

Cleavage of the Ge-S and C-H bonds in the reaction of electron-deficient $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ with Ph_3GeSPh : Generation of thiophenol derivatives $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm})]$

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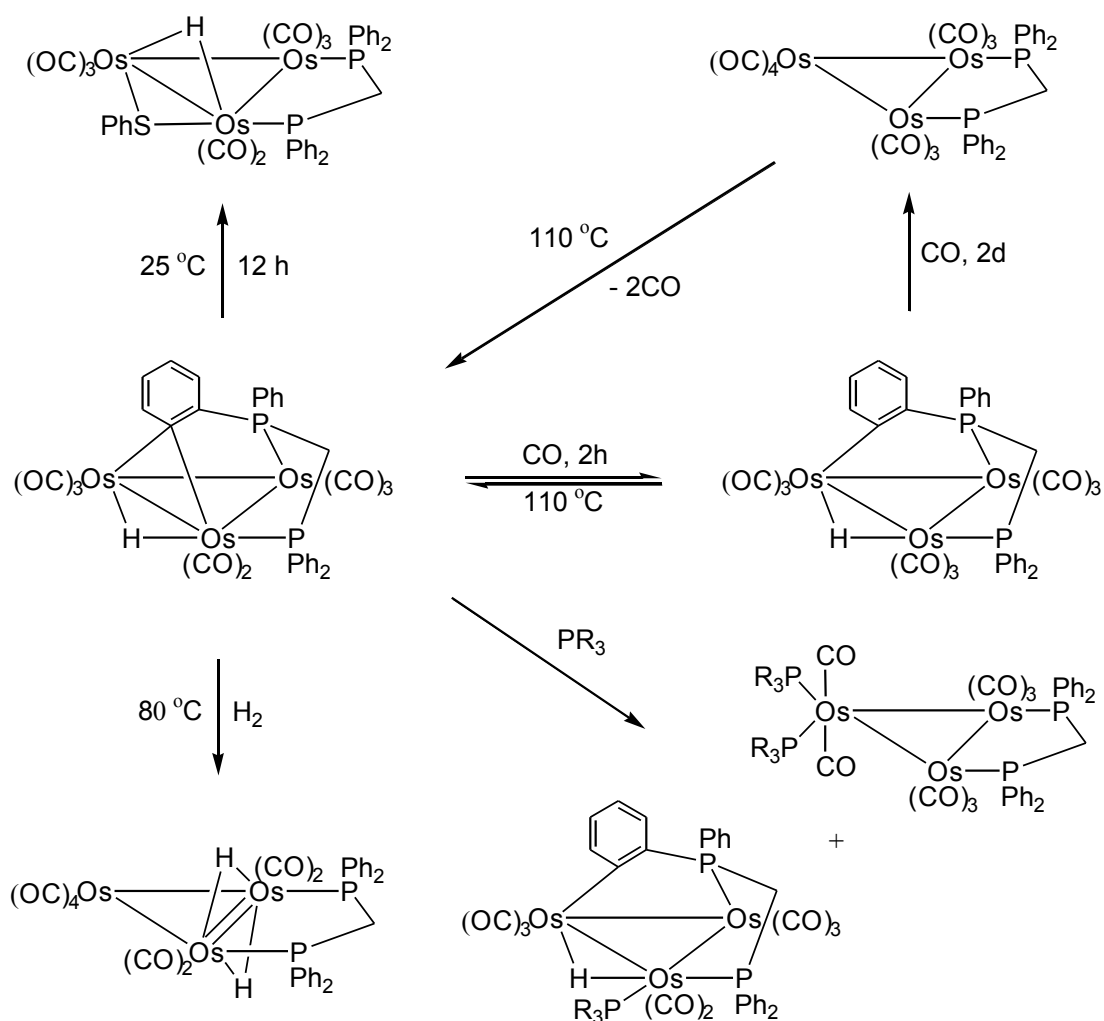
Abstract

Heating the electron-deficient $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ (**1**) and Ph_3GeSPh in benzene at 80 °C led to the thiolato bridged compounds, $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ (**2**) and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm})]$ (**3**), formed by cleavage of Ge-S and C-S bond cleavage 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 **2** crystallizes in the triclinic space group *P*-1 with $a = 11.5072(8)$, $b = 12.3475(8)$, $c = 15.1330(10)$ Å, $\beta = 98.894(1)^\circ$, $Z = 4$ and $V = 5105.07(14)$ Å³ and **3** crystallizes in the monoclinic space group *P*2₁/*n* with $a = 9.9678(2)$, $b = 28.0191(2)$, $c = 18.5013(3)$ Å, $\beta = 98.894(1)^\circ$, $Z = 4$ and $V = 5105.07(14)$ Å³. Compound **3** contains an open triangle of osmium atoms bridged by a SPh and SC₆H₄ 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.

