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# Synthesis of novel quadruply bridged $M_2Se_4$ clusters *trans*/*anti* and *trans*/*syn*-$[(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$ (M = Mo, W) via an unexpected reaction of M≡M triply bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ with dibenzyl diselenide. Crystal structures of a pair of isomers *trans*/*anti*- and *trans*/*syn*-$[(\eta^5\text{-}EtO_2CC_5H_4)_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$

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## Abstract

The unexpected reaction of triply bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ with dibenzyl diselenide $(PhCH_2)_2Se_2$ in toluene at reflux gave a series of isomeric $M_2Se_4$ clusters *trans*/*anti*-$[(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$ (**1a**, M = Mo, R = MeCO; **2a**, Mo, $MeO_2C$; **3a**, Mo, $EtO_2C$; **4a**, W, MeCO; **5a**, W, $MeO_2C$; **6a**, W, $EtO_2C$) and *trans*/*syn*-$[(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$ (**1b**, M = Mo, R = MeCO; **2b**, Mo, $MeO_2C$; **3b**, Mo, $EtO_2C$; **4b**, W, MeCO; **5b**, W, $MeO_2C$; **6b**, W, $EtO_2C$) in combined 20–41% yields. In addition, the reaction of $[(\eta^5\text{-}MeO_2CC_5H_4)_2W_2(CO)_4]$ with $(PhCH_2)_2Se_2$ in solid state at 90°C also afforded **5a** and **5b** in a total of 32% yield. The structures of these new clusters were fully characterized by elemental analysis and spectroscopy; those for **3a** and **3b** were confirmed by single-crystal X-ray diffraction techniques. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* $(PhCH_2)_2Se_2$; Metal–metal multiple bond; $Mo_2Se_2$ clusters; $W_2Se_2$ clusters; Crystal structures

## 1. Introduction

Over the last two decades, considerable attention has been paid to studies on the chemistry of transition metal–metal triply bonded complexes, such as Group 6 metal–metal triply bonded dimers $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ (M = Cr, Mo, W; $\eta^5\text{-}RC_5H_4$ is parent or substituted cyclopentadienyl ligands) [1]. On the other hand, the chemistry of transition metal complexes containing both Group 6 metals and chalcogenido ligands has also been extensively studied, not only because of their importance to biology and catalysis [2–6], but also because of their novel structures and widespread use for the synthesis of organometallic compounds, and particularly organometallic clusters [7–13]. Recently, based on our previous studies associated with such organometallic systems [14], we continued to investigate the reaction of triply bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ (M = Mo, W) with dibenzyl diselenide in refluxing toluene. Interestingly, this reaction has unexpectedly led us to obtain a series of quadruply bridged $M_2Se_4$ isomers *trans*/*anti*- and *trans*/*syn*-$[(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$ (M = Mo, W). Herein we wish to report on such an unexpected result by describing the synthetic procedures and characterization of these novel isomers, including the X-ray structural analyses for one pair of those isomers.

## 2. Results and discussion

### 2.1. Synthesis and characterization of 1a,b–6a,b

It was found that an equimolar amount of triply bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ (M = Mo,

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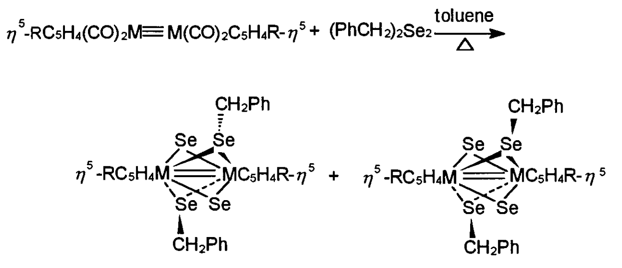
W; R = MeCO, $MeO_2C$, $EtO_2C$) reacted with $(PhCH_2)_2Se_2$ in refluxing toluene, after separation by preparative thin-layer chromatography (TLC), to afford a series of $M_2Se_4$ clusters, namely *trans/anti*- and *trans/syn*-$[(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SeCH_2Ph)_2]$ (**1a,b**–**6a,b**) (Scheme 1).

As shown in Scheme 1, while isomers **1a**–**6a** and **1b**–**6b** all have their two $\eta^5$-$RC_5H_4$, two naked Se and two $PhCH_2Se$ ligands in the *trans* arrangement with respect to the M–M vector, isomers **1a**–**6a** have their two benzyl groups attached to Se atoms in the *anti* orientation and isomers **1b**–**6b** in the *syn* orientation with respect to the four-membered $M_2Se_2$ (selenolato) ring. The structures of products **1a,b**–**6a,b** have been well characterized by IR, $^1H$-NMR and $^{77}Se$-NMR spectroscopies, and especially by crystal X-ray diffraction analyses of **3a** and **3b**. The IR spectra of **1a,b**–**6a,b** exhibited one strong absorption band at 1674–1680 or 1704–1720 cm$^{-1}$ characteristic of their corresponding ketonic and ester carbonyls, respectively. The $^1H$-NMR spectra of these isomers displayed a singlet at 2.79–3.06 ppm, assigned to their methylene hydrogen atoms of the benzyl groups. The other signals appeared in their $^1H$-NMR spectra indicated the presence of their respective acetyl, methoxy or ethoxy carbonyls, phenyl and cyclopentadienyl groups. Fig. 1 represents the $^1H$-NMR spectra of a pair of isomers, **6a** and **6b**, from which it can be seen that such two isomers have quite different $^1H$-NMR patterns in the spectral part caused by the four hydrogens of each substituted Cp ring. That is, **6a** has three sets of multiplets, one at 5.96–6.18 ppm, attributed to $H^3/H^4$ remote from the substituent, and



