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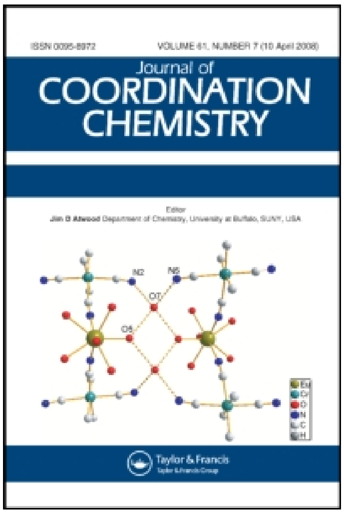

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Syntheses and crystal structures of butterfly M_2Te_2 complexes of molybdenum and tungsten with functionalized cyclopentadienyl ligands

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Syntheses and crystal structures of butterfly M_2Te_2 complexes of molybdenum and tungsten with functionalized cyclopentadienyl ligands

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Reactions of singly-bonded dinuclear complexes $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2M_2(CO)_6]$ (**I**, M = Mo; **II**, M = W) with the diarenylditelluride $[4\text{-}CH_3C_6H_4Te]_2$ in refluxing toluene for 4–6 h afforded dinuclear complexes **1** and **2** *trans*/ae-$[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4(\mu\text{-}ArTe)_2]$ (Ar = 4-$CH_3C_6H_4Te$). Complexes **1** and **2** were also synthesized by reactions of triply-bonded dinuclear complexes $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2M_2(CO)_4]$ (**III**, M = Mo; **IV**, M = W) with $[4\text{-}CH_3C_6H_4Te]_2$ in refluxing toluene for 1 h. Both complexes have been characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and IR spectroscopy and X-ray diffraction. Preliminary low-temperature NMR experiments on complexes **1** and **2** have revealed that in solution each complex goes through a rapid inversion of the butterfly four-membered ring M_2Te_2.

Keywords: Metal–metal bond; Molybdenum complex; Tungsten complex; Crystal structure

1. Introduction

During the past two decades, group 6 metal triply-bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_4]$ (η^5-RC_5H_4 = parent and substituted cyclopentadienyls; M = Cr, Mo, W) have attracted much interest because of their novel reactions and widespread use for syntheses of organometallic compounds [1–8]. However, the chemistry of the corresponding metal–metal singly-bonded complexes $[(\eta^5\text{-}RC_5H_4)_2M_2(CO)_6]$ has been less explored [9–12]. Recently, I have found that reaction of singly-bonded dimolybdenum complexes $[(\eta^5\text{-}RC_5H_4)_2Mo_2(CO)_6]$ (R = CH_3CO, C_6H_5CO, CH_3O_2C, $C_2H_5O_2C$) with diphenylditelluride in the presence of ^{n}Bu$_4$NI affords quadruply-bridged dimolybdenum complexes *cis*/ae-$[(\eta^5\text{-}RC_5H_4)_2Mo_2(\mu\text{-}Te)_2(\mu\text{-}TePh)_2]$ [12]. In continuation of this work I report here the syntheses and crystal structures of butterfly M_2Te_2 complexes with functionalized cyclopentadienyl ligands (M = Mo, W).

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2. Experimental

All reactions were carried out under purified dinitrogen using standard Schlenk techniques. Toluene was distilled from Na/benzophenone under dinitrogen. Singly-bonded dinuclear complexes $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2M_2(CO)_6]$ (**I**, M = Mo; **II**, M = W), triply-bonded dinuclear complexes $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2M_2(CO)_4]$ (**III**, M = Mo; **IV**, M = W) and $(4\text{-}CH_3C_6H_4)_2Te_2$ were prepared according to literature methods [13–15]. Progress of the reactions was monitored periodically by TLC. The products were separated by preparative TLC (silica gel H, 10–40 µm) in air and further recrystallized from deoxygenated solvents (CH_2Cl_2/petroleum ether). NMR spectra were determined by using a Bruker Avance 600 spectrometer with TMS as external standard in D_3COCD_3. IR spectra were recorded on a Perkin-Elmer 402 instrument as KBr disks in the range 400–4000 cm^{-1}. C and H analyses were performed on an Elementa Vario EL III instrument. Melting points were measured on a Yanagimoto instrument and are uncorrected.

