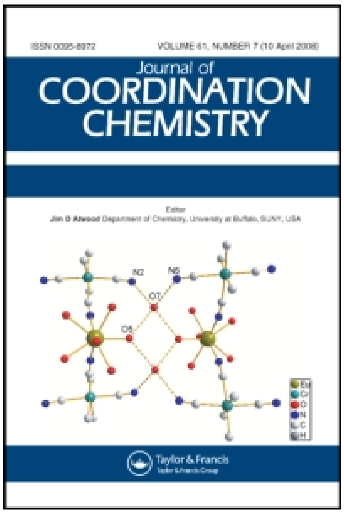

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SYNTHESIS AND CHARACTERIZATION OF W=W DOUBLY-BONDED DIMERS $[\eta^5\text{-RC}_5H_4W(CO)(\mu\text{-SPh})]_2$ AND $[\eta^5\text{-RC}_5H_4W(\mu\text{-Se})(\mu\text{-SPh})]_2$ (R=MeO_2C, EtO_2C). CRYSTAL AND MOLECULAR STRUCTURE OF *TRANS/SYN*-$[\eta^5\text{-EtO}_2CC_5H_4W\ (\mu\text{-SPh})]_2$

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SYNTHESIS AND CHARACTERIZATION OF W=W DOUBLY-BONDED DIMERS $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}(\mu\text{-SPh})]_2$ AND $[\eta^5\text{-RC}_5\text{H}_4\text{W}(\mu\text{-Se})(\mu\text{-SPh})]_2$ (R=MeO_2C, EtO_2C). CRYSTAL AND MOLECULAR STRUCTURE OF *TRANS/SYN*-$[\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{W}(\mu\text{-Se})(\mu\text{-SPh})]_2$

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The reaction of triply-bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{W}]_2$ with diphenyldisulfide affords doubly-bridged and doubly-bonded dimers *trans/anti*-$[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}(\mu\text{-SPh})]_2$ (**1a**, R = MeO_2C; **2a**, R = EtO_2C) and *trans/syn*-$[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}(\mu\text{-SPh})]_2$ (**1b**, R = MeO_2C; **2b**, R = EtO_2C). Further reaction of a mixture of the *trans/anti* and *trans/syn* isomers with elemental selenium leads to quadruply-bridged and doubly-bonded dimers, *trans/anti*-$[\eta^5\text{-RC}_5\text{H}_4\text{W}(\mu\text{-Se})(\mu\text{-SPh})]_2$ (**3a**, R = MeO_2C; **4a**, R = EtO_2C) and *trans/syn*-$[\eta^5\text{-RC}_5\text{H}_4\text{W}(\mu\text{-Se})(\mu\text{-SPh})]_2$ (**3b**, R = MeO_2C; **4b**, R = EtO_2C). All the above bridged W = W doubly-bonded dimers have been characterized by analysis, IR, ^{1}H NMR and MS spectroscopies, as well as for **4b** by X-ray crystallography.

Keywords: Tungsten multiple bond; diphenyldisulfide; selenium; synthesis; crystal structure

INTRODUCTION

The group 6 metal–metal doubly-bonded dimers $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}(\mu\text{-SR}')]_2$ (M = Cr, Mo, W; η^5-RC_5H_4 = parent and substituted cyclopentadienyls) are of great interest and potentially useful in synthesizing group 6 metal-containing organometallic complexes.[1–4] However, although the synthesis,

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* Corresponding author.

structure and reactivities of the molybdenum dimers have been well-documented, those of the tungsten analogues are little explored and only one such tungsten dimer has been reported in the literature.[5] In this paper we describe the synthesis of four doubly-bridged and doubly-bonded tungsten dimers, *trans/anti*-$[\eta^5\text{-RC}_5H_4W(CO)(\mu\text{-SPh})]_2$ (**1a**, R = MeO_2C; **2a**, R = EtO_2C) and *trans/syn*-$[\eta^5\text{-RC}_5H_4W(CO)(\mu\text{-SPh})]_2$ (**1b**, R = MeO_2C; **2b**, R = EtO_2C) and the reaction of **1a–b** or **2a–b** with elemental selenium to afford four quadruply-bridged and doubly-bonded tungsten dimers, *trans/anti*-$[\eta^5\text{-RC}_5H_4W(\mu\text{-Se})(\mu\text{-SPh})]_2$ (**3a**, R = MeO_2C; **4a**, R = EtO_2C) and *trans/syn*-$[\eta^5\text{-RC}_5H_4W(\mu\text{-Se})(\mu\text{-SPh})]_2$ (**3b**, R = MeO_2C; **4b**, R = EtO_2C), as well as the molecular structure of **4b** determined by X-ray diffraction methods.

