

## Syntheses of Tetranuclear Tungsten Sulfide Clusters with Raft-type and Tetrahedral Core Structures

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Reaction of  $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$  with  $(\text{Me}_3\text{Si})_2\text{S}-\text{MeOH}$  gives a raft-type tetranuclear tungsten sulfide cluster  $[\text{W}_4(\mu_3\text{-S})_2(\mu\text{-S})_4(\text{SH})_2(\text{PMe}_2\text{Ph})_6]$  **2**, which is converted to a tetrahedral cluster  $[\text{W}_4(\mu\text{-S})_6(\text{PMe}_2\text{Ph})_4]$  **5** upon treatment with  $\text{SnCl}_2$  followed by reduction with  $\text{Na}/\text{Hg}$ ; the molecular structures of **2** and **5** are determined by X-ray crystallography.

Transition-metal sulfide clusters have been the subject of increased attention as synthetic analogues for non-molecular sulfides,<sup>1</sup> which show unique physical properties such as superconductivity in Chevrel phases. Structural properties<sup>2</sup> and reactivities of sulfide clusters are also of significant interest in relation to biological<sup>3</sup> and industrial<sup>4</sup> catalysis. These potential characteristics of sulfide clusters prompted us to investigate the preparation of di- and tri-ruthenium complexes with bridging sulfur-donor ligands,<sup>5</sup> and mixed-metal sulfide clusters containing  $\text{WRu}_2$ ,<sup>6</sup>  $\text{PtRu}_2$ ,<sup>6</sup>  $\text{Pd}_2\text{Ru}_2$ ,<sup>6</sup> and  $\text{PdMo}_3$ <sup>7</sup> cores, for some of which intriguing reactivities towards various substrates including alkynes,  $\text{H}_2$ ,  $\text{CO}$ , alkyl halides, and hydrazines have already been demonstrated. In this paper, we wish to report the syntheses of two types of novel tetranuclear tungsten sulfide clusters containing either a raft-type or a tetrahedral core framework (Scheme 1).

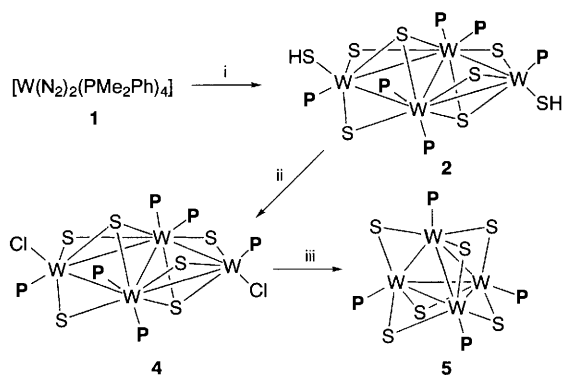
Treatment of *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$  **1** with  $(\text{Me}_3\text{Si})_2\text{S}$  (2 equiv. per **1**) and  $\text{MeOH}$  (10 equiv. per **1**) in toluene at  $50^\circ\text{C}$  for 4 h under vacuum afforded  $[\text{W}_4(\mu_3\text{-S})_2(\mu\text{-S})_4(\text{SH})_2(\text{PMe}_2\text{Ph})_6]$  **2** in 43% yield as dark green microcrystals upon recrystallization from THF–diethyl ether.† A single-crystal X-ray analysis has shown that **2** consists of the tetranuclear tungsten core arranged in a raft-type or planar butterfly geometry (Fig. 1).‡ The  $\text{W}_4\text{S}_6$  framework comprises two fused incomplete cubanes in a face-sharing manner; the two  $\text{W}_3$  triangles are capped by  $\mu_3$ -sulfide ligands and the four peripheral  $\text{W}-\text{W}$  edges in the raft are bridged by  $\mu$ -sulfide ligands. The sulfur atom terminally bound to the wingtip tungsten proved to be a thiol sulfur atom, since the final Fourier map unambiguously showed the presence of a hydrogen atom attached to this sulfur. This is further confirmed by the appearance of a weak  $\nu(\text{SH})$  band at  $2512\text{ cm}^{-1}$  in the IR spectrum (KBr disk). There are 10 *d* electrons in **2** corresponding to the existence of five  $\text{W}-\text{W}$  bonds. These structural features allow us to tentatively assign a 14-electron  $d^2$  configuration to the wingtip tungstens with two  $\text{W}-\text{W}$  bonds and an 18-electron  $d^3$  configuration to the hinge tungstens with three  $\text{W}-\text{W}$  bonds, respectively. It is to be noted that bond

distances between the wingtip  $\text{W}$  and the  $\mu\text{-S}$  [2.274(2)–2.279(2) Å] are substantially shorter than those between the hinge  $\text{W}$  and the  $\mu\text{-S}$  [2.435(3) Å].