KEY WORDS: Triosmium clusters; bond cleavage (Ge-S, C-H); thiophenol; dppm; X-ray structures.

Introduction

The electron-deficient triosmium cluster $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ (**1**) derived from the decarbonylation of the decacarbonyl compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ 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 Electron-deficiency in **1** makes it more vulnerable to attack by nucleophiles and practically it reacts with a wide range of electron donor ligands under mild conditions relative to electron precise complexes.



Scheme 1.

The reactions **1** with a wide variety of small inorganic and organic ligands such as CO,⁴ H₂,⁵ PR₃,⁶ P(OR)₃ (R = Me, Et, Prⁱ, Bu, Ph),⁶ PPh₂H,⁷ RC≡CR (R = Ph, C₆H₄Me, Me, CF₃),⁸ [Au(PPh₃)]PF₆,⁹ EtSH,¹⁰ CH₃CH(CH₃)SH,¹⁰ PhSH,¹⁰ pySH,¹¹ HSCH₂CH₂SH,¹² HSCH₂CH₂CH₂SH,¹² Se,¹³ HX (X = Cl, Br, F, CF₃CO₂, CH₃CO₂),¹⁴ CH₂CN₂,¹⁵ silane¹⁶ and Ph₃SnH¹⁷ 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. [Ru₃(CO)₈(μ-SPh)₂(μ₃-SnPh₂)(SnPh₃)₂] and [Ru₃(CO)₈(μ-SPh)₂(μ₃-GePh₂)(GePh₃)₂], from the reactions of Ph₃SnSPh and Ph₃GeSPh with [Ru₃(CO)₁₂], respectively.¹⁸ We also reported the Os-Sn compound [Os₃(CO)₉(μ-SPh)(μ₃-SnPh₂)(NCMe)(η¹-C₆H₅)₂] from the reaction of [Os₃(CO)₁₀(NCMe)₂] with Ph₃SnSPh.

As a part of our work on going studies on bimetallic Os-Ge clusters, we set out to investigate the reactivity of the electron-deficient **1** with Ph₃GeSPh. 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 [Os₃(CO)₈(μ-H)(μ-SPh)(μ-dppm)] (**2**) and [(Os₃(CO)₇(μ-H)(μ-SPh)(μ₃-SC₆H₄)(μ-dppm)] (**3**).

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 [Os₃(CO)₈(μ-H)(μ₃-Ph₂PCH₂P(Ph)C₆H₄)] (**1**) and the ligand Ph₃GeSPh 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 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.

*Reaction of [Os₃(CO)₈(μ-H)(μ₃-Ph₂PCH₂P(Ph)C₆H₄)] (**1**) with Ph₃GeSPh*

A benzene (20 mL) solution of **1** (50 mg, 0.042 mmol) and Ph₃GeSPh (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/CH₂Cl₂ (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 $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ (**2**) (22 mg, 40%) as orange crystals and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm}))]$ (**3**) (10 mg, 17%) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Spectral data for **2**: Anal. Calcd. for $\text{C}_{39}\text{H}_{28}\text{O}_8\text{Os}_3\text{P}_2\text{S}$: C, 36.33; H, 2.19. Found: C, 36.55; H, 2.23%. IR (ν_{CO} , 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). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ -24.1 (br, s), -24.8 (br, s). FAB mass spectrum: m/z 1290 (M^+), 1262 ($\text{M}^+ - \text{CO}$), 1234 ($\text{M}^+ - 2\text{CO}$), 1206 ($\text{M}^+ - 3\text{CO}$), 1178 ($\text{M}^+ - 4\text{CO}$), 1150 ($\text{M}^+ - 5\text{CO}$), 1122 ($\text{M}^+ - 6\text{CO}$), 1094 ($\text{M}^+ - 7\text{CO}$), 1066 ($\text{M}^+ - 8\text{CO}$). Spectral data for **3**: Anal. Calcd. For $\text{C}_{44}\text{H}_{32}\text{O}_7\text{Os}_3\text{P}_2\text{S}_2$: C, 38.59; H, 2.36. Found: C, 38.73; H, 2.41%. IR (ν_{CO} , 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). $^{31}\text{P}\{-^1\text{H}\}$ 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 ($\text{M}^+ - \text{CO}$), 1314 ($\text{M}^+ - 2\text{CO}$), 1286 ($\text{M}^+ - 3\text{CO}$), 1258 ($\text{M}^+ - 4\text{CO}$), 1230 ($\text{M}^+ - 5\text{CO}$), 1202 ($\text{M}^+ - 6\text{CO}$), 1174 ($\text{M}^+ - 7\text{CO}$).

