

Reactions of metal–metal triply bonded complexes [[η^5 -RC₅H₄)₂M₂(CO)₄] (M = Mo, W) with diphenyl ditelluride. Crystal structures of [[η^5 -MeC₅H₄)Mo₂(CO)₄(μ -TePh)₃] and [[η^5 -EtO₂CC₅H₄)₂W₂(CO)₄(μ -TePh)₂]

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Abstract

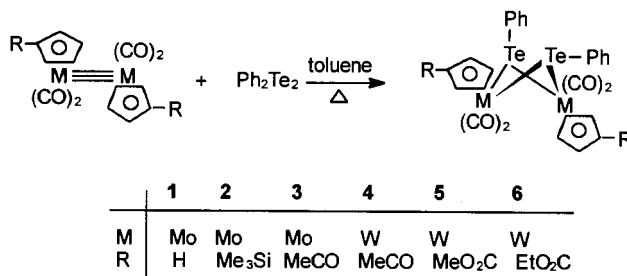
Reactions of triply bonded complexes [[η^5 -RC₅H₄)₂M₂(CO)₄] with Ph₂Te₂ in solution and solid state were investigated. While [[η^5 -RC₅H₄)₂M₂(CO)₄] (M = Mo, R = H, Me₃Si, MeCO; M = W, R = MeCO, MeO₂C, EtO₂C) reacted with Ph₂Te₂ in toluene at reflux to give a series of doubly bridged complexes [[η^5 -RC₅H₄)₂M₂(CO)₄(μ -TePh)₂] (**1**, M = Mo, R = H; **2**, Mo, Me₃Si; **3**, Mo, MeCO; **4**, W, MeCO; **5**, W, MeO₂C; **6**, W, EtO₂C), the reaction of [[η^5 -MeC₅H₄)₂Mo₂(CO)₄] with Ph₂Te₂ under the same conditions produced not only the corresponding doubly bridged complex [[η^5 -MeC₅H₄)₂Mo₂(CO)₄(μ -TePh)₂] (**7**) but also the unexpected triply bridged complex [[η^5 -MeC₅H₄)Mo₂(CO)₄(μ -TePh)₃] (**8**). For these bridged dinuclear complexes structural characterization and conformational analysis were carried out, while the crystal structures of **6** and **8**, representing the two types of the structures of complexes **1**–**8**, were successfully determined by single crystal X-ray diffraction techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ph₂Te₂; Metal–metal triple bond; Mo₂Te₂ complex; W₂Te₂ complex; Mo₂Te₃ complex; Crystal structure

1. Introduction

It is well known that reactions of Group 6 metal–metal triply bonded complexes [[η^5 -RC₅H₄)₂M₂(CO)₄] (M = Mo, W; η^5 -RC₅H₄ is the parent or a substituted cyclopenta-dienyl ligand) have been extensively studied and widely used in the synthesis of a variety of transition metal complexes, particularly organometallic clusters [1–6]. However, among the reactions studied so far only a few are reactions of Mo≡Mo triply bonded complexes [[η^5 -RC₅H₄)₂Mo₂(CO)₄] with Ph₂Te₂ [7,8] and not one is a reaction of a W≡W triply bonded complex [[η^5 -RC₅H₄)₂W₂(CO)₄] with Ph₂Te₂. So, we initiated a systematic study on reactions of M≡M triply

bonded complexes [[η^5 -RC₅H₄)₂M₂(CO)₄] (M = Mo, W) with Ph₂Te₂, in order to know the possible influences of the substituents R and metals M upon the reactions and to synthesize the two interesting μ -PhTe bridged transition metal compounds, in particular the new type of more μ -PhTe bridged dinuclear complexes.



Scheme 1.

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other. The distance between W1 and W2 (5.279 Å) is greater than the sum of the van der Waals radii of two tungsten atoms [11], which implies that there are no

bonding interactions between W1 and W2. However, since the distance between Te1 and Te2 (2.81 Å) is much less than the sum of the van der Waals radii of