When **1** was treated with  $(\text{Me}_3\text{Si})_2\text{S}$  alone at  $50^\circ\text{C}$ , no reaction occurred. This suggests that hydrogen sulfide generated *in situ* from  $(\text{Me}_3\text{Si})_2\text{S}$  and  $\text{MeOH}$  reacts with **1** to give the tetranuclear sulfide cluster **2**. Indeed, the  $^1\text{H}$  NMR spectrum of the reaction mixture obtained from treatment of **1** with  $\text{H}_2\text{S}$  gas indicated the formation of **2**, although the isolation of pure **2** in high yield has not yet been successful. Oxidative addition of hydrogen sulfide to low-valent metal complexes provides a potential synthetic method to prepare sulfide clusters.<sup>8</sup> As to related reactions reported to date,  $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2\text{H})]$  is known to react with  $\text{H}_2\text{S}$  to give a mononuclear bis(sulfide) complex  $[\text{W}(\text{S})_2(\text{PMe}_3)_4]$ ,<sup>9</sup> while the reactions of *trans*- $[\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4]$  with thiols produce mononuclear hydride–thiolate complexes  $[\text{MoH}(\text{SR})_3(\text{PMePh}_2)]$  ( $\text{R} = \text{C}_6\text{H}_2\text{R}'_3\text{-2,4,6}$ ;  $\text{R}' = \text{Me}, \text{Pr}^i$ ).<sup>10</sup> It is also to be noted that the isostructural Mo cluster  $[\text{Mo}_4(\mu_3\text{-S})_2(\mu\text{-S})_4(\text{SH})_2(\text{PMe}_3)_6]$  **3** was prepared from the reaction of  $[\text{Mo}_3\text{S}(\text{S}_2)_6]^{2-}$  with  $\text{PMe}_3$ –butylamine and characterised by X-ray analysis.<sup>11</sup>

Reaction of **2** with  $\text{SnCl}_2$  (1 equiv. per **2**) in THF at reflux resulted in the formation of the chloro-substituted cluster  $[\text{W}_4(\mu_3\text{-S})_2(\mu\text{-S})_4\text{Cl}_2(\text{PMe}_2\text{Ph})_6]$  **4**, which has been characterised by IR,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy as well as X-ray analysis.§ The core structure of **4** is identical with that of **2** and this also substantiates the characterisation of the terminal sulfur atom in **2** as a thiol type sulfur atom. Saito and coworkers have recently reported that similar replacement of the SH group in **3** by a chloride ligand also takes place to afford the corresponding Mo cluster  $[\text{Mo}_4(\mu_3\text{-S})_2(\mu\text{-S})_4\text{Cl}_2(\text{PMe}_3)_6]$ .<sup>12</sup>

We have further found that treatment of  $\text{W}^{\text{III}}\text{W}^{\text{IV}}_2$  cluster **4** with an excess amount of  $\text{Na}/\text{Hg}$  in THF at room temperature



Scheme 1 Reagents and conditions: i,  $(\text{Me}_3\text{Si})_2\text{S}$ ,  $\text{MeOH}$ , toluene,  $50^\circ\text{C}$ ; ii,  $\text{SnCl}_2$ , THF, reflux; iii,  $\text{Na}/\text{Hg}$ , THF, room temp. ( $\text{P} = \text{PMe}_2\text{Ph}$ )