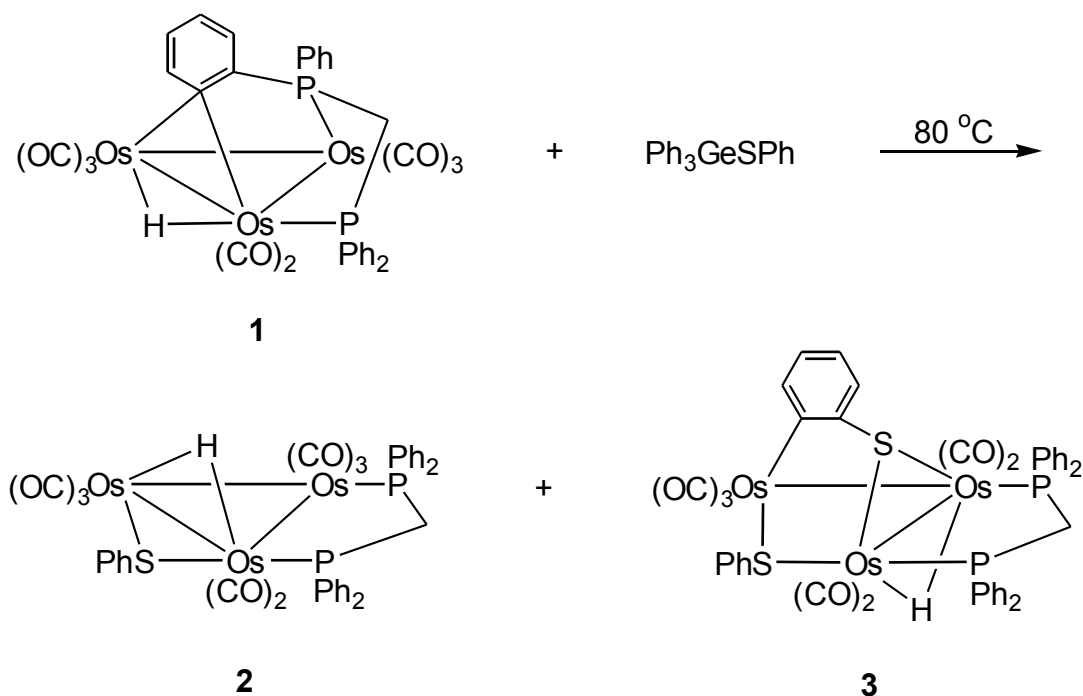
X-ray crystallography

Single crystals were mounted on fibres and diffraction data collected at low temperatures (see Table 1) on Bruker AXS SMART APEX CCD diffractometers using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection, indexing and initial cell refinements were all done using SMART²⁰ software. Data reduction was done with SAINT²¹ software and the SADABS program²² was used to apply empirical absorption corrections. The structures were solved by direct methods²³ 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. Scattering factors were taken from International Tables for X-ray Crystallography.²⁵ All pertinent crystal data and other experimental conditions and refinement details are summarized in Table 1.

Results and discussion

Reaction of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ (**1**) with Ph_3GeSPh in refluxing benzene for 9 h resulted in the isolation of two triosmium compounds, $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-$

SPh)(μ -dppm)] (**2**) and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm}))]$ (**3**) in 40 and 17% yields, respectively (Scheme 2). Compound **2** was previously reported from the reactions of thiophenol with $[\text{Os}_3(\text{CO})_9(\text{NCMe})(\mu\text{-dppm})]^{26}$ and **1**¹⁰ at ambient temperature and with $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]^{27}$ at 110 °C and was characterized spectroscopically. Compounds **2** and **3** do not contain any Ph_3Ge -derived ligand. Compound **2** does not seem to be a precursor of **3** as attempts to obtain **3** by treating **2** with thiophenol in refluxing benzene for 24 h or in refluxing toluene for 8 h have failed.



Scheme 2.

The solid-state molecular structure of **2** is shown in Fig. 1, crystallographic data are collected in Table 1, and selected bond lengths and angles are presented in Table 2. The structure is based upon a triangular arrangement of three osmium atoms coordinated by eight carbonyl ligands, a bridging bis(diphenylphosphino)methane (dppm) ligand, a bridging phenylsulfido ligand and a bridging hydride. The three osmium atoms define an approximate isosceles triangle of osmium atoms with one long {Os(1)–Os(2) 2.8877(5) Å} and two comparatively short bonds {Os(1)–Os(3) 2.8549(5) Å and Os(2)–Os(3) 2.8588(5) Å}. The eight terminal carbonyl ligands are all terminal, three of which are bonded to each of Os(1) and Os(3) while the other two to Os(2). The phenylsulfido ligand spans across the Os(1)–Os(2) edge {Os(1)–S(1) 2.412(2) Å and Os(2)–S(1) 2.414(2) Å} almost