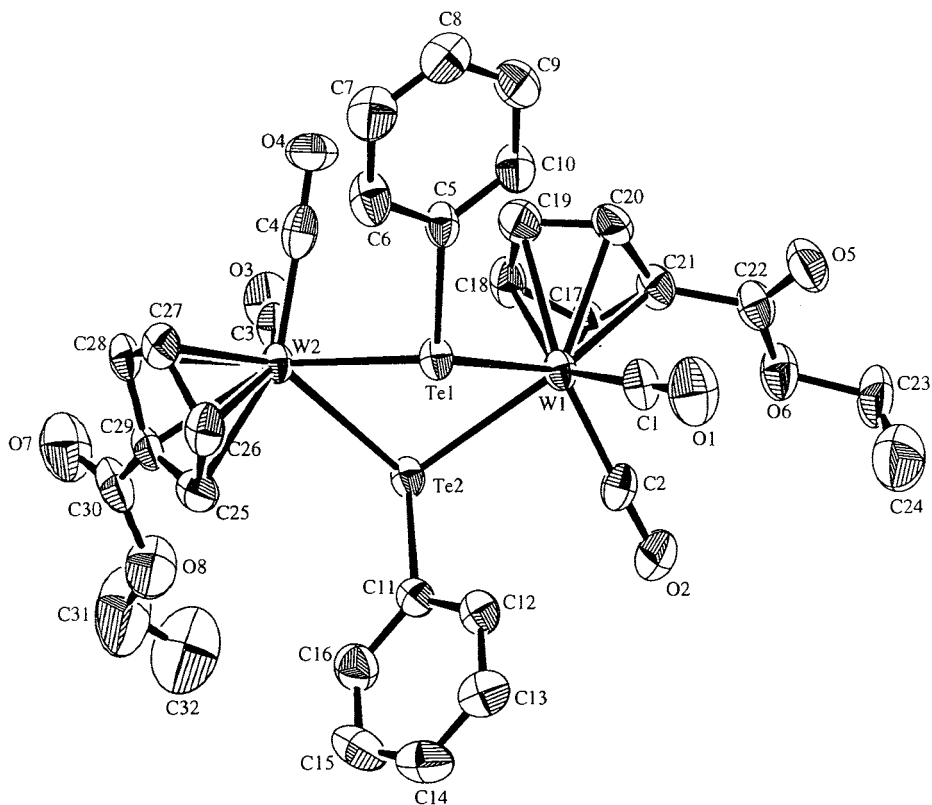


Fig. 1. ORTEP drawing of **6** with atom-labeling scheme.

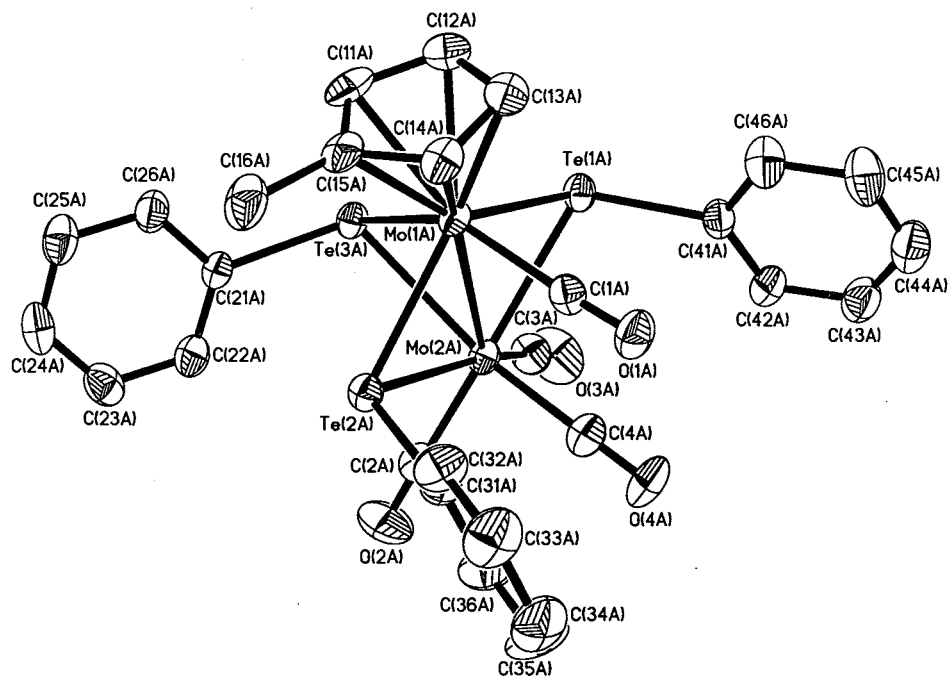


Fig. 2. ORTEP drawing of **8** with atom-labeling scheme.

