

# Reactions of $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$ with $\text{CuBr}$ in $\text{CHCl}_3$ : isolation and structures of an octanuclear cluster $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$ and a trinuclear cluster $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$

Jian-Ping Lang, Kazuyuki Tatsumi \*

Research Center for Materials Science, and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

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## Abstract

Reaction of  $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  with two equivalents of  $\text{CuBr}$  in  $\text{CHCl}_3$  produced an intriguing octanuclear cluster  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$  (**1**) in 80% yield. When this reaction was carried out in the presence of excess  $\text{PPh}_3$ , a trinuclear cluster  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$  (**2**) was isolated in 87% yield. Both **1** and **2** were characterized fully. In the structure of **1**, four  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  fragments are linked by Cu atoms through interactions with  $\mu_2\text{-S}$  and  $\mu_3\text{-S}$  bridges, forming an unusual square  $\text{W}_4\text{Cu}_4$  core with an approximate  $S_4$  symmetry, while **2** consists of an incomplete cubane  $[\text{WS}_3\text{Cu}_2\text{Br}]$  core. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Tungsten complex; Copper complex; Sulfide; Cluster

## 1. Introduction

In the past 2 decades, chemistry of transition metal chalcogenide clusters [1–7], especially those derived from thiomolybdates and thiotungstates, has been developed due to their relevance to biological systems [8–10], catalysis [11–13], and photonic materials [14–16]. It is known that selection of suitable solvents is critically important for the preparation of specific chalcogenide cluster complexes. In some cases, a given reaction system may produce different compounds depending on the choice of the solvent [17–20]. For instance, the reaction of  $[\text{NiCl}_2(\text{PPh}_3)_2]$  with two equivalents of  $(\text{Me}_3\text{Si})_2\text{Se}$  in toluene was reported to give a neutral cluster  $[\text{Ni}_{34}\text{Se}_{22}(\text{PPh}_3)_{10}]$  [17], while in acetonitrile it led to isolation of an anionic cluster  $[\text{Ni}_{12}\text{Se}_{11}\text{Cl}(\text{PPh}_3)_8][\text{NiCl}_3(\text{PPh}_3)_2]$  [18]. We have interested in construction of heterometallic clusters based on

the organometallic trisulfido complex anions,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MS}_3]^{n-}$  ( $\text{M}=\text{Nb}, \text{Ta}$  ( $n=2$ ) [21,22];  $\text{M}=\text{W}, \text{Mo}$  ( $n=1$ ) [23,24]) [25–30]. Recently we communicated that the reaction of  $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  with  $\text{CuBr}$  in  $\text{CH}_3\text{CN}$  produced a double incomplete-cubane cluster  $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_3]_2$  [26], which in turn reacted with excess  $\text{PPh}_3$  to yield a tetranuclear cluster  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_2(\text{PPh}_3)_2]$  [29]. Re-examination of the above reaction in  $\text{CHCl}_3$  resulted in isolation of an unusual octanuclear neutral cluster  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$  (**1**). When an excess amount of  $\text{PPh}_3$  was added to the reaction system in  $\text{CHCl}_3$ , a neutral trinuclear cluster  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$  (**2**) was generated. Herein, we report the syntheses and structural characterization of these two new clusters.

## 2. Results and discussion

When two equivalents of  $\text{CuBr}$  were added to a red solution of  $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  in  $\text{CHCl}_3$ , the color