EXPERIMENTAL

All reactions were carried out under a highly pre-purified nitrogen atmosphere using vacuum-line techniques. Toluene was distilled from sodium-benzophenone ketyl under nitrogen. Preparative TLC was carried out on glass plates (26 × 19 cm) coated with silica gel G (10–40 μm). Gray selenium powder was of commercial origin and used as received; $[\eta^5\text{-RC}_5H_4(CO)_2W]_2$ (R = MeO_2C, EtO_2C)[6] and Ph_2S_2[7] were prepared according to literature methods. IR spectra were recorded on Nicolet FT-5DX and Bio-Rad FTS-40 infrared spectrophotometers. ^1H NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer. C/H analyses and MS determinations were performed by a 240 C analyzer and HP 5988A spectrometer, respectively. Melting points were determined on a Yanaco MP-500 micro-melting point apparatus.

Trans/anti-$[\eta^5\text{-MeO}_2CC_5H_4W(CO)(\mu\text{-SPh})]_2$ (1a) and *Trans/syn*-$[\eta^5\text{-MeO}_2CC_5H_4W(CO)(\mu\text{-SPh})]_2$ (1b)

A 100 cm³ two-necked flask fitted with a magnetic stir-bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.150 g (0.207 mmol) of $[\eta^5\text{-MeO}_2CC_5H_4(CO)_2W]_2$, 0.045 g (0.206 mmol) of Ph_2S_2 and 15 cm³ of toluene. The mixture was refluxed for 3 h. Solvent was removed and the residue was subjected to column chromatography using CH_2Cl_2 as eluent. The first green band gave 0.069 g (38%) of **1a**, the following brown-purple band gave 0.050 g (27%) of **1b**; **1a**: m.p. 213–215°C; *anal.* calcd. for $C_{28}H_{24}O_6S_2W_2$(%): C, 37.85; H, 2.72; found: C, 37.50; H, 2.89; IR (KBr disc): $\nu_{C\equiv O}$ 1860(vs); $\nu_{C=O}$ 1713(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.60 (s, 6H, $2CH_3$), 5.44 (m, 2H of $2C_5H_4$ rings), 5.76 (m, 4H of $2C_5H_4$ rings), 5.96 (m, 2H of $2C_5H_4$ rings), 7.20–7.52 (m, 10H, $2C_6H_5$) ppm; **1b**: m.p. 202–203°C; *anal.* calcd. for $C_{28}H_{24}O_6S_2W_2$(%): C, 37.85; H, 2.72; found: C, 37.86; H, 2.77; IR (KBr disc): $\nu_{C\equiv O}$ 1852(vs), 1918(s); $\nu_{C=O}$ 1721(s) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.52 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 5.50 (t, 2H, (H^3, H^4)), 5.78 (t, 2H, (H^2, H^5)), 5.96 (t, 2H, (H^3, H^4)), 6.08 (t, 2H, (H^2, H^5)), 7.08–7.48 (m, 10H, $2C_6H_5$) ppm; MS (EI), *m/z* (relative intensity); 523[$(MeO_2CC_5H_4)W_2S^+$, 1.1], 307($MeO_2CC_5H_4W^+$, 0.8), 186 (Ph_2S^+, 3.6), 184 (W^+, 1.9), 154 (Ph_2^+, 13.0), 109 (PhS^+, 10.4), 92 ($C_5H_4(CO)^+$, 55.0), 77 (Ph^+, 100).

