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Cleavage of Ge–S and C–H bonds in the reaction of electron-deficient $[Os_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4)]$ with Ph_3GeSPh: Generation of thiophenol derivatives $[Os_3(CO)_8(\mu\text{-}H)(\mu\text{-}SPh)(\mu\text{-}dppm)]$ and $[Os_3(CO)_7(\mu\text{-}H)(\mu\text{-}SPh)(\mu_3\text{-}SC_6H_4)(\mu\text{-}dppm)]$

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ABSTRACT

Heating the electron-deficient $[Os_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4)]$ (**1**) and Ph_3GeSPh in benzene at 80 °C led to the thiolato bridged compounds, $[Os_3(CO)_8(\mu\text{-}H)(\mu\text{-}SPh)(\mu\text{-}dppm)]$ (**2**) and $[Os_3(CO)_7(\mu\text{-}H)(\mu\text{-}SPh)(\mu_3\text{-}SC_6H_4)(\mu\text{-}dppm)]$ (**3**), formed by cleavage of Ge–S and C–S bonds of the ligand, in 40% and 17% yields, respectively. Both compounds **2** and **3** have been characterized by a combination of elemental analysis, infrared and ^1H NMR spectroscopic data together with single crystal X-ray crystallography. Compound **3** contains an open triangle of osmium atoms bridged by a SPh and SC_6H_4 ligands on opposite sides of the cluster with a dppm ligand bridging one of the Os–Os edges. Compound **2** consists of a closed triangular cluster of osmium atoms with a bridging SPh, and a bridging hydride ligand on the same Os–Os edge, and a dppm ligand bridging one of the remaining Os–Os edges.

1. Introduction

The electron-deficient triosmium cluster $[Os_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4)]$ (**1**) derived from the decarbonylation of the decacarbonyl compound $[Os_3(CO)_{10}(\mu\text{-}dppm)]$ has attracted considerable interest for many years and its chemistry has been thoroughly investigated during the last decade to reveal its catalytic potential as well as applications in organic synthesis [1–15]. With an electron count of 46, cluster **1** is electron-deficient with respect to the noble gas rule which requires 48 electrons for a closed trinuclear cluster; for this reason it is susceptible to nucleophilic attack and reacts with a wide range of electron donor ligands under mild conditions relative to electron precise complexes.

The reactions of **1** with a wide variety of small inorganic and organic ligands such as CO [4], H_2 [5], PR_3 [6], $P(OR)_3$ (R = Me, Et, Pr^i, Bu, Ph) [6], PPh_2H [7], $RC{\equiv}CR$ (R = Ph, C_6H_4Me, Me, CF_3) [8], $[Au(PPh_3)]PF_6$ [9], EtSH [10], $CH_3CH(CH_3)SH$ [10], PhSH [10], pySH [11], $HSCH_2CH_2SH$ [12], $HSCH_2CH_2CH_2SH$ [12], Se [13], HX (X = Cl, Br, F, CF_3CO_2, CH_3CO_2) [14], CH_2N_2 [15], silane [16] and Ph_3SnH [17] that afford many interesting and potentially useful compounds have been investigated (Scheme 1). We have recently reported some unusual bimetallic Ru–Sn, Ru–Ge clusters, e.g. $[Ru_3(CO)_8(\mu\text{-}SPh)_2(\mu_3\text{-}SnPh_2)(SnPh_3)_2]$ and $[Ru_3(CO)_8(\mu\text{-}SPh)_2(\mu_3\text{-}GePh_2)(GePh_3)_2]$, from the reactions of Ph_3SnSPh or Ph_3GeSPh with $[Ru_3(CO)_{12}]$, respectively [18]. We also reported the Os-Sn compound $[Os_3(CO)_9(\mu\text{-}SPh)(\mu_3\text{-}SnPh_2)(NCMe)(\eta^1\text{-}C_6H_5)_2]$ from the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with Ph_3SnSPh.