| M | R | trans/anti | trans/syn |
|---|---|---|---|
| Mo | MeCO | **1a** | **1b** |
| Mo | $MeO_2C$ | **2a** | **2b** |
| Mo | $EtO_2C$ | **3a** | **3b** |
| W | MeCO | **4a** | **4b** |
| W | $MeO_2C$ | **5a** | **5b** |
| W | $EtO_2C$ | **6a** | **6b** |

Scheme 1.

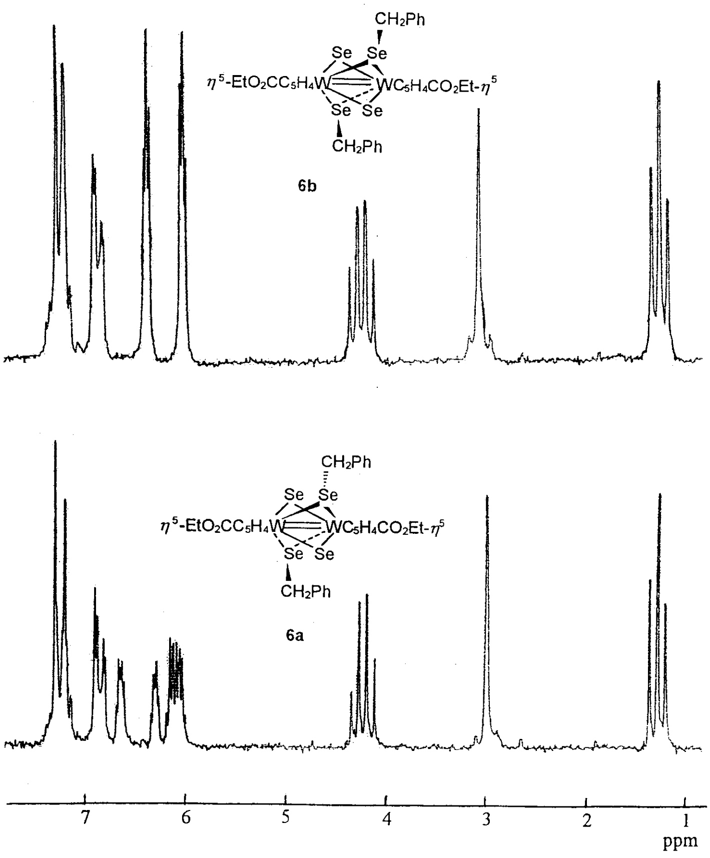


Fig. 1. $^1H$-NMR spectra of one pair of isomers **6a** and **6b**.