symmetrically with the phenyl ring perpendicularly oriented in space with respect to the trimetallic plane. The hydride ligand is located crystallographically but not refined which also spans the Os(1)–Os(2) edge but lies on the opposite side of the Os₃ plane relative to the phenylsulfido ligand. This observation is consistent with the lengthening of the Os(1)–Os(2) edge and the opening out of the carbonyl ligands along this edge {C(1)–Os(1)–Os(2) 116.8(3)°, C(4)–Os(2)–Os(1) 115.1(3)°, and C(5)–Os(2)–Os(1) 119.7(3)°}. The dppm ligand bridges the Os(2)–Os(3) edge a little bit asymmetrically {Os(2)–P(1) 2.317(2) Å and Os(3)–P(2) 2.333(2) Å} and the phosphorus atoms of the ligand occupy equatorial site on both osmium atoms as expected. However, the Os–S and Os–P bond distances in **2** are similar to those observed in related complexes¹⁰⁻¹² and the overall structural features are similar to the corresponding ruthenium compound [Ru₃(CO)₈(μ-H)(μ-SPh)(μ-dppm)]²⁸ and the ethanethiol analog [Os₃(CO)₈(μ-H)(μ-SC₂H₅)(μ-dppm)]¹⁰. The spectroscopic data of **2** are consistent with the solid-state structure and are very similar to those reported previously.^{10,}

27

The solid-state molecular structure of **3** is depicted in Fig. 2, crystallographic data are collected in Table 1, and selected bond lengths and angles are listed in Table 3. The molecule consists of an open triangle of three osmium atoms with two distinctly different metal-metal bonds {Os(1)–Os(2) 2.9817(10) Å and Os(2)–Os(3) 2.9160(10) Å}, seven carbonyl ligands, a bridging phenylsulfido ligand, a bridging dppm ligand, a triply bridging SC₆H₄ ligand, and a bridging hydride. The carbonyl ligands are terminally bonded, two of which are bonded to each of Os(1) and Os(2) while the other three to Os(3). An interesting structural feature of **3** is the *ortho* C–H bond activation of the phenyl ring of one phenylsulfido ligand thus forming a μ₃-SC₆H₄ ligand on the cluster surface which spatially oriented in space such that the plane constituted by the atoms of this ligand is almost perpendicular to the Os₃ plane. The covalent Os–C distance in **3** {Os(3)–C(12) 2.143(17) Å} is quite similar to those observed in related complexes.^{10, 12, 26} The phenylsulfido ligand which lies on the opposite side of the μ₃-SC₆H₄ ligand asymmetrically bridges the open Os(1)–Os(3) edge {Os(1)–S(2) 2.424(4) Å and Os(3)–S(2) 2.459(5) Å} through the sulfur atom while the μ₃-SC₆H₄ ligand similarly spans across the Os(1)–Os(2) bonding edge {Os(1)–S(1) 2.446(4) Å and Os(2)–S(1) 2.404(4) Å}. The hydride ligand is located in the structural analysis but not refined which bridges the Os(1)–Os(2) bonding edge and is *cis* to both Os(1)–C(1) and Os(1)–C(3) bonds. This is also supported by the lengthening of this edge and widening of the C(1)–Os(1)–Os(2) and C(3)–Os(2)–Os(1) angles {121.6(5)° and

115.6(5)°}. The dppm ligand also bridges the same Os–Os edge and the Os–P bond distances are within the range reported for related compounds.^{7, 10-12, 26, 27} The Os–S bond distances in **3** are also in the range found in literature.¹⁰⁻¹² The C–C bond lengths within the phenyl ring of the μ_3 -SC₆H₄ ligand fall in the range of 1.37(2) – 1.44(3) Å, suggesting unperturbed benzenoid character in the ring. All other features of the molecule are within the expected range and the molecule is a 50-electron cluster with two formal metal-metal bonds assuming the phenylsulfido and μ_3 -SC₆H₄ ligands serve as three and four electron donor, respectively.

The spectroscopic data of **3** support the solid-state structure. The infrared spectrum exhibits absorption bands characteristic for terminally bonded carbonyl ligands. In addition to the usual aromatic resonances for the phenyl protons, the ¹H NMR spectrum shows a virtual triplet at δ –15.66 ($J = 7.2$ Hz) for the bridging hydride ligand while the ³¹P-¹H NMR spectrum displays two equal intensity doublets at δ 17.2 ($J = 94.8$ Hz) and 21.3 ($J = 94.8$ Hz) due to the phosphorus atoms of the dppm ligand. The FAB mass spectrum shows the parent molecular ion peak at m/z 1370 together with fragmentation peaks due to the sequential loss of all seven carbonyl groups which are also consistent with the solid-state structure.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number (space group $P -1$) and (space group $P2_1/n$). Copies of this information can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.ac.uk>).