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2.1. *Synthesis of* $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_4(\mu\text{-}TeAr)]_2$ *(Ar = 4-*$CH_3C_6H_4$*)*

Method A. A 100-mL Schlenk flask fitted with a magnetic stir-bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 0.606 g (1 mmol) of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_6]$ and 0.438 g (1 mmol) of Ar_2Te_2 in 40 mL of toluene. The mixture was refluxed for 4 h. The resulting brown mixture was evaporated to dryness under vacuum. The residue was subjected to preparative TLC using CH_2Cl_2/petroleum ether (4:1) as eluant. The main band afforded 0.869 g (88%) of complex **1** as a brown solid.

Method B. The similar reaction of 0.138 g (0.25 mmol) of $(\eta^5\text{-}CH_3O_2CC_5H_4)_2$ $Mo_2(CO)_4]$ and 0.110 g (0.25 mmol) of Ar_2Te_2 for 1 h afforded 0.200 g (83%) of complex **1**. Mp 172.3–174.2°C. Anal. Calcd. for $C_{32}H_{28}Mo_2O_8Te_2$(%): C, 38.92; H, 2.86. Found: C, 39.21; H, 3.04. IR (KBr disk): terminal carbonyl 1938 (vs), 1875 (sh, vs), 1858 (vs); ester carbonyl 1723 (s) cm^{-1}. ^1H NMR (600 MHz, D_3COD_3): δ 2.354 (s, 6H, $2CH_3$), 3.734 (s, 6H, $2OCH_3$), 5.597, 5.681, 5.786, 5.900 (4s, 2H, 2H, 2H, 2H, $2C_5H_4$), 7.082–7.095, 7.453–7.466 (2s, 4H, 4H, $2C_6H_4$). ^{13}C NMR (600 MHz, D_3COD_3): δ 20.194 (CH_3), 51.276 (OCH_3), 90.717, 94.185, 94.753, 98.254, 98.306, 100.047 (C_5H_4), 129.371, 137.192, 138.310 (C_6H_4), 164.959 (C=O), 205.266 (C≡O).

2.2. *Synthesis of* $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2W_2(CO)_4(\mu\text{-}TeAr)]_2$ *(Ar = 4-*$CH_3C_6H_4$*)*

Method A. The similar reaction of 0.782 g (1 mmol) of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2W_2(CO)_6]$ and 0.438 g (1 mmol) of Ar_2Te_2 for 6 h after preparative TLC using CH_2Cl_2/petroleum ether (4:1) as eluant afforded 0.991 g (85%) of complex **2** as a brown solid.

Method B. The similar reaction of 0.182 g (0.25 mmol) of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2$ $W_2(CO)_4]$ and 0.110 g (0.25 mmol) of Ar_2Te_2 for 1 h afforded 0.233 g (80%) of complex **2**. Mp 183.1–184.8°C. Anal. Calcd. for $C_{32}H_{28}W_2O_8Te_2$(%): C, 33.03; H, 2.43. Found: C, 33.39; H, 2.78. IR (KBr disk): terminal carbonyl 1931 (vs), 1861 (sh, vs), 1845 (vs); ester carbonyl 1724 (s) cm^{-1}. ^1H NMR (600 MHz, D_3COD_3): δ 2.308 (s, 6H, $2CH_3$), 3.720 (s, 6H, $2OCH_3$), 5.635, 5.711–5.750, 5.833–5.865, 5.940–6.022 (4m, 2H, 2H,

Table 1. Crystallographic data and structure refinements for complexes **1** and **2**.