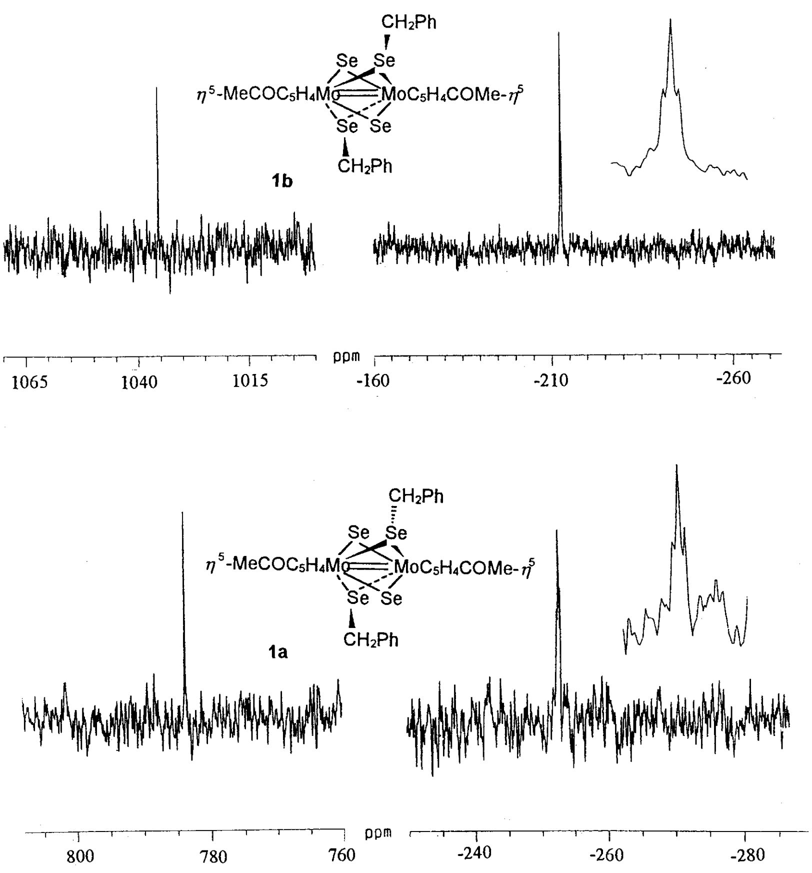


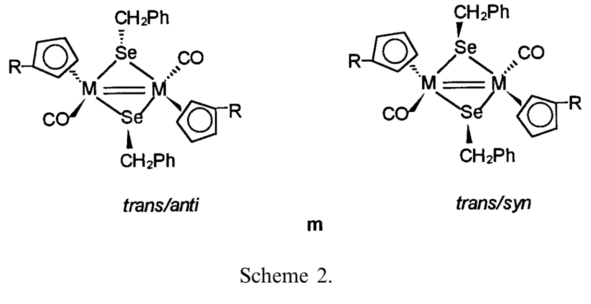
Fig. 2. $^{77}$Se-NMR spectra of one pair of isomers **1a** and **1b**.

the other two at 6.20–6.36 and 6.52–6.68 ppm, assigned to $H^2/H^5$ close to the substituent [15], whereas **6b** has two sets of apparent triplets, one at 6.03 ppm and the other at 6.38 ppm assigned to $H^3/H^4$ and $H^2/H^5$ [15], respectively.

Since $^{77}$Se-NMR spectroscopy is a very useful tool for characterization of organometallic selenium complexes [16], we determined the $^{77}$Se-NMR spectra of representatives **1a**, **1b**, **4a** and **5b** among isomers **1a**,**b**–**6a**,**b**. Fig. 2 shows the $^{77}$Se-NMR spectra of a pair of isomers, **1a** and **1b**, in which the singlets at 783.9 and 1035.5 ppm can be assigned to the naked Se atoms of **1a** and **1b**, the triplets at $-252.8$ and $-212.8$ ppm can be assigned to the Se atoms attached to benzyl groups of **1a** and **1b**, respectively. The coupling constants $^2J_{SeH}$ for the triplets caused by coupling of the Se atom with two methylene H atoms of the benzyl group are 19.2 Hz (**1a**) and 16.9 Hz (**1b**), 17.7 Hz (**4a**) and 16.6 Hz (**5b**), which are very close to those of the compounds containing similar structural units, such as $Fe_2(\mu\text{-}SeCH)$ in $[Fe_2(CO)_6\{\mu\text{-}SeCHC(O)CRCPhCr(CO)_3CPhS\text{-}\mu\}]$ (R = H, Ph) [17].

It is worth to point out that isomers **5a**,**b** could also be synthesized through the reaction under solid state conditions in comparable yields. For example, an equimolar amount of $[(\eta^5\text{-}MeO_2CC_5H_4)_2W_2(CO)_4]$ reacted with $(PhCH_2)_2Se_2$ at 90°C for 3 h to give **5a** and **5b** in 21 and 11% yields, respectively.

So far, the pathway for production of such quadruply bridged $M_2Se_4$ clusters is not completely clear. However, a possible pathway might be suggested, which involves the two $PhCH_2Se$ bridged intermediates **m** (Scheme 2) produced through reaction of triply bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ with $(PhCH_2)_2Se_2$ and subsequent reaction of **m** with elemental selenium generated in situ from the decomposition of $(PhCH_2)_2Se_2$ to finally give **1a**,**b**–**6a**,**b**. This suggested pathway is primarily based on the following facts. (i) The triply bonded complexes can react with $Ph_2Se_2$ to give fully characterized analogs of the intermediates **m** $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_2(\mu\text{-}SePh)_2]$ [18]. (ii) Treatment of such analogs with elemental selenium



Scheme 2.

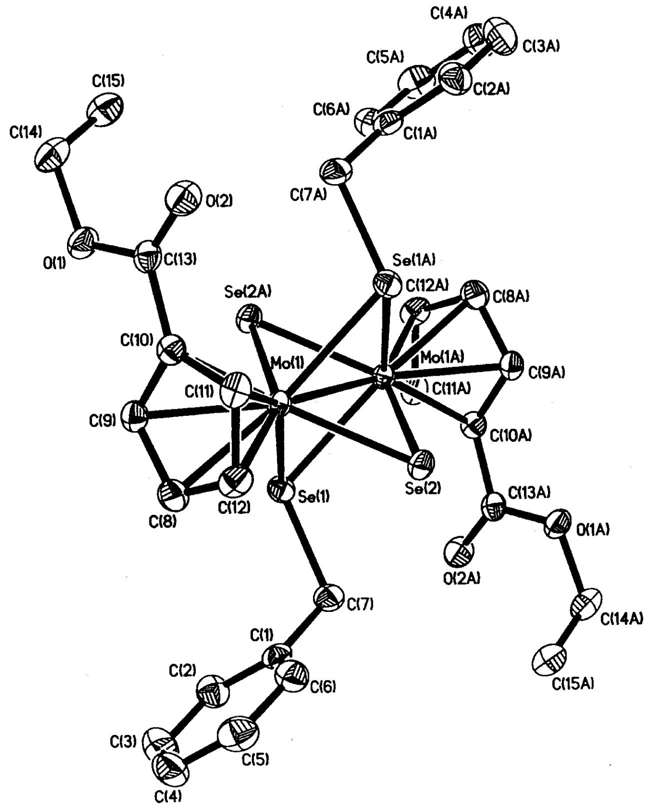


Fig. 3. ORTEP drawing of **3a** with atom-labeling scheme.