***Trans/anti*-[η^5-$EtO_2CC_5H_4W(CO)(\mu$-SPh)]$_2$ (2a) and *Trans/syn*-[η^5-$EtO_2CC_5H_4W(CO)(\mu$-SPh)]$_2$ (2b)**

A similar reaction of 0.150 g (0.199 mmol) of [η^5-$EtO_2CC_5H_4(CO)_2W]_2$, and 0.044 g (0.202 mmol) of Ph_2S_2 in 15 cm^3 of toluene afforded 0.079 g (43%) of **2a** and 0.064 g (35%) of **2b**; **2a**: m.p. 203–205°C; *anal.* calcd. for $C_{30}H_{28}O_6S_2W_2$(%): C, 39.32; H, 3.08; found: C, 39.12; H, 3.06; IR (KBr disc): $\nu_{C\equiv O}$ 1868(vs); $\nu_{C=O}$ 1713(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.12 (s, 6H, $2CH_3$), 4.06 (q, 4H, $2CH_2$), 5.36 (m, 2H of $2C_5H_4$ rings), 5.72 (m, 4H of $2C_5H_4$ rings), 5.88 (m, 2H of $2C_5H_4$ rings), 7.00–7.52 (m, 10H, $2C_6H_5$) ppm; MS (EI), *m/z* (relative intensity): 888 ($(M-CO)^+$, 1.0), 860 ($(M-2CO)^+$, 2.7) 665 ($(C_5H_4)_2W_2(CO)S(SPh)^+$, 1.1), 650 ($C_5H_4W_2(SPh)_2^+$, 1.4), 637 ($(C_5H_4)_2W_2S(SPh)^+$, 1.9), 586 ($W_2(SPh)_2^+$, 3.1), 560 ($(C_5H_4)_2W_2S_2^+$, 1.4), 528 ($(C_5H_4)_2W_2S^+$, 3.0), 509 ($W_2S(SPh)^+$, 1.4), 496 ($(C_5H_4)_2W_2^+$, 0.8), 432 ($W_2S_2^+$, 0.3), 368 ($W_2^+$, 0.6), 109 ($PhS^+$, 3.3), 92 ($C_5H_4(CO)^+$, 14.6), 77 ($Ph^+$, 16.5); **2b**: m.p. 179–181°C; *anal.* calcd. for $C_{30}H_{28}O_6S_2W_2$(%): C, 39.32; H, 3.08; found: C, 39.35; H, 2.87; IR (KBr disc): $\nu_{C\equiv O}$ 1836(vs), 1918(vs); $\nu_{C=O}$ 1713(s) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 0.84 (t, 3H, CH_3, J = 7.2 Hz), 1.16 (t, 3H, CH_3, J = 7.2 Hz), 3.88 (q, 2H, CH_2, J = 7.2 Hz), 4.14 (q, 2H, CH_2, J = 7.2 Hz), 5.40 (t, 2H, (H^3, H^4)), 5.68 (t, 2H, (H^2, H^5)), 5.86 (t, 2H, (H^3, H^4)), 5.96 (t, 2H, (H^2, H^5)), 7.04–7.40 (m, 10H, $2C_6H_5$) ppm.

***Trans/anti*-[η^5-$MeO_2CC_5H_4W(\mu$-Se)(μ-SPh)]$_2$ (3a) and *Trans/syn*-[η^5-$MeO_2CC_5H_4W(\mu$-Se)(μ-SPh)]$_2$ (3b)**

A flask as described above was charged with 0.405 g (0.456 mmol) of [η^5-$MeO_2CC_5H_4W(CO)(\mu$-SPh)]$_2$, 0.144 g (1.824 mmol) of selenium powder and 30 cm^3 of toluene. The mixture was refluxed for 2 h. Solvent was removed and the residue was subjected to preparative TLC separation using CH_2Cl_2 as eluent to give two purple bands, from which 0.074 g (16%) of **3a** and 0.028 g (6%) of **3b** were obtained; **3a**: m.p. 262–263°C; *anal.* calcd. for $C_{26}H_{24}O_4S_2Se_2W_2$(%): C, 31.54; H, 2.44; found: C, 31.67; H, 2.34; IR (CsI disc): $\nu_{C=O}$ 1711(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.78 (s, 6H, $2CH_3$), 6.36–7.16 (4m, 18H, $2C_5H_4+2C_6H_5$); MS (EI), *m/z* (relative intensity): 640 ($((C_5H_4)_2W_2S_2Se^+$, 1.8), 608 ($((C_5H_4)_2W_2SSe^+$, 1.9), 186 (Ph_2S^+, 5.4), 157 ($PhSe^+$, 11.8), 154 (Ph_2^+, 4.7), 109 (PhS^+, 26.8), 92 ($(C_5H_4(CO))^+$, 50.8), 77 (Ph^+, 100); **3b**: m.p. 169°C (dec.); *anal.* calcd. for $C_{26}H_{24}O_4S_2Se_2W_2$(%): C, 31.54; H, 2.44; found: C, 31.54; H, 2.19; IR (CsI disc): $\nu_{C=O}$ 1715(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 3.77 (s, 6H, $2CH_3$), 6.56–7.00 (2m, 18H, $2C_5H_4+2C_6H_5$) ppm; MS (EI), *m/z* (relative intensity): 186 (Ph_2S^+, 2.4), 184 (W^+, 1.5), 157 ($PhSe^+$, 1.9), 154 (Ph_2^+, 4.1), 109 (PhS^+, 27.8), 92 ($((C_5H_4(CO))^+$, 11.2), 77 (Ph^+, 20.8).