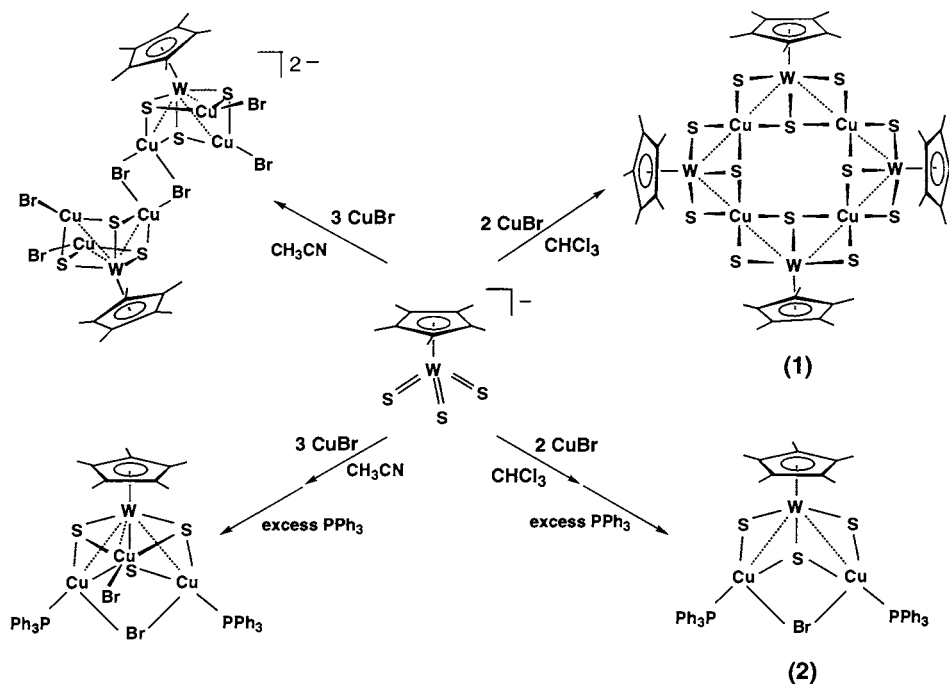
\* Corresponding author.

turned dark red immediately. The solution was stirred at room temperature overnight and then concentrated. By layering Et<sub>2</sub>O onto the concentrated solution, [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu]<sub>4</sub> (**1**) was isolated as dark red crystals in 80% yield. The formation of the octanuclear cluster **1** contrasts to the analogous reaction carried out in CH<sub>3</sub>CN, which gave a double incomplete-cubane cluster [PPh<sub>4</sub>]<sub>2</sub>[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>3</sub>Br<sub>3</sub>]<sub>2</sub> [26]. The remarkable difference in products between the two reactions may be ascribed to different solubility in CHCl<sub>3</sub> and CH<sub>3</sub>CN. Compound **1** is very soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, while it is nearly insoluble in CH<sub>3</sub>CN. On the contrary, [PPh<sub>4</sub>]<sub>2</sub>[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>3</sub>Br<sub>3</sub>]<sub>2</sub> does not dissolve in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, but dissolves readily in CH<sub>3</sub>CN. An interesting facet of the reaction in CHCl<sub>3</sub> is that, the bromine atom of CuBr is removed completely, while for the reaction in CH<sub>3</sub>CN, the CuBr unit is intact. Complete loss of halide or pseudohalide of M'X (M' = Cu(I), Ag(I); X = Cl, Br, I, CN, NCS) is rare in the cluster forming reactions with [MO<sub>4-n</sub>S<sub>n</sub>]<sup>2-</sup> (M = Mo, W; n = 1 ~ 4). The single example is the formation of an anionic icosanuclear cluster [Bu<sub>4</sub>N]<sub>4</sub>[(MoS<sub>4</sub>)<sub>8</sub>Cu<sub>12</sub>] [31], which was prepared from the solid state reaction of (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] with CuCN and Bu<sub>4</sub>NBr at 90°C. In this case, all the cyanide groups of CuCN are lost during the reaction. On the other hand, treatment of [PPh<sub>4</sub>][(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>] in CHCl<sub>3</sub> with two equivalents of CuBr followed by addition of excess PPh<sub>3</sub> afforded a neutral trinuclear cluster [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>2</sub>Br(PPh<sub>3</sub>)<sub>2</sub>] (**2**) in 83% yield. Again, this product is different from

the tetranuclear neutral cluster [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>3</sub>Br<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] which was isolated from the analogous reaction carried out in CH<sub>3</sub>CN [29] (Scheme 1).

Both **1** and **2** are stable toward oxygen and moisture, and **2** is again soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, but is only slightly soluble in CH<sub>3</sub>CN. As the electronic spectrum of [PPh<sub>4</sub>][(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>] in CHCl<sub>3</sub> features a strong absorption band at 381 nm, the bands at 421 (**1**) and 391 (**2**) nm observed in the spectra of **1** and **2** in CHCl<sub>3</sub> are probably originated from sulfur-to-tungsten charge-transfer transitions of the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub> moiety. The <sup>1</sup>H-NMR spectrum of **1** in CDCl<sub>3</sub> shows a single η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> signal at 2.13 ppm, while that of **2** in CD<sub>2</sub>Cl<sub>2</sub> consists of a singlet at 1.97 ppm for η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> and multiplets in the 7.36–7.68 ppm region for PPh<sub>3</sub>. In the <sup>31</sup>P {<sup>1</sup>H}-NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub>, the signal at 9.54 (w<sub>1/2</sub> = 154 Hz) is broadened slightly, probably due to couplings between the <sup>31</sup>P and <sup>63</sup>Cu(<sup>65</sup>Cu) nuclei. The FT-IR spectra of **1** and **2** display bands arising from the W–S<sub>br</sub> stretching vibrations at 454/435/405 (**1**) and 430/405 (**2**) cm<sup>-1</sup>, respectively.