yields a series of analogs of **1a,b**–**6a,b** [$(\eta^5\text{-}RC_5H_4)_2M_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$] [19]. (iii) $(PhCH_2)_2Se_2$ is thermally less stable than $Ph_2Se_2$ and thus can be decomposed at higher temperatures to give elemental Se [20]. (iv) After about 15 min in reaction of [$(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4$] (M = Mo, R = $EtO_2C$) with $(PhCH_2)_2Se_2$, TLC showed that two contiguous green and brown spots appeared, which were also observed to correspond to *trans*/*anti*- and *trans*/*syn*-[$(\eta^5\text{-}RC_5H_4)_2M_2(CO)_2(\mu\text{-}SePh)_2$], yielded from the reaction with $Ph_2Se_2$ [18]. In addition, with the lapse of reaction time, TLC showed that the two spots completely disappeared and instead two new green spots appeared, which have been fully characterized as **3a** and **3b**. However, to further support this pathway more work needs to be done in the future.

### 2.2. Crystal structures of *3a* and *3b*

To confirm the *trans*/*anti* and *trans*/*syn* structures of **1a,b**–**6a,b**, we carried out the single-crystal X-ray diffraction analyses for one pair of isomers, **3a** and **3b**. The ORTEP plots of **3a** and **3b** are shown in Figs. 3 and 4, whereas the selected bond lengths and angles of **3a** and **3b** are listed in Tables 1 and 2, respectively.

As seen from Figs. 3 and 4, the molecules of **3a** and **3b** both contain two naked Se and two $PhCH_2Se$ ligands, quadruply bridged to two Mo atoms, each carrying one $\eta^5\text{-}EtO_2CC_5H_4$ ligand. In addition, while for **3a** and **3b** the two naked Se, the two $PhCH_2Se$ and the two $\eta^5\text{-}EtO_2CC_5H_4$ are *trans* to each other with respect to the Mo–Mo vector, for **3a** the two methylene carbon atoms of two benzyl groups are attached to Se atoms in the *anti* orientation with respect to the $Mo_2Se_2$ (seleno-

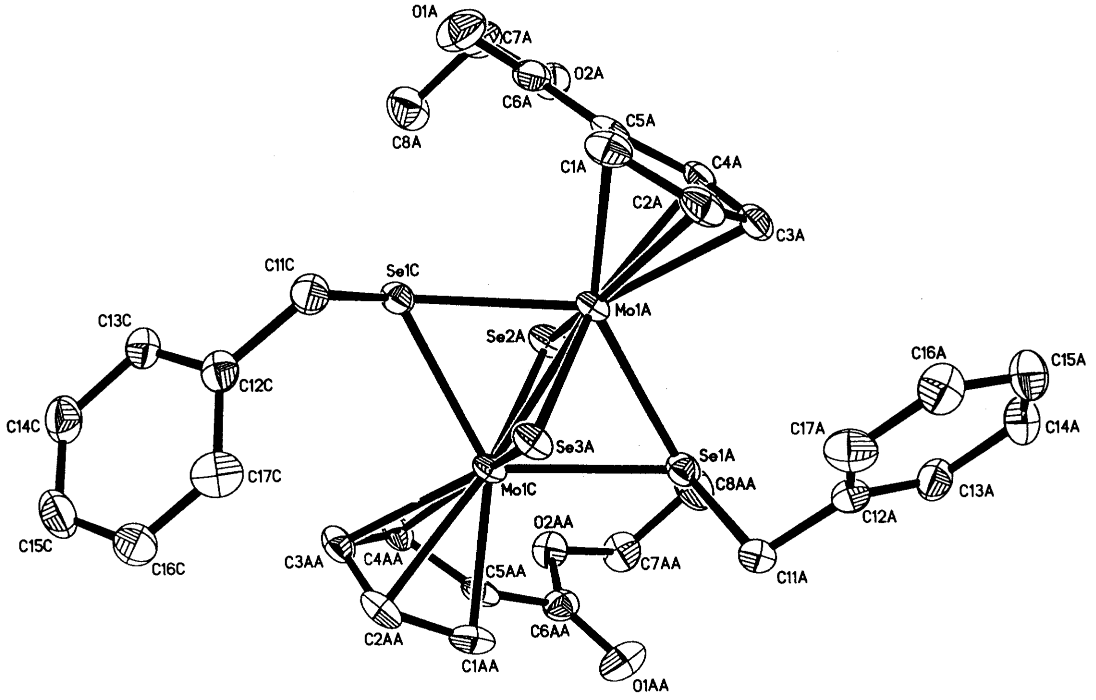


Fig. 4. ORTEP drawing of **3b** with atom-labeling scheme.

