Investigations on Novel Tandem Reaction of Three Components, $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$, Ph_2Te_2, and Cp_2TiCl_2, Cp_2ZrCl_2, or Cp_2ZrBr_2. Synthesis and Structural Characterization of Tetrakis- and Bis-Bridged Dimolybdenum Complexes $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (R = MeCO, MeO_2C, EtO_2C), $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (R = MeCO, MeO_2C, EtO_2C), $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-Br})(\mu\text{-PhTe})_3$ (R = MeO_2C, EtO_2C), and $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\mu\text{-PhTe})_2$ (R = MeO_2C, EtO_2C)

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While reaction of triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ (R = MeCO, MeO_2C) with Ph_2Te_2 in xylene at 110 °C and subsequent treatment with Cp_2TiCl_2 at reflux gives novel tetrakis-bridged complexes $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (**1**, R = MeCO; **3**, R = MeO_2C) and $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (**2a**,**b**, R = MeCO; **4a**,**b**, R = MeO_2C), the dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ (R = MeO_2C, EtO_2C) reacted with Ph_2Te_2 and Cp_2ZrCl_2 or Cp_2ZrBr_2 under similar conditions to afford novel tetrakis-bridged complexes $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (**3**, R = MeO_2C; **5**, R = EtO_2C), $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (**4a**,**b**, R = MeO_2C; **6a**,**b**, R = EtO_2C), and $(\eta^5\text{-RC}_5\text{H}_4\text{Mo})_2(\mu\text{-Br})(\mu\text{-PhTe})_3$ (**7a**,**b**, R = MeO_2C; **8a**,**b**, R = EtO_2C). A possible pathway for production of such tetrakis-bridged complexes has been suggested primarily on the basis of the following facts: (i) Treatment of triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ (R = MeO_2C, EtO_2C) with Ph_2Te_2 in xylene at 110 °C produces bis-bridged complexes $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\mu\text{-PhTe})_2$ (**9**, R = MeO_2C; **10**, R = EtO_2C) and (ii) reaction of **9** with Cp_2MCl_2 (M = Ti, Zr) yields tetrakis-bridged complexes **3** and **4a**,**b**. All the new products **1**−**10** are fully characterized by elemental analysis and IR, ^{1}H, and ^{125}Te NMR spectroscopies, and **4b** and **9** by single-crystal X-ray diffraction techniques.

Introduction

The group 6 metal−metal triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{M}]_2$ (M = Cr, Mo, W; $\eta^5\text{-RC}_5\text{H}_4$ = parent and substituted cyclopentadienyls) are of considerable interest since they are important synthons to react with organic, inorganic, and organometallic substrates, yielding a great variety of novel group 6 metal-containing complexes.[1] Some years ago, we started a project regarding such dimers, aimed to develop their new reaction modes and to prepare new types of group 6 metal-containing complexes, particularly organometallic clusters. Among our published papers related to this project[2] is an interesting tandem reaction of triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{M}]_2$ (M = Mo, W) with $[\text{Et}_3\text{NH}][(\mu\text{-R'S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]$ and oxygen, which affords a novel type of thiolato-bridged and oxo-capped trimetallic clusters $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{MFe}_2(\mu_3\text{-O})(\mu\text{-R'S})(\text{CO})_6$.[2g] As a continuation of this project, we recently carried out another tandem reaction of triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ with Ph_2Te_2 and subsequently with Cp_2TiCl_2, Cp_2ZrCl_2, or Cp_2ZrBr_2. Herein we report the results obtained from this study.

Results and Discussion

Tandem Reaction of $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$, Ph_2Te_2, and Cp_2MX_2 (M = Ti, Zr; X = Cl, Br). Synthesis and Characterization of 1−8. We found that the Mo−Mo

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(2) For example see: (a) Song, L.-C.; Wang J.-Q.; Hu, Q.-M.; Gao, W.-Q.; Han, B.-S. *Polyhedron* **1997**, *16*, 481. (b) Song, L.-C.; Wang, J.-Q.; Hu, Q.-M.; Huang, X.-Y. *Polyhedron* **1997**, *16*, 2249. (c) Song, L.-C.; Wang, J.-Q.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W. *Inorg. Chim. Acta* **1997**, *256*, 129. (d) Song, L.-C.; Wang, J.-Q.; Hu, Q.-M.; Sun, J. *J. Coord. Chem.* **1997**, *42*, 63. (e) Song, L.-C.; Shi, Y.-C.; Hu, Q.-M.; Du, F.; Mao, X.-A. *Polyhedron* **1998**, *18*, 19. (f) Song, L.-C.; Wang, J.-Q.; Hu, Q.-M.; Huang, X.-Y. *J. Coord. Chem.* **1999**, *46*, 245. (g) Song, L.-C.; Fan, H.-T.; Hu, Q.-M.; Qin, X.-D.; Zhu, W.-F.; Chen, Y.; Sun, J. *Organometallics* **1998**, *17*, 3454.

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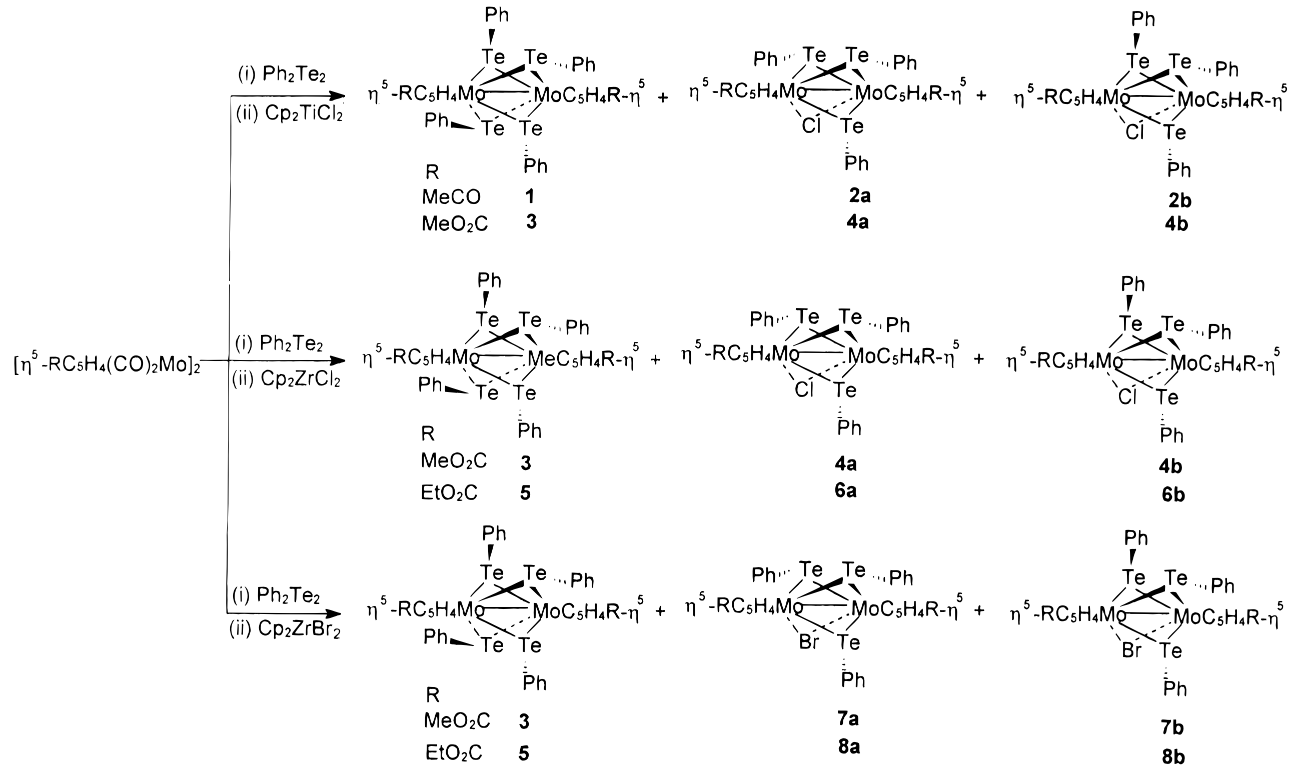
Scheme 1