Table 1
Selected bond lengths (Å) and angles (°) for **6**

| Bond lengths | | | |
|------------------|----------|------------------|----------|
| W(1)–Te(1) | 2.817(1) | W(1)–Te(2) | 2.819(1) |
| W(2)–Te(1) | 2.795(1) | W(2)–Te(2) | 2.833(1) |
| W(1)–C(17) | 2.280(8) | Te(1)–C(5) | 2.152(8) |
| W(2)–C(25) | 2.371(9) | Te(2)–C(11) | 2.138(8) |
| Bond angles | | | |
| W(1)–Te(1)–W(2) | 98.08(2) | Te(1)–W(1)–Te(2) | 71.09(2) |
| W(1)–Te(2)–W(1) | 97.16(2) | Te(1)–W(2)–Te(2) | 71.20(2) |
| W(1)–Te(1)–C(5) | 110.0(2) | W(1)–Te(2)–C(11) | 106.8(2) |
| Te(1)–W(1)–C(17) | 144.5(2) | Te(1)–W(2)–C(25) | 103.7(3) |

Table 2
Selected bond lengths (Å) and angles (°) for **8**

| Bond lengths | | | |
|----------------------|------------|----------------------|------------|
| Mo(1A)–Mo(2A) | 2.9354(8) | Mo(2A)–Te(1A) | 2.8035(8) |
| Mo(1A)–Te(1A) | 2.7232(7) | Mo(2A)–Te(2A) | 2.7880(7) |
| Mo(1A)–Te(2A) | 2.7173(7) | Mo(2A)–Te(3A) | 2.8305(7) |
| Mo(1A)–Te(3A) | 2.8344(7) | | |
| Bond angles | | | |
| Mo(1A)–Te(1A)–Mo(2A) | 64.144(19) | Mo(1A)–Te(2A)–Mo(2A) | 64.427(19) |
| Mo(1A)–Te(3A)–Mo(2A) | 62.418(18) | Te(1A)–Mo(1A)–Mo(2A) | 59.256(18) |
| Te(2A)–Mo(2A)–Mo(1A) | 56.619(18) | Te(3A)–Mo(1A)–Mo(2A) | 58.726(17) |
| Te(2A)–Mo(1A)–Te(3A) | 78.46(2) | Te(2A)–Mo(2A)–Te(3A) | 77.378(19) |
| Te(1A)–Mo(1A)–Te(2A) | 117.97(2) | Te(1A)–Mo(2A)–Te(2A) | 113.00(2) |

two tellurium atoms (4.4 Å) [11] and particularly less than the suggested value of 3.3 Å for possible interactions between Te atoms [12], we might suggest the existence of partial bonding interactions between Te1 and Te2 [12] (the single bond length of Te–Te is 2.71 Å in a typical Te–Te containing compound Ph₂Te₂ [13]).

It is worth noting that although the structure of **6** is similar to those of its molybdenum analogs [Cp₂Mo₂(CO)₄(μ-TePh)₂] (the Mo···Mo distance is 4.23 Å and the Te···Te distance is 3.24 Å) [7] and [(η⁵-MeO₂CC₅H₄)₂Mo₂(CO)₄(μ-TePh)₂] (the Mo···Mo distance is 4.259(3) Å and the Te···Te distance is 3.32 Å) [8], complex **6** is the first example of such a butterfly W₂Te₂ complex to be synthesized and structurally characterized.

More interesting is the structure of the unprecedented type of complex **8** shown in Fig. 2. X-ray diffraction analysis shows that it contains two butterfly skeletons Mo(1A)Mo(2A)Te(1A)Te(3A) and Mo(1A)Mo(2A)Te(2A)Te(3A). The shared butterfly wing Mo(1A)Mo(2A)Te(3A) is almost perpendicular (92.2°) to the plane comprising Mo(1A), Te(1A), Mo(2A) and Te(2A).

