Note

Synthesis and structure of sulfur and selenium capped dihydride triruthenium clusters [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-E)] (E = S, Se)

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ABSTRACT

Reaction of [Ru$_3$(CO)$_{10}$(μ-dppm)] (1) with H$_2$S at 66 °C affords high yields of the sulfur-capped dihydride [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-S)] (2), formed by oxidative-addition of both hydrogen–sulfur bonds. Hydrogenation of [Ru$_3$(CO)$_7$(μ-dppm)(μ$_3$-CO)(μ$_3$-S)] (3) at 110 °C also gives 2 in similar yields, while hydrogenation of [Ru$_3$(CO)$_7$(μ-dppm)(μ$_3$-CO)(μ$_3$-Se)] (4) affords [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-Se)] (5) in 85% yield. The molecular structures of 2 and 5 reveal that the diphosphine and one hydride simultaneously bridge the same ruthenium–ruthenium edge with the second hydride spanning one of the non-bridged edges. Both 2 and 5 are fluxional at room temperature being attributed to hydride migration between the non-bridged edges. Addition of HBF$_4$ to 2 affords the cationic trihydride [Ru$_3$(CO)$_7$(μ-H)$_3$(μ-dppm)(μ$_3$-S)][BF$_4$] (6) in which the hydrides are non-fluxional due to the blocking of the free ruthenium–ruthenium edge.

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1. Introduction

Transition-metal carbonyl clusters containing triply-bridging chalcogenide ligands are of interest since they can often be used to facilitate the synthesis of higher nuclearity clusters [1–4]. In recent work we have been examining the reactivity of [M$_3$(CO)$_{10}$(μ-dppm)] (M = Os, Ru), [Ru$_3$(CO)$_{12}$] and [Os$_3$(CO)$_{10}$(μ$_3$-CO)(μ$_3$-S)(μ-dppm)] with a variety of chalcogen-containing ligands in an effort to develop methods for the systematic synthesis of trimetallic clusters containing capping chalcogenide ligands for use in cluster growth reactions [3–9]. In an earlier paper we reported the synthesis of [Os$_3$(CO)$_7$(μ-dppm)(μ$_3$-S)$_2$] from the reaction of [Os$_3$(CO)$_{10}$(μ-dppm)] with tetramethylthiourea [8], which we later successfully converted into hexanuclear [Os$_6$(CO)$_{12}$(μ-dppm)$_2$(μ$_3$-S)$_2$] via a Me$_3$NO-initiated thermal decarbonylation [3]. In related work, Predieri et al. have reported the preparation of the corresponding hexaruthenium cluster, [Ru$_6$(CO)$_{12}$(μ-dppm)$_2$(μ$_3$-Se)$_2$], from a similar self-condensation reaction [10].
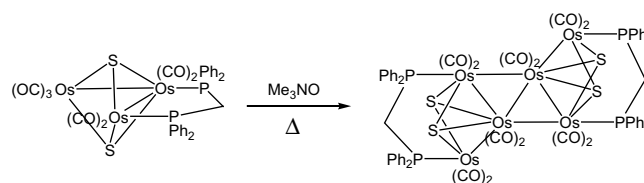
In developing our work we sought high yielding routes to the diphosphine-substituted trinuclear clusters [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-E)] (E = S, Se) since the presence of the small bite-angle dppm ligand has been shown to both activate [M$_3$(CO)$_{10}$(μ-dppm)] towards CO loss while also serving to maintain the integrity of the trinuclear unit [11]. Herein we describe the successful synthesis of both of these target molecules from reactions of the dppm-substituted triruthenium clusters [Ru$_3$(CO)$_{10}$(μ-dppm)] and [Ru$_3$(CO)$_7$(μ-dppm)(μ$_3$-CO)(μ$_3$-E)] with the catalytically important H$_2$S and H$_2$, respectively.