The molecular structure of **1** is shown in Fig. 1 and the selected bond distances and angles are given in Table 1. The molecule is composed of four (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub> units connected by four Cu atoms, forming a 'four-flier pin-wheel' structure with an approximate S<sub>4</sub> symmetry. The W<sub>4</sub>Cu<sub>4</sub> core structure resembles those of [Et<sub>4</sub>N]<sub>4</sub>[MOS<sub>3</sub>Cu]<sub>4</sub> (M=Mo, W) [32], in which four [MOS<sub>3</sub>]<sup>2-</sup> moieties are linked by four Cu atoms via sulfur bridges. Within the W<sub>4</sub>Cu<sub>4</sub> cluster core of **1**, the



Scheme 1.

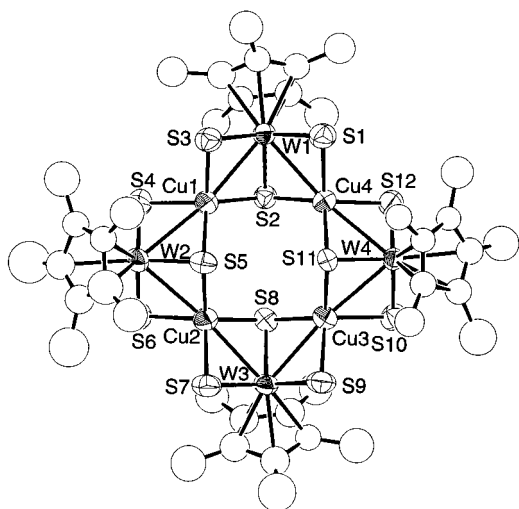


Fig. 1. Molecular structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$  (**1**), with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity

four W and four Cu atoms are coplanar, with the maximum deviation from the least-squares plane being 0.3 Å. Each copper atom moves inward from the midpoint of each edge of the  $W_4$  square, and the average W–Cu–W angle is  $172^\circ$ . The  $\eta^5\text{-C}_5\text{Me}_5$  groups are situated alternatively above and below the  $W_4\text{Cu}_4$  mean plane, and so are the bridging sulfur atoms. Each of the four  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  units adopts a slightly distorted three-legged piano-stool structure, and the  $S_3$  plane parallels to the  $\eta^5\text{-C}_5\text{Me}_5$  ring (dihedral angle =  $0.76 \sim 1.97^\circ$ ). The average W– $\mu_3$ -S and W– $\mu_2$ -S bond lengths, 2.287 and 2.213 Å, are comparable to those of  $[\text{PPh}_4][\{(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\}_3\text{S}_2]$  ((W– $\mu_3$ -S)<sub>av</sub> = 2.292 Å, (W– $\mu_2$ -S)<sub>av</sub> = 2.232 Å) [28]. The mean W–Cu bond length of 2.751 Å, which is similar to that of  $[\text{Et}_4\text{N}]_4[\text{WOS}_3\text{Cu}]_4$  (2.747 Å) and is slightly longer than those of  $[\text{PPh}_4][\{(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\}_3\text{S}_2]$  (2.678 Å) [28] and  $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_3]_2$  (2.660 Å) [26], suggests the presence of weak metal–metal interactions between  $d^{10}$  Cu<sup>I</sup> and  $d^0$  W<sup>VI</sup>. All the Cu atoms adopt a tetrahedral geometry coordinated by two  $\mu_2$ -S and two  $\mu_3$ -S atoms. The mean Cu–S bond length of 2.290 Å is normal, being similar to those of  $[\text{PPh}_4][\{(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\}_3\text{S}_2]$  (2.222 Å) and  $[\text{PPh}_4]_2[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_3]_2$  (2.230 Å). Interestingly, the average Cu–( $\mu_3$ -S)–Cu bond angle ( $104^\circ$ ) is somewhat smaller than that of  $[\text{Et}_4\text{N}]_4[\text{WOS}_3\text{Cu}]_4$  ( $112^\circ$ ). The cavity of the tetrahedral hollow site at the center of the molecule is small, where the distances between the  $\mu_3$ -S atoms are in the range from 3.77 to 3.90 Å.