Acknowledgement

AKR gratefully acknowledges the University Grants Commission of Bangladesh for a scholarship.

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Table 1. Crystal and Structural Refinement Data for [Os₃(CO)₈(μ-H)(μ-SPh)(μ-dppm)] (2) and [(Os₃(CO)₇(μ-H)(μ-SPh)(μ₃-SC₆H₄)(μ-dppm)] (3)

Empirical formula	C ₃₉ H ₂₈ O ₈ Os ₃ P ₂ S	C ₄₄ H ₃₂ O ₇ Os ₃ P ₂ S
CCDC deposit no.
Formula weight	1289.21	1368.35
Temperature (K)	150(2)	89(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic

Space group	$P-1$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.5072(8)	10.9678(2)
b (Å)	12.3475(8)	28.0191(2)
c (Å)	15.1330(10)	18.5013(3)
α (°)	112.9460(10)	90
β (°)	91.0800(10)	98.894(1)
γ (°)	106.5390(10)	90
Volume (Å ³)	1877.5(2)	5105.07(14)
Z	2	4
Density (calculated) (Mg/m ³)	2.281	1.780
Absorption coefficient (mm ⁻¹)	10.320	7.735
$F(000)$	1200	2564
Crystal size (mm ³)	0.44 × 0.32 × 0.04	0.22 × 0.10 × 0.05
θ range for data collection (°)	2.77 – 28.30	1.33 – 25.72
Index ranges	$-15 \leq h \leq 15$ $-16 \leq k \leq 16$ $-20 \leq l \leq 20$	$-12 \leq h \leq 12$ $-33 \leq k \leq 33$ $-16 \leq l \leq 22$
Reflections collected	16053	28287
Independent reflections	8500 [$R(\text{int}) = 0.0295$]	9664 [$R(\text{int}) = 0.1269$]
Completeness to $\theta = 67.10^\circ$	96.7 %	99.3 %
Max. and min. transmission	0.0926 and 0.6830	0.7014 and 0.2844
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8500/0/478	6267/0/516
Goodness-of-fit on F^2	0.933	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0383$, $wR_2 = 0.1333$	$R_1 = 0.0743$, $wR_2 = 0.1528$
R indices (all data)	$R_1 = 0.0479$, $wR_2 = 0.1711$	$R_1 = 0.1343$, $wR_2 = 0.1700$
Largest diff. peak and hole (eÅ ⁻³)	2.3471 and -2.284	2.540 and -2.132

Table 2. Selected Bond Distances (Å) and Angles (°) for $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ (**2**)