2. Experimental

All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried using standard procedures and were freshly distilled prior to use. Infrared spectra were recorded

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on a Shimadzu FTIR 8101 spectrometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX 400 instrument. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and to external 85% H_3PO_4 for ^{31}P chemical shifts. Elemental analyses were performed by the Microanalytical Laboratories, University College London. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. The clusters [Ru$_3$(CO)$_{10}$(μ-dppm)] [12], [Ru$_3$(CO)$_7$(μ_3-CO)(μ_3-S)(μ-dppm)] [7] and [Ru$_3$(CO)$_7$(μ_3-CO)(μ_3-Se)(μ-dppm)] [7] were prepared according to published procedures.

2.1. Reaction of [Ru$_3$(CO)$_{10}$(μ-dppm)] (1) with H$_2$S

Hydrogen sulfide was bubbled through a boiling THF solution (50 mL) of **1** (125 mg, 0.129 mmol) for 1 h. The solvent was removed under reduced pressure and the residue chromatographed over a column of silica gel. Elution with hexane/CH$_2$Cl$_2$ (2:1, v/v) gave a single orange band which on removal of solvent afforded [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ_3-S)] (**2**) (0.092 g, 80%) as orange crystals from hexane/CH$_2$Cl$_2$ at 20 °C. Anal. Calc. for C$_{32}$H$_{24}$O$_7$P$_2$Ru$_3$S: C, 41.88; H, 2.64. Found: C, 41.98; H, 2.78%. IR υ(CO) (CH$_2$Cl$_2$): 2062 vs, 2041 vs, 2000 vs, 1993 s, 1943 w, 1869 w cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 7.54–7.02 (m, 20 H), 3.87 (m, 1H), 3.31 (m, 1H), −17.93 (brs, 2H). ^{1}H NMR (CD$_2$Cl$_2$, 213 K): δ 7.59–7.04 (m, 20 H), 3.92 (m, 1H), 3.32 (m, 1H), −17.88 (t, J 6.0, 1H), −18.06 (d, J 28.0, 1H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ 21.8 (s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 213K): δ 22.3 (d, J 56.7), 20.6 (d, J 56.7). Mass spectrum: m/z 919.

2.2. Hydrogenation of [Ru$_3$(CO)$_7$(μ_3-CO)(μ_3-S)(μ-dppm)] (3)

Hydrogen was bubbled through a boiling toluene solution (20 mL) of [Ru$_3$(CO)$_7$(μ_3-CO)(μ_3-S)(μ-dppm)] (**3**) (85 mg, 0.090 mmol) for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH$_2$Cl$_2$ (7:3, v/v) gave an orange band, which afforded **2** (65 mg, 78%).

2.3. Hydrogenation of [Ru$_3$(CO)$_7$(μ-dppm)(μ_3-CO)(μ_3-Se)] (4)

A similar hydrogenation of **4** (75 mg, 0.076 mmol) for 1 h followed by chromatographic work-up afforded [Ru$_3$(CO)$_7$-(μ-H)$_2$(μ-dppm)(μ_3-Se)] (**5**) (62 mg, 85%) as orange crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. Anal. Calc. for C$_{32}$H$_{24}$O$_7$P$_2$Ru$_3$Se: C, 39.84; H, 2.51. Found: C, 40.05; H, 2.71%. IR υ(CO) (CH$_2$Cl$_2$): 2062 vs, 2041 vs, 2000 vs, 1993 s, 1943 w, 1869 w cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 293K): δ 7.50–7.18 (m, 20 H), 3.92 (m, 1H), 3.27 (m, 1H), −17.88 (s, 2H). ^{31}P{^{1}H} NMR(CD$_2$Cl$_2$, 213 K): δ 24.2 (s). Mass spectrum: m/z 965.

2.4. Protonation of 2

Addition of a drop of HBF$_4$ · Et$_2$O to an orange CD$_2$Cl$_2$ solution of **2** led to its rapid decolourisation and clean formation of [Ru$_3$(CO)$_7$(μ-H)$_3$(μ-dppm)(μ_3-S)][BF$_4$] (**6**). IR υ(CO) (CH$_2$Cl$_2$): 2122 s, 2070 vs, 2021 m cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.69–7.20 (m, 20 H), 4.14 (m, 1H), 3.68 (m, 1H), −18.03 (m, 1H), −18.15 (m, 2H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 213 K): δ 29.2 (s).