Table 1
Selected bond lengths (Å) and angles (°) for **3a**

| | | | |
|---|---|---|---|
| *Bond length* | | | |
| Mo(1)–Se(2) | 2.4793(5) | Mo(1)–Se(1) | 2.5880(5) |
| Mo(1)–Se(2A) | 2.4751(5) | Mo(1)–Se(1A) | 2.5984(5) |
| Mo(1)–Mo(1A) | 2.6484(7) | Se(1)–Mo(1A) | 2.5984(5) |
| Se(2)–Mo(1A) | 2.4751(5) | Se(1)–C(7) | 1.999(4) |
| *Bond angles* | | | |
| Se(2A)–Mo(1)–Se(2) | 115.374(18) | Se(2A)–Mo(1)–Se(1) | 70.366(18) |
| Se(2)–Mo(1)–Se(1) | 78.058(18) | Se(2A)–Mo(1)–Se(1A) | 77.936(18) |
| Se(1)–Mo(1)–Se(1A) | 118.588(17) | Se(2A)–Mo(1)–Mo(1A) | 57.763(15) |
| Se(2)–Mo(1)–Mo(1A) | 57.611(15) | Se(1)–Mo(1)–Mo(1A) | 59.486(15) |
| Mo(1)–Se(1)–Mo(1A) | 61.412(17) | Mo(1A)–Se(2)–Mo(1) | 64.626(17) |

Table 2
Selected bond lengths (Å) and angles (°) for **3b**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Mo(1A)–Se(3A) | 2.4732(9) | Mo(1A)–Se(2A) | 2.4774(10) |
| Mo(1A)–Se(1C) | 2.5839(8) | Mo(1A)–Se(1A) | 2.5868(8) |
| Mo(1A)–Mo(1C) | 2.6498(9) | Se(1A)–Mo(1C) | 2.5839(8) |
| Se(2A)–Mo(1C) | 2.4774(10) | Se(3A)–Mo(1C) | 2.4732(9) |
| *Bond angles* | | | |
| Se(3A)–Mo(1A)–Se(2A) | 115.28(2) | Se(3A)–Mo(1A)–Se(1C) | 77.13(2) |
| Se(2A)–Mo(1A)–Se(1C) | 71.03(2) | Se(3A)–Mo(1A)–Se(1A) | 77.08(2) |
| Se(2A)–Mo(1A)–Se(1A) | 70.98(2) | Se(1C)–Mo(1A)–Se(1A) | 117.86(2) |
| Se(3A)–Mo(1A)–Mo(1C) | 57.609(16) | Me(1C)–Se(1A)–Mo(1A) | 61.66(2) |
| Mo(1C)–Se(2A)–Mo(1A) | 64.66(3) | Mo(1A)–Se(3A)–Mo(1C) | 64.78(3) |

lato) ring, and for **3b** in the *syn* orientation. Interestingly, for **3a** and **3b**, the two Mo and the two naked Se atoms, as well as the two Mo and the two selenolato Se atoms are respectively coplanar and the two planes are perpendicular to each other. In addition, for **3a** and **3b** the two naked and two selenolato Se atoms are found to be symmetrically bonded to the two Mo atoms, respectively, and the four Se atoms lie in a plane, which is perpendicular to the above two planes through the midpoint of the Mo–Mo bond. In fact, the corresponding bond lengths and angles in **3a** and **3b** are almost the same. For example, the Mo=Mo double bond lengths equal 2.648 for **3a** and 2.650 for **3b**, which are very close to that of *trans*/*syn*-[$Cp_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$] (2.653) [21]. In addition, the average Mo–Se (naked)–Mo and Mo–Se (selenolato)–Mo bond angles are 64.63°, 61.41° for **3a** and 64.72°, 61.66° for **3b**, respectively, which are very close to corresponding those of *trans*/*syn*-[$Cp_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}SePh)_2$] (64.6° and 61.4°) [21]. It is worth noting that while **3a** is centrosymmetric, **3b** is non-centrosymmetric due to the *syn* orientation of the two methylene carbon atoms of its two benzyl groups. In addition, for both **3a** and **3b**, the two phenyl groups attached to *anti*- or *syn*-methylene carbon atoms all bent toward the directions far away from the $EtO_2C$ substituents in order to minimize the strong steric repulsions between them.

## 3. Experimental

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk or vacuum-line techniques. Toluene was distilled from sodium-benzophenone ketyl under nitrogen. $(PhCH_2)_2Se_2$ [22] and [$(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4$] (M = Mo, W; R = MeCO, $MeO_2C$, $EtO_2C$) [23,24] were prepared according to literature methods. The products were separated by preparative TLC (glass plates, 20 × 25 × 0.25 cm; silica gel H, 10–40 μm). All samples for analyses were recrystallized in a mixed $CH_2Cl_2$/hexane solvent. IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer. $^1H$- and $^{77}Se$-NMR spectra were recorded on a JEOL FX-90Q and a Bruker ARX-500 NMR spectrometers. $^{77}Se$-NMR spectra were referenced to $Ph_2Se_2$($\delta$ 0). C/H analysis and melting point (m.p.) determination were performed on a Yanaco CHN corder MT-3 analyzer and on a Yanaco Mp-500 apparatus, respectively.