Trans/*anti*-[η^5-$EtO_2CC_5H_4W(\mu\text{-}Se)(\mu\text{-}SPh)]_2$ (4a) and *Trans*/*syn*-[η^5-$EtO_2CC_5H_4W(\mu\text{-}Se)(\mu\text{-}SPh)]_2$ (4b)

A flask as described above was charged with 0.400 g (0.436 mmol) of [η^5-$EtO_2CC_5H_4W(CO)(\mu\text{-}SPh)]_2$, 0.138 g (1.748 mmol) of selenium powder and 30 cm^3 of toluene. Similar work-up was followed to give 0.131 g (30%) of **4a** and 0.069 g (16%) of **4b**; **4a**: m.p. 260–261°C; *anal.* calcd. for $C_{28}H_{28}O_4S_2Se_2W_2$(%): C, 33.03; H, 2.77; found: C, 33.02; H, 2.62; IR (CsI disc): $\nu_{C=O}$ 1705(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.20(t, 6H, $2CH_3$, J = 7.2 Hz), 4.26 (q, 4H, $2CH_2$, J = 7.2 Hz), 6.28–7.16 (4m, 18H, $2C_5H_4+2C_6H_5$) ppm; **4b**: m.p. 212°C (dec.); *anal.* calcd. for $C_{28}H_{28}O_4S_2Se_2W_2$(%): C, 33.03; H, 2.77; found: C, 32.62; H, 2.70; IR (CsI disc): $\nu_{C=O}$ 1706(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 1.22 (t, 6H, $2CH_3$, J = 7.2 Hz), 4.27 (q, 4H, $2CH_2$, J = 7.2 Hz), 6.56–7.08 (2m, 18H, $2C_5H_4+2C_6H_5$) ppm; MS (EI), *m/z* (relative intensity): 831 ($(M-Se-PhS)^+$, 1.1), 656 ($((C_5H_4)_2W_2S_2Se_2^+$, 4.5), 642 ($((EtO_2CC_5H_4)_2W_2^+$, 3.7), 640 ($((C_5H_4)_2W_2S_2Se^+$, 4.3), 186 (Ph_2S^+, 5.3), 157 ($PhSe^+$, 2.9), 154 (Ph_2^+, 4.0), 109 (PhS^+, 28.3), (η^5-$C_5H_5W(CO)$-(μ-$SCHMe_2$)), 92 ($(C_5H_4(CO))^+$, 42.9), 77 (Ph^+, 46.4).

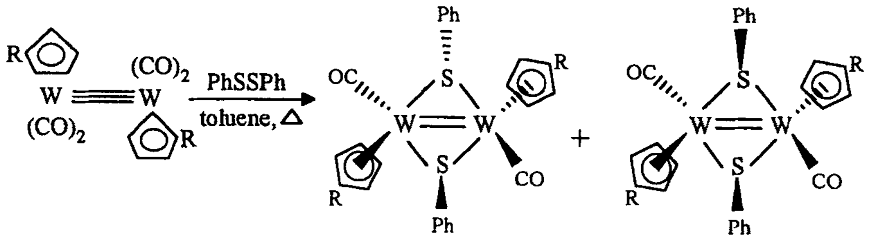
Single-Crystal Structural Determination of 4b

Suitable crystals of **4b** for an X-ray diffraction study were obtained by slow evaporation of a hexane/CH_2Cl_2 solution. A single crystal with dimensions 0.60 × 0.12 × 0.08 mm was mounted on a glass fibre with epoxy resin. Data collection was performed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Lorentz and polarization corrections and an empirical absorption correction were applied to the data. Details of crystal parameters, data collection and structure refinement are summarized in Table IV.

The structure was solved by direct methods (MITHRIL). Final refinement was carried out using full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a Micro-VAX II computer using the TEXSAN program package.