triply bonded dimers $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$ (R = MeCO, MeO_2C) reacted with Ph_2Te_2 in xylene at 110 °C followed by treatment with Cp_2TiCl_2 at this temperature and then at reflux to give tetrakis-bridged complexes $(\eta^5\text{-}RC_5H_4Mo)_2(\mu\text{-}PhTe)_4$ (**1,** R = MeCO; **3,** R = MeO_2C) and $(\eta^5\text{-}RC_5H_4Mo)_2(\mu\text{-}Cl)(\mu\text{-}PhTe)_3$ (**2a**,**b**, R = MeCO; **4a**,**b**, R = MeO_2C), whereas reaction of $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$ (R = MeO_2C, EtO_2C) with Ph_2Te_2 and subsequently with Cp_2ZrCl_2 or Cp_2ZrBr_2 under similar conditions afforded tetrakis-bridged complexes $(\eta^5\text{-}RC_5H_4Mo)_2(\mu\text{-}PhTe)_4$ (**3**, R = MeO_2C; **5**, R = EtO_2C), $(\eta^5\text{-}RC_5H_4Mo)_2(\mu\text{-}Cl)(\mu\text{-}PhTe)_3$ (**4a**,**b**, R = MeO_2C; **6a**,**b**, R = EtO_2C), and $(\eta^5\text{-}RC_5H_4Mo)_2(\mu\text{-}Br)(\mu\text{-}PhTe)_3$ (**7a**,**b**, R = MeO_2C; **8a**,**b**, R = EtO_2C), as shown in Scheme 1.

While products **1**, **3**, and **5** belong to homo-tetrakis-bridged complexes which contain four identical PhTe ligands, products **2**, **4**, **6**, **7**, and **8** are mixed-tetrakis-bridged complexes, which have one halogenido (Cl or Br) and three PhTe ligands. The mixed-bridged complexes each have two isomers **a** and **b**, in which isomer **a** has two phenyl groups attached to the planar four-membered ring Mo_2Te_2 cis to the halogenido ligand, whereas isomer **b** has these two phenyl groups cis and trans to the halogenido ligand with respect to the planar Mo_2Te_2 ring, respectively. Although isomers **a** and **b** both contain two consecutive Mo_2Te_2 butterfly structural units, isomer **a** has two equatorial Ph groups in one of its butterfly units, whereas **b** has one axial Ph group and one equatorial Ph group in its corresponding one butterfly unit (for details, see crystal structure of **4b**). The homo-bridged complexes could be regarded as being generated by replacement of the halogenido ligand in isomer **a** or **b** by one PhTe ligand. Such homo-bridged complexes consist of four sequential Mo_2Te_2 butterfly structural units, each of which contains one axial Ph group and one equatorial Ph group. It is worth noting 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. In fact, all the products shown in Scheme 1 are new types of tetrakis-bridged complexes, which have been characterized by elemental analysis, by IR and NMR spectroscopies, and particularly by an X-ray diffraction analysis of isomer **4b**.

The IR spectra of **1** and **2a**,**b** showed one absorption band at about 1657 cm^{-1} for their acetyl groups, and those of **3**, **4a**,**b**, **5**, **6a**,**b**, **7a**,**b**, and **8a**,**b** exhibited one absorption band at around 1703 cm^{-1} for their ester groups. The ^1H NMR spectra of **1** and **2a**,**b** showed a singlet at ca. 2.1 ppm for their methyl groups of acetyls, whereas those of **3**, **4a**,**b**, and **7a**,**b** displayed a singlet at ca. 3.5 ppm for their methyl groups of methoxycarbonyls and those of **5, 6a**,**b**, and **8a**,**b** exhibited a triplet at ca. 1.2 ppm and a quartet at ca. 4.1 ppm for their ethoxycarbonyls. In addition, all the complexes **1**−**8** showed one multiplet at between 6.80 and 7.76 ppm for their phenyl groups and two multiplets for their monosubstituted Cp rings, one between 5.56 and 6.20 ppm assigned to H^2 and H^5 protons close to the substituents and the other between 5.40 and 5.86 ppm attributed to H^3 and H^4 protons remote from the substituents since the substituents are electron-withdrawing.[3−6] It is noteworthy that the two isomers for the Mo_2Te_3X (X = Cl, Br) complexes have similar but slightly different physical and spectroscopic properties. For example, the melting points and R_f values of isomer type **a** are greater than those of type **b**. In addition, as can be seen from the ^1H NMR spectra of one representative pair of

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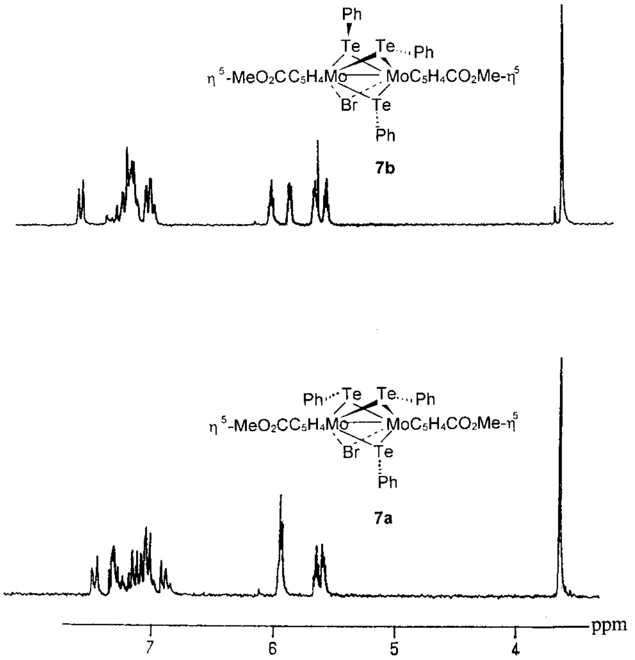

Figure 1. ^{1}H NMR spectra of one pair of isomers **7a** and **7b**.

isomers **7a** and **7b** (Figure 1), the ^{1}H NMR spectral patterns, particularly the shapes of the substituted Cp rings for isomers of type **a**, are somewhat different from those for isomers of type **b**.