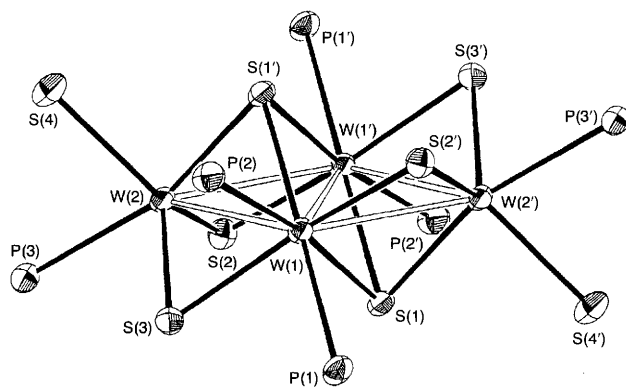
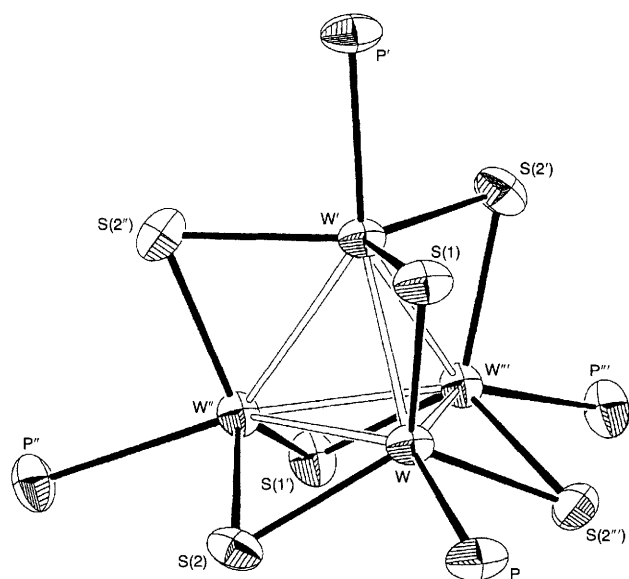


Fig. 1 Molecular structure of **2** (carbon and hydrogen atoms are omitted for clarity). The molecule has a crystallographically imposed inversion centre. Selected bond distances (Å):  $\text{W}(1)-\text{W}(1')$  2.8373(8),  $\text{W}(1)-\text{W}(2)$  2.8114(7),  $\text{W}(1)-\text{W}(2')$  2.8118(6),  $\text{W}(1)-\text{S}(1)$  2.380(2),  $\text{W}(1)-\text{S}(1')$  2.374(2),  $\text{W}(1)-\text{S}(2)$  2.435(3),  $\text{W}(1)-\text{S}(3)$  2.435(3),  $\text{W}(2)-\text{S}(1')$  2.393(2),  $\text{W}(2)-\text{S}(2')$  2.279(2),  $\text{W}(2)-\text{S}(3)$  2.274(2),  $\text{W}(2)-\text{S}(4)$  2.390(2),  $\text{W}(1)-\text{P}(1)$  2.606(3),  $\text{W}(1)-\text{P}(2)$  2.592(2),  $\text{W}(2)-\text{P}(3)$  2.513(3).



**Fig. 2** Molecular structure of **5** (carbon and hydrogen atoms are omitted for clarity). The molecule has a crystallographically imposed  $S_4$  axis passing through S(1) and S(1'). Selected bond distances (Å) and angles ( $^\circ$ ): W–W' 2.634(3), W–W'' 2.634(2), W–S(1) 2.32(1), W–S(2) 2.323(7), W–P 2.533(10), W'–W–W'' 60.00(3), W''–W–W''' 60.00(6), S(1)–W–S(2) 119.98(3), S(2)–W–S(2'') 119.99(6), S(1)–W–P 88.8(3), S(2)–W–P 89.5(2).

gives the  $W_4S_6$  cluster  $[W_4(\mu-S)_6(PMe_2Ph)_4]$  **5** in 10% yield as purple crystals upon recrystallization from THF–diethyl ether. $\S$  The structure of **5** determined by X-ray analysis consists of an almost regular tetrahedron of tungsten atoms with each edge bridged by a  $\mu$ -sulfido ligand; the  $W_4S_6P_4$  core has pseudo  $T_d$  symmetry (Fig. 2). $\ddagger$  The W–W bond lengths in **5** [2.634(3) Å] are substantially shorter than those in **2** [2.8114(7)–2.8373(8) Å]. There are six W–W bonds, which is consistent with the presence of 12  $d$  electrons in **5**.