RESULTS AND DISCUSSION

As described in the experimental section, in order to synthesize the doubly-bonded tungsten dimers *trans/anti-* and *trans/syn*-[η^5-$RC_5H_4W(CO)$(μ-SPh)]$_2$ ($R = MeO_2C$, EtO_2C) (**1a–b**) and (**2a–b**), the reaction of an equivalent of tungsten triply-bonded dimers [η^5-$RC_5H_4(CO)_2W]_2$ with PhSSPh was carried out in toluene at reflux. After a reaction time of 5 h, TLC showed that the dinuclear tungsten starting materials had completely disappeared and two spots in green and brown-purple colours could be seen. The reaction mixture was subjected to column chromatography to afford dimers **1a–b** and **2a–b** in 65% and 78% overall yields, respectively (Scheme 1).



trans/anti

1a $R = MeO_2C$
2a $R = EtO_2C$

trans/syn

1b $R = MeO_2C$
2b $R = EtO_2C$

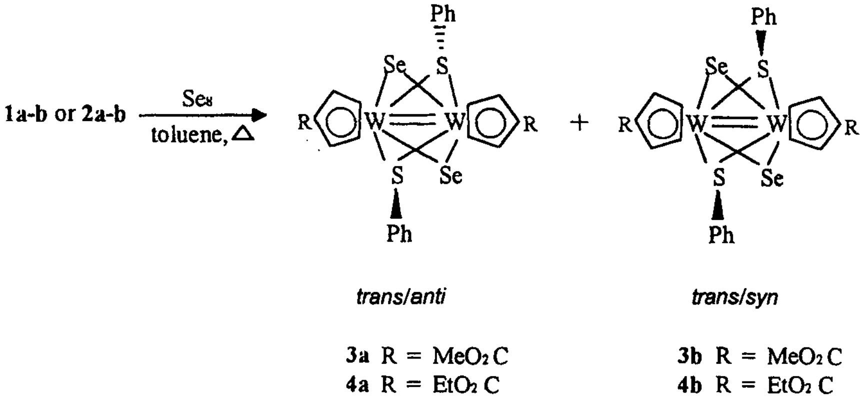
SCHEME 1

Products **1a** and **1b**, **2a** and **2b** are *trans/anti* and *trans/syn* isomers, which can be viewed formally as derived from the exchange of PhS ligands in PhSSPh with CO ligands of the triply-bonded starting materials

$[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{W}]_2$. Although for compounds of the type $[\eta^5\text{-RC}_5\text{H}_4\text{W}(\text{CO})(\mu\text{-SPh})]_2$ five isomers, namely *trans/anti*, *trans/syn*, *cis/anti* and two *cis/syn* isomers are possible (based on *trans/cis* arrangement of RC_5H_4 and carbonyl ligands and *anti/syn* orientation of phenyl groups with respect to the planar W_2S_2 ring), the reaction mentioned above produced only *trans/anti* and *trans/syn* isomers, and the other three isomers (note that for the two *cis/syn* isomers, one has two Ph groups and two RC_5H_4 ligands on the same side of the planar W_2S_2 ring, and the other on the opposite side of the W_2S_2 ring), which all have RC_5H_4 or carbonyl ligands in *cis* positions, were not obtained. This is most likely due to the *cis* isomers having very strong internal steric repulsions, and thus being highly unstable, as had been confirmed by X-ray diffraction analyses of the Mo analogues *trans/anti* and *trans/syn*-$[\text{RC}_5\text{H}_4\text{Mo}(\text{CO})(\mu\text{-SPh})]_2(\text{R} = \text{MeCO})$.[8] It is worth noting that the first related tungsten dimer $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})(\mu\text{-SCHMe}_2)]_2$ had been prepared in 14.6% yield by Shaver[5] through thermal reaction of $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\text{PPh}_3)\text{SCHMe}_2$ or $[\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\mu\text{-SCHMe}_2)]_2$, which was obtained only as the *trans/anti* isomer; other isomers were not detected by ^{1}H NMR spectroscopy. However, compared to Shaver's method, our procedure gave both *trans/anti* and *trans/syn* isomers **1a–b** and **2a–b**, and yields are much higher than that obtained by Shaver.[5]

The complexes **1a–b** and **2a–b** were characterized by elemental analysis, IR, ^{1}H NMR and MS spectroscopies. For the *trans/anti* isomers, due to their centrosymmetric geometries, the ^{1}H NMR spectra show one singlet at 3.60 ppm for methyl groups in **1a**, one triplet at 1.12 ppm and one quartet at 4.60 ppm for ethyl groups in **2a**, and three multiplets between 5.36 and 5.96 ppm for the protons of cyclopentadienyl rings in both **1a** and **2a**. However, for the *trans/syn* isomers having non-centrosymmetric geometries, the ^{1}H NMR spectra exhibit two singlets at 3.52 and 3.76 ppm for methyl groups in **1b**, two triplets at 0.84 and 1.16 ppm and two quartets at 3.88 and 4.14 ppm for ethyl groups in **2b**, and four triplets between 5.40 and 6.08 ppm assigned to the protons of cyclopentadienyl rings in both **1b** and **2b**. IR spectra of the *trans/anti* and *trans/syn* isomers all show one ester carbonyl band at 1705–1721 cm^{-1}, but one terminal carbonyl absorption band at about 1864 cm^{-1} for *trans/anti* isomers **1a** and **2a** and two terminal carbonyl bands at 1836–1918 cm^{-1} for *trans/syn* isomers **1b** and **2b**, this also due to their different geometries.