The molecular structure of **2** is shown in Fig. 2, and the selected bond lengths and angles are listed in Table 2. The structure of **2** is very close to that of

Table 1

Bond distances (Å) and angles ( $^\circ$ ) for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$  (**1**)

W(1)–Cu(1)	2.750(3)	W(1)–Cu(4)	2.754(3)
W(2)–Cu(1)	2.745(3)	W(2)–Cu(2)	2.745(3)
W(3)–Cu(2)	2.742(3)	W(3)–Cu(3)	2.753(3)
W(4)–Cu(3)	2.761(3)	W(4)–Cu(4)	2.758(3)
W(1)–S(1)	2.191(7)	W(1)–S(2)	2.297(6)
W(1)–S(3)	2.218(6)	W(2)–S(4)	2.205(7)
W(2)–S(5)	2.300(7)	W(2)–S(6)	2.227(7)
W(3)–S(7)	2.211(6)	W(3)–S(8)	2.270(6)
W(3)–S(9)	2.206(8)	W(4)–S(10)	2.227(7)
W(4)–S(11)	2.282(5)	W(4)–S(12)	2.221(6)
Cu(1)–S(2)	2.292(6)	Cu(1)–S(3)	2.292(7)
Cu(1)–S(4)	2.304(8)	Cu(1)–S(5)	2.279(7)
Cu(2)–S(5)	2.271(7)	Cu(2)–S(6)	2.313(8)
Cu(2)–S(7)	2.294(7)	Cu(2)–S(8)	2.274(6)
Cu(3)–S(8)	2.273(7)	Cu(3)–S(9)	2.294(7)
Cu(3)–S(10)	2.314(7)	Cu(3)–S(11)	2.274(7)
Cu(4)–S(1)	2.311(7)	Cu(4)–S(2)	2.265(7)
Cu(4)–S(11)	2.289(6)	Cu(4)–S(12)	2.305(7)
S(2)AS(5)	3.90	S(2)AS(8)	3.77
S(2)AS(11)	3.88	S(5)AS(8)	3.82
S(5)AS(11)	3.76	S(8)AS(11)	3.86
Cu(1)–W(1)–Cu(4)	80.89(9)	Cu(1)–W(2)–Cu(2)	81.52(9)
Cu(2)–W(3)–Cu(3)	82.27(9)	Cu(3)–W(4)–Cu(4)	80.70(9)
S(1)–W(1)–S(2)	106.6(2)	S(1)–W(1)–S(3)	103.2(3)
S(2)–W(1)–S(3)	106.7(2)	S(4)–W(2)–S(5)	107.0(2)
S(4)–W(2)–S(6)	103.2(3)	S(5)–W(2)–S(6)	106.9(2)
S(7)–W(3)–S(8)	106.8(2)	S(7)–W(3)–S(9)	103.5(3)
S(8)–W(3)–S(9)	106.4(2)	S(10)–W(4)–S(11)	106.5(2)
S(10)–W(4)–S(12)	103.6(3)	S(11)–W(4)–S(12)	106.8(2)
W(1)–Cu(1)–W(2)	170.3(1)	W(2)–Cu(2)–W(3)	173.6(1)
W(3)–Cu(3)–W(4)	171.5(1)	W(1)–Cu(4)–W(4)	171.4(1)
Cu(1)–S(2)–Cu(4)	103.2(3)	Cu(1)–S(5)–Cu(2)	103.9(3)
Cu(2)–S(8)–Cu(3)	105.3(3)	Cu(3)–S(11)–Cu(4)	103.1(3)