2.5. X-ray structure determinations

Crystals of **2** and **5** suitable for X-ray analyses were mounted on fibres and diffraction data collected at low temperature on a Nonious Kappa CCD (Bruker AXS) and SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collection, indexing

Table 1
Crystal data and structure refinement parameters for **2** and **5**.

	2	5
Empirical formula	C$_{32}$H$_{24}$O$_7$P$_2$Ru$_3$S	C$_{32}$H$_{24}$O$_7$P$_2$Ru$_3$Se
Formula weight	917.72	964.62
Temperature (K)	150(2)	293(2)
Wave length (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P$\bar{1}$	P$\bar{1}$
a (Å)	10.5188(3)	10.2649(6)
b (Å)	11.2719(3)	12.4663(7)
c (Å)	16.5144(5)	14.0895(8)
α (°)	94.344(1)	95.781(1)
β (°)	104.757(2)	90.329(1)
γ (°)	112.509(1)	111.099(1)
V (Å^3)	1716.01(8)	1671.8(2)
Z	2	2
$d_{calcd.}$ (g cm^{-3})	1.776	1.916
Absorption coefficient (cm^{-1})	15.01	25.67
$F(000)$	900	936
Crystal size (mm)	0.25 × 0.15 × 0.15	0.47 × 0.15 × 0.12
θ range for data collection (°)	2.95–26.04	1.76–28.29
Limiting indices	−12 ⩽ h ⩽ 12	−13 ⩽ h ⩽ 13
	−13 ⩽ k ⩽ 13	−15 ⩽ k ⩽ 16
	−19 ⩽ l ⩽ 20	−18 ⩽ l ⩽ 18
Reflections collected	26723	14875
Independent reflections [$R_{(int)}$]	6677 (0.0700)	7713 (0.0158)
Data/restraints/parameters	6677/12/436	7713/0/492
Goodness-of-fit (GOF) on F^2	1.027	1.016
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.042,	R_1 = 0.035,
	wR_2 = 0.098	wR_2 = 0.089
R indices (all data)	R_1 = 0.055,	R_1 = 0.040,
	wR_2 = 0.103	wR_2 = 0.092
Largest difference peak/hole (e Å^{-3})	1.994/−1.154	1.754 /−1.78

and initial cell refinements were all done using SMART [13] software. Data reduction was accomplished with SAINT [14] software and the SADABS program [15] was used to apply empirical absorption corrections. The structures were solved by direct methods [16] and refined by full matrix least-squares [17]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. The phenyl rings of the dppm ligand of compound **2** were disordered with the occupancy of 50:50, the carbon–carbon distance was restrained to 1.39 Å and the 1,3-related distance to 2.408 Å for the pair of unprimed (C(8) to C(13)) and primed (C(8′) to C(13′)) atoms. Additional details of data collection and structure refinement are given in Table 1.

3. Results and discussion

No reaction was observed between [Ru$_3$(CO)$_{10}$(μ-dppm)] (**1**) and H$_2$S at room temperature, however, in boiling thf the sulfur-capped dihydride [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ_3-S)] (**2**) was isolated in 80% yield after chromatographic separation. The latter was also obtained in similar yields from the reaction of [Ru$_3$(CO)$_7$(μ-dppm)(μ_3-CO)(μ_3-S)] (**3**) with H$_2$ (1 atm) in toluene at 110 °C. The high temperatures required for this second transformation are not surprising since the addition of dihydrogen to a saturated 48-electron cluster is expected to have a high activation energy. Since H$_2$Se is not readily available due to its toxicity, we utilized the hydrogenation of [Ru$_3$(CO)$_7$(μ-dppm)(μ_3-CO)(μ_3-Se)] (**4**) to give [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ_3-Se)] (**5**) in 85% yield (Scheme 1). Both **2** and **5** were readily characterised on the basis of analytical and spectroscopic data, while single crystal X-ray diffraction studies were also carried out on both the results of which are summarized in Figs. 1 and 2 and Table 1.