	1	**2**
Formula	$C_{32}H_{28}Mo_2O_8Te_2$	$C_{32}H_{28}W_2O_8Te_2$
Formula weight	987.62	1163.44
Crystal size (mm)	$0.5 \times 0.4 \times 0.3$	$0.18 \times 0.14 \times 0.12$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.610(2)	11.635(4)
b (Å)	12.360(3)	12.393(5)
c (Å)	13.630(3)	13.633(5)
α (°)	72.56(3)	72.552(6)
β (°)	66.69(3)	66.516(5)
γ (°)	76.81(3)	76.682(6)
V (Å^3)	1700.2(6)	1706.0(11)
Z	2	2
D_c (g cm^{-1})	1.929	2.265
F (000)	944	1072
T (K)	293(2)	293(2)
μ (Mo Kα) (mm^{-1})	2.466	8.460
Scan mode	ω–2θ	ϕ–ω
Θ range (°)	1.67; 24.98	1.67; 26.37
Limiting indices	$0 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 16$	$-14 \le h \le 13$, $-9 \le k \le 15$, $-15 \le l \le 17$
Absorption correction	PSI-scan	Multi-scan
Reflections collected	6286	9819
Independent reflections	5964 [$R_{\text{int}} = 0.0331$]	6886 [$R_{\text{int}} = 0.0290$]
No. of parameters refined	397	397
Final R indices [$I > 2.0\sigma(I)$]	$R = 0.0381$, $Rw = 0.1846$	$R = 0.0364$, $Rw = 0.0778$
R indices (all data)	$R = 0.0466$, $Rw = 0.1914$	$R = 0.0679$, $Rw = 0.1059$
Goodness of fit	1.294	1.054
Max. peak and hole (e Å^{-3})	1.024 and −1.155	1.390 and −1.506

2H, 2H, $2C_5H_4$), 7.105–7.158, 7.485–7.503 (2m, 4H, 4H, $2C_6H_4$). ^{13}C NMR (600 MHz, D_3COD_3): δ 20.157 (CH_3), 51.314 (OCH_3), 88.799, 91.759, 92.110, 98.367, 99.860, 100.114 (C_5H_4), 129.498, 136.602, 138.255 (C_6H_4), 164.944 (C=O), 205.222 (C≡O).

2.3. *Crystal structure determination*

Bright red, single crystals for X-ray determination were obtained by layering the CH_2Cl_2 solutions of complexes **1** and **2** with petroleum ether at *ca* 5°C. For each complex, a selected single crystal was mounted on a glass fiber with epoxy resin. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer for complex **1** and a Bruker SMART CCD area detector diffractometer for complex **2** using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data were corrected using PSI-scan for complex **1** and Multi-scan for complex **2**. The structures were solved by direct methods and refined by full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. All computations were carried out using SHELXS-97 and SHELXL-97 programs [16,17]. ORTEP and PLUTON drawings were made with the WinGx Program System [18]. Crystal data and details of data collection and structure refinement are summarized in table 1. Selected bond lengths and angles of complexes **1** and **2** are listed in tables 2 and 3.

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Table 2. Selected bond lengths (Å) and angles (°) for complex **1**.