### 3.1. Preparation of *1a* and *1b*

A 100-ml three-necked flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 0.777 g (1.5 mmol) of [$(\eta^5\text{-}MeCOC_5H_4)_2Mo_2(CO)_4$] and 0.510 g (1.5 mmol) of $(PhCH_2)_2Se_2$ in 40 ml of toluene. The mixture was refluxed for 2 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using $CH_2Cl_2$ as eluent. The first main band afforded 0.138 g (10%) of **1a** as a green solid. M.p. 176–178°C. Anal. Found: C, 37.15; H, 3.14. $C_{28}H_{28}Mo_2O_2Se_4$ Calc.: C, 37.19; H, 3.12. IR (KBr disk): acetyl carbonyl C=O 1680s $cm^{-1}$. $^1H$-NMR ($CDCl_3$): 2.44 (s, 6H, $2CH_3$), 2.84 (s, 4H, $2CH_2$), 6.04–6.20, 6.48–6.60, 6.72–6.82 (3m, 8H, $2C_5H_4$), 6.84–6.96, 7.12–7.24 (2m, 10H, $2C_6H_5$). $^{77}Se$-NMR ($Ph_2Se_2$, $CDCl_3$): $-252.8$ (t, $^2J_{SeH} = 19.2$ Hz, $2SeCH_2Ph$), 783.97 (s, 2Se). The second main band afforded 0.139 g (10%) of **1b** as a green solid. M.p. 168–169°C. Anal. Found: C, 37.12; H, 2.80. $C_{28}H_{28}Mo_2O_2Se_4$ Calc.: C, 37.19; H, 3.12. IR (KBr disk): acetyl carbonyl C=O 1678s $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.41 (s, 6H, $2CH_3$), 2.84 (s, 4H, $2CH_2$), 6.01, 6.22 (2t, 8H, $2CH_5H_4$), 6.72–7.00, 7.08–7.27 (2m, 10H, $2C_6H_5$). $^{77}$Se-NMR ($Ph_2Se_2$, $CDCl_3$): −212.8 (t, $^2J_{SeH} = 16.9$ Hz, $2SeCH_2Ph$), 1035.5 (s, 2Se).

### *3.2. Preparation of **2a** and **2b***

The same procedure as that for **1a** and **1b** was followed, but 0.825 g (1.5 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)_2Mo_2(CO)_4]$ was used instead of $[(\eta^5\text{-}MeCOC_5H_4)_2Mo_2(CO)_4]$. The first main band afforded 0.162 g (12%) of **2a** as a green solid. M.p. (dec.) 168°C. Anal. Found: C, 36.20; H 3.22. $C_{28}H_{28}Mo_2O_4Se_4$ Calc.: C, 35.92; H, 3.01. IR (KBr disk): ester carbonyl C=O 1719s $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.83 (s, 4H, $2CH_2$), 3.73 (s, 6H, $2CH_3$), 5.90–6.10, 6.27–6.31, 6.59–6.63 (3m, 8H, $2C_5H_4$), 6.72–6.88, 7.10–7.25 (2m, 10H, $2C_6H_5$). The second main band afforded 0.176 g (13%) of **2b** as a green solid. M.p. 150–151°C. Anal. Found: C, 36.24; H, 2.80. $C_{28}H_{28}Mo_2O_4Se_4$ Calc.: C, 35.92; H, 3.01. IR (KBr disk): ester carbonyl C=O 1720s $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.82 (s, 4H, $2CH_2$), 3.72 (s, 6H, $2CH_3$), 5.91, 6.40 (2t, 8H, $2C_5H_4$), 6.68–6.96, 7.08–7.22 (2m, 10H, $2C_6H_5$).

### *3.3. Preparation of **3a** and **3b***

The same procedure as that for **1a** and **1b** was followed, but 0.867 g (1.5 mmol) of $[(\eta^5\text{-}EtO_2CC_5H_4)_2Mo_2(CO)_4]$ was used instead of $[(\eta^5\text{-}MeCOC_5H_4)_2Mo_2(CO)_4]$. The first main band afforded 0.172 g (12%) of **3a** as a green solid. M.p. (dec.) 158–159°C. Anal. Found: C, 37.40; H 2.95. $C_{30}H_{32}Mo_2O_4Se_4$ Calc.: C, 37.37; H, 3.34. IR (KBr disk): ester carbonyl C=O 1713s $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 1.30 (t, $J = 7.2$ Hz, 6H, $2CH_3$) 2.88 (s, 4H, $2CH_2Ph$), 4.24 (q, $J = 7.2$ Hz, 4H, $2\mathit{CH_2}CH_3$), 5.96–6.12, 6.20–6.32, 6.56–6.68 (3m, 8H, $2C_5H_4$), 6.76–6.96, 7.14–7.36 (2m, 10H, $2C_6H_5$). The second main band afforded 0.175 g (12%) of **3b** as a green solid. M.p. 131–132°C. Anal. Found: C, 37.38; H, 3.25. $C_{30}H_{32}Mo_2\ O_4Se_4$ Calc.: C, 37.37; H, 3.34. IR (KBr disk): ester carbonyl C=O 1704vs $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 1.23 (t, $J = 7.2$ Hz, 6H, $2CH_3$), 2.79 (s, 4H, $2CH_2Ph$), 4.18 (q, $J = 7.2$ Hz, 4H, $2\mathit{CH_2}CH_3$), 5.90, 6.29 (2t, 8H, $2C_5H_4$), 6.72–6.90, 7.04–7.24 (2m, 10H, $2C_6H_5$).