During recent years, ^{125}Te NMR spectroscopy has been developed as an important tool for characterizing Te-containing organometallic compounds.[7-10] To further characterize our homo- and mixed-tetrakis-bridged complexes, the ^{125}Te NMR spectra of representatives **3** and **4b** (Figure 2) were determined with reference to external Ph_2Te_2. As seen from Figure 2, while **3** showed one singlet at −139 ppm, **4b** displayed three singlets at 113, −9, and −249 ppm. Apparently, this is consistent with the homo-bridged complexes having four environmentally identical Te atoms and the mixed-bridged complexes containing three environmentally different bridging Te atoms, respectively.

Crystal Structure of 4b. To unequivocally confirm the structures of isomer type **a** and type **b** for the mixed-tetrakis-bridged complexes and to provide more structural evidence for the homo-tetrakis-bridged complexes, we carried out the single-crystal diffraction analysis for isomer **4b**. The ORTEP drawing and unit cell plot of **4b** are shown in Figures 3 and 4. Table 1 lists its selected bond lengths and angles. As seen from Figure 4, in the unit cell each molecule of **4b** carries two solvent molecules of CH_2Cl_2. Figure 3 shows that **4b** consists of two substituted cyclopentadienyl ligands η^5-$MeO_2CC_5H_4$, three PhTe ligands, one Cl ligand, and two Mo atoms. The two η^5-$MeO_2CC_5H_4$ ligands are trans to each other with respect to the Mo(1)−Mo(2) bond, and the three PhTe and one Cl are bridged to the Mo(1)−Mo(2) bond. The dihedral angle between the two cyclopentadienyl planes C(11) through C(15) and C(21) through C(25) is calculated as 9.69°. In addition, Mo(1), Mo(2), Te(1), and Te(2) atoms, as well as Mo(1), Mo(2), Te(3), and Cl(1) atoms, are calculated to be coplanar, and the two planes are actually perpendicular, with a dihedral angle of 89.14°. It is noteworthy that the two phenyl groups attached to Te(1) and Te(2) are trans to each other with respect to the plane Mo(1)Mo(2)Te(1)Te(2), whereas the phenyl group bonded to Te(3) is cis to the phenyl group attached to Te(2). Interestingly, Te(1), Te(2), Te(3), and Cl(1) atoms are also coplanar. This plane is perpendicular to both Mo(1)Mo(2)Te(1)Te(2) and Mo(1)Mo(2)Te(3)Cl(1) planes, which is passed through the midpoint of the Mo(1)−Mo(2) bond. The bond angles Mo(1)−Te(1)−Mo(2), Mo(1)−Te(2)−Mo(2), and Mo(1)−Te(3)−Mo(2) are virtually the same (59.2(2)°, 59.1(2)°, and 59.4(1)°, respectively), which are smaller than that of Mo(1)−Cl(1)−Mo(2) (66.2(1)°). While the bond lengths of Mo−Cl equal 2.486(2) and 2.487(2) Å, those of Mo−Te are between 2.735(1) and 2.756(3)Å, which are very close to those in $Cp_2Mo_2(CO)_4(\mu\text{-}TePh)_2$ (2.785(4)−2.865(4)Å).[11] The bond length of Mo(1)−Mo(2) is 2.714(6) Å, which is slightly longer than that of $Cp_2Mo_2(\mu\text{-}SMe)_4$ (2.603(2) Å)[12] and very close to that in $Cp_2Mo_2(CO)_2(\mu\text{-}SMe)_3Br$ (2.785(2) Å).[13] Since the oxidation state of Mo(1) and Mo(2) is +III, **4b** belongs to a d^3−d^3 type of complex, and the electronic configuration of the Mo(1)−Mo(2) single bond would be best described as $\sigma^2\delta^2\delta^{*2}$.[14] In view of the determined structure of isomer **4b**, we might suggest that isomer **4a** would have the phenyl group attached to Te(2) in the cis position to both the Cl ligand and the phenyl group attached to Te(1). This is because it is impossible for all three phenyl groups to be in cis positions with respect to Mo(1)Mo(2)Te(1)Te(2) plane, due to very strong steric repulsion between the two phenyl groups axially bonded to Te(1) and Te(3) in the butterfly-shaped skeleton Mo(1)Mo(2)Te(1)Te(3).[15]

Reaction of $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$ with Ph_2Te_2. Synthesis and Characterization of 9 and 10. To know the pathway for production of the tetrakis-bridged dimolybdenum complexes **1**−**8** from the novel tandem reaction, we carried out the reaction of an equimolar amount of $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$ (R = MeO_2C, EtO_2C) with Ph_2Te_2 in xylene at 110 °C. As a result, two homo-bis-bridged dimolybdenum complexes **9** and **10** were obtained in high yields without tetrakis-bridged dimolybdenum complexes **3** and **5** produced, as shown in Scheme 2.

It is worth noting that when the triply bonded dimer $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$ reacted with Ph_2Te_2 in 1:2 molar ratio at higher temperature (in refluxing xylene, about 145 °C), only 14% of **9** was obtained (primarily due to serious thermal decomposition of the triply bonded dimer) and no tetrakis-bridged dimolybdenum

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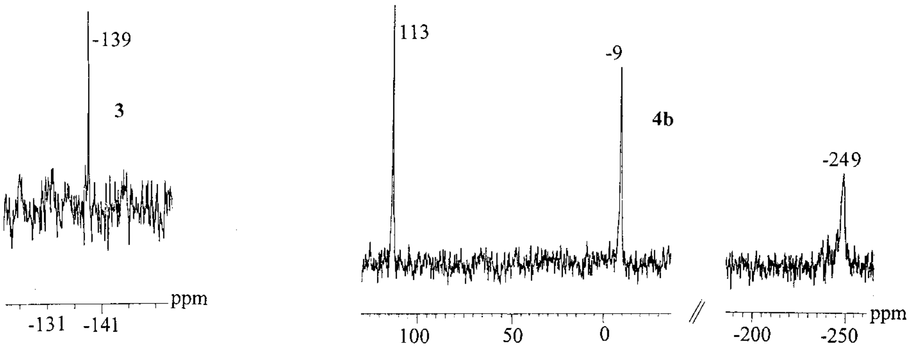


Figure 2. ^{125}Te NMR spectra of $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (**3**) and $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (**4b**).