<u>Bond distances</u>			
Os(1)–C(2)	1.905(12)	Os(1)–C(1)	1.908(12)
Os(1)–C(3)	1.918(11)	Os(1)–S(1)	2.412(2)
Os(1)–Os(3)	2.8549(5)	Os(1)–Os(2)	2.8877(5)
Os(2)–C(4)	1.881(9)	Os(2)–C(5)	1.892(11)
Os(2)–P(1)	2.317(2)	Os(2)–S(1)	2.414(2)
Os(2)–Os(3)	2.8588(5)	Os(3)–C(7)	1.895(9)
Os(3)–C(6)	1.931(8)	Os(3)–C(8)	1.938(9)
Os(3)–P(2)	2.333(2)	S(1)–C(35)	1.806(9)
P(1)–C(11)	1.820(9)	P(1)–C(10)	1.830(9)
P(1)–C(17)	1.830(9)	P(2)–C(29)	1.831(10)
P(2)–C(23)	1.839(8)	P(2)–C(10)	1.838(9)
<u>Bond angles</u>			
C(2)–Os(1)–C(1)	95.4(5)	C(2)–Os(1)–C(3)	93.4(4)
C(1)–Os(1)–C(3)	94.4(4)	C(2)–Os(1)–S(1)	93.2(3)
C(1)–Os(1)–S(1)	94.7(3)	C(3)–Os(1)–S(1)	168.2(3)
C(2)–Os(1)–Os(3)	86.1(3)	C(1)–Os(1)–Os(3)	175.7(3)
C(3)–Os(1)–Os(3)	89.5(3)	S(1)–Os(1)–Os(3)	81.16(5)
C(2)–Os(1)–Os(2)	133.0(3)	C(1)–Os(1)–Os(2)	116.8(3)
C(3)–Os(1)–Os(2)	115.5(3)	S(1)–Os(1)–Os(2)	53.28(5)
Os(3)–Os(1)–Os(2)	59.709(12)	C(4)–Os(2)–C(5)	93.4(4)
C(4)–Os(2)–P(1)	89.4(3)	C(5)–Os(2)–P(1)	92.1(3)
C(4)–Os(2)–S(1)	168.1(3)	C(5)–Os(2)–S(1)	95.1(3)
P(1)–Os(2)–S(1)	98.55(8)	C(4)–Os(2)–Os(3)	90.7(3)
C(5)–Os(2)–Os(3)	175.6(3)	P(1)–Os(2)–Os(3)	86.36(5)
S(1)–Os(2)–Os(3)	81.04(5)	C(4)–Os(2)–Os(1)	115.1(3)
C(5)–Os(2)–Os(1)	119.7(3)	P(1)–Os(2)–Os(1)	136.48(5)
S(1)–Os(2)–Os(1)	53.22(5)	Os(3)–Os(2)–Os(1)	59.575(12)
C(7)–Os(3)–C(6)	89.9(4)	C(7)–Os(3)–C(8)	92.1(4)
C(6)–Os(3)–C(8)	170.9(4)	C(7)–Os(3)–P(2)	97.4(3)
C(6)–Os(3)–P(2)	95.7(2)	C(8)–Os(3)–P(2)	92.8(3)
C(7)–Os(3)–Os(1)	109.1(3)	C(6)–Os(3)–Os(1)	88.1(2)
C(8)–Os(3)–Os(1)	82.8(3)	P(2)–Os(3)–Os(1)	153.27(6)
C(7)–Os(3)–Os(2)	169.2(3)	C(6)–Os(3)–Os(2)	93.1(3)
C(8)–Os(3)–Os(2)	83.4(3)	P(2)–Os(3)–Os(2)	92.62(5)
Os(1)–Os(3)–Os(2)	60.716(12)	C(35)–S(1)–Os(1)	111.7(3)
C(35)–S(1)–Os(2)	110.3(3)	Os(1)–S(1)–Os(2)	73.50(6)
C(11)–P(1)–C(10)	108.0(4)	C(11)–P(1)–C(17)	104.5(4)
C(10)–P(1)–C(17)	101.4(4)	C(11)–P(1)–Os(2)	115.5(3)
C(10)–P(1)–Os(2)	111.6(3)	C(17)–P(1)–Os(2)	114.7(3)
C(29)–P(2)–C(23)	100.5(4)	C(29)–P(2)–C(10)	105.1(4)
C(23)–P(2)–C(10)	102.5(4)	C(29)–P(2)–Os(3)	113.3(3)
C(23)–P(2)–Os(3)	120.3(3)	C(10)–P(2)–Os(3)	113.3(3)

Table 3. Selected Bond Distances (Å) and Angles (°) for [(Os₃(CO)₇(μ-H)(μ-SPh)(μ₃-SC₆H₄)(μ-dppm)] (3)

Bond distances

Os(1)–C(2)	1.871(17)	Os(3)–C(6)	1.88(2)
Os(1)–C(1)	1.932(18)	Os(3)–C(7)	1.92 (2)
Os(1)–P(1)	2.349(5)	Os(3)–C(5)	1.981(19)
Os(1)–S(2)	2.424(4)	Os(3)–C(12)	2.143(17)
Os(1)–S(1)	2.446(4)	Os(3)–S(2)	2.459(5)
Os(1)–Os(2)	2.9817(10)	P(1)–C(31)	1.809(16)
Os(2)–C(4)	1.869(18)	P(1)–C(8)	1.844(17)
Os(2)–C(3)	1.886(17)	P(1)–C(41)	1.858(18)
Os(2)–P(2)	2.387 (5)	P(2)–C(61)	1.829(19)
Os(2)–S(1)	2.404(4)	P(2)–C(51)	1.856(18)
Os(2)–Os(3)	2.9160(10)	P(2)–C(8)	1.845(17)