Mo(1)–Te(1)	2.798(1)	O(7)–C(9)	1.15(1)
Mo(1)–Te(2)	2.810(2)	O(8)–C(10)	1.17(1)
Mo(2)–Te(1)	2.787(1)	C(2)–C(11)	1.53(2)
Mo(2)–Te(2)	2.839(1)	C(7)–C(43)	1.49(2)
Mo(1)–C(4)	1.96(1)	O(1)–C(2)	1.19(2)
Mo(1)–C(5)	1.94(1)	O(2)–C(2)	1.32(2)
Mo(2)–C(9)	1.96(1)	O(2)–C(1)	1.53(2)
Mo(2)–C(10)	1.95(1)	O(5)–C(7)	1.21(2)
Te(1)–C(23)	2.13(1)	O(6)–C(7)	1.34(2)
Te(2)–C(34)	2.147(9)	O(6)–C(6)	1.46(2)
O(3)–C(4)	1.13(1)	C(14)$\cdots$O(4)$^{\text{i}}$	3.37(2)
O(4)–C(5)	1.17(1)	C(32)$\cdots$O(1)$^{\text{ii}}$	3.47(2)
Mo(1)–Te(1)–Mo(2)	99.42(4)	Mo(2)–C(10)–O(8)	178(1)
Mo(1)–Te(2)–Mo(2)	97.90(4)	O(1)–C(2)–C(11)	122 (2)
Te(1)–Mo(1)–Te(2)	70.94(3)	O(1)–C(2)–O(2)	128(2)
Te(1)–Mo(2)–Te(2)	70.66(4)	O(2)–C(2)–C(11)	110(2)
Mo(1)–Te(1)–C(23)	105.9(3)	C(1)–O(2)–C(2)	107(2)
Mo(1)–Te(2)–C(34)	106.3(3)	O(5)–C(7)–C(43)	125(1)
Mo(2)–Te(1)–C(23)	112.0(3)	O(5)–C(7)–O(6)	124(1)
Mo(2)–Te(2)–C(34)	106.3(3)	O(6)–C(7)–C(43)	111(1)
Mo(1)–C(4)–O(3)	176(1)	C(6)–O(6)–C(7)	117(1)
Mo(1)–C(5)–O(4)	179(1)	C(14)–H(14A)$\cdots$O(4)$^{\text{i}}$	166
Mo(2)–C(9)–O(7)	178(1)	C(32)–H(32A)$\cdots$O(1)$^{\text{ii}}$	159

Symmetry codes: (i) $1-x$, $3-y$, $1-z$; (ii) $-x$, $2-y$, $2-z$.

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

W(1)–Te(1)	2.799(1)	O(3)–C(3)	1.17(1)
W(1)–Te(2)	2.812(1)	O(4)–C(4)	1.15(1)
W(2)–Te(1)	2.791(1)	C(5)–C(10)	1.53(2)
W(2)–Te(2)	2.844(1)	C(12)–C(17)	1.50(2)
W(1)–C(1)	1.96(1)	O(5)–C(10)	1.18(2)
W(1)–C(2)	1.95(1)	O(6)–C(10)	1.30(2)
W(2)–C(3)	1.96(1)	O(6)–C(11)	1.473(9)
W(2)–C(4)	1.98(1)	O(7)–C(17)	1.18(1)
Te(1)–C(19)	2.146(9)	O(8)–C(17)	1.32(2)
Te(2)–C(26)	2.142(9)	O(8)–C(18)	1.47(2)
O(1)–C(1)	1.15(1)	C(7)$\cdots$O(2)$^{\text{i}}$	3.36(2)
O(2)–C(2)	1.16(1)	C(18)$\cdots$O(1)$^{\text{ii}}$	3.45(2)
W(1)–Te(1)–W(2)	99.53(3)	W(2)–C(4)–O(4)	176(1)
W(1)–Te(2)–W(2)	97.98(3)	O(5)–C(10)–C(5)	121(2)
Te(1)–W(1)–Te(2)	71.08(3)	O(5)–C(10)–O(6)	128(2)
Te(1)–W(2)–Te(2)	70.73(2)	O(6)–C(10)–C(5)	111(2)
W(1)–Te(1)–C(19)	105.4(2)	C(10)–O(6)–C(11)	107(2)
W(1)–Te(2)–C(26)	105.7(3)	O(7)–C(17)–C(12)	123(1)
W(2)–Te(1)–C(19)	112.1(3)	O(7)–C(17)–O(8)	128(1)
W(2)–Te(2)–C(26)	106.6(2)	O(8)–C(17)–C(12)	109(1)
W(1)–C(1)–O(1)	177(1)	C(17)–O(8)–C(18)	114(1)
W(1)–C(2)–O(2)	179.1(9)	C(7)–H(7)$\cdots$O(2)$^{\text{i}}$	174
W(2)–C(3)–O(3)	178.1(9)	C(18)–H(18C)$\cdots$O(1)$^{\text{ii}}$	160

Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) $1-x$, $-y$, $1-z$.