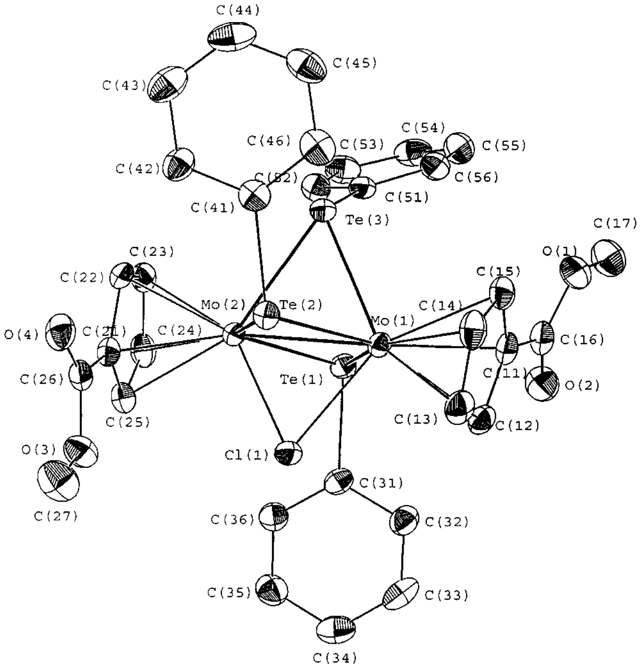


Figure 3. ORTEP drawing of **4b** with atom-labeling scheme.

complex **3** was isolated. These experiments imply that the homo-tetrakis-bridged complexes **1**, **3**, and **5** could not be produced directly from reaction of triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ with Ph_2Te_2 in the absence of Cp_2MX_2 (M = Ti, Zr; X = Cl, Br). In addition, TLC showed that the reaction of **9** with Ph_2Te_2 in 1:1 molar ratio in xylene at lower temperatures than that of refluxing xylene such as 105, 115, 125, or 135 °C for 2 h also gave no homo-tetrakis-bridged complex **3**, both starting materials **9** and Ph_2Te_2 being basically unchanged with trace amounts of immobile residue (CH_2Cl_2 as eluent) left on the original spot.

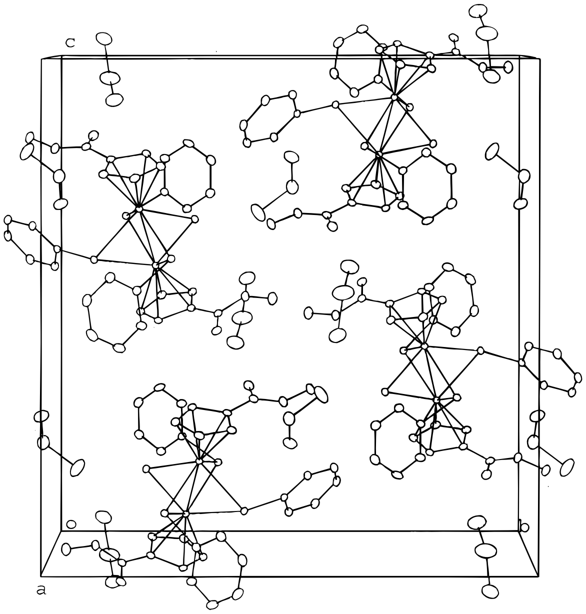
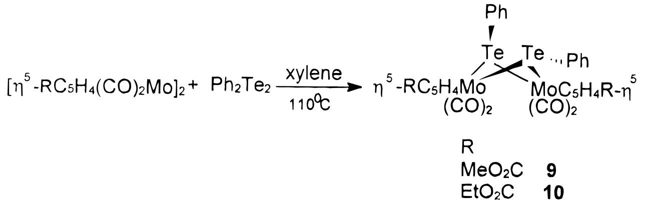


Figure 4. Unit cell plot of **4b**.

Table 1. Selected Bond Lengths (Å) and Bonds Angles (deg) for 4b

Mo(1)−Mo(2)	2.714(6)	Te(1)−Mo(2)	2.747(4)
Te(1)−Mo(1)	2.752(2)	Te(2)−Mo(1)	2.748(4)
Te(2)−Mo(2)	2.756(3)	Te(3)−Mo(2)	2.735(1)
Te(3)−Mo(1)	2.741(1)	Mo(1)−Cl(1)	2.487(2)
Mo(2)−Cl(1)	2.486(2)	Te(1)−C(31)	2.140(6)
Mo(1)−C(12)	2.242(6)	Mo(2)−C(22)	2.237(5)
Mo(2)−Te(1)−Mo(1)	59.2(2)	Mo(1)−Te(2)−Mo(2)	59.1(2)
Mo(2)−Te(3)−Mo(1)	59.4(1)	Mo(2)−Mo(1)−Te(3)	60.18(6)
Mo(2)−Mo(1)−Te(2)	60.60(4)	Mo(2)−Mo(1)−Te(1)	60.3(2)
Te(3)−Mo(1)−Te(2)	76.93(8)	Mo(1)−Mo(2)−Te(3)	60.40(8)
Mo(1)−Mo(2)−Te(1)	60.53(4)	Mo(1)−Mo(2)−Te(2)	60.3(2)
Te(3)−Mo(2)−Te(1)	76.2(1)	Te(3)−Mo(2)−Te(2)	76.90(5)
Te(1)−Mo(2)−Te(2)	120.8(2)	Mo(2)−Cl(1)−Mo(1)	66.2(1)

Scheme 2



9 and **10** are new and have been fully characterized by combustion analysis and IR and NMR spectroscopy, as well as by an X-ray diffraction analysis for **9** . The IR spectra of **9** and **10** each showed one absorption band at 1720 or 1716 cm^{-1} for their ester functionalities and four to five absorption bands in the range 1954−1846 cm^{-1} for their terminal carbonyls. The ^{1}H NMR spectra showed the signals assignable to all the hydrogen-containing groups, whereas the ^{125}Te NMR spectra each displayed one broad peak at −1160 or −1164 ppm with reference to external Ph_2Te_2 (Figure 5). It is interesting to note that such high-field ^{125}Te NMR values, compared to those of **3** and **4b**, imply that the Te atoms in bis-bridged complexes **9** and **10** are much more shielded than those in the tetrakis-bridged complexes by corresponding structural units around Te atoms. In addition, such high-field ^{125}Te NMR values were also observed in other tellurium-containing organometallic com-

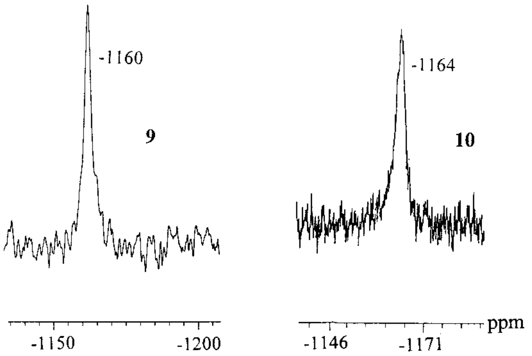


Figure 5. ^{125}Te NMR spectra of [η^5-$MeO_2CC_5H_4Mo$]$_2$(μ-PhTe)$_2$ (**9**) and [η^5-$EtO_2CC_5H_4(CO)_2Mo$]$_2$(μ-PhTe)$_2$ (**10**).