The two structures are very similar and hence the discussion will focus on that of **2**. The molecule consists of a triangle of ruthenium atoms characterized by three similar but distinct ruthenium-
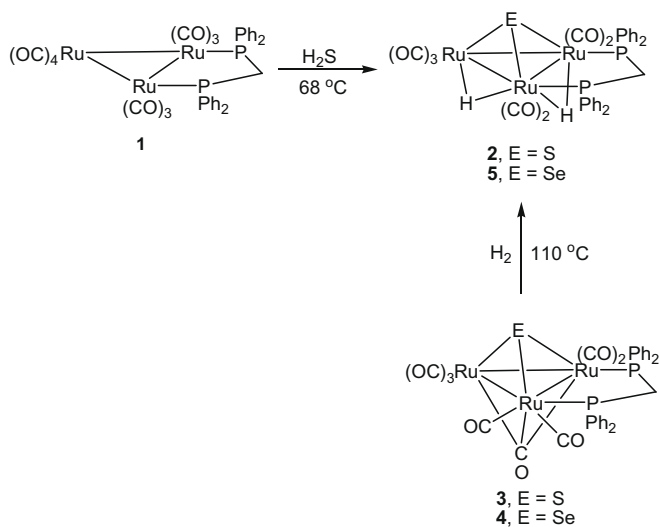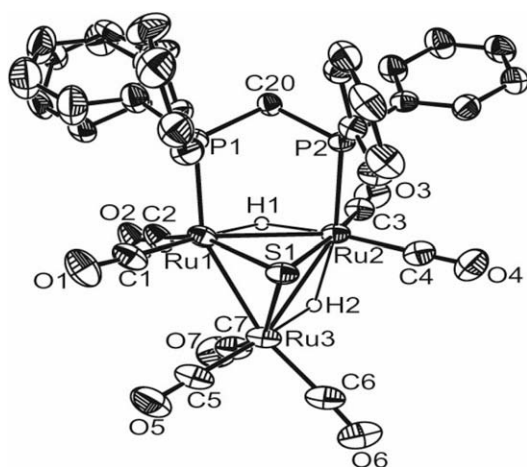
Scheme 1.

Fig. 1. Molecular structure of [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-S)] (**2**) showing 50% probability thermal ellipsoids. Hydrogen atoms of the phenyl rings are omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.8723(6), Ru(1)–Ru(3) 2.7395(6), Ru(2)–Ru(3) 2.9030(5), Ru(1)–S(1) 2.365(1), Ru(3)–S(1) 2.358(1), Ru(2)–S(1) 2.367(1), Ru(1)–P(1) 2.322(1), Ru(2)–P(2) 2.328(1), Ru(1)–Ru(2)–Ru(3) 56.630(14), Ru(3)–Ru(1)–Ru(2) 62.25(2), Ru(1)–Ru(3)–Ru(2) 61.12(1), Ru(3)–S(1)–Ru(2) 75.83(4), Ru(3)–S(1)–Ru(1) 70.92(4), Ru(1)–S(1)–Ru(2) 74.75(4), S(1)–Ru(3)–Ru(1) 54.66(3), S(1)–Ru(2)–Ru(1) 52.59(3), S(1)–Ru(1)–Ru(2) 52.66(3), S(1)–Ru(1)–Ru(3) 54.42(3), S(1)–Ru(3)–Ru(2) 52.23(3), S(1)–Ru(2)–Ru(3) 51.94(3), P(2)–C(20)–P(1) 113.5(2).