In order to further explore the reactivity of **1a–b** and **2a–b**, we carried out reactions with selenium in toluene. After the reaction mixture was refluxed for 2 h, we found that the tungsten materials disappeared and the reaction mixture turned purple. After removal of the solvent, the residue was subjected to TLC to give quadruply-bridged dimers **3a–b** and **4a–b** in 22% and 46% overall yields, respectively (Scheme 2).



SCHEME 2

Products **3a–b** and **4a–b** can be regarded formally as resulting from the substitution of CO ligands of **1a–b** and **2a–b** by the selenido ligands generated from selenium powder. These products are also *trans/anti* and *trans/syn* isomers in terms of the *trans/cis* arrangement of RC_5H_4 and selenido ligands and *anti/syn* orientation of phenyl groups with respect to the W_2S_2 ring. Elemental analyses, IR, ^1H NMR and MS spectroscopies for these isomers are in accordance with their structures. For example, the IR spectra of **3a–b** and **4a–b** all display one ester carbonyl band at 1705–1715 cm^{-1}, without showing any absorption signals for a terminal CO ligand. Since *trans/anti* isomers **3a** and **3b** are centrosymmetric and *trans/syn* isomers **4a** and **4b** each has a symmetric plane, the ^1H NMR spectra of **3a** and **3b** all show one singlet at 3.78 and 3.77 ppm for the methyl groups, whereas those of **4a** and **4b** all exhibit one triplet at 1.20 and 1.22 ppm and one quartet at 4.26 and 4.27 ppm for the ethyl groups.

We have unambiguously confirmed the molecular structure of **4b** by X-ray diffraction techniques. The structure is shown in Figure 1. Tables I–III list the positional parameters, selected bond lengths (Å) and selected bond angles (°). As seen from Figure 1, two η^5-$EtO_2CC_5H_4W$ moieties are metal–metal bonded and quadruply-bridged by *trans* benzenethiolato and selenido ligands, which form an unprecedented $W_2Se_2S_2$ cluster skeleton and the two phenyl groups on sulfur atoms adopt a *syn* orientation. Such a structure with a mixed and quadruple Se_2S_2 bridge on a W = W double bond is similar to those with a quadruple S_4 or Se_4 bridge on a Mo = Mo

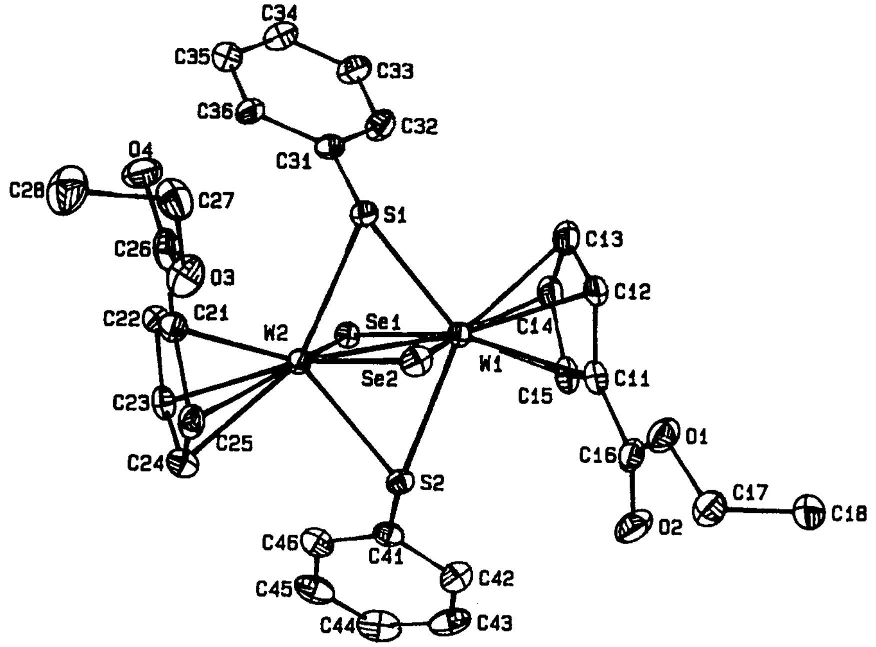


FIGURE 1 Structure of **4b** showing the atom numbering scheme.

