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Syntheses and structural characterisation of triosmium carbonyl clusters containing bis(diphenylthiophosphinoyl)amine

Emmie Ngai-Man Ho and Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

The reaction of $[Os_3(CO)_{11}(NCMe)]$ with bis(diphenylthiophosphinoyl)amine $[Ph_2P(S)NHP(S)Ph_2]$ in dichloromethane at room temperature afforded two yellow products $[Os_3(CO)_{10}\{Ph_2P(SH)NP(S)Ph_2\text{-}S,S\}]$ and $[Os_3H(CO)_9\{Ph_2P(S)NP(S)Ph_2\text{-}S,S\}]$ in which the ligand adopts a novel co-ordination mode.

The co-ordination chemistry of the $[Ph_2P(E)NP(E)Ph_2]^-$ anions (E = O, S or Se) has attracted attention because of their selective complexation properties towards 'hard/soft' metal ions.[1–3] However, the chemistry of the undissociated form $Ph_2P(E)NHP(E)Ph_2$ is relatively unexplored.[4–6] We are interested in the chemistry of osmium carbonyl clusters containing S or S and O mixed-donor ligands.[7–9] Herein, we report the reactivity of $Ph_2P(S)NHP(S)Ph_2$ towards the activated triosmium cluster $[Os_3(CO)_{11}(NCMe)]$ which resulted in the isolation of two novel triosmium clusters containing the bis(diphenylthiophosphinoyl)amine ligand.

Treatment of 1 equivalent of $Ph_2P(S)NHP(S)Ph_2$ with $[Os_3(CO)_{11}(NCMe)]$ in CH_2Cl_2 at room temperature (r.t.) for 12 h gives two yellow products (*ca.* 25% each), $[Os_3(CO)_{10}\{Ph_2P(SH)NP(S)Ph_2\text{-}S,S\}]$ **1** and $[Os_3H(CO)_9\{Ph_2P(S)NP(S)Ph_2\text{-}S,S\}]$ **2**. The molecular structures of **1** and **2** together with selected bond parameters are depicted in Figs. 1 and 2. The molecular geometries of clusters **1** and **2** are similar in that the two sulfur atoms of the ligand bridge above and below the osmium triangle over the open Os–Os edge [Os(2)···Os(3) 3.422(1) in **1** and 3.383(1) Å in **2**]. This is similar to that observed for $[Os_3(CO)_{10}(\mu\text{-dmpymt})_2]$ (dmpymt = 4,6-dimethylpyrimidine-2-thione).[10] The Os–Os bonds in **1** [Os(1)–Os(2) 2.866(2) and Os(1)–Os(3) 2.871(2) Å] are significantly shorter than those in **2** [Os(1)–Os(2) 2.913(3) and Os(1)–Os(3) 2.943(3) Å] but are comparable to the Os–Os bonds in $[Os_3(CO)_{10}(\mu\text{-dmpymt})_2]$ (2.895 Å). The cluster **1** is very symmetrical and possesses approximate C_{2v} symmetry with Os(1), Os(2), Os(3), N(1), C(1)–O(1), C(3)–O(3), C(5)–O(5) and C(7)–O(7) in the crystallographic mirror plane as refined in the space group $P2_1/m$. However, we expected the structure of **1** to be more complicated in both the solid state and in solution. This is evident from the ^{31}P NMR spectroscopic data. Two distinct signals for the phosphorus atom with mutual coupling and roughly equal intensity suggests that both P resonances are from the same molecule rather than from other isomers present in solution. The position of hydrogen on the organic moiety cannot be located with certainty from X-ray work alone. Placing the hydrogen atom on N(1) **1a** will fit the crystallographic symmetry requirement. Introducing the hydrogen on one of the sulfur atoms **1b** will give a structure that is consistent with all the spectroscopic data obtained in solution (see Scheme 1). In structure **1b** we assume that one of the sulfur atoms is sp^3 hybridised and acts as a four-electron donor. Therefore, the neutral $Ph_2P(S)NHP(S)Ph_2$ ligand in **1a** is considered to contribute six electrons to the cluster. This results in an overall count of 50 cluster valence electrons and this is consistent with the observed metal core geometry according to the effective atomic number rule. In order to resolve the two types of PS linkage in the ligand, we have attempted to refine the structure in space group $P2_1$ (non-centrosymmetric alternative for $P2_1/m$). Unfortunately, we were unable to break the pseudo-mirror plane symmetry associated with the molecule. The refinement does not converge, with heavy correlations observed between positional parameters. In the cluster **2**, the deprotonated $Ph_2P(S)NP(S)Ph_2$ ligand acts as a seven-electron donor with electrons delocalised over the SPNPS moiety. The SPNPS moiety in both **1** and **2** is essentially planar (maximum deviation 0.03 Å for **2**) and mutually perpendicular to the triosmium plane (dihedral angles 90° for **1**, 89.7° for **2**). The position of the hydride in **2** is estimated from potential energy calculations.[11] The solution spectroscopic data † of **2** are fully consistent with