ruthenium bond lengths: Ru(1)–Ru(3) 2.7395(6), Ru(1)–Ru(2) 2.8723(6), Ru(2)–Ru(3) 2.9030(5) Å. The diphosphine bridges the Ru(3)–Ru(2) edge with the phosphorus atoms occupying approximately equatorial positions and the ruthenium-phosphorus distances [Ru(1)–P(1) 2.322(1), Ru(2)–P(2) 2.328(1) Å] being comparable to those in [Ru$_3$(CO)$_{10}$(μ-dppm)] [2.322(2) and 2.334(2) Å] [18]. Both hydrides were crystallographically located (not refined) across the Ru(1)–Ru(2) and Ru(2)–Ru(3) edges and their elongation is consistent with hydride bridging [19]. The non-hydride bridged Ru(1)–Ru(3) edge is significantly shorter than the average ruthenium–ruthenium distance in [Ru$_3$(CO)$_{12}$] [2.854(7) Å] [20] and the unsupported ruthenium-ruthenium bonds in **1** [2.860(1) and 2.841(1) Å] but comparable to non-hydride bridged ruthenium–ruthenium distance in [Ru$_3$(CO)$_9$(μ-

H)$_2$(μ$_3$-S)] [2.760(1) Å] [21]. The triply-bridging sulfide ligand caps the ruthenium triangle in a symmetrical manner, the ruthenium-sulfur distances [Ru(1)–S(1) 2.365(1), Ru(2)–S(1) 2.367(1), Ru(3)–S(1) 2.358(1) Å] lying in the range found for [Ru$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-S)] [21]. Selenide-capped **5** is very similar. The hydrides were again crystallographically located on the Ru(2)–Ru(3) and Ru(1)–Ru(2) edges and the non-hydride bridged Ru(1)–Ru(3) edge is significantly shorter than these. The triply-bridging selenide ligand symmetrically caps the ruthenium triangle with ruthenium–selenium distances in the narrow-range of 2.4772(5)–2.4901(5) Å. The overall structure of **2** and **5** are very similar to that of the osmium cluster, [Os$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-S)], obtained from the reaction of [Os$_3$(CO)$_9$(μ-H)$_2$(μ$_3$-S)] with dppm [22]. Both contain 48 valence electrons and therefore, each ruthenium atom formally has an 18-electron configuration.

The carbonyl region of the IR spectrum of **2** and **5** are also similar to that observed for [Os$_3$(CO)$_7$(μ-dppm)(μ$_3$-CO)(μ$_3$-S)] indicating that they are also structurally similar in solution. At room temperature, the ^{1}H NMR spectrum of **2** shows multiplets in the aromatic region and at δ 3.87 and 3.31 assigned to the dppm ligand. The hydride region of the spectrum contains a broadened singlet resonance at δ −17.94 resulting from the rapid exchange of the hydrides between the non-diphosphine bridged ruthenium-ruthenium edges on the NMR timescale (Scheme 2). The VT-^{1}H NMR spectra of **2** in the hydride region are depicted in Fig. 3. The exchange of the hydrides is also apparent in the
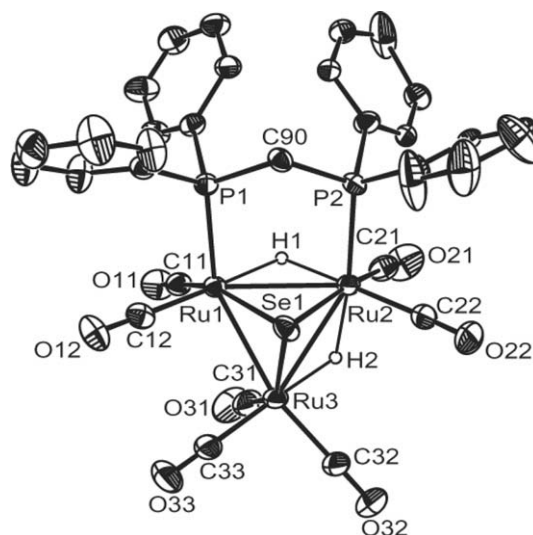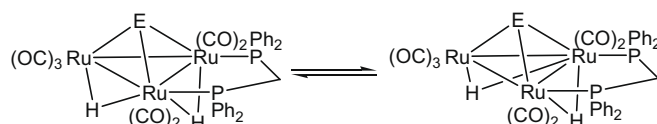