As a part of our studies on bimetallic Os–Ge clusters, we set out to investigate the reactivity of the electron-deficient **1** with Ph_3GeSPh. Unfortunately, the reaction does not appear to give any Os–Ge product, instead only the thiolato part of the ligand incorporated into the cluster resulting in the formation of $[Os_3(CO)_8(\mu\text{-}H)(\mu\text{-}SPh)(\mu\text{-}dppm)]$ (**2**) and $[Os_3(CO)_7(\mu\text{-}H)(\mu\text{-}SPh)(\mu_3\text{-}SC_6H_4)(\mu\text{-}dppm)]$ (**3**).

2. Experimental

All the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. The starting complex $[Os_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}Ph_2PCH_2P(Ph)C_6H_4)]$ (**1**) and the ligand Ph_3GeSPh were prepared according to published procedures [4,19]. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX 400 spectrometer. Elemental analyses were performed by

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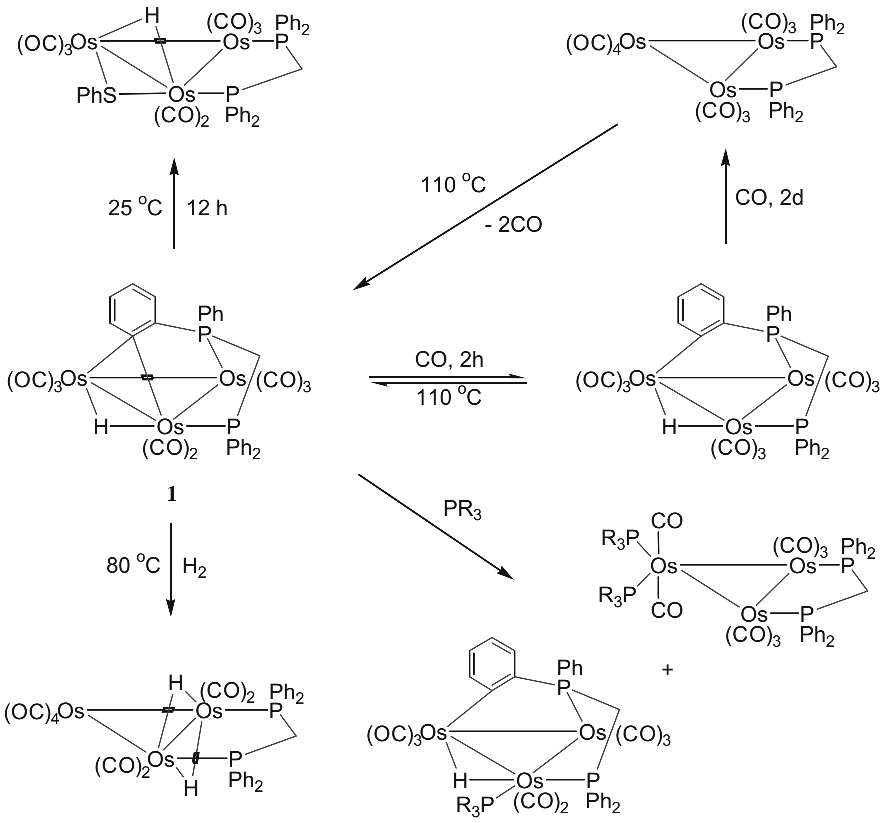

Scheme 1.

Microanalytical Laboratories, University College London. Fast atom bombardment mass spectra were obtained on a JEOLSX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant.