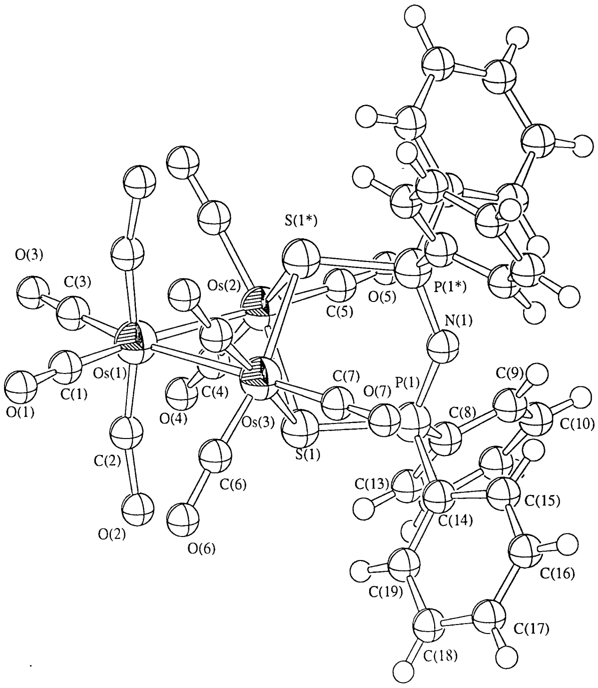

Fig. 1 Molecular structure of complex **1** with selected bond distances (Å) and angles (°): Os(1)–Os(2) 2.866(2), Os(1)–Os(3), 2.871(2), Os(2)–S(1) 2.465(5), Os(3)–S(1) 2.470(5), P(1)–S(1) 2.070(8), P(1)–N 1.572(10); Os(2)–Os(1)–Os(3) 73.24(4), Os(2)–S(1)–Os(3) 87.8(2), S(1)–Os(2)–S(1′) 82.2(3), P(1)–N–P(1′) 137(1), S(1)–P(1)–N 115.6(9)

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† Spectroscopic data for complex **1**. IR [ν(CO), CH_2Cl_2]: 2111w, 2096w, 2073vs, 2065s, 2026vs and 2007s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.69 (m, 20 H) and 3.74 (t, $J_{PH} = 5.9$ Hz, 1 H). ^{31}P NMR ($CDCl_3$): δ 48.6 (d, $J_{PP} = 19.4$) and 41.1 (d, $J_{PP} = 19.4$ Hz). FAB mass spectrum: *m/z* 1300 (calc. 1300), M^+ (Found: C, 31.7; H, 1.55; N, 1.1; P, 4.3. $C_{34}H_{21}NO_{10}Os_3P_2S_2$ requires C, 31.4; H, 1.65; N, 1.1; P, 4.75%). Complex **2**. IR [ν(CO), CH_2Cl_2]: 2084m, 2046s, 1999vs, 1983s and 1920w cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.06 (m, 8 H), 7.58 (m, 12 H) and −6.57 [t, $J_{PH} = 11.5$ Hz, 1 H]. ^{31}P NMR ($CDCl_3$): δ 35.40. FAB mass spectrum: *m/z* 1272 (calc. 1272), M^+ (Found: C, 30.95; H, 1.5; N, 1.0; P, 4.65. $C_{33}H_{21}NO_9Os_3P_2S_2$ requires C, 31.15; H, 1.65; N, 1.1; P, 4.85%).