Fig. 2. Molecular structure of [Ru$_3$(CO)$_7$(μ-H)$_2$(μ-dppm)(μ$_3$-Se)] (**5**) showing 50% probability thermal ellipsoids. Hydrogen atoms of the phenyl rings are omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(3) 2.7445(4), Ru(1)–Ru(2) 2.8843(4), Ru(2)–Ru(3) 2.9111(4), Ru(1)–P(1) 2.3165(9), Ru(2)–P(2) 2.3393(9), Ru(1)–Se(1) 2.4772(5), Ru(2)–Se(1) 2.4901(5), Ru(3)–Se(1) 2.4813(5), Se(1)–Ru(1)–Ru(3) 56.46(1), Se(1)–Ru(1)–Ru(2) 54.71(1), C(11)–Ru(1)–Ru(2) 114.3(1), Ru(1)–Ru(3)–Ru(2) 61.24(1), Ru(1)–Ru(2)–Ru(3) 56.53(1), Ru(1)–Ru(3)–Ru(2) 61.24(1), C(21)–Ru(2)–Ru(3) 113.4(1), Ru(3)–Ru(1)–Ru(2) 62.23(1), Se(1)–Ru(2)–Ru(1) 54.30(1), Se(1)–Ru(3)–Ru(1) 56.32(1), Se(1)–Ru(3)–Ru(2) 54.30(1), P(1)–Ru(1)–Ru(2) 94.28(3), Se(1)–Ru(2)–Ru(3) 54.02(1), P(2)–Ru(2)–Ru(1) 91.85(3), Ru(1)–Ru(2)–Ru(3) 56.53(1), Ru(1)–Se(1)–Ru(3) 67.21(1), Ru(1)–Se(1)–Ru(2) 70.99(1), Ru(3)–Se(1)–Ru(2) 71.69(2), P(2)–C(90)–P(1) 116.8(2).
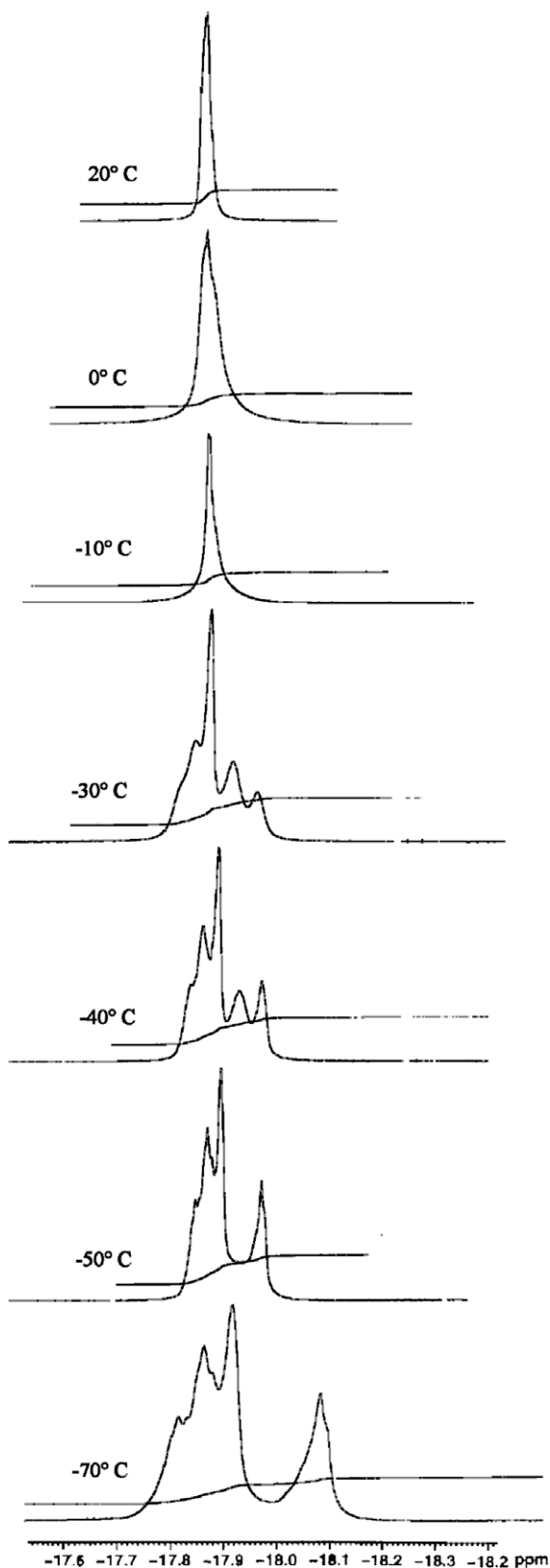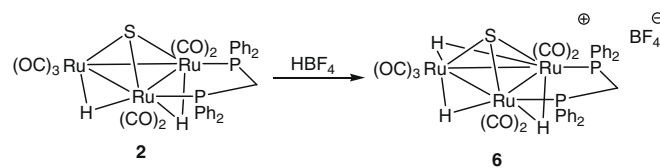