### *3.4. Preparation of **4a** and **4b***

The same procedure as that for **1a** and **1b** was followed, but 1.041 g (1.5 mmol) of $[(\eta^5\text{-}MeCOC_5H_4)_2W_2(CO)_4]$ was used instead of $[(\eta^5\text{-}MeCOC_5H_4)_2Mo_2(CO)_4]$ and the reaction mixture was refluxed for 1 h. The first main band afforded 0.396 g (24%) of **4a** as a purple solid. M.p. (dec.) 182°C. Anal. Found: C, 30.89; H 2.32. $C_{28}H_{28}O_2\ Se_4W_2$ Calc.: C, 31.14%; H, 2.61. IR (KBr disk): ester carbonyl C=O 1677vs $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.44 (s, 6H, $2CH_3$), 2.96 (s, 4H, $2CH_2$), 6.04–6.28, 6.44–6.62, 6.68–6.78 (3m, 8H, $2C_5H_4$), 6.80–6.96, 7.12–7.24 (2m, 10H, $2C_6H_5$). $^{77}$Se-NMR ($Ph_2Se_2$, $CDCl_3$): −458.8 (t, $^2J_{SeH} = 17.7$ Hz, $2SeCH_2Ph$), 1073.4 (s, 2Se). The second main band afforded 0.282 g (17%) of **4b** as a purple solid. M.p. 207–208°C. Anal. Found: C, 31.18; H, 2.52. $C_{28}H_{28}O_2\ Se_4W_2$ Calc.: C, 31.14; H, 2.61. IR (KBr disk): ester carbonyl C=O 1674vs $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.44 (s, 6H, $2CH_3$), 3.05 (s, 4H, $2CH_2$), 6.09, 6.29 (2t, 8H, $2C_5H_4$), 6.77–7.00, 7.16–7.26 (2m, 10H, $2C_6H_5$).

### *3.5. Preparation of **5a** and **5b***

The same procedure as that for **4a** and **4b** was followed, but 1.089 g (1.5 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)_2W_2(CO)_4]$ was used instead of $[(\eta^5\text{-}MeCOC_5H_4)_2W_2(CO)_4]$. The first main band afforded 0.413 g (25%) of **5a** as a purple-red solid. M.p. (dec.) 162°C. Anal. Found: C, 29.83; H 2.04. $C_{28}H_{28}O_4Se_4W_2$ Calc.:C, 30.24; H, 2.54. IR (KBr disk): ester carbonyl C=O 1718vs $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 2.96 (s, 4H, $2CH_2$), 3.74 (s, 6H, $2CH_3$), 5.88–6.20, 6.28–6.42, 6.58–6.72 (3m, 8H, $2C_5H_4$), 6.76–6.96, 7.08–7.26 (2m, 10H, $2C_6H_5$). The second main band afforded 0.234 g (14%) of **5b** as a purple-red solid. M.p. 159–161°C. Anal. Found: C, 30.45; H, 2.25. $C_{28}H_{28}O_4Se_4W_2$ Calc.: C, 30.24; H, 2.54. IR (KBr disk): ester carbonyl C=O 1718vs $cm^{-1}$. $^1$H-NMR ($CDCl_3$): 3.03 (s, 4H, $2CH_2$), 3.74 (s, 6H, $2CH_3$), 6.00, 6.41 (2t, 8H, $2C_5H_4$), 6.72–6.96, 7.08–7.24 (2m, 10H, $2C_6H_5$). $^{77}$Se-NMR ($Ph_2Se_2$, $CDCl_3$): −412.5 (t, $^2J_{SeH} = 16.6$ Hz, $2SeCH_2Ph$), 735.5 (s, 2Se). **5a** and **5b** were also synthesized through the solid state reaction method described below. To a 50-ml Schenk flask, 0.520 g (0.717 mmol) of $[(\eta^5\text{-}MeO_2CC_5H_4)_2W_2(CO)_4]$ and 0.244 g (0.717 mmol) $(PhCH_2)_2Se_2$ were added. The finely powdered and uniformly mixed reaction mixture was heated at 90°C for 3 h. After cooling to room temperature, the mixture was subjected to TLC separation using $CH_2Cl_2$ as eluent to give 0.168 g (21%) of **5a** and 0.087 g (11%) of **5b**.