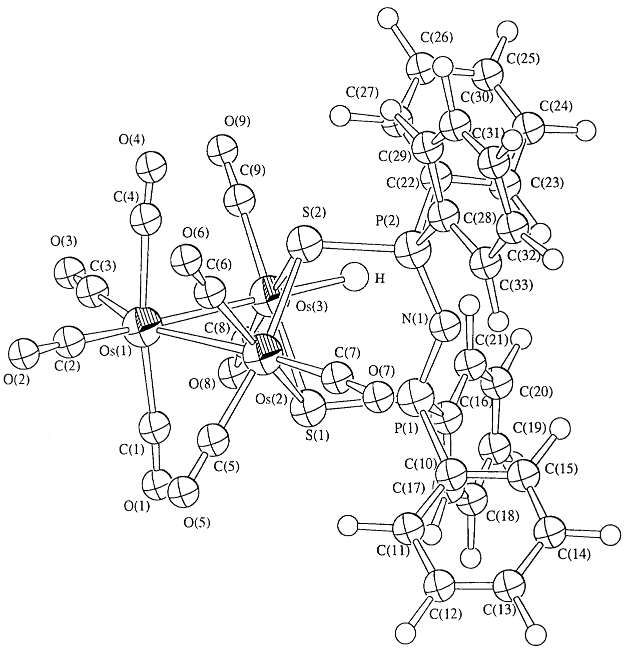
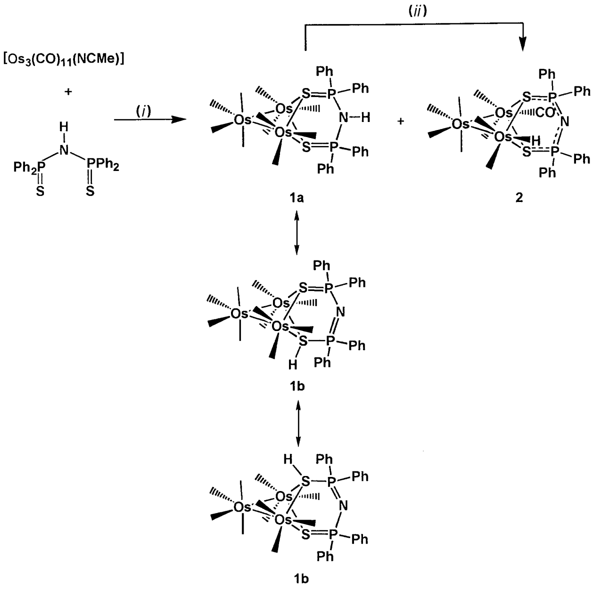


Fig. 2 Molecular structure of complex **2** with selected bond distances (Å) and angles (°): Os(1)–Os(2) 2.913(3), Os(1)–Os(3) 2.943(3), Os(2)–S(1) 2.48(1), Os(3)–S(1) 2.49(1), Os(2)–S(2) 2.46(1), Os(3)–S(2) 2.47(1), P(1)–S(1) 2.08(2), P(2)–S(2) 2.08(2), P(1)–N 1.57(4), P(2)–N 1.61(4), Os(3)–H 1.88; Os(2)–Os(1)–Os(3) 70.57(7), Os(2)–S(1)–Os(3) 85.8(4), Os(2)–S(2)–Os(3) 86.5(4), S(1)–P(1)–N 117(1), S(2)–P(2)–N 116(1), P(1)–N–P(2) 134(2)