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3. Results and discussion

3.1. *Syntheses of complexes*

Reaction of singly-bonded dinuclear complexes $[(\eta^5\text{-CH}_3\text{O}_2\text{CC}_5\text{H}_4)_2\text{M}_2(\text{CO})_6]$ (**I**, M = Mo; **II**, M = W) with the ditelluride $[4\text{-CH}_3\text{C}_6\text{H}_4\text{Te}]_2$ in refluxing toluene for 4–6 h gave, after the removal of solvent and preparative TLC, dinuclear complexes **1** and **2** as dark brown, crystalline solids. Complexes **1** and **2** were characterized by elemental analyses, ^{1}H NMR, ^{13}C NMR and IR spectroscopies. All data are consistent with their formulation $[(\eta^5\text{-CH}_3\text{O}_2\text{CC}_5\text{H}_4)_2\text{M}_2(\text{CO})_4(\mu\text{-}(4\text{-CH}_3\text{C}_6\text{H}_4\text{Te}))_2]$ (**1**, M = Mo; **2**, M = W). The complexes can also be prepared from triply-bonded dinuclear complexes $[(\eta^5\text{-CH}_3\text{O}_2\text{CC}_5\text{H}_4)_2\text{M}_2(\text{CO})_4]$ (**III**, M = Mo; **IV**, M = W) in good yields. As air-sensitive triply-bonded dinuclear complexes are generated from the corresponding singly-bonded complexes, the former might serve as a simpler and more convenient method of synthesizing the ArTe bridged dinuclear complexes described above.

3.2. *Crystal structures of complexes 1 and 2*

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Theoretically, the complexes of type $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{M}_2(\text{CO})_4(\mu\text{-TeAr})_2]$ (M = Mo, W) may have six isomers as follows: *cis* /aa, *cis*/ae, *cis*/ee, *trans*/aa, *trans*/ae and *trans*/ee. The *cis* and *trans* refer to the two arrangements of either η^5-RC$_5$H$_4$ or carbonyl ligands with respect to the M···M vector and a and e refer to the mutual orientations of the two substituents (Ar) in the butterfly four-membered ring M_2Te_2 [6,8]. As shown in figures 1 and 2, complexes **1** and **2** are essentially isostructural with a butterfly M_2Te_2 skeleton (M = Mo, W); the M(1) and M(2) atoms each carry one substituted Cp ring and two terminal carbonyls *trans* to each other whereas the Te(1) and Te(2) are attached to two Ar groups by an axial and an equatorial bond. Therefore, complexes **1** and **2** exist as *trans*/ae isomers in the solid state. The distance between Mo(1) and Mo(2) [4.260(2) Å] is greater than the sum of the van der Waals radii of two molybdenum atoms, suggesting that there is no bonding interaction between them. However, the distance between Te(1) and Te(2) [3.254(1) Å] is much less than the sum of the van der Waals radii of two tellurium atoms (4.4 Å) and particularly less than the suggested value for possible interaction between Te atoms (3.3 Å), indicating a partial bonding interaction between Te(1) and Te(2). The above distances are very close to the values in the complex $[(\eta^5\text{-H}_3\text{O}_2\text{CC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4(\mu\text{-TePh})_2]$ [the Mo···Mo distance is 4.260(3) Å and the Te···Te distance is 3.273(2) Å] [6,11]. Similarly, the distances between W(1) and W(2) [4.268(2) Å] and between Te(1) and Te(2) [3.262(2) Å] indicate no bonding between W(1) and W(2) and the existence of partial bonding interaction between Te(1) and Te(2). In addition, the distances in complex **2** are close to those in the complex $[(\eta^5\text{-C}_2\text{H}_5\text{O}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4(\mu\text{-TePh})_2]$ [the W···W distance is 4.238(2) Å and the Te···Te distance is 3.277(2) Å] [8]. The lack of bonds between two M atoms is consistent with the 18 valence-electron rule because **1** and **2** are d^4–d^4 dimers [9,12]. As shown in tables 2 and 3, like the complexes $[(\eta^5\text{-CH}_3\text{O}_2\text{CC}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_4(\mu\text{-TePh})_2]$ and $[(\eta^5\text{-C}_2\text{H}_5\text{O}_2\text{CC}_5\text{H}_4)_2\text{W}_2(\text{CO})_4(\mu\text{-TePh})_2]$, the M–Te(1) [Te(1) attached to the e bond] bond lengths are smaller than those of M–Te(2) [Te(2) attached to the a bond]. Interestingly, the Te(1)–C(23) bond length is smaller than that of the Te(2)–C(34) bond in **1** whereas the Te(1)–C(19) bond length is larger than that of the Te(2)–C(26) bond in **2**. Two substituted cyclopentadienyl rings and two

