-substituted complexes [Ru₃ $(CO)_9(PR_3)(\mu$ -dppm)] behave in a similar fashion. Studies to determine this are on-going, especially with respect to the relatively facile addition of molecular oxygen, which remains an unusual transformation in low-valent cluster chemistry [39-48,59].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No 795599 for compound **2** and 795600 for compound **8**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or URL: http:// www.ccdc.ac.uk)

Acknowledgement

We are grateful to the Ministry of Science and Information & Communication Technology, Government of the People's Republic of Bangladesh for financial support.

References

- D. Fenske, J.F. Corrigan, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, vol. 3, VCH, Weinheim, 1999, p. 1302.
- [2] S. Ulvenlund, A. Bengtsson-Kloo, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, vol. 1, VCH, Weinheim, 1999, p. 561.
- [3] M.L. Steigerwald, T. Siegrist, E.M. Gyorgy, B. Hessen, Y.-U. Kwon, S.M. Tanzler, Inorg. Chem. 33 (1994) 3389.
- [4] G. Longoni, M.C. Japalucci, Clusters and Colloids, VCH, Weinheim, 1994. p. 132.
 [5] K.H. Whitmire, J. Coord. Chem. 17 (1988) 95.
- [6] T. Shibihara, Coord. Chem. Rev. 123 (1993) 73.
- [7] S.W.A. Fong, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (1999) 639.