Bond angles

C(2)–Os(1)–C(1)	89.5(7)		
C(2)–Os(1)–P(1)	92.2(5)	P(2)–Os(2)–Os(3)	169.80(11)
C(1)–Os(1)–P(1)	93.7(5)	S(1)–Os(2)–Os(3)	83.64(11)
C(2)–Os(1)–S(2)	94.4(5)	C(4)–Os(2)–Os(1)	151.3(5)
C(1)–Os(1)–S(2)	88.1(5)	C(3)–Os(2)–Os(1)	115.6(5)
P(1)–Os(1)–S(2)	173.12(16)	P(2)–Os(2)–Os(1)	91.19(12)
C(2)–Os(1)–S(1)	97.6(5)	S(1)–Os(2)–Os(1)	52.71(11)
C(1)–Os(1)–S(1)	172.8(5)	Os(3)–Os(2)–Os(1)	83.70(3)
P(1)–Os(1)–S(1)	85.10(15)	C(6)–Os(3)–C(7)	91.1(8)
S(2)–Os(1)–S(1)	92.25(15)	C(6)–Os(3)–C(5)	98.6(7)
C(2)–Os(1)–S(2)	148.5(5)	C(7)–Os(3)–C(5)	91.1(8)
C(1)–Os(1)–Os(2)	121.6(5)	C(6)–Os(3)–C(12)	84.0(7)
P(1)–Os(1)–Os(2)	90.96(12)	C(7)–Os(3)–C(12)	93.0(8)
S(2)–Os(1)–Os(2)	82.44(11)	C(5)–Os(3)–C(12)	175.0(7)
S(1)–Os(1)–Os(2)	51.44(10)	C(6)–Os(3)–S(2)	171.5(6)
C(4)–Os(2)–C(3)	92.1(7)	C(7)–Os(3)–S(2)	96.3(6)
C(4)–Os(2)–P(2)	91.6(6)	C(5)–Os(3)–S(2)	85.7(5)
C(3)–Os(2)–P(2)	99.6(5)	C(12)–Os(3)–S(2)	91.2(5)
C(4)–Os(2)–S(1)	99.0(5)	C(6)–Os(3)–Os(2)	89.5(6)
C(3)–Os(2)–S(1)	167.4(5)	C(7)–Os(3)–Os(2)	179.2(6)
P(2)–Os(2)–S(1)	86.25(15)	C(5)–Os(3)–Os(2)	88.2(6)
C(4)–Os(2)–Os(3)	88.7(5)	C(12)–Os(3)–Os(2)	87.6(5)
C(3)–Os(2)–Os(3)	90.6(5)	S(2)–Os(3)–Os(2)	83.27(10)

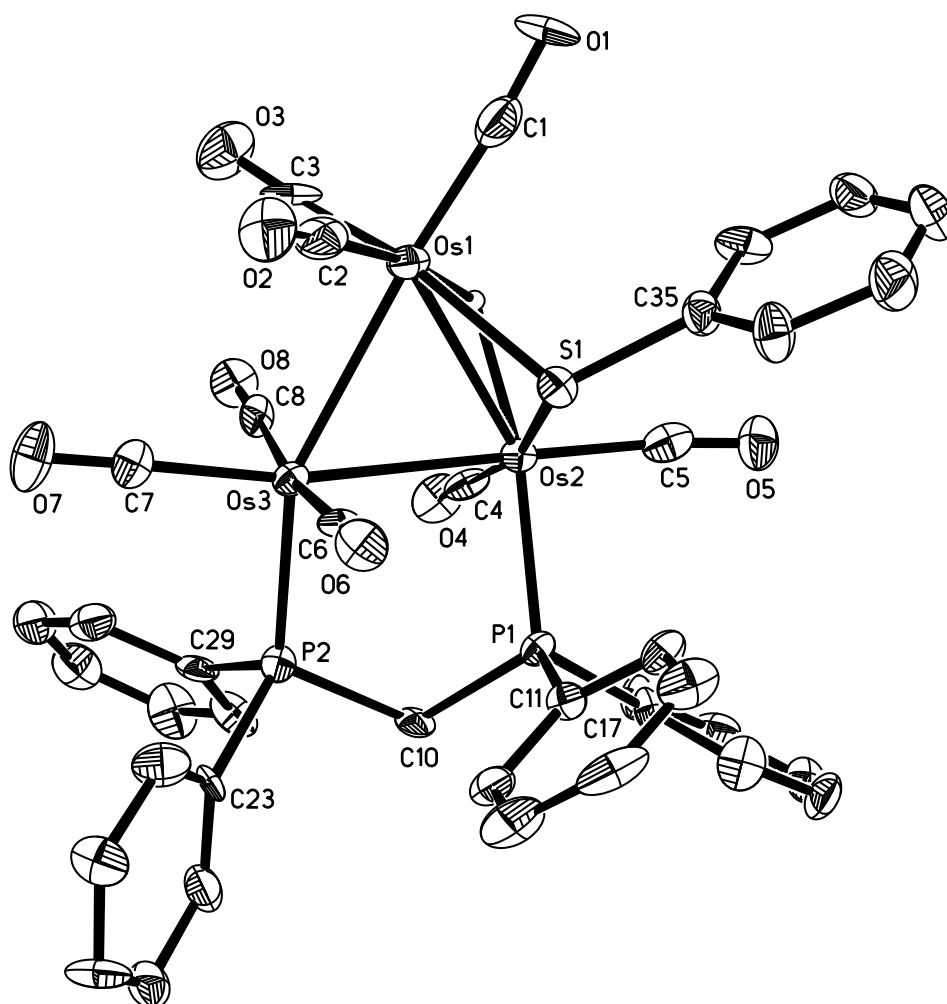


Figure 1. Molecular structure of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Ring hydrogen atoms are omitted for clarity.