The  $W_4S_6$  framework in **5** may be regarded as an adamantanoid core, which occurs in the cubic metal sulfide lattice known as the sphalerite or zinc blende structure. However, the coordination geometry around the W atom in **5** is fairly distorted from an ideal tetrahedral environment [S–W–P 89.2, S–W–S 120.0 $^\circ$  (mean)] due to the presence of W–W interactions. Atom connectivity of this type has previously been observed only in some discrete cluster molecules containing post-transition metals such as  $[M_{10}S_4(SPh)_{16}]^{4-}$  ( $M = Zn, Cd$ ) $^{13}$  and  $[Ge_4S_6Br_4]$ , $^{14}$  although thiolate-bridged  $M_4(SR)_6$  adamantanoid cores are more precedented. $^{15}$

Reductive condensation of sulfide–chloride clusters is now known as a practical synthetic method for sulfide clusters. $^{16}$  However, reductive core rearrangement of sulfide clusters maintaining the cluster nuclearity is less common and the present results may give a new rational route to prepare novel cluster cores. Further studies on the reactivities of tetratungsten sulfide clusters **2**, **4** and **5** towards organic, inorganic, and organometallic compounds are now in progress.

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## Footnotes

$\dagger$   $^1H$  NMR ( $[^2H_8]THF$ ):  $\delta$  8.12–7.06 (m, 30 H,  $PMe_2Ph$ ), 2.34 (d, 12 H,  $J = 7.9$  Hz, wingtip  $PMe_2Ph$ ), 1.61, 1.35 (br d, 12 H each,  $J = 6.8$  Hz, hinge  $PMe_2Ph$ ). Signals due to SH protons were not assignable.  $^{31}P\{^1H\}$  NMR ( $[^2H_8]THF$ ):  $\delta$  –17.9 ( $^1J_{WP} = 175$  Hz, wingtip  $PMe_2Ph$ ), –52.3 ( $^1J_{WP} = 167$  Hz, hinge  $PMe_2Ph$ ).

$\ddagger$  Crystal data for **2**:  $M = 1822.79$ ; monoclinic, space group  $P2_1/c$ ,  $a = 11.158(4)$ ,  $b = 21.408(1)$ ,  $c = 13.765(1)$  Å,  $\beta = 113.53(1)^\circ$ ,  $V = 3014(1)$  Å $^3$ ,  $Z = 2$ ,  $D_c = 2.008$  g cm $^{-3}$ ,  $\mu = 80.83$  cm $^{-1}$ ,  $F(000) = 1740$ ,  $R = 0.037$  and  $R_w = 0.026$  for 298 variables and 4266 unique reflections [ $I > 3.0\sigma(I)$ ]. For **5**:  $M = 1480.35$ ; tetragonal, space group  $I4_1/amd$ ,  $a = 23.160(4)$ ,  $c = 9.939(4)$  Å,  $V = 5331(2)$  Å $^3$ ,  $Z = 4$ ,  $D_c = 1.844$  g cm $^{-3}$ ,  $\mu = 89.86$  cm $^{-1}$ ,  $F(000) = 2752$ ,  $R = 0.049$  and  $R_w = 0.047$  for 61 variables and 717 unique reflections [ $I > 3.0\sigma(I)$ ]. Intensity data were collected on a Rigaku AFC7R diffractometer with the use of graphite-monochromated Mo–K $\alpha$  radiation and corrected for Lorentz-polarization effect as well as for absorption ( $\psi$  scans). Structure solution and refinements were carried out by using the TEXSAN program package. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

$\S$  Yield 63%.  $^1H$  NMR ( $[^2H_8]THF$ ):  $\delta$  7.98–7.08 (m, 30 H,  $PMe_2Ph$ ), 2.15 (br d, 12 H,  $J = 7.9$  Hz, wingtip  $PMe_2Ph$ ), 1.27 (br s, 12 H, hinge  $PMe_2Ph$ ). A signal ascribed to another hinge  $PMe_2Ph$  might be overlapping on the signals of non-deuteriated THF at  $\delta$  1.73.  $^{31}P\{^1H\}$  NMR ( $[^2H_8]THF$ ):  $\delta$  –18.3 (br s, wingtip  $PMe_2Ph$ ), –52.6 (s,  $^1J_{WP} = 169$  Hz, hinge  $PMe_2Ph$ ). Details of the structure of **4** will be reported elsewhere.

$\P$   $^1H$  NMR ( $[^2H_8]THF$ ):  $\delta$  8.00–7.25 (m, 20 H,  $PMe_2Ph$ ), 2.42 (d, 24 H,  $J = 6.3$  Hz,  $PMe_2Ph$ ).  $^{31}P\{^1H\}$  NMR ( $[^2H_8]THF$ ):  $\delta$  –3.8 (s,  $^1J_{WP} = 141$  Hz).

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