silver analogue which we reported earlier [27]. The W– $\mu_2$ -S (2.224 Å) and W– $\mu_3$ -S (2.296 Å) bond lengths are similar to the corresponding distances of **1** and  $[(\mu^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Ag}_2\text{Br}(\text{PPh}_3)_2]$  ((W– $\mu_2$ -S)<sub>av</sub> = 2.213 Å, W– $\mu_3$ -S = 2.275 Å) [27], while the mean W–Cu bond of 2.704 Å is shortened slightly compared with that of **1**. Each Cu atom is bound to  $\mu_2$ -Br, P(PPh<sub>3</sub>),  $\mu_2$ -S, and one  $\mu_3$ -S, forming a distorted tetrahedral coordination geometry. It is interesting to compare the structure of **2** with that of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_2(\text{PPh}_3)_2]$  [29]. Formally, the latter structure is made by addition of one CuBr group to the cluster framework of **2**, forming an open  $\text{WS}_3\text{Cu}_3\text{Br}$  cube where one Cu–Br bond is broken. Like in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_2(\text{PPh}_3)_2]$ , the bridging Br atom in **2** moves out of the triangular face of Cu(1), S(1) and Cu(2). The bond angle, Cu(1)–( $\mu_2$ -Br)–Cu(2) ( $66^\circ$ ), is more acute than that of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_2(\text{PPh}_3)_2]$  ( $68^\circ$ ). The mean Cu– $\mu_2$ -Br length (2.640 Å) within this linkage is similar to that of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_3\text{Br}_2(\text{PPh}_3)_2]$  (2.646 Å), but is much longer than those of  $[\text{Et}_4\text{N}]_4[\text{Cu}_2\text{Br}_4]$  (2.448 Å) [33] and  $[\text{Pr}_4\text{N}]_4[\text{Cu}_4\text{Br}_6]$  (2.398 Å) [34].

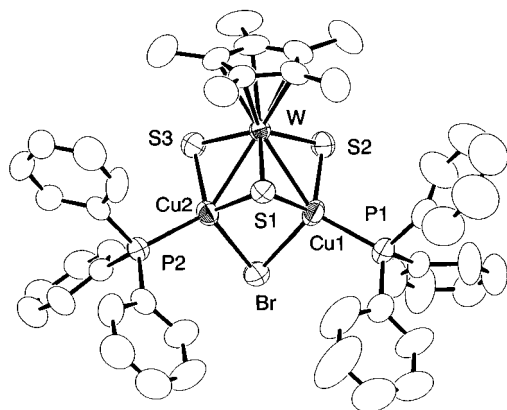


Fig. 2. Molecular structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$  (**2**), with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity

### 3. Experimental

#### 3.1. General

All manipulations were carried out under argon using standard Schlenk techniques. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon.  $^1\text{H-NMR}$  spectra were recorded at an ambient temperature on a Varian UNITYplus-500 spectrometer.  $^1\text{H-NMR}$  chemical shifts were referenced to the  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  signal, and the  $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shift for **2** was relative to 85%  $\text{H}_3\text{PO}_4$ . FT-IR spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer using KBr discs. UV-vis spectra were measured on a JASCO V-560 spectrophotometer. The elemental analyses for C, H, and S were performed on a LECO-CHNS microanalyzer, using the samples dried in vacuo for a prolonged period in order to remove crystal solvents.

Table 2  
Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$  (**2**)

W–Cu(1)	2.706(1)	W–Cu(2)	2.701(1)
W–S(1)	2.296(2)	W–S(2)	2.226(2)
W–S(3)	2.223(3)	Cu(1)–S(1)	2.281(3)
Cu(1)–S(2)	2.255(3)	Cu(2)–S(1)	2.281(3)
Cu(2)–S(3)	2.259(3)	Cu(1)–Br	2.668(2)
Cu(2)–Br	2.612(2)	Cu(1)–P(1)	2.217(3)
Cu(2)–P(2)	2.215(3)		
S(1)–W–S(2)	105.18(9)	S(1)–W–S(3)	105.53(9)
S(2)–W–S(3)	104.71(10)	Cu(1)–W–Cu(2)	64.18(4)
S(1)–Cu(1)–S(2)	104.75(1)	S(1)–Cu(2)–S(3)	104.83(9)
W–S(1)–Cu(1)	72.48(7)	W–S(1)–Cu(2)	72.35(8)
W–S(2)–Cu(1)	72.48(7)	W–S(3)–Cu(2)	72.35(8)
Cu(1)–S(1)–Cu(2)	78.05(8)	Cu(1)–Br–Cu(2)	65.90(4)
Br–Cu(1)–S(1)	102.07(8)	Br–Cu(1)–S(2)	108.99(9)
Br–Cu(2)–S(3)	108.90(8)	Br–Cu(2)–S(1)	103.83(8)