While Mo(1A) carries one Me-substituted cyclopentadienyl and one terminal CO ligand, Mo(2A) carries three terminal CO ligands. In addition, the two phenyl groups attached to Te(1A) and Te(2A) are *cis* to each other with respect to the plane Mo(1A)Te(1A)Mo(2A)Te(2A), whereas the phenyl group bonded to Te(3A) is in an equatorial position [10] in the first butterfly skeleton Mo(1A)Mo(2A)Te(1A)Te(3A) (note that in any two contiguous butterfly units if the Ph group attached to the Te atom of the common wing is equatorial in the first unit, then it will be axial in the second unit and vice versa [10]). So, although four isomers *cis/e*, *cis/a*, *trans/e* and *trans/a* are possible for **8** in terms of the *cis* or *trans* arrangements of the two Ph groups attached to Te(1A) and Te(2A) with respect to the plane mentioned above and the *a* or *e* orientations of the Ph group attached to Te(3A) in the first butterfly skeleton [10], the single crystal molecule of **8** has proved to be a *cis/e* isomer. However, the ¹H-NMR spectrum of **8** exhibited two singlets at 2.38 and 2.29 ppm in the ratio 3:2 for its Me substituent. So, this implies that **8** is originally a mixture of two isomers including *cis/e* and one of the other three in the ratio 3:2, and that the pure isomer *cis/e* was actually obtained during the single crystal growing process. The dihedral angles between the substituted Cp ring and the above-mentioned three Ph rings are 72.42, 83.92 and 88.95°, respectively. The bond lengths between Te(1A), Te(2A) or Te(3A) and Mo(1A) or Mo(2A) are within 2.7173(7)–2.8344(7) Å, whereas the bond angles Mo(1A)–Te(1A)–Mo(2A), Mo(1A)–Te(2A)–Mo(2A) and Mo(1A)–Te(3A)–Mo(2A) are within 62.418(18)–64.427(19)°. The single bond length of Mo(1A)–Mo(2A) is 2.9354(8) Å, which is slightly longer than the corresponding one (2.714(6) Å) in [(η⁵-MeO₂CC₅H₄)₂Mo₂(μ-Cl)(μ-TePh)₃] [8], but very close to that (2.93 Å) in [(η⁷-C₇H₇)Mo₂(CO)₃(μ-SBu-*t*)₃] [14]. Fig. 3 is the unit cell plot of **8**, from which it can be seen that each molecule of **8** carries one solvent molecule of acetone. This is in good agreement with its elemental analysis.

Finally, it should be noted that in contrast to **6**, since the distances of the two tellurium atoms Te(1A)···Te(3A) (3.38 Å) and Te(2A)···Te(3A) (3.51 Å) are greater than the suggested value of 3.3 Å for possible interactions between Te atoms [12], it seems likely that the partial bonding interactions between Te(3A) and Te(1A) or Te(2A) cannot exist.

3. Experimental

All the reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk or vacuum-line techniques. Toluene was distilled from

sodium-benzophenone ketyl under nitrogen. Ph_2Te_2 [15], $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{M}_2(\text{CO})_4]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{H}, \text{Me}, \text{Me}_3\text{Si}, \text{MeCO}, \text{MeO}_2\text{C}, \text{EtO}_2\text{C}$) [7a,16–19] were prepared according to the methods in the literature. The products were separated by preparative TLC (glass plates, $20 \times 25 \times 0.25 \text{ cm}^3$; 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. $^1\text{H-NMR}$ spectra were recorded on a JEOL FX-90Q or a Bruker AC-P 200 NMR spectrometer. C/H analysis and melting point determination were performed on a Yanaco CHN Corder MT-3 analyzer and on a Yanaco Mp-500 apparatus, respectively.

3.1. Preparation of 1

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 0.434 g (1.0 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$ and 0.409 g (1.0 mmol) of Ph_2Te_2 in 40 ml of toluene. The mixture was refluxed for 6 h. The solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone–petroleum ether ($v/v = 1:8$) as the eluent. The main band afforded 0.582 g (69%) of **1** as a brown solid, which has been identified by comparison of its IR and $^1\text{H-NMR}$ spectra with those of an authentic sample [7a].

3.2. Preparation of 2

The same procedure as that for **1** was followed, but 0.578 g (1.0 mmol) of $[(\eta^5\text{-Me}_3\text{SiC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4]$ was used instead of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. The main band was eluted with acetone–petroleum ether ($v/v = 1:5$) to give 0.774 g (83%) of **2** as a brown solid. m.p. 75–77°C. Anal. Found: C, 38.99; H, 3.79. Calc. for $\text{C}_{32}\text{H}_{36}\text{Mo}_2\text{O}_4\text{Si}_2\text{Te}_2$: C, 38.91; H, 3.67%. IR (KBr disk, cm^{-1}): terminal $\text{C}=\text{O}$ 1920s, 1925vs, 1852vs. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 0.13$ (s, 18H, 2 Me_3Si), 5.02–5.26 (m, 4H, 2 H^2 , 2 H^5), 5.42–5.71 (m, 4H, 2 H^3 , 2 H^4), 7.13–7.48 (m, 10H, 2 C_6H_5).