- [8] M. Shieh, M.-H. Hsu, J. Cluster Sci. 15 (2004) 91.
- [9] T. Akter, N. Begum, D.T. Haworth, D.W. Bennett, S.E. Kabir, M.A. Miah, N.C. Sarker, T.A. Siddiquee, E. Rosenberg, J. Organomet. Chem. 689 (2004) 2571.
- [10] S.E. Kabir, S.J. Ahmed, M.I. Hyder, M.A. Miah, D.W. Bennett, D.T. Haworth, T.A. Siddiquee, E. Rosenberg, J. Organomet. Chem. 689 (2004) 3412.
- M.I. Hyder, G.M.G. Hossain, S.E. Kabir, M.A. Miah, Polyhedron 24 (2005) 872.
 H. Akter, A.J. Deeming, G.M.G. Hossain, S.E. Kabir, D.N. Mondol, E. Nordlander, A. Sharmin, D.A. Tocher, J. Organomet. Chem. 690 (2005) 4628.
- [13] N. Begum, M.I. Hyder, M.R. Hassan, S.E. Kabir, D.W. Bennett, D.T. Haworth, T.A. Siddiquee, D. Rokhsana, A. Sharmin, E. Rosenberg, Organometallics 27 (2008) 1550.
- [14] M.L. Steigerwald, Polyhedron 13 (1994) 1245.
- [15] R.D. Adams, M. Tasi, J. Cluster Sci. 1 (1990) 249.
- [16] R.D. Adams, Polyhedron 4 (1985) 2003.
- [17] R.D. Adams, I.T. Horvath, L.W. Yang, J. Am. Chem. Soc. 105 (1983) 1533.
- [18] R.D. Adams, I.T. Horvath, P. Mathur, B.E. Segmuller, Organometallics 2 (1983) 1078.
- [19] R.D. Adams, Z. Dawoodi, D.F. Foust, Organometallics 1 (1982) 411.
- [20] D. Cauzzi, C. Graiff, G. Predieri, A. Tiripicchio, P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, vol. 3, VCH, Weinheim, 1999, p. 193.
- [21] P. Baistrocchi, D. Cauzzi, M. Lanfranchi, G. Predieri, A. Tiripicchio, M.T. Camellini, Inorg. Chim. Acta 235 (1995) 173.
- [22] P. Baistrocchi, M. Careri, D. Cauzzi, C. Graiff, M. Lanfranchi, P. Manini, G. Predieri, A. Tiripicchio, Inorg. Chim. Acta 252 (1996) 367.
- [23] G. Hogarth, N.J. Taylor, A.J. Carty, A. Meyer, J. Chem. Soc., Chem. Commun. (1988) 834.
- [24] D. Cauzzi, C. Graiff, C. Massera, G. Predieri, A. Tiripicchio, Inorg. Chim. Acta 300-302 (2000) 259.
- [25] R.D. Adams, O.-S. Kwon, S. Sanyl, J. Organomet. Chem. 681 (2003) 258.
- [26] P. Braunstein, C. Graiff, C. Massera, G. Predieri, J. Rose, Inorg. Chem. 41 (2002) 1372.
- [27] D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri, A. Tiripicchio, J. Organomet. Chem. 536–537 (1995) 497.
- [28] D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri, A. Tiripicchio, J. Chem. Soc., Dalton Trans. (1995) 2321.
- [29] D. Cauzzi, C. Graiff, M. Lanfranchi, G. Mori, G. Predieri, A. Tiripicchio, J. Chem. Soc., Dalton Trans. (1998) 321.
- [30] S.E. Kabir, S. Pervin, N.C. Sarker, A. Yesmin, A. Sharmin, T.A. Siddiquee, D.T. Haworth, D.W. Bennett, K.M.A. Malik, J. Organomet. Chem. 681 (2003) 237.
- [31] J. Zhang, W.K. Leong, J. Chem. Soc., Dalton Trans. (2000) 1249.
- [32] P.V. Broadhurst, B.F.G. Johnson, J. Lewis, J. Chem. Soc., Dalton Trans. (1982) 1881.
- [33] A.J. Arce, P. Arrojo, Y.D. Sanctis, A.J. Deeming, D.J. West, Polyhedron 11 (1992) 1013.
- [34] A.J. Arce, P. Arrojo, Y.D. Sanctis, A.J. Deeming, J. Chem. Soc., Chem. Commun. (1991) 1491.
- [35] S.E. Kabir, N. Begum, M.M. Hassan, M.I. Hyder, H. Nur, D.W. Bennett, T.A. Siddiquee, D.T. Haworth, E. Rosenberg, J. Organomet. Chem. 689 (2004) 1569.
- [36] S.E. Kabir, M.S. Saha, D.A. Tocher, G.M.G. Hossain, E. Rosenberg, J. Organomet. Chem. 691 (2006) 97.
- [37] C.A. Hunter, Chem. Soc. Rev. (1994) 101.
- [38] B.F.G. Johnson, J. Lewis, P.G. Lodge, P.R. Raithby, K. Henrick, M. McPartlin, J. Chem. Soc., Chem. Commun. (1979) 719.
- [39] J.T. Park, J.R. Shapley, C. Bueno, J.W. Ziller, M.R. Churchill, Organometallics 7 (1988) 2307.
- [40] L. Xu, K.H. Whitmire, Organometallics 21 (2002) 2581.
- [41] J.-H. Gong, D.-K. Hwang, C.-W. Tsay, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 13 (1994) 1720.
- [42] M.R. Churchill, C. Bueno, J.T. Park, J.R. Shapley, Inorg. Chem. 23 (1984) 1017.
- [43] Y. Chi, L. Hwang, G.-H. Lee, S.-M. Peng, J. Chem. Soc., Chem. Commun. (1988) 1456.
- [44] Y. Chi, J.R. Shapley, J. Ziller, M.R. Churchill, Organometallics 6 (1987) 301.
- [45] R.J. Goudsmit, B.F.G. Johnson, J. Lewis, P.R. Raithby, K.H. Whitmire, J. Chem. Soc., Chem. Commun. (1983) 246.
- [46] G. Lavigne, N. Lugan, J.-J. Bonnet, Nouv. J. Chim. 5 (1981) 423.
- [47] S. Ghosh, G. Hogarth, S.E. Kabir, M.A. Miah, L. Salassa, S. Sultana, C. Garino, Organometallics 28 (2009) 7047.
- [48] A. Colombie, J.J. Bonnet, P. Fompeyrine, G. Lavigne, S. Sunshine, Organometallics 5 (1986) 1154.
- [49] S.E. Kabir, G. Hogarth, Coord. Chem. Rev. 253 (2009) 1285.
- [50] M.N. Uddin, N. Begum, M.R. Hassan, G. Hogarth, S.E. Kabir, M.A. Miah, E. Nordlander, D.A. Tocher, J. Chem. Soc., Dalton Trans. (2008) 6219.
- [51] SMART and SAINT Software for CCD diffractometers, version 6.1, Madison, WI (2000).
- [52] G.M. Sheldrick, SHELXTL PLUS, version 6.10, Bruker AXS, Madison, W1 (2000).
- [53] M.I. Bruce, B.K. Nicholson, M.L. Williams, Inorg. Synth. 26 (1990) 265.
- [54] D.M.P. Mingos, Acc. Chem. Res. 17 (1984) 311.
- [55] Crystallographic data of **5**: space group $P\bar{1}$, with a = 12.952(4) Å, b = 19.365(6) Å, c = 21.712(6) Å, $\alpha = 74.708(6)^\circ$, $\beta = 89.961(6)^\circ$, $\gamma = 70.581(6)^\circ$.
- [56] S.J. Ahmed, M.I. Hyder, S.E. Kabir, M.A. Miah, A.J. Deeming, E. Nordlander, J. Organomet. Chem. 691 (2006) 309.
- [57] M.I. Hyder, N. Begum, M.D.H. Sikder, G.M.G. Hossain, G. Hogarth, S.E. Kabir, C.J. Richard, J. Organomet. Chem. 694 (2009) 304.
- [58] R.G. Teller, R. Bau, Struct. Bonding 41 (1981) 1.
- [59] G. Hogarth, S.E. Kabir, E. Nordlander, Dalton Trans. 39 (2010) 6153.