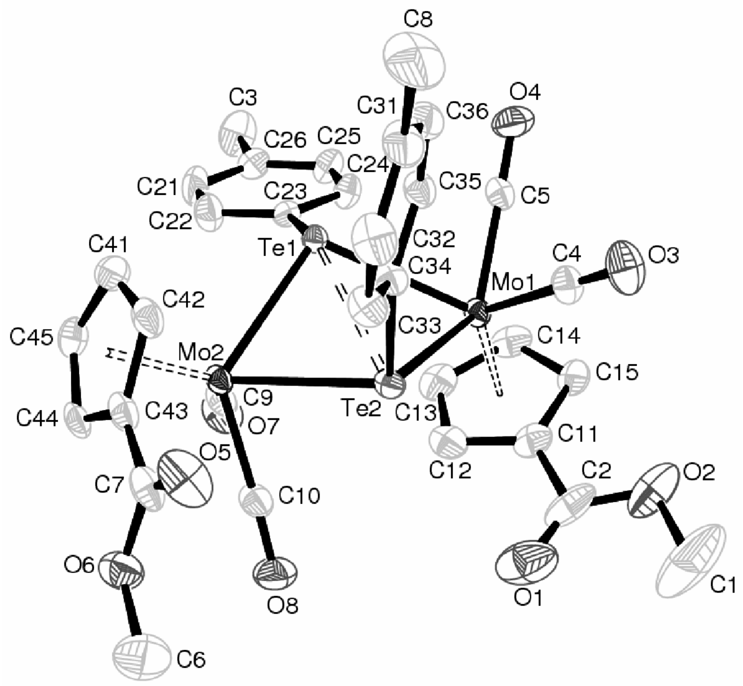

Figure 1. Molecular structure of complex **1** drawn with 30% probability ellipsoids.