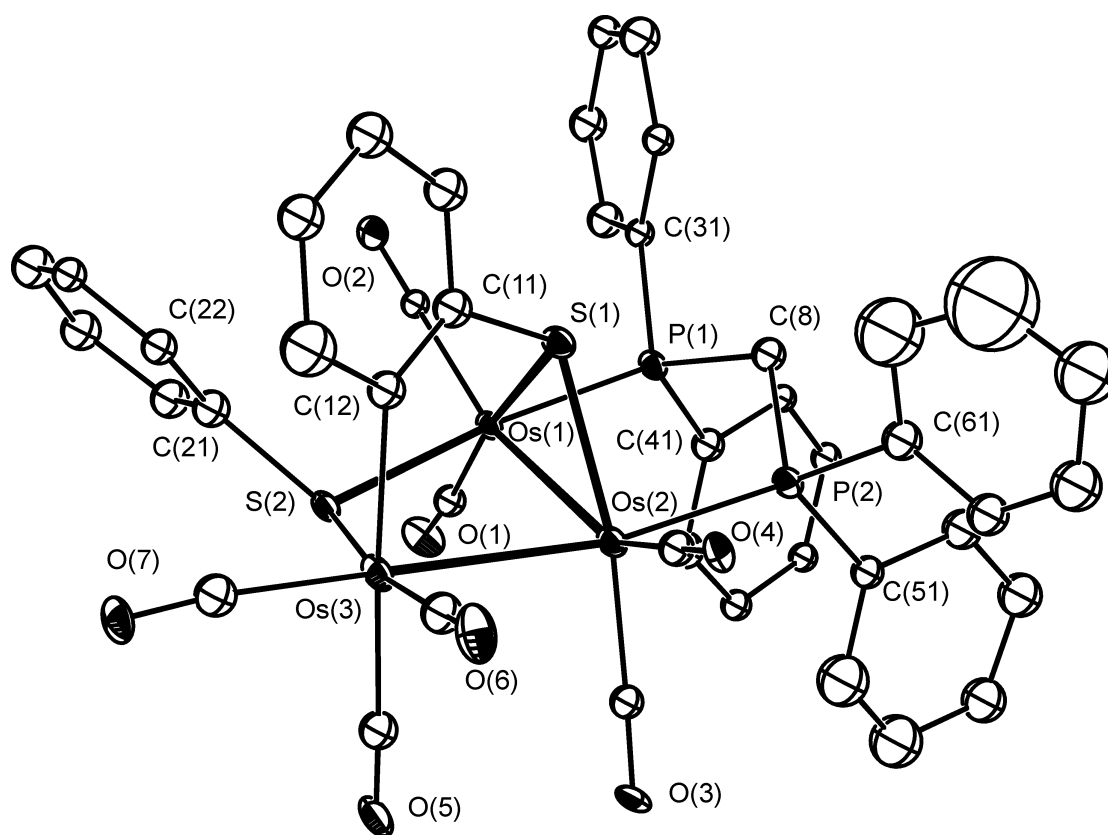
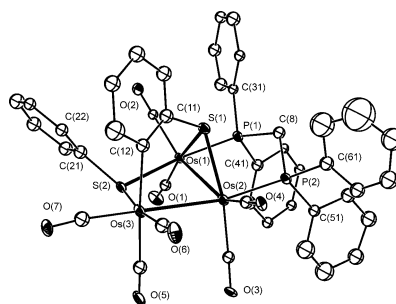
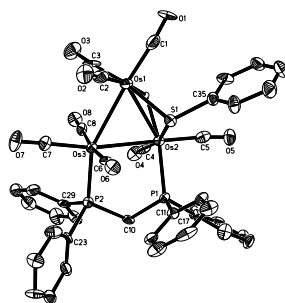


Figure 2. Molecular structure of $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm})]$ (**3**) with thermal ellipsoids drawn at the 30% probability level. Ring hydrogen atoms are omitted for clarity.

INDEX ABSTRACT

Reaction of the electron-deficient $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ (**1**) with Ph_3GeSPh at $80\text{ }^\circ\text{C}$ led to two triosmium compounds, $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ (**2**) and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm})]$ (**3**). Compound **3** represents a rare example of triosmium complex bearing a $\mu_3\text{-SC}_6\text{H}_4$ ligand.



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X-ray crystal structures of $[\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-SPh})(\mu\text{-dppm})]$ and $[(\text{Os}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-SPh})(\mu_3\text{-SC}_6\text{H}_4)(\mu\text{-dppm})]$