#### 3.2. Syntheses

##### 3.2.1. $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}]_4$ (**1**)

To a red solution of  $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  (0.13 g, 0.17 mmol) in  $\text{CHCl}_3$  ( $25\text{ cm}^3$ ) was added  $\text{CuBr}$  (0.050 g, 0.34 mmol). The solution became dark red within minutes and was allowed to stir at room temperature overnight. After the solution was concentrated to ca.  $3\text{ cm}^3$  in vacuo and filtered. The filtrate was layered with  $\text{Et}_2\text{O}$  ( $6\text{ cm}^3$ ) to produce dark red prisms of **1**· $2\text{CHCl}_3$  in 4 days, which were collected by filtration, washed with  $\text{CHCl}_3/\text{Et}_2\text{O}$  (1:4), and dried in vacuo. Yield: 0.065 g, 79.9% (Found: C, 25.24; H, 3.15; S, 19.48.  $\text{C}_{40}\text{H}_{60}\text{Cu}_4\text{S}_{12}\text{W}_4$  requires C, 25.08; H, 3.16; S, 20.09%).  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): d 2.21 (60H, s,  $\eta^5\text{-C}_5\text{Me}_5$ ). IR ( $\tilde{\nu}\text{ cm}^{-1}$ ): 1375 (s), 1109 (w), 1022 (s), 804 (w), 454 (m), 435 (s), 405 (w)  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ) ( $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$ )): 421 (17300).

##### 3.2.2. $[(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3\text{Cu}_2\text{Br}(\text{PPh}_3)_2]$ (**2**)

To a red solution of  $[\text{PPh}_4][(\eta^5\text{-C}_5\text{Me}_5)\text{WS}_3]$  (0.12 g, 0.16 mmol) in  $\text{CHCl}_3$  ( $30\text{ cm}^3$ ) was added  $\text{CuBr}$  (0.05 g, 0.32 mmol) with stirring. After 24 h,  $\text{PPh}_3$  (0.25 g, 0.96 mmol) was added to the solution and stirred for another 1 h. The solution was then concentrated to ca.  $3\text{ cm}^3$  in vacuo and layered by diethyl ether ( $6\text{ cm}^3$ ). Dark red prisms of **2**· $2\text{CHCl}_3$  were formed after 2 days, which were collected by filtration, washed with  $\text{CHCl}_3/\text{Et}_2\text{O}$  (1:4), and dried in vacuo. Yield: 0.16 g (87.2%) (Found: C, 48.32; H, 3.91; S, 8.89.  $\text{C}_{46}\text{H}_{45}\text{BrCu}_2\text{P}_2\text{S}_3\text{W}$  requires C, 48.17; H, 3.96; S, 8.39%).  $^1\text{H-NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ): d 7.36–7.68 (30H, m,  $\text{PPh}_3$ ), 1.97 (15H, s,  $\eta^5\text{-C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ): d 9.54 (br s,  $w_{1/2} = 154\text{ Hz}$ ). IR ( $\tilde{\nu}\text{ cm}^{-1}$ ): 1480 (s), 1436 (vs), 1374 (m), 1183 (w), 1096 (s), 1027 (m), 745 (s), 694 (vs), 521 (vs), 430 (m), 405 (w)  $\text{cm}^{-1}$ . UV-vis ( $\text{CHCl}_3$ ) ( $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$ )): 391 (9400).

#### 3.3. X-ray crystallography

X-ray quality crystals of **1**· $2\text{CHCl}_3$  and **2**· $2\text{CHCl}_3$  were obtained by recrystallization from  $\text{CHCl}_3/\text{Et}_2\text{O}$ . Diffraction data were collected on a Rigaku AFC7R diffractometer at ambient temperature by using graphite-monochromatized  $\text{Mo-K}\alpha$  radiation ( $0.71079\text{ \AA}$ ). A dark red single crystal of **1**· $2\text{CHCl}_3$  with dimensions  $0.25 \times 0.40 \times 0.30\text{ mm}$  was sealed in a capillary under argon, while a dark red single crystal of **2**· $2\text{CHCl}_3$  with dimensions  $0.45 \times 0.35 \times 0.30\text{ mm}$  was mounted on the top of a glass fiber. Cell constants and an orientation matrix for data collection were obtained from least-squares refinements using the setting angles of  $23^\circ$  (**1**· $2\text{CHCl}_3$ ) and  $25^\circ$  (**2**· $2\text{CHCl}_3$ ) carefully centered reflections in the range  $29.75^\circ < 2\theta < 31.37^\circ$  for **1**· $2\text{CHCl}_3$  and  $22.33^\circ < 2\theta < 24.81^\circ$  for **2**· $2\text{CHCl}_3$ . The intensities of three representative reflections monitored

