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Note

Synthesis and structure of sulfur and selenium capped dihydride triruthenium clusters $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}dppm)(\mu_3\text{-}E)]$ (E = S, Se)

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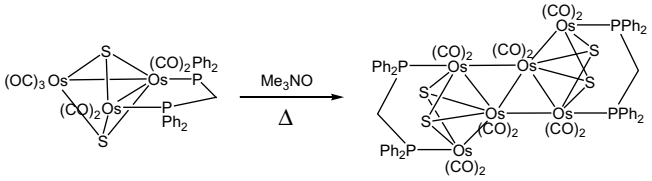
ABSTRACT

Reaction of $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ (**1**) with H_2S at 66 °C affords high yields of the sulfur-capped dihydride $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}dppm)(\mu_3\text{-}S)]$ (**2**), formed by oxidative-addition of both hydrogen–sulfur bonds. Hydrogenation of $[Ru_3(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}CO)(\mu_3\text{-}S)]$ (**3**) at 110 °C also gives **2** in similar yields, while hydrogenation of $[Ru_3(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}CO)(\mu_3\text{-}Se)]$ (**4**) affords $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}dppm)(\mu_3\text{-}Se)]$ (**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 $[Ru_3(CO)_7(\mu\text{-}H)_3(\mu\text{-}dppm)(\mu_3\text{-}S)][BF_4]$ (**6**) in which the hydrides are non-fluxional due to the blocking of the free ruthenium–ruthenium edge.

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 $[M_3(CO)_{10}(\mu\text{-}dppm)]$ (M = Os, Ru), $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)]$ 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 $[Os_3(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}S)_2]$ from the reaction of $[Os_3(CO)_{10}(\mu\text{-}dppm)]$ with tetramethylthiourea [8], which we later successfully converted into hexanuclear $[Os_6(CO)_{12}(\mu\text{-}dppm)_2(\mu_3\text{-}S)_2]$ *via* a Me_3NO-initiated thermal decarbonylation [3]. In related work, Predieri et al. have reported the preparation of the corresponding hexaruthenium cluster, $[Ru_6(CO)_{12}(\mu\text{-}dppm)_2(\mu_3\text{-}Se)_2]$, from a similar self-condensation reaction [10].



In developing our work we sought high yielding routes to the diphosphine-substituted trinuclear clusters $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}dppm)(\mu_3\text{-}E)]$ (E = S, Se) since the presence of the small bite-angle dppm ligand has been shown to both activate $[M_3(CO)_{10}(\mu\text{-}dppm)]$ 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 $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ and $[Ru_3(CO)_7(\mu\text{-}dppm)(\mu_3\text{-}CO)(\mu_3\text{-}E)]$ with the catalytically important H_2S 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 $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ [12], $[Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-S})(\mu\text{-dppm})]$ [7] and $[Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-Se})(\mu\text{-dppm})]$ [7] were prepared according to published procedures.

2.1. Reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**1**) with H_2S

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_2Cl_2 (2:1, v/v) gave a single orange band which on removal of solvent afforded $[Ru_3(CO)_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-S})]$ (**2**) (0.092 g, 80%) as orange crystals from hexane/CH_2Cl_2 at 20 °C. Anal. Calc. for $C_{32}H_{24}O_7P_2Ru_3S$: C, 41.88; H, 2.64. Found: C, 41.98; H, 2.78%. IR υ(CO) (CH_2Cl_2): 2062 vs, 2041 vs, 2000 vs, 1993 s, 1943 w, 1869 w cm^{-1}. ^{1}H NMR (CD_2Cl_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_2Cl_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_2Cl_2, 293 K): δ 21.8 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, 213K): δ 22.3 (d, J 56.7), 20.6 (d, J 56.7). Mass spectrum: *m/z* 919.

2.2. Hydrogenation of $[Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-S})(\mu\text{-dppm})]$ (**3**)

Hydrogen was bubbled through a boiling toluene solution (20 mL) of $[Ru_3(CO)_7(\mu_3\text{-CO})(\mu_3\text{-S})(\mu\text{-dppm})]$ (**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_2Cl_2 (7:3, v/v) gave an orange band, which afforded **2** (65 mg, 78%).

2.3. Hydrogenation of $[Ru_3(CO)_7(\mu\text{-dppm})(\mu_3\text{-CO})(\mu_3\text{-Se})]$ (**4**)

A similar hydrogenation of **4** (75 mg, 0.076 mmol) for 1 h followed by chromatographic work-up afforded $[Ru_3(CO)_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-Se})]$ (**5**) (62 mg, 85%) as orange crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. Anal. Calc. for $C_{32}H_{24}O_7P_2Ru_3Se$: C, 39.84; H, 2.51. Found: C, 40.05; H, 2.71%. IR υ(CO) (CH_2Cl_2): 2062 vs, 2041 vs, 2000 vs, 1993 s, 1943 w, 1869 w cm^{-1}. ^{1}H NMR (CD_2Cl_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_2Cl_2, 213 K): δ 24.2 (s). Mass spectrum: *m/z* 965.

2.4. Protonation of **2**

Addition of a drop of $HBF_4 \cdot Et_2O$ to an orange CD_2Cl_2 solution of **2** led to its rapid decolourisation and clean formation of $[Ru_3(CO)_7(\mu\text{-H})_3(\mu\text{-dppm})(\mu_3\text{-S})][BF_4]$ (**6**). IR υ(CO) (CH_2Cl_2): 2122 s, 2070 vs, 2021 m cm^{-1}. ^{1}H NMR (CD_2Cl_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_2Cl_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 Nonius Kappa CCD (Bruker AXS) and SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collection, indexing 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.

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

	2	**5**
Empirical formula	$C_{32}H_{24}O_7P_2Ru_3S$	$C_{32}H_{24}O_7P_2Ru_3Se$
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	$-12 \leqslant h \leqslant 12$ $-13 \leqslant k \leqslant 13$ $-19 \leqslant l \leqslant 20$	$-13 \leqslant h \leqslant 13$ $-15 \leqslant k \leqslant 16$ $-18 \leqslant l \leqslant 18$
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, wR_2 = 0.098	R_1 = 0.035, wR_2 = 0.089
R indices (all data)	R_1 = 0.055, wR_2 = 0.103	R_1 = 0.040, wR_2 = 0.092
Largest difference peak/hole (e Å^{-3})	1.994/−1.154	1.754 /−1.78

3. Results and discussion

No reaction was observed between $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**1**) and H_2S at room temperature, however, in boiling thf the sulfur-capped dihydride $[Ru_3(CO)_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-S})]$ (**2**) was isolated in 80% yield after chromatographic separation. The latter was also obtained in similar yields from the reaction of $[Ru_3(CO)_7(\mu\text{-dppm})(\mu_3\text{-CO})(\mu_3\text{-S})]$ (**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_2Se is not readily available due to its toxicity, we utilized the hydrogenation of $[Ru_3(CO)_7(\mu\text{-dppm})(\mu_3\text{-CO})(\mu_3\text{-Se})]$ (**4**) to give $[Ru_3(CO)_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-Se})]$ (**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-