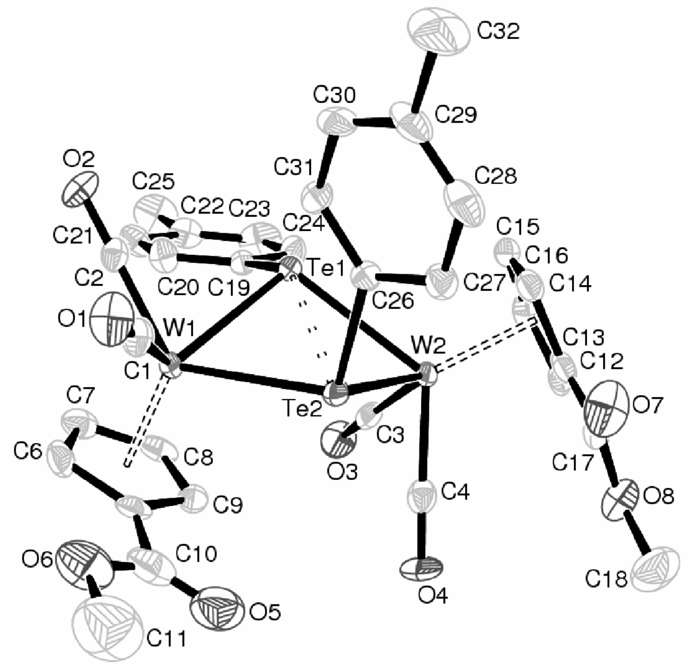

Figure 2. Molecular structure of complex **2** drawn with 30% probability ellipsoids.

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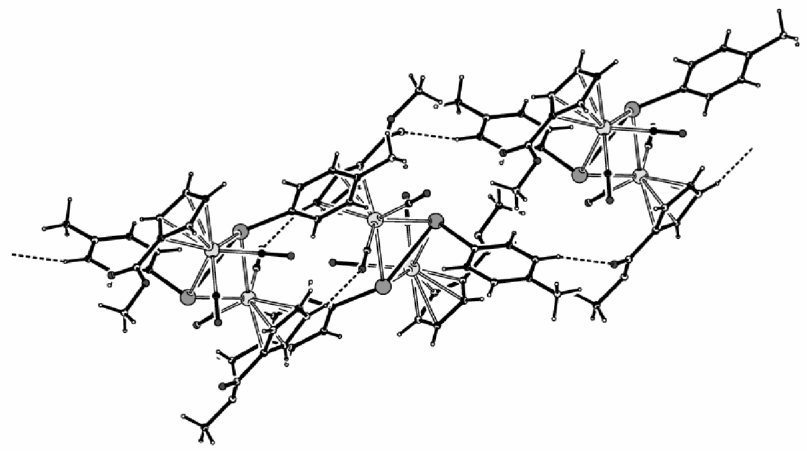

Figure 3. Packing view of complex **1** in the B plane.

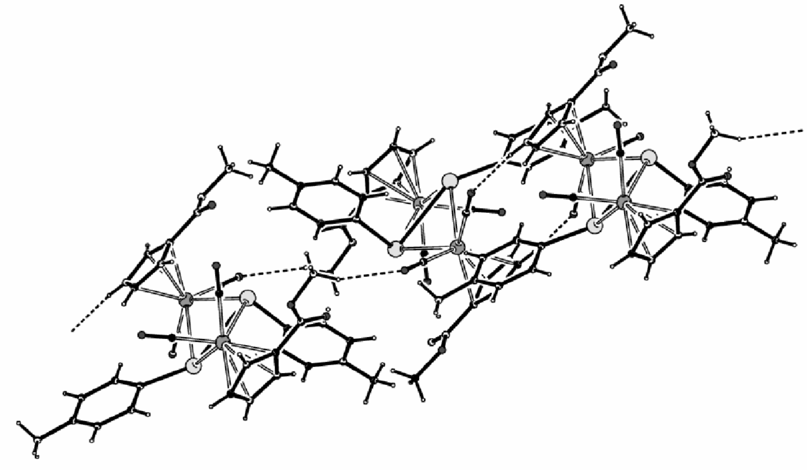

Figure 4. Packing view of complex **2** in the B plane.

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substituted benzene rings in **1** form dihedral angles of 45.8(8) and 75.3(6)°, whereas in **2** the corresponding dihedral angles are 44.7(7) and 74.3(6)°.