3.3. Preparation of 3

1. *Solution reaction method.* The same procedure as that for **1** was followed, but 0.518 g (1.0 mmol) of $[(\eta^5\text{-MeCOC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4]$ was used instead of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. Using CH_2Cl_2 as eluent, the main band afforded 0.802 g (86%) of **3** as a brown solid. m.p. 158–159°C. Anal. Found: C, 38.56; H, 2.71. Calc. for $\text{C}_{30}\text{H}_{24}\text{Mo}_2\text{O}_6\text{Te}_2$: C, 38.85; H, 2.61%. IR (KBr disk, cm^{-1}): acetyl carbonyl $\text{C}=\text{O}$ 1678s; terminal $\text{C}=\text{O}$ 1954vs, 1932vs, 1905s, 1875vs, 1848vs. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 1.98$ (s, 6H, 2 CH_3), 5.24–5.70 (m, 8H, 2 C_5H_4), 6.72–7.52 (m, 10H, 2 C_6H_5).

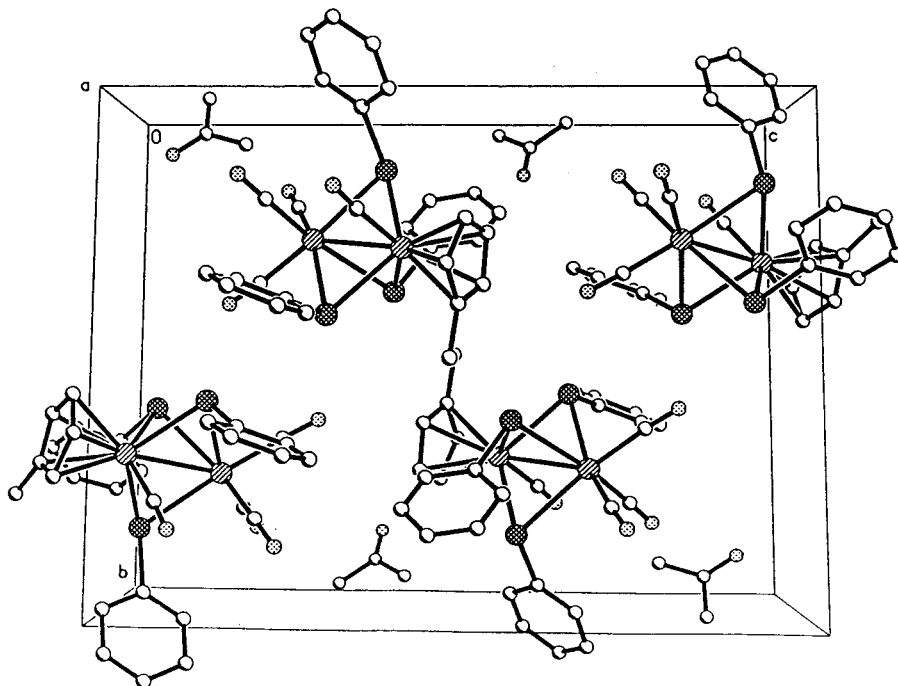


Fig. 3. The unit cell plot of **8**.

2. *Solid state reaction method.* A 50-ml Schlenk flask was charged with 0.155 g (0.3 mmol) of $[(\eta^5\text{-MeCOC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4]$ and 0.123 g (0.3 mmol) of Ph_2Te_2 . The finely powdered and uniformly mixed reaction mixture was heated at 60°C for 3 h. After TLC separation using CH_2Cl_2 as eluent, 0.245 g (88%) of **3** was obtained.

3.4. Preparation of **4**

The same procedure as that for **1** was followed, but 0.694 g (1.0 mmol) of $[(\eta^5\text{-MeCOC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4]$ was used instead of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. Using CH_2Cl_2 as eluent, the main band afforded 0.870 g (79%) of **4** as a brown solid. m.p. 147–148°C. Anal. Found: C, 32.14; H 2.12. Calc. for $\text{C}_{30}\text{H}_{24}\text{O}_6\text{Te}_2\text{W}_2$: C, 32.66; H, 2.19%. IR (KBr disk, cm^{-1}): acetyl carbonyl C=O 1682s; terminal C≡O 1927vs, 1859vs, 1835s. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 2.12$ (s, 6H, 2 CH_3), 5.44–5.90 (m, 8H, 2 C_5H_4), 7.04–7.60 (m, 10H, 2 C_6H_5).