double bond, for example *trans/anti*-[η^5-$MeC_5H_4Mo(\mu$-$S)(\mu$-$SMe)]_2$,[9] *trans/anti*-[η^5-$Me_5C_5Mo(\mu$-$S)(\mu$-$SMe)]_2$,[10] *trans/syn*-(η^5-${}^iPrC_5H_4)_2Mo_2(\mu$-$S)_2(\mu$-$S^tBu)_2$,[11] and *trans/syn*-(η^5-$C_5H_5)_2Mo_2(\mu$-$Se)_2(\mu$-$SePh)_2$.[12] The W_2S_2 and W_2Se_2 rings are all planar and the two planes are mutually perpendicular (90.35°). The four bridgehead atoms S_2Se_2 also constitute a plane, which basically parallels the two substituted cyclopentadienyl rings (the dihedral angle between the two rings = 2.87°) and bisects the W–W vector. The non-bonding distances between bridgehead atoms are 2.865(3) (Se(2)–S(1)), 2.848(3) (Se(2)–S(2)), 3.076(3) (Se(1)–S(1)) and 3.089(3) (Se(1)–S(2)) Å. These distances are less than the sum of the van der Waals radii of sulfur and selenium atoms, which indicates some weak interactions between the bridgehead atoms. Compound **4b** contains two W atoms each in oxidation state +IV and thus is a d^2–d^2 dimer with $\sigma^2\delta^2$ electronic configuration.[13,14] This would suggest a double bond between the tungsten atoms. The W–W double bond length of 2.625(3) Å is reasonable and near the W–W double bond length of 2.602(5) Å in *trans/anti*-[η^5-$C_5H_5W(CO)(\mu$-$SCHMe_2)]_2$.[5] In addition, the four W–S bond lengths of **4b** are almost the same (2.468(3)–2.488(2) Å), slightly longer than those in *trans/anti*-[η^5-$C_5H_5W(CO)(\mu$-$SCHMe_2)]_2$ (2.411(3) and 2.412(4) Å).[5]

TABLE I Positional parameters of non-hydrogen atoms and equivalent isotropic thermal parameters for **4b**

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
W(1)	0.09928(3)	0.76519(3)	−0.06102(3)	1.98(1)
W(2)	0.37273(3)	0.86643(3)	0.11586(3)	1.90(1)
Se(1)	0.2281(1)	0.65945(7)	0.04077(7)	2.30(2)
Se(2)	0.2433(1)	0.97486(7)	0.01439(8)	2.64(3)
S(1)	0.1401(2)	0.8785(2)	0.1449(2)	2.31(6)
S(2)	0.3330(2)	0.7800(2)	−0.0912(2)	2.19(6)
O(1)	−0.0353(8)	0.8700(6)	−0.3091(5)	3.6(2)
O(2)	0.0399(9)	0.7156(7)	−0.3860(6)	4.6(3)
O(3)	0.5096(8)	1.2013(5)	0.3377(6)	3.8(2)
O(4)	0.4516(8)	1.1093(6)	0.4378(6)	4.0(2)
C(11)	−0.059(1)	0.7252(8)	−0.2489(8)	2.8(3)
C(12)	−0.126(1)	0.7807(9)	−0.1768(8)	3.1(3)
C(13)	−0.170(1)	0.706(1)	−0.1303(8)	3.8(3)
C(14)	−0.127(1)	0.604(1)	−0.1745(8)	3.6(3)
C(15)	−0.059(1)	0.6173(8)	−0.2466(8)	3.5(3)
C(16)	−0.011(1)	0.7678(8)	−0.3217(8)	3.2(3)
C(17)	−0.006(1)	0.9200(9)	−0.3813(9)	3.6(3)
C(18)	−0.142(1)	0.875(1)	−0.4953(9)	4.0(3)
C(21)	0.538(1)	1.0170(8)	0.2957(8)	2.7(3)
C(22)	0.536(1)	0.9109(8)	0.3069(7)	2.8(3)
C(23)	0.597(1)	0.8483(8)	0.2331(8)	2.9(3)
C(24)	0.640(1)	0.9154(8)	0.1822(8)	3.2(3)
C(25)	0.604(1)	1.0175(8)	0.2160(8)	3.0(3)
C(26)	0.493(1)	1.1131(8)	0.3646(8)	3.2(3)
C(27)	0.478(1)	1.3029(8)	0.407(1)	3.8(3)
C(28)	0.613(1)	1.386(1)	0.521(1)	4.9(4)
C(31)	0.092(1)	0.7926(7)	0.2148(7)	2.4(2)
C(32)	−0.033(1)	0.6969(8)	0.1573(8)	3.5(3)
C(33)	−0.074(1)	0.6420(9)	0.2198(9)	3.8(3)
C(34)	0.010(1)	0.6857(9)	0.3372(9)	3.6(3)
C(35)	0.138(1)	0.7820(9)	0.3948(8)	3.4(3)
C(36)	0.178(1)	0.8360(8)	0.3350(8)	3.0(3)
C(41)	0.373(1)	0.6456(7)	−0.1470(8)	2.6(3)
C(42)	0.305(1)	0.5805(8)	−0.2688(8)	3.3(3)
C(43)	0.340(1)	0.4810(9)	−0.321(1)	4.2(4)
C(44)	0.446(1)	0.4493(9)	−0.252(1)	4.5(4)
C(45)	0.518(1)	0.515(1)	−0.132(1)	4.3(4)
C(46)	0.481(1)	0.6123(8)	−0.0793(9)	3.2(3)