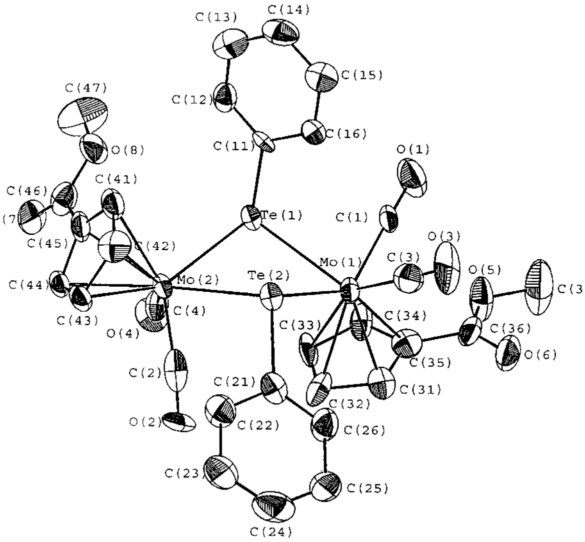


Figure 6. ORTEP drawing of **9** with atom-labeling scheme.

pounds, such as (μ-Te_2)[Cp*Re(CO)$_2$]$_2$,[16] (μ-Te_2)$Fe_2(CO)_6$,[17] [η^5-$MeC_5H_4MoFeTe_2(CO)_5$]SbF_6,[18] and [$(CO)_3Fe(\mu\text{-}CH_2)Te$]$_2$.[19]

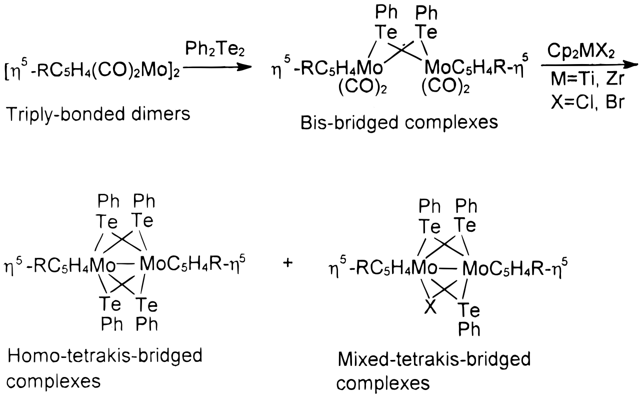
Theoretically, the bridged complexes of type [η^5-$RC_5H_4(CO)_2Mo$](μ-ER)$_2$ (η^5-RC_5H_4 = parent and substituted Cp; M = Cr, Mo, W; E = S, Se, Te) may have six isomers (namely, trans/ae, trans/ee, trans/aa, cis/ae, cis/ee, and cis/aa; a = axial, e = equatorial), in terms of the trans or cis arrangement of either η^5-RC_5H_4 or carbonyl ligands with respect to the M···M vector and the ae, ee, or aa orientations of two R groups bonded to the bridged E atoms in the butterfly skeleton M_2E_2.[20] So, to further establish the structures of **9** and **10**, we carried out the crystallographic study of **9** by X-ray diffraction techniques.

The ORTEP plot of **9** is presented in Figure 6, and its selected bond lengths and angles are listed in Table 2. As seen in Figure 6, this molecule contains a butterfly Mo(1)Mo(2)Te(1)Te(2) skeleton; the Mo(1) and Mo(2) atoms each carry one substituted Cp ring and two terminal carbonyls trans to each other, whereas the Te(1) and Te(2) atoms are attached to two phenyl groups by an axial and an equatorial bond, respectively. So, **9** belongs to the trans/ae isomer.[20] While the dihedral angle between the two cyclopentadienyl planes C(31) through C(35) and C(41) through C(45) is 44.27°, that between the two benzene ring planes C(11) through C(16) and C(21) through C(26) equals 72.41°. It is worth noting that the distance between Mo(1) and Mo(2) is 4.259(3) Å, which is even longer than those in its analogues [$CpMo(CO)_2$]$_2$(μ-EPh)$_2$ (E = S,[21] 3.940 Å; E = Se,[11] 4.054 Å, E = Te,[22] 4.23 Å). This implies that there is no bonding interactions between the two Mo atoms in **9**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 9

Mo(1)−Mo(2)	4.259(3)	Te(1)−Mo(1)	2.825(2)
Te(1)−Mo(2)	2.829(2)	Te(2)−Mo(2)	2.811(2)
Te(2)−Mo(1)	2.824(2)	Te(1)−C(11)	2.13(1)
Te(2)−C(21)	2.15(2)	Mo(1)−C(1)	1.95(2)
Te(2)−Mo(1)−Te(1)	70.81(6)	Te(2)−Mo(2)−Te(1)	70.94(6)
Mo(1)−Te(1)−Mo(2)	97.76(6)	Mo(2)−Te(2)−Mo(1)	98.19(6)
C(11)−Te(1)−Mo(1)	106.3(4)	C(11)−Te(1)−Mo(2)	105.8(4)
C(21)−Te(2)−Mo(2)	106.9(4)	C(21)−Te(2)−Mo(1)	108.3(4)
C(1)−Mo(1)−C(3)	78.8(8)	C(2)−Mo(2)−C(4)	76.5(7)

Scheme 3



Mechanistic Considerations for the Tandem Reaction. To further reveal the pathway for the tandem reaction, we carried out the reaction of an equimolar amount of **9** with Cp_2TiCl_2 or Cp_2ZrCl_2 in xylene at reflux. As a result, 34% of **4a** and a much less amount of **4b** and **3** (for Cp_2TiCl_2) and 9% of **4a** and trace of amounts of **4b** and **3** (for Cp_2ZrCl_2) were produced, respectively. So, based on these results and the above facts indicated by reaction of [η^5-$RC_5H_4(CO)_2Mo$]$_2$ with equimolar or excess Ph_2Te_2, a plausible pathway for the tandem reaction might be proposed as shown in Scheme 3.