*2.1. Reaction of [$Os_3(CO)_8(\mu$-H)(μ_3-$Ph_2PCH_2P(Ph)C_6H_4$)] (**1**) with Ph_3GeSPh*

A benzene (20 mL) solution of **1** (50 mg, 0.042 mmol) and Ph_3GeSPh (35 mg, 0.084 mmol) was heated to reflux for 9 h during which time the color changed from green to yellow. The progress of the reaction was followed by spot TLC. 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) developed three bands. The second band gave the unreacted starting compound **1** (6 mg) while the first and third bands afforded [$Os_3(CO)_8(\mu$-H)(μ-SPh)(μ-dppm)] (**2**) (22 mg, 40%) as orange crystals and [$Os_3(CO)_7(\mu$-H)(μ-SPh)(μ_3-SC_6H_4)(μ-dppm)] (**3**) (10 mg, 17%) as pale yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. Spectral data for **2**: Anal. Calc. for $C_{39}H_{28}O_8Os_3P_2S$: C, 36.33; H, 2.19. Found: C, 36.55; H, 2.23%. IR (νCO, CH_2Cl_2): 2067 vs, 2023 m, 1993 vs, 1970 m, 1955 m, 1923 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.66 (m, 2H), 7.53 (m, 3H), 7.42 (m, 5H), 7.32 (m, 6H), 7.13 (m, 9H), 5.73 (dd, 1H, $J = 24.2$, 12.5 Hz), 4.56 (dd, 1H, $J = 24.2$, 12.5 Hz), −15.76 (d, 1H, $J = 29.6$ Hz). ^{31}P-{^1H} NMR ($CDCl_3$): δ −24.1 (br, s), −24.8 (br, s). FAB mass spectrum: *m*/*z* 1290 (M^+), 1262 (M^+−CO), 1234 (M^+−2CO), 1206 (M^+−3CO), 1178 (M^+−4CO), 1150 (M^+−5CO), 1122 (M^+−6CO), 1094 (M^+−7CO), 1066 (M^+−8CO). Spectral data for **3**: Anal. Calc. for $C_{44}H_{32}O_7Os_3P_2S_2$: C, 38.59; H, 2.36. Found: C, 38.73; H, 2.41%. IR (νCO, CH_2Cl_2): 2056 s, 2041 vs, 1996 s, 1983 vs, 1953 w, 1940 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.83 (dd, 1H, $J = 6.8$, 3.6 Hz), 7.64 (dd, 1H, $J = 6.0$, 3.6 Hz), 7.58 (m, 3H), 7.38 (m, 8H), 7.26 (m, 3H), 7.12 (m, 5H), 6.90 (m, 6H), 6.72 (m, 2H), 2.97 (m, 1H), 1.58 (m, 1H), −15.66 (t, 1H, $J = 7.2$ Hz). ^{31}P-{^1H} NMR ($CDCl_3$): δ 17.2 (d, $J = 94.8$ Hz), 21.3 (d, $J = 94.8$ Hz). FAB mass spectrum: *m*/*z* 1370 (M^+), 1342 (M^+−CO), 1314 (M^+−2CO), 1286 (M^+−3CO), 1258 (M^+−4CO), 1230 (M^+−5CO), 1202 (M^+−6CO), 1174 (M^+−7CO).

2.2. X-ray crystallography

Single crystals were mounted on fibres and diffraction data collected at low temperatures (see Table 1) on Bruker AXS SMART APEX CCD diffractometers using Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection, indexing and initial cell refinements were all done using SMART [20] software. Data reduction was done with SAINT [21] software and the SADABS program [22] was used to apply empirical absorption corrections. The structures were solved by direct methods [23] and refined by full matrix least-squares on F^2 [24]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. For compound **3** the refinement with just the cluster molecule included converged with $R_1 = 0.093$. There was considerable diffuse electron density still remaining (2–3 e A^{-3}) and PLATON calculated very large voids in the lattice. Obviously very poorly ordered solvent, probably CH_2Cl_2 was present. Since this could not be modeled, it was eliminated using SQUEEZE procedures [25]. After this treatment refinement converged to $R_1 = 0.074$. The disordered solvent, combined with a small poorly diffracting crystal, meant that refinement was less successful than normal. Only the Os, S, P, and O atoms were refined anisotropically, since several of the carbon atoms gave positive definite ellipsoids if released from isotropic modeling. The hydride ligand could not be located directly but the disposition of the CO ligands suggest strongly that it bridges the Os(1)–Os(2) edge. Scattering factors were taken from International Tables for X-ray