Table 3  
Crystallographic data for **1**·2CHCl<sub>3</sub> and **2**·2CHCl<sub>3</sub>

	<b>1</b> ·2CHCl <sub>3</sub>	<b>2</b> ·2CHCl <sub>3</sub>
Empirical formula	C <sub>42</sub> H <sub>62</sub> Cl <sub>6</sub> Cu <sub>4</sub> S <sub>12</sub> W <sub>4</sub>	C <sub>48</sub> H <sub>47</sub> BrCl <sub>6</sub> Cu <sub>2</sub> P <sub>2</sub> S <sub>3</sub> W
<i>M<sub>r</sub></i>	2153.97	1385.59
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	17.035(6)	14.644(6)
<i>b</i> (Å)	14.014(6)	19.068(8)
<i>c</i> (Å)	26.507(8)	10.620(5)
$\alpha$ (°)	–	102.41(4)
$\beta$ (°)	94.62(3)	103.01(3)
$\gamma$ (°)	–	102.16(4)
<i>V</i> (Å <sup>3</sup> )	6319(3)	2715(2)
<i>Z</i>	4	2
$\lambda$ (Mo–K $\alpha_1$ ) (Å)	0.71069	0.71069
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	2.264	1.695
$\mu$ (cm <sup>-1</sup> )	92.55	41.31
2 $\theta$ <sub>max</sub> (°)	45.0	50.0
No. reflections collected	9016	10202
No. independent reflections	8673	9585
No. observed reflections ( <i>I</i> > 3.00 $\sigma$ ( <i>I</i> ))	4614	7227
No. parameters refined	373	544
<i>R</i> <sup>a</sup>	0.058	0.049
<i>R<sub>w</sub></i> <sup>b</sup>	0.068	0.065
GOF <sup>c</sup>	1.91	1.98
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	2.83	2.64
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.89	–2.66

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = \{ \sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2 \}^{1/2}$$

<sup>c</sup> GOF =  $\{ \sum w (|F_o| - |F_c|)^2 / (M - N) \}^{1/2}$ , where *M* = number of reflections and *N* = number of parameters.

every 150 reflections showed no sign of significant decay. An empirical absorption correction using the  $\psi$  scan technique was applied, which resulted in transmission factors ranging from 0.38 to 1.00 for **1**·2CHCl<sub>3</sub> and from 0.59 to 1.00 for **2**·2CHCl<sub>3</sub>. The data were also corrected for Lorentz and polarization effects.

The structures of **1**·2CHCl<sub>3</sub> and **2**·2CHCl<sub>3</sub> were solved by direct methods [35,36] and expanded using Fourier techniques [37]. All non-hydrogen atoms, apart from the C atoms of  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> groups in **1**·2CHCl<sub>3</sub>, were refined anisotropically, and hydrogen atoms were put at calculated positions without refinement. Some carbon atoms from the phenyl groups in **2**·2CHCl<sub>3</sub> were refined with relatively high anisotropic temperature factors. The crystal of **1** appears to contain two CHCl<sub>3</sub> solvent molecules in an asymmetric unit. One CHCl<sub>3</sub> solvent molecule was located clearly and the atom positions were refined isotropically. The other CHCl<sub>3</sub> was found to be disordered severely and we could locate a fully occupied C position and three Cl atom positions with a half occupancy. The crystal of **2** contains two CHCl<sub>3</sub> solvent molecules in an asymmetric unit. One was refined anisotropically. The carbon in the other CHCl<sub>3</sub> was found on the Fourier map and put on

the fixed position, and the three Cl atoms were refined isotropically. Neutral atom scattering factors were taken from Cromer and Waber [38], and anomalous dispersion effects were included in *F<sub>c</sub>* [39]. Crystallographic calculations were carried out with a teXsan crystallographic software package of the Molecular Structure Corp. (1985 and 1992). Crystallographic data for **1**·2CHCl<sub>3</sub> and **2**·2CHCl<sub>3</sub> are summarized in Table 3.

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