In the first step of the tandem reaction, the Mo−Mo triply bonded dimers react with Ph_2Te_2 to give intermediate bis-bridged complexes [η^5-$RC_5H_4(CO)_2Mo$]$_2$(μ-PhTe)$_2$, and in the second step the bis-bridged complexes will further react with Cp_2MX_2 to give homo- and mixed-tetrakis-bridged complexes (η^5-RC_5H_4Mo)$_2$(μ-PhTe)$_4$ and (η^5-RC_5H_4 Mo)$_2$(μ-X)(μ-PhTe)$_3$. Apparently, in the second step Cp_2MX_2 played an important role both as a Cl or

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Br source and causing the transformation of the bis-bridged complexes $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\mu\text{-PhTe})_2$ into homo- and mixed-tetrakis-bridged products. It should be further pointed out that (i) the homo- and mixed-tetrakis-bridged complexes are most likely produced independently from the intermediate bis-bridged complexes under the action of Cp_2MX_2, since reaction of **3** with Cp_2TiCl_2 or **4b** with Ph_2Te_2 under those conditions gave no corresponding RTe/Cl ligand exchange products and about 90% of starting material **3** or **4b** was recovered. (ii) While n-Bu_4NBr can replace Cp_2ZrBr_2 as a bromide source in reaction of $[\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ with Ph_2Te_2 to give **7a** and **7b**, Me_4NCl cannot replace Cp_2MCl_2 (M = Ti, Zr) as a chloride source to give the expected **4a** and **4b**, possibly due to its very low solubility in xylene. (iii) We have never found any TLC isolated products that contain a Cp_2M unit, which should remain in the insoluble residues. It is believed that Cp_2MX_2 are not simply halide sources but are responsible for production of homo-tetrakis-bridged complexes **1**, **3**, and **5.** The metallocenes in this tandem reaction should be involved in the redox process, through which each Mo atom with an oxidation state of +I in triply bonded dimers is oxidized to the Mo atom with an oxidation state of +III in products **1**−**8**. However, at present the detailed pathway regarding this tandem reaction is still unclear, and more work remains to be studied in the future.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk and vacuum-line techniques. Xylene was distilled from sodium-benzophenone ketyl under nitrogen. Me_4NCl and n-Bu_4NBr were commercially available. Ph_2Te_2,[23] $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$,[24] Cp_2TiCl_2,[25] Cp_2ZrCl_2,[25] and $\text{Cp}_2\text{Zr Br}_2$[26] were prepared according to the literature. The products were separated by TLC (20 × 25 × 0.25 cm, silica gel G) and further purified by recrystallization from CH_2Cl_2/hexane. The yields of the products were calculated based on Mo−Mo triply bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$. IR spectra were recorded on a Nicolet FT-IR 170 SX spectrophotometer; ^{1}H and ^{125}Te NMR spectra were recorded on Brucker AC-P 200 and Bruker ARX-500 NMR spectrometers. ^{125}Te NMR spectra were referenced to Ph_2Te_2 (δ 0). Combustion analyses were performed on a Yanaco CHN corder MT-3 analyzer, and melting points were determined on Yanaco Mp-500 apparatus.

Preparation of $(\eta^5\text{-MeCOC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (1) and $(\eta^5\text{-MeCOC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (2a,b). 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 0.518 g (1.00 mmol) of $[\eta^5\text{-MeCOC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$, 0.470 g (1.15 mmol) of Ph_2Te_2, and 40 mL of xylene. The mixture was stirred at 110 °C for 1 h, and then 0.249 g (1.00 mmol) of Cp_2TiCl_2 was added. The mixture was stirred at 110 °C for 2 h and then at reflux (ca. 140 °C) for an additional 4 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 (11%) of **1** as a brown solid, mp 212−213 °C. Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{Mo}_2\text{Te}_4$: C, 37.26; H, 2.80. Found: C, 37.47; H, 2.85. IR (KBr disk): $\nu_{\text{C=O}}$ 1654(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 2.14(s, 6H, 2CH_3), 5.48−5.78(m, 4H, 2H^3, 2H^4), 5.84−6.12(m, 4H, 2H^2, 2H^5), 6.80−7.60(m, 20H, $4\text{C}_6\text{H}_5$) ppm. The second main band afforded 0.196 g (19%) of **2a** as a brown solid, mp 222 °C dec. Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{ClMo}_2\text{O}_2\text{Te}_3$: C, 36.41; H, 2.77. Found: C, 36.50; H, 2.71. IR (KBr disk): $\nu_{\text{C=O}}$ 1654(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 2.12(s, 6H, 2CH_3), 5.48−5.62(m, 4H, 2H^3, 2H^4), 5.63−5.86(m, 4H, 2H^2, 2H^5), 6.88−7.39(m, 15H, $3\text{C}_6\text{H}_5$) ppm. The third main band afforded 0.379 g (37%) of **2b** as a black-brown solid, mp 210 °C dec. Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{ClMo}_2\text{O}_2\text{Te}_3$: C, 36.41; H, 2.77. Found: C, 36.25; H, 2.63. IR (KBr disk): $\nu_{\text{C=O}}$ 1660(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 2.00(s, 6H, 2CH_3), 5.40−5.72(m, 4H, 2H^3, 2H^4), 5.80−6.12(m, 4H, 2H^2, 2H^5), 6.92−7.56(m, 15H, $3\text{C}_6\text{H}_5$) ppm.

Preparation of $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (3) and $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})(\mu\text{-PhTe})_3$ (4a,b). The same procedure as that for **1** and **2a**,**b** was followed, but 0.550 g (1.00 mmol) of $[\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ was used instead of $[\eta^5\text{-MeCOC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$. Using 4:1 (v/v) CH_2Cl_2/petroleum ether as eluent, the first main band afforded 0.159 g (13%) of **3** as a brown solid, mp 208−210 °C. Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{Mo}_2\text{O}_4\text{Te}_4$: C, 36.31; H, 2.73. Found: C, 36.25; H, 2.56. IR (KBr disk): $\nu_{\text{C=O}}$ 1707(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 3.62(s, 6H, 2CH_3), 5.60−5.76(m, 4H, 2H^3, 2H^4), 5.92−6.02(m, 4H, 2H^2, 2H^5), 6.88−7.56(m, 20H, $4\text{C}_6\text{H}_5$) ppm. ^{125}Te NMR (CDCl_3, Ph_2Te_2): −139(s) ppm. The second main band afforded 0.114 g (10%) of **4a** as a dark green solid, mp 216−218 °C. Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{ClMo}_2\text{O}_4\text{Te}_3$: C, 35.32; H, 2.71. Found: C, 35.60; H, 3.13. IR (KBr disk): $\nu_{\text{C=O}}$ 1706(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 3.63(s, 6H, 2CH_3), 5.56−5.76(m, 4H, 2H^3, 2H^4), 5.92−6.04(m, 4H, 2H^2, 2H^5), 6.88−7.56(m, 15H, $3\text{C}_6\text{H}_5$) ppm. The third main band afforded 0.421 g (39%) of **4b** as a dark green solid, mp 198−202 °C. Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{ClMo}_2\text{O}_4\text{Te}_3$: C, 35.32; H, 2.71. Found: C, 35.46; H, 2.50. IR (KBr disk): $\nu_{\text{C=O}}$ 1707(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 3.56(s, 6H, 2CH_3), 5.52−5.68(m, 4H, 2H^3, 2H^4), 5.84−6.04(m, 4H, 2H^2, 2H^5), 6.88−7.76(m, 15H, $3\text{C}_6\text{H}_5$) ppm. ^{125}Te NMR (CDCl_3, Ph_2Te_2): 113, −9, −249(s, s, s) ppm. In addition, while 0.096 g (8%) of **3**, 0.078 g (7%) of **4a**, and 0.189 g (17%) of **4b** could be also prepared from 0.550 g (1.00 mmol) of $[\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{ Mo}]_2$, 0.615 g (1.50 mmol) of Ph_2Te_2, and 0.292 g (1.00 mmol) of Cp_2ZrCl_2, the reaction of 0.712 g (1.3 mmol) of $[\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$, 0.532 g (1.3 mmol) of Ph_2Te_2, and 0.142 g (1.3 mmol) of Me_4NCl under similar conditions did not give any amount of **3** and **4a**,**b**.

Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (5) and $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-Cl})\ (\mu\text{-PhTe})_3$ (6a,b). Similarly, 0.578 g (1.00 mmol) of $[\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ reacted with 0.615 g (1.50 mmol) of Ph_2Te_2 and 0.292 g (1.00 mmol) of Cp_2ZrCl_2 to give three main bands. The first main band afforded 0.153 g (12%) of **5** as a green solid, mp 202−204 °C. Anal. Calcd for $\text{C}_{40}\text{H}_{38}\text{Mo}_2\text{O}_4\text{Te}_4$: C, 37.38; H, 2.98. Found: C, 37.29; H, 3.11. IR (KBr disk): $\nu_{\text{C=O}}$ 1702(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.19(t, J = 7.2 Hz, 6H, 2CH_3), 4.11(q, J = 7.2 Hz, 4H, 2CH_2), 5.56−5.68(m, 4H, 2H^3, 2H^4), 5.94−6.00(m, 4H, 2H^2, 2H^5), 6.80−7.52(m, 20H, $4\text{C}_6\text{H}_5$) ppm. The second main band afforded 0.196 g (18%) of **6a** as a yellow-green solid, mp 209−211 °C. Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{ClMo}_2\text{O}_4\text{Te}_3$: C, 36.59; H, 3.01. Found: C, 36.51; H, 3.07. IR (KBr disk): $\nu_{\text{C=O}}$ 1702(vs) cm^{-1}. ^{1}H NMR (CDCl_3): 1.21(t, J = 7.2 Hz, 6H, 2CH_3), 4.15(q, J = 7.2 Hz, 4H, 2CH_2), 5.54(br.s, 4H, 2H^3, 2H^4), 5.56−5.92(m, 4H, 2H^2, 2H^5), 6.88−7.24(m, 15H, $3\text{C}_6\text{H}_5$) ppm. The third main band afforded 0.374 g (34%) of **6b** as a dark green solid, mp 176−178 °C. Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{ClMo}_2\text{ O}_4\text{Te}_3$: C, 36.59; H, 3.01. Found: C, 36.60; H, 3.37. IR (KBr disk): $\nu_{\text{C=O}}$ 1703(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.10(t, J = 7.2 Hz, 6H, 2CH_3), 4.14(q, J = 7.2 Hz, 4H, 2CH_2), 5.60−5.80(m, 4H, 2H^3, 2H^4), 5.98−6.20(m, 4H, 2H^2, 2H^5), 7.00−7.76(m, 15H, $3\text{C}_6\text{H}_5$) ppm.

Preparation of $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-PhTe})_4$ (3) and $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Mo})_2(\mu\text{-Br})(\mu\text{-PhTe})_3$ (7a,b). Similarly, 0.550 g (1.00 mmol) of $[\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ reacted with 0.615

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g (1.50 mmol) of Ph_2Te_2 and 0.379 g (1.00 mmol) of Cp_2ZrBr_2 to give three main bands. The first main band afforded 0.049 g (4%) of **3**. The second main band afforded 0.096 g (9%) of **7a** as black-green solid, mp 214−216 °C. Anal. Calcd for $C_{32}H_{29}BrMo_2O_4Te_3$: C, 33.95; H, 2.58. Found: C, 33.85; H, 2.51. IR (KBr disk): $\nu_{C=O}$ 1705(vs) cm^{-1}. ^1H NMR (acetone-d_6): 3.63(s, 6H, $2CH_3$), 5.56−5.68(m, 4H, $2H^3$, $2H^4$), 5.88−6.00(m, 4H, $2H^2$, $2H^5$), 6.84−7.52(m, 15H, $3C_6H_5$) ppm. The second main band afforded 0.218 g (19%) of **7b** as a yellow-green solid, mp 192−194 °C. Anal. Cacld for $C_{32}H_{29}BrMo_2O_4Te_3$: C, 33.95; H, 2.58. Found: C, 34.12; H, 2.60. IR (KBr disk): $\nu_{C=O}$ 1707(vs) cm^{-1}. ^1H NMR (acetone-d_6): 3.58(s, 6H, $2CH_3$), 5.48−5.68(m, 4H, $2H^3$, $2H^4$), 5.76−6.00(m, 4H, $2H^2$, $2H^5$), 6.97−7.56(m, 15H, $3C_6H_5$) ppm. However, when 0.550 g (1 mmol) of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$ and 0.409 g (1 mmol) of Ph_2Te_2 reacted with 0.322 g (1 mmol) of n-Bu_4NBr under conditions similar to those in the case of Cp_2ZrBr_2, 0.042 g (4%) of **7a** and 0.285 g (26%) of **7b** were obtained without any amount of **3** isolated.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4Mo)_2(\mu\text{-}PhTe)_4$ (5) and $(\eta^5\text{-}EtO_2CC_5H_4Mo)_2(\mu\text{-}Br)(\mu\text{-}PhTe)_3$ (8a,b). Similarly, 0.578 g (1.00 mmol) of $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$ reacted with 0.615 g (1.50 mmol) of Ph_2Te_2 and 0.379 g (1.00 mmol) of Cp_2ZrBr_2 to give three main bands. The first main band afforded 0.046 g (4%) of **5**. The second main band afforded 0.112 g (10%) of **8a** as a black-green solid, mp 206−208 °C. Anal. Calcd for $C_{34}H_{33}BrMo_2O_4Te_3$: C, 35.20; H, 2.87. Found: C, 35.49; H, 2.92. IR (KBr disk): $\nu_{C=O}$ 1700(vs) cm^{-1}. ^1H NMR (acetone-d_6): 1.18(t, $J = 7.2$ Hz, 6H, $2CH_3$), 4.11(q, $J = 7.2$ Hz, 4H, $2CH_2$), 5.56−5.68(m, 4H, $2H^3$, $2H^4$), 5.88−6.00(m, 4H, $2H^2$, $2H^5$), 6.84−7.56(m, 15H, $3C_6H_5$) ppm. The second main band afforded 0.236 g (20%) of **8b** as a yellow-green solid, mp 188−192 °C. Anal. Calcd for $C_{34}H_{33}BrMo_2O_4Te_3$: C, 35.20; H, 2.87. Found: C, 34.83; H, 3.02. IR (KBr disk): $\nu_{C=O}$ 1707(vs) cm^{-1}. ^1H NMR (acetone-d_6): 1.10(t, $J = 7.2$ Hz, 6H, $2CH_3$), 4.08(q, $J = 7.2$ Hz, 4H, $2CH_2$), 5.48−5.68(m, 4H, $2H^3$, $2H^4$), 5.76−6.04(m, 4H, $2H^2$, $2H^5$), 6.88−7.60(m, 15H, $3C_6H_5$) ppm.