TABLE II Selected bond lengths (Å) for the complex **4b**

W(1)–W(2)	2.625(3)	S(1)–C(31)	1.811(8)
W(1)–Se(1)	2.464(2)	S(2)–C(41)	1.790(9)
W(1)–S(2)	2.479(2)	O(1)–C(16)	1.34(1)
W(1)–S(1)	2.481(3)	O(1)–C(17)	1.44(1)
W(1)–Se(2)	2.490(3)	O(2)–C(16)	1.20(1)
W(2)–Se(1)	2.463(3)	O(3)–C(26)	1.32(1)
W(2)–S(2)	2.468(3)	O(3)–C(27)	1.46(1)
W(2)–S(1)	2.488(2)	O(4)–C(26)	1.21(1)
W(2)–Se(2)	2.493(2)		

TABLE III Selected bond angles (°) for the complex **4b**

Se(1)-W(1)-S(2)	77.36(6)	S(2)-W(2)-S(1)	115.48(9)
Se(1)-W(1)-S(1)	76.93(7)	S(2)-W(2)-Se(2)	70.08(7)
Se(1)-W(1)-Se(2)	116.05(7)	S(2)-W(2)-W(1)	58.15(7)
Se(1)-W(1)-W(2)	57.79(6)	S(1)-W(2)-Se(2)	70.24(6)
S(2)-W(1)-S(1)	115.3(1)	S(1)-W(2)-W(1)	57.97(6)
S(2)-W(1)-Se(2)	69.95(8)	Se(2)-W(2)-W(1)	58.16(6)
S(2)-W(1)-W(2)	57.75(6)	W(2)-Se(1)-W(1)	64.39(6)
S(1)-W(1)-Se(2)	70.4(1)	W(1)-Se(2)-W(2)	63.57(7)
S(1)-W(1)-W(2)	58.23(8)	C(31)-S(1)-W(1)	115.9(3)
Se(2)-W(1)-W(2)	58.26(8)	C(31)-S(1)-W(2)	114.3(3)
Se(1)-W(2)-S(2)	77.6(1)	W(1)-S(1)-W(2)	63.79(8)
Se(1)-W(2)-S(1)	76.82(8)	C(41)-S(2)-W(2)	117.9(3)
Se(1)-W(2)-Se(2)	115.99(7)	C(41)-S(2)-W(1)	116.2(3)
Se(1)-W(2)-W(1)	57.83(8)	W(2)-S(2)-W(1)	64.10(8)

TABLE IV Details of crystal parameters, data collection and structure refinement for **4b**

Molecular formula	$C_{28}H_{28}O_4S_2Se_2W_2$
Molecular weight	1018.27
Space group	triclinic, $P1$
a (Å)	9.904(3)
b (Å)	12.917(8)
c (Å)	13.561(7)
α (°)	111.38(6)
β (°)	110.47(4)
γ (°)	98.74(6)
V (Å^3)	1434(2)
Z	2
Radiation used, λ(Å)	MoKα (0.71073 Å)
$Dcalc$ (g cm^{-3})	2.36
μ (cm^{-1})	108.77
Temperature (K)	296
Scan mode	ω–2θ
Measured reflections	5344
Observed reflections $I > 3\sigma(I)$	4157
θ_{max} (°)	25
R	0.034
R_w	0.045
$\Delta\rho_{max}$ (e Å^{-3})	1.33

Supplemental Material

Tables of fractional atomic coordinates, thermal parameters, interatomic distances, and observed and calculated structure factors are available on request from the authors.

Acknowledgments

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