Scheme 2.

Scheme 3.

(−35 °C) the free energy of activation for hydride exchange is estimated as 46 ± 1 kJ mol^{-1}. At −70 °C the hydride region also shows two signals, a doublet at δ −18.06 (J_{PH} 28.0 Hz) and a triplet at δ −17.88 (J_{PH} 6.0 Hz). The triplet is assigned to H(2) which bridges the Ru(2)–Ru(3) edge, and the doublet to H(1) which bridges the Ru(2)–Ru(1) edge. Data for **5** were similar and will not be discussed further.

The hydride fluxionality observed for **2** and **5** is possible since one of the ruthenium-ruthenium edges is always non-bridged. This edge should be basic enough to bind a proton, which in turn should block hydride migration. Indeed, addition of $HBF_4 \cdot Et_2O$ to a CD_2Cl_2 solution of **2** resulted in the rapid and quantitative formation of the trihydride $[Ru_3(CO)_7(\mu-H)_3(\mu-dppm)(\mu_3-S)][BF_4]$ (**6**) (Scheme 3). This was easily shown by ^{31}P NMR spectroscopy, the initial singlet at 21.8 ppm being replaced by another at 29.2 ppm. Two distinct hydride signals are now observed in a 2:1 ratio, both appearing as complex multiplets. Lowering the temperature to −60 °C had little effect on these (or other) signals and we conclude that, as expected, **6** is non-fluxional.

4. Conclusions

The new clusters $[Ru_3(CO)_7(\mu-H)_2(\mu-dppm)(\mu_3-S)]$ (**2**) and $[Ru_3(CO)_7(\mu-H)_2(\mu-dppm)(\mu_3-Se)]$ (**5**) have been synthesized in high yields from the reactions of $[Ru_3(CO)_7(\mu-dppm)(\mu_3-CO)(\mu_3-S)]$ (**3**) and $[Ru_3(CO)_7(\mu-dppm)(\mu_3-CO)(\mu_3-Se)]$ (**4**) with molecular hydrogen (1 atm). Cluster **2** is also obtained from $[Ru_3(CO)_{10}(\mu-dppm)]$ (**1**) and H_2S. The coordination mode adopted by the ligands in **2** and **5** has been established by NMR spectroscopy and X-ray crystallography. The hydrogenation of **3** and **4** to give **2** and **5** is in contrast to that reported for **1** which afforded $[Ru_3(CO)_9(\mu-H)(\mu_3-PhPCH_2PPh_2)]$ by loss of a phenyl group by cleavage of a phosphorus-carbon bond [23,24]. Unfortunately, all attempts at both thermal and Me_3NO-initiated decarbonylation reactions of **2** and **5** in efforts to prepare high nuclearity clusters resulted only in non-specific decomposition.

Supplementary material

CCDC 694984 and 698813 contain the supplementary crystallographic data for **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Fig. 3. The hydride region of the VT-^{1}H NMR spectra of $[Ru_3(CO)_7(\mu-H)_2(\mu-dppm)(\mu_3-S)]$ (**2**).

$^{31}P\{^1H\}$ NMR spectrum which shows a singlet at 21.88 ppm in CD_2Cl_2. Upon cooling this signal broadens and at −60 °C appears as an AB doublet (J_{PP} 56.7 Hz). From the coalescence temperature

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