3.5. Preparation of **5**

1. *Solution reaction method.* The same procedure as that for **1** was followed, but 0.725 g (1.0 mmol) of $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4]$ was used instead of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. Using CH_2Cl_2 as eluent, the main band gave 0.929 g (82%) of **5** as a brown solid. m.p. 139–141°C. Anal. Found: C, 31.89; H, 2.12. Calc. for $\text{C}_{30}\text{H}_{24}\text{O}_8\text{Te}_2\text{W}_2$: C, 31.74; H, 2.13%. IR (KBr disk, cm^{-1}): ester carbonyl C=O 1720s; terminal C≡O 1956vs, 1919vs, 1894vs, 1865s, 1824s. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 3.73$ (s, 6H, 2 CH_3), 5.36–5.70 (m, 4H, 2 H^3 , 2 H^4), 5.74–5.96 (m, 4H, 2 H^2 , 2 H^5), 7.00–7.64 (m, 10H, 2 C_6H_5).
2. *Solid state reaction method.* A 50-ml Schlenk flask was charged with 0.218 g (0.3 mmol) of $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4]$ and 0.123 g (0.3 mmol) of Ph_2Te_2 . The finely powdered and uniformly mixed reaction mixture was heated at 60°C for 3 h. After TLC separation using CH_2Cl_2 as eluent, 0.285 g (84%) of **5** was obtained.

3.6. Preparation of **6**

1. *Solution reaction method.* The same procedure as that for **1** was followed, but 0.754 g (1.0 mmol) of $[(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4]$ was used instead of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. Using CH_2Cl_2 as eluent, the main band afforded 0.898 g (77%) of **6** as a brown solid. m.p. 154–156°C. Anal. Found: C, 32.96; H, 2.50. Calc. for $\text{C}_{32}\text{H}_{28}\text{O}_8\text{Te}_2\text{W}_2$: C, 33.04; H, 2.43%. IR (KBr disk, cm^{-1}): ester carbonyl C=O 1713vs; terminal C≡O 1948vs, 1919vs, 1890vs, 1871s, 1828vs. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 1.26$ (t, $J = 7.2$ Hz, 6H,

2 CH_3), 4.22 (q, $J = 7.2$ Hz, 4H, 2 CH_2), 5.40–5.70 (m, 4H, 2 H^3 , 2 H^4), 5.74–5.94 (m, 4H, 2 H^2 , 2 H^5), 7.08–7.62 (m, 10H, 2 C_6H_5).

2. *Solid state reaction method.* A 50-ml Schlenk flask was charged with 0.226 g (0.3 mmol) of $[(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4]$ and 0.123 g (0.3 mmol) of Ph_2Te_2 . The finely powdered and uniformly mixed reaction mixture was heated at 60°C for 3 h. After TLC separation using CH_2Cl_2 as eluent, 0.282 g (81%) of **6** was obtained.

3.7. Preparation of **7** and **8**

The same procedure as that for **1** was followed, but 0.462 g (1.0 mmol) of $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4]$ was used instead of $[(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$. Using acetone–petroleum ether ($v/v = 1:5$) as eluent, from the first main band 0.276 g (34%) of **7** was obtained as a brown solid. m.p. 135–137°C. Anal. Found: C, 38.54; H, 2.72. Calc. for $\text{C}_{28}\text{H}_{24}\text{Mo}_2\text{O}_4\text{Te}_2$: C, 38.29; H, 2.97%. IR (KBr disk, cm^{-1}): terminal C≡O 1943s, 1916vs, 1846vs, 1829s. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 1.96$ (s, 6H, 2 CH_3), 5.02–5.32 (m, 8H, 2 C_5H_4), 7.12–7.50 (m, 10H, 2 C_6H_5). The second main band afforded 0.196 g (24%) of **8** as a green solid. m.p. 178–180°C. Anal. Found: C, 33.76; H, 2.03. Calc. for $\text{C}_{31}\text{H}_{28}\text{Mo}_2\text{O}_5\text{Te}_3$: C, 33.72; H, 2.22%. IR (KBr disk, cm^{-1}): terminal C≡O 1981vs, 1955vs, 1920s, 1861s. $^1\text{H-NMR}$ ($\text{CHCl}_3\text{-}d$): $\delta = 2.29$, 2.38 (s,s, 3H, CH_3), 5.34–5.68 (m, 4H, C_5H_4), 6.96–7.42 (m, 15H, 3 C_6H_5). Crystal growing of **8** in acetone–hexane ($v/v = 1:3$) gave **8** with one molecule of acetone, as a green crystal. Anal. Found: C, 35.01; H, 2.91. Calc. for $\text{C}_{31}\text{H}_{28}\text{Mo}_2\text{O}_5\text{Te}_3 \cdot \text{C}_2\text{H}_6\text{O}$: C, 35.28; H, 2.67%.