Scheme 1 (*i*) CH_2Cl_2, r.t., 12 h; (*ii*) refluxing $CHCl_3$, 1 h

the observed structure obtained in the solid state.‡ The terminal hydride resonance in **2** is observed at δ −6.57 as a triplet. Such a chemical shift is comparable to other osmium clusters containing terminal hydride, for example $[Os_3H_2(CO)_{11}]$ (δ −10).[14]

It is reasonable to propose that the cluster **1** is an intermediate in the formation of **2**. To support this, thermolysis of **1** in refluxing $CHCl_3$ for 1 h produces **2** and two other uncharacterised products in low yields. It is well documented that Brønsted acids, HX, will undergo oxidative addition with $[Os_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$ or 2) to give $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-X})]$.[15–17] However, the detailed mechanism of this reaction is not well understood. Isolation of cluster **2** is useful in the construction of a reaction sequence for this type of reaction. The study of the reactivities of other osmium clusters of bis(diphenylthiophosphinoyl)amine is underway.

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‡ Crystal data for complex **1**. $[Os_3(CO)_{10}\{Ph_2P(SH)NP(S)Ph_2\text{-}S,S\}]\cdot CH_2Cl_2$, $C_{34}H_{21}NO_{10}Os_3P_2S_2\cdot CH_2Cl_2$, $M = 1385.14$, monoclinic, space group $P2_1/m$ (no. 11), $a = 9.956(1)$, $b = 16.727(1)$, $c = 12.521(1)$ Å, $\beta = 95.79(2)°$, $U = 2074.5(3)$ Å^3, $Z = 2$, $D_c = 2.217$ g cm^{-3}, $F(000) = 1288$, Mo-Kα radiation, $T = 295$ K, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 95.19 cm^{-1}, yellow needle 0.12 × 0.14 × 0.32 mm, 3422 unique data measured on a MAR research image-plate scanner, 65 3° frames with exposure time of 5 min per frame. 2039 Observed reflections $[I > 3\sigma(I)]$. Structure solved by direct methods (SIR 92)[12] and Fourier-difference techniques. Full-matrix least-squares refinement on F was employed and Os, Cl, S, P and N atoms refined anisotropically; $R = 0.067$ and $R' = 0.067$, $w = [\sigma^2(F_o)]^{-1}$. Refinements of the structure have also been attempted with space group $P2_1$ (no. 4). However, it led to unreasonable atomic positional parameters for many non-hydrogen atoms. Also refinement did not converge and heavy correlation between parameters resulted.

Crystal data for complex **2**: $[Os_3H(CO)_9\{Ph_2P(S)NP(S)Ph_2\text{-}S,S\}]$, $C_{33}H_{21}NO_9Os_3P_2S_2$, $M = 1272.20$, orthorhombic, space group $Pbcn$ (no. 60), $a = 18.478(1)$, $b = 18.180(1)$, $c = 21.553(2)$ Å, $U = 7240.3(7)$ Å^3, $Z = 8$, $D_c = 2.334$ g cm^{-3}, $F(000) = 4704$, Mo-Kα radiation, $T = 295$ K, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 107.54 cm^{-1}, yellow block 0.27 × 0.28 × 0.31 mm, 6818 unique data measured on a MAR research image-plate scanner, 70 3° frames with exposure time of 6 min per frame. 2694 Observed reflections $[I > 3\sigma(I)]$. Structure solved by direct methods (SIR 92)[12] and Fourier-difference techniques. Full-matrix least-squares refinement on F was employed and Os, S, P and N atoms refined anisotropically; $R = 0.052$ and $R' = 0.098$, $w = [\sigma^2(F_o)]^{-1}$. Calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[13] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/423.

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