Preparation of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2(\mu\text{-}PhTe)_2$ (9). To the same equipped flask described above were added 0.550 g (1.00 mmol) of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$ 0.409 g (1.00 mmol) of Ph_2Te_2, and 40 mL of xylene. The mixture was stirred at 110 °C for 6 h. Solvent was removed under reduced pressure. The residue was subjected to column chromatography using CH_2Cl_2 as eluent. From the main brown band was obtained 0.850 g (89%) of **9** as a brown solid, mp 149−150 °C. Anal. Calcd for $C_{30}H_{24}Mo_2O_8Te_2$: C, 37.55; H, 2.52. Found: C, 37.51; H, 2.40. IR (KBr disk): $\nu_{C\equiv O}$ 1954(s), 1936(vs), 1898(m), 1875(vs), 1863(s); $\nu_{C=O}$1720(vs) cm^{-1}. ^1H NMR ($CDCl_3$): 3.72(s, 6H, $2CH_3$), 5.28−5.58(m, 4H, $2H^3$, $2H^4$), 5.58−5.86(m, 4H, $2H^2$, $2H^5$), 7.00−7.64(m, 10H, $2C_6H_5$) ppm. ^{125}Te NMR ($CDCl_3$, Ph_2Te_2): −1160(s) ppm. However, when 0.275 g (0.50 mmol) of $[\eta^5\text{-}MeO_2C\ C_5H_4(CO)_2Mo]_2$ reacted with 0.409 g (1 mmol) of Ph_2Te_2 in 40 mL of xylene at reflux for 4 h, a much less amount of **9** (0.067 g, 14%) was obtained.

Preparation of $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2(\mu\text{-}PhTe)_2$ (10). The same procedure as that for **9** was followed, but 0.578 g (1.00 mmol) of $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$ was used instead of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$. The main brown band afforded 0.857 g (87%) of **10** as a brown solid, mp 124−125 °C. Anal. Calcd for $C_{32}H_{28}Mo_2O_8Te_2$: C, 38.92; H, 2.86. Found: C, 39.00; H, 3.01. IR (KBr disk): $\nu_{C\equiv O}$ 1954(s), 1938(vs), 1882(vs), 1846(vs); $\nu_{C=O}$1716(s) cm^{-1}. ^1H NMR ($CDCl_3$): 1.27(t, $J = 7.2$ Hz, 6H, $2CH_3$), 4.26(q, $J = 7.2$ Hz, 4H, $2CH_2$), 5.40−5.62(m, 4H, $2H^3$, $2H^4$), 5.62−5.94(m, 4H, $2H^2$, $2H^5$), 7.08−7.68(m, 10H, $2C_6H_5$) ppm. ^{125}Te NMR ($CDCl_3$, Ph_2Te_2): −1164(s) ppm.

Reaction of 9 with Cp_2TiCl_2 or Cp_2ZrCl_2. To the same equipped flask described above were added 0.480 g (0.50 mmol) of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2(\mu\text{-}PhTe)_2$ (**9**), 0.125 g (0.50 mmol) of Cp_2TiCl_2, and 40 mL of xylene. The mixture was stirred at reflux for 4 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether as eluent. The dark green main band afforded 0.185 g (34%) of **4b** and a much less amount (not weighed) of **4a** and **3**. When 0.146 g (0.50 mmol) of Cp_2ZrCl_2 was used in place of Cp_2TiCl_2, 0.054 g (10%) of **4b** and a much less amount of **4a** and **3** were produced.

Table 3. Crystalllographic Data for 4b and 9

	4b	9
mol formula	$C_{32}H_{29}ClMo_2O_4Te_3\cdot 2CH_2Cl_2$	$C_{30}H_{24}Mo_2O_8Te_2$
mol wt	1257.58	959.59
cryst dimens, mm	0.90 × 0.40 × 0.30	0.60 × 0.20 × 0.10
cryst syst	monoclinic	triclinic
space group	$P21/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.856(3)	11.949(4)
b, Å	19.4599(6)	12.809(7)
c, Å	20.418(3)	11.503(4)
α, deg		82.48(4)
β, deg	95.91(3)	78.62(2)
γ, deg		73.92(4)
V, Å^3	3895(2)	1653(3)
Z	4	2
density(calcd), g/cm^{-3}	2.083	1.960
F(000)	2304	928
μ(Mo Kα), cm^{-1}	32.18	25.24
diffractometer	Enraf-Nonius CAD 4	Rigaku-AFC 5R
temp, °C	23	23
scan type	$\omega/2\theta$	$\omega/2\theta$
R	0.034	0.073
R_w	0.047	0.094
S	1.38	2.30
largest peak (e/Å^{-3})	0.706	2.76

Reaction of 3 with Cp_2TiCl_2. A mixture of 0.063 g (0.05 mmol) of **3** and 0.013 g (0.05 mmol) of Cp_2TiCl_2 in 40 mL of xylene was stirred and refluxed for 6 h. After removal of solvent under vacuum the residue was subjected to TLC separation using CH_2Cl_2 as eluent to recover 0.055 g (87%) of starting material **3**.

Reaction of 4b with Ph_2Te_2. A mixture of 0.109 g (0.10 mmol) of **4b** and 0.082 g (0.20 mmol) of Ph_2Te_2 in 40 mL of xylene was stirred at reflux for 6 h. After the same workup as above, 0.099 g (91%) of starting material **4b** was recovered.

Single-Crystal Structure Determinations of 4b and 9. Single crystals of **4b** and **9** suitable for X-ray diffraction analyses were grown from CH_2Cl_2/hexane solutions at about 5 °C. A crystal was mounted on a glass fiber and placed on the diffractometer with a graphite monochromator with Mo−Kα radiation. A total of 7502 (**4b**) or 6128 (**9**) independent reflections were collected at 23 °C by the $\omega/2\theta$ scan mode, of which 7189 (**4b**) or 5820 (**9**) 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. Crystallographic data are listed in Table 3.

The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and H atoms were included but not refined. The final refinement by a full-matrix least-squares method with non-H atoms converged to give the unweighted and weighted agreement factors. All calculations were performed using the TEXSAN program system crystallographic software of the Molecular Structure Corporation.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **4b** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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