3.8. X-ray structure determination of **6**

Single crystals of **6** suitable for X-ray diffraction analysis were grown by slow evaporation of its CH_2Cl_2 –hexane ($v/v = 1:2$) solution at about 5°C. The single crystal of **6** ($0.2 \times 0.2 \times 0.3$ mm³) was glued to a glass fiber and mounted on a Rigaku ACF 7R diffractometer. Data were collected at room temperature, using graphite-monochromated Mo– K_α radiation ($\lambda = 0.71069$ Å). A total of 4397 independent reflections were collected at 20°C by the ω – 2θ scan mode, of which 3923 independent reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinement. The data were corrected for Lorentz polarization factors and empirical absorption. Crystallographic data are listed in Table 3.

3.9. X-ray structure determination of **8**

Single crystals of **8** suitable for X-ray diffraction analysis were grown by slow evaporation of its acetone–hexane ($v/v = 1:3$) solution at about 5°C. The

Table 3
Crystal data and structure refinements for **6** and **8**

| | 6 | 8 |
|--|---|--|
| Empirical formula | C ₃₂ H ₃₀ O ₉ Te ₂ W ₂ | C ₃₁ H ₂₈ Mo ₂ O ₅ Te ₃ |
| Formula weight | 1181.48 | 1055.21 |
| Temperature (K) | 293(2) | 298(2) |
| Crystal system | Triclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ (# 2) | <i>P</i> $\bar{1}$ |
| <i>a</i> (Å) | 12.278(5) | 10.5927(7) |
| <i>b</i> (Å) | 13.115(5) | 15.6762(10) |
| <i>c</i> (Å) | 11.708(4) | 20.4673(13) |
| α (°) | 97.55(3) | 89.2850(10) |
| β (°) | 101.60(3) | 87.3820(10) |
| γ (°) | 71.16(3) | 80.2460(10) |
| <i>V</i> (Å ³) | 1743(1) | 3346.0(4) |
| <i>Z</i> | 2 | 4 |
| <i>D_c</i> (g cm ⁻³) | 2.251 | 2.095 |
| Scan type | ω -2 θ | ω -2 θ |
| Absorption coefficient (mm ⁻¹) | 8.291 | 3.349 |
| <i>F</i> (000) | 1092 | 1976 |
| Reflections collected | 4656 | 13968 |
| Independent reflections | 4397 | 11756 |
| | [<i>R</i> _{int} = 0.067] | [<i>R</i> _{int} = 0.0368] |
| Goodness-of-fit on <i>F</i> ² | 1.56 | 1.049 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | | <i>R</i> ₁ = 0.0387, <i>wR</i> ₂ = 0.0950 |
| <i>R</i> indices (all data) | | <i>R</i> ₁ = 0.0545, <i>wR</i> ₂ = 0.1055 |
| <i>R</i> | 0.025 | |
| <i>R_w</i> | 0.036 | |
| Largest difference peak and hole (e Å ⁻³) | 0.86 and -0.73 | 1.110 and -0.849 |

single crystal of **8** (0.52 × 0.19 × 0.09 mm³) was glued to a glass fiber and mounted on a Bruker Smart 1000 automated diffractometer. Data were collected at 25°C, using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) in the ω -2 θ scan mode. The structure was solved by direct methods and refined by the full-matrix least-squares techniques (SHELXL-97) on *F*². Hydrogen atoms were located by using the geometric method. The crystal data and structural refinement details are summarized in Table 3.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge

Crystallographic Data Center, CCDC nos. 152543 for **6** and 152544 for **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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