### *3.6. Preparation of **6a** and **6b***

The same procedure as that for **4a** and **4b** was followed, but 1.131 g (1.5 mmol) of $[(\eta^5\text{-}EtO_2CC_5H_4)_2W_2(CO)_4]$ was used instead of $[(\eta^5\text{-}MeCOC_5H_4)_2W_2(CO)_4]$. The first main band afforded 0.393 g (23%) of **6a** as a purple-red solid. M.p. 170–172°C. Anal. Found: C, 31.64; H 2.31. $C_{30}H_{32}O_4Se_4W_2$

Calc.: C, 31.61; H, 2.63. IR (KBr disk): ester carbonyl C=O 1713s cm$^{-1}$. $^1$H-NMR (CDCl$_3$): 1.27 (t, $J = 7.2$ Hz, 6H, 2CH$_3$), 2.97 (s, 4H, 2CH$_2$Ph), 4.22 (q, $J = 7.2$ Hz, 4H, 2*CH$_2$*CH$_3$), 5.96–6.18, 6.20–6.36, 6.52–6.68 (3m, 8H, 2C$_5$H$_4$), 6.72–7.00, 7.04–7.24 (2m, 10H, 2C$_6$H$_5$). The second main band afforded 0.266 g (16%) of **6b** as a purple-red solid. M.p. 141–142°C. Anal. Found: C, 31.64; H, 2.61. $C_{30}H_{32}O_4Se_4W_2$ Calc.: C, 31.61; H, 2.63. IR (KBr disk): ester carbonyl C=O 1706s cm$^{-1}$. $^1$H-NMR (CDCl$_3$): 1.28 (t, $J = 7.2$ Hz, 6H, 2CH$_3$), 3.06 (s, 4H, 2CH$_2$Ph), 4.22 (q, $J = 7.2$ Hz, 4H, 2*CH$_2$*CH$_3$), 6.03, 6.38 (2t, 8H, 2C$_5$H$_4$), 6.72–7.00, 7.12–7.44 (2m, 10H, 2C$_6$H$_5$).

### *3.7. X-ray structure determinations of **3a** and **3b***

Single crystals of **3a** and **3b** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH$_2$CH$_2$:petroleum ether (1:2, v/v) solutions in a refrigerator. The single crystal of **3a** (0.20 × 0.15 × 0.10 mm) or that of **3b** (0.3 × 0.25 × 0.2 mm) was glued to a glass fiber and mounted on a Bruker Smart 1000 automated diffractometer. Data were collected at room temperature, using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) in the scanning mode. The structures of **3a** and **3b** were solved by direct methods and refined by full-matrix least-squares techniques (SHELXL-97) on $F^2$. Hydrogen atoms were located using the geometric method. A weight scheme of $w = 1/\sigma^2(F_0^2) + (0.0284P)^2 + 0.0000P$ [where $P = (F_0^2 + 2F_c^2)/3$] was applied to the data for **3a** and $w = 1/\sigma^2(F_0^2) + (0.0241P)^2 + 0.6395P$ [where $P = (F_0^2 + 2F_c^2)/3$] was applied to the data for **3b**. The crystal data and structural refinements details are summarized in Table 3.

Table 3
Crystal data and structure refinements for **3a** and **3b**

| | **3a** | **3b** |
|---|---|---|
| Empirical formula | $C_{30}H_{32}Mo_2O_4Se_4$ | $C_{30}H_{32}Mo_2O_4Se_4$ |
| Formula weight | 964.28 | 964.28 |
| Temperature (K) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ | *Cccm* |
| Unit cell dimensions | | |
| *a* (Å) | 13.0323(15) | 14.1150(11) |
| *b* (Å) | 10.4638(12) | 15.8498(11) |
| *c* (Å) | 11.9818(13) | 27.7442(2) |
| $\beta$ (°) | 108.758(2) | 90 |
| $V$ (Å$^3$) | 1547.1(3) | 6206.8(8) |
| $Z$ | 2 | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 2.070 | 2.064 |
| Scan type | ω scans | ω scans |
| Absorption coefficient (mm$^{-1}$) | 5.550 | 5.534 |
| $F$(000) | 928 | 3712 |
| Theta range for data collection (°) | 1.65–26.44 | 2.07–26.34 |
| Reflections collected | 7158 | 14 081 |
| Independent reflections | 3169 ($R_{int} = 0.0526$) | 5374 ($R_{int} = 0.0500$) |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0322$, $wR_2 = 0.0614$ | |
| Final $R$ indices [$I > 4\sigma(I)$ | | $R_1 = 0.0311$, $wR_2 = 0.0773$ |
| $R$ indices (all data) | $R_1 = 0.0494$, $wR_2 = 0.0662$ | $R_1 = 0.0367$, $wR_2 = 0.0799$ |
| Goodness-of-fit on $F^2$ | 0.937 | 1.093 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.547 and −0.682 | 0.813 and −0.543 |

## 4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 141747 for compound **3a** and 141746 for compound **3b.** Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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