Although the two complexes display very similar axis lengths, their molecules show different packing modes, as shown in figures 3 and 4. Complex **1** participates in two types of intermolecular hydrogen bonds through two donors from two CH groups of the substituted cyclopentadienyl ring and the substituted benzene ring in the same molecule and two acceptors from one carbonyl oxygen and one methoxycarbonyl oxygen of two other molecules: one $O(4)^{i}\cdots H(14A)–C(14)$ [the distance of $O(4)^{i}\cdots C(14)$ is 3.37(2) Å; symmetry code: (i), $1-x$, $3-y$, $1-z$], and the other $O(1)^{ii}\cdots H(32A)–C(32)$ [the distance of $O(4)^{i}\cdots C(14)$ is 3.47(2) Å; symmetry code: (ii), $-x$, $2-y$, $2-z$]. Complex **2** involves two types of intermolecular hydrogen bonds through two donors from one CH group and one ester methyl group of two substituted cyclopentadienyl rings in the same molecule and two acceptors from two carbonyl oxygens of two other molecules: one $O(2)^{i}\cdots H(7A){-}C(7)$ [the distance is 3.36(2) Å; symmetry code: (i), $2-x$, $1-y$, $-z$], and the other $O(1)^{ii}\cdots C(18)$ [the distance is 3.45(2) Å; symmetry code: (ii), $1-x$, $-y$, $1-z$].

3.3. *Spectroscopies of complexes*

Complexes **1** and **2** are isostructural and therefore display similar spectroscopies. In ^{1}H NMR spectra, methyl groups of benzene rings and methoxycarbonyls show two singlets at 2.354 and 3.734 ppm for **1** and at 2.308 and 3.720 ppm for **2**. Substituted cyclopentadienyl rings exhibit four multiplets between 5.597 and 5.900 ppm for **1** and between 5.711 and 6.022 ppm for **2**. Substituted benzene rings appear as two multiplets between 7.082 and 7.466 ppm for **1** and between 7.105 and 7.503 ppm for **2**. Indeed, the above room-temperature ^{1}H NMR spectra do not agree with crystal structures of **1** and **2**, indicating that in solution these complexes are fluxional. At 0°C ^{1}H NMR spectra were the same as the room-temperature ^{1}H NMR spectra. However, ^{1}H NMR spectra of the complexes show that absorptions of substituted cyclopentadienyl rings and benzene rings broaden as the temperature is lowered and complex resonance patterns are observed at −60°C. At −75°C, ^{1}H NMR spectra of complexes are similar to those at −60°C although further broadened. Absorptions of the methyl groups of the benzene rings and methoxycarbonyls remain as two singlets at this temperature, respectively. As indicated in figures 1 and 2, although a butterfly M_2Te_2 ring contains two types of substituted benzene rings, in solution each of complexes **1** and **2** must go through rapid inversion of the butterfly ring between two conformers. In one conformer Te(1) is bonded to the Ar group through an equatorial bond and in the other Te(1) is bonded to the Ar group through an axial bond and vice versa for Te(2), and therefore its NMR spectrum shows average resonances [19–22]. In ^{13}C NMR spectra, methyl groups of benzene rings and methoxycarbonyls show two absorptions at 20.194 and 51.276 ppm for **1** and at 20.157 and 51.314 ppm for **2**. The substituted cyclopentadienyl rings display five absorptions in the range 90.717–100.047 ppm for **1** and six absorptions in the range 88.799–100.114 ppm for **2** whereas the phenyl groups exhibit three absorptions in the range 129.371–138.310 ppm. In addition, absorptions of the ester carbonyls appear at 164.959 and 164.944 ppm and those of the terminal carbonyls at 205.266 and 205.222 ppm [23].

In the IR spectra, terminal carbonyls display three strong absorption bands at 1938, 1875 and 1858 cm^{-1} for complex **1** and 1931, 1861, 1845 cm^{-1} for complex **2**, while ester carbonyls appear at 1723 and 1724 cm^{-1}.

Supplementary data

Full crystallographic data (CCDC 233540 for complex **1** and CCDC 233541 for complex **2**) have been deposited at the Cambridge Crystallographic Data Centre and are available on request 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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