Journal of Organometallic Chemistry, *453* (1993) 105–109

JOM 23442

Synthesis and characterization of homo- and heterobimetallic complexes $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_2]_2$ (W≡W) and $\eta^5\text{-RC}_5\text{H}_4\text{(CO)}_3\text{WCo(CO)}_4$ (W–Co). X-ray molecular structure of $[\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{W(CO)}_2]_2$

Li-Cheng Song, Ji-Quan Wang, Wei-Jun Zhao, Qing-Mei Hu, Yan-Quan Fang and Shu-Ji Zhang
Department of Chemistry, Nankai University, Tianjin, 300071 (People's Republic of China)

Ru-Ji Wang and Hong-Gen Wang
Central Laboratory, Nankai University, Tianjin, 300071 (People's Republic of China)

(Received October 23, 1992; in revised form December 3, 1992)

Abstract

The thermal decarbonylation of metal–metal singly bonded complexes $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_3]_2$ in diglyme affords, in 23–34% yields, the corresponding triply bonded dimer $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_2]_2$ (**1**) (R = MeCO, MeO_2C, and EtO_2C). Further reaction of **1** (R = MeCO and MeO_2C) with $\text{Co}_2\text{(CO)}_8$ in toluene at ambient temperature produces the heterobimetallic compounds $\eta^5\text{-RC}_5\text{H}_4\text{(CO)}_3\text{WCo(CO)}_4$ (**2**) (R = MeCO and MeO_2C) in 51 and 40% yields, respectively. Structures for all these compounds have been deduced from elemental analysis, IR, ^{1}H NMR and MS spectroscopies and the structure of **1** (R = EtO_2C) has been unequivocally confirmed by single crystal X-ray diffraction analysis.

1. Introduction

Although metal–metal bonded bimetallic compounds containing a $\text{Cp}^\star\text{(CO)}_n\text{M}$ fragment ($\text{Cp}^\star$ = Cp and alkyl substituted Cp; $n = 2, 3$; M = Cr, Mo, W) have been extensively studied [1–4], no compounds of the types $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}_2]_2$ (M≡M) and $\eta^5\text{-RC}_5\text{H}_4\text{(CO)}_3\text{MCo(CO)}_4$ (M–Co) (R = functionally substituted group) have been known up to now. In a previous paper we reported the synthesis and characterization of the metal–metal singly bonded compounds of the type $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}_3]_2$ (R = MeCO, MeO_2C or EtO_2C; M = Mo, W) [5]. Therefore, it would be interesting to investigate the possibility of preparing unknown triply bonded compounds of the type $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}_2]_2$ (M≡M) through thermal reaction of the singly bonded complex $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}_3]_2$. Additionally, we have found that the complexes of $[\eta^5\text{-RC}_5\text{H}_4\text{M(CO)}_2]_2$ (R = MeCO or MeO_2C; M = W) (**1**), in contrast to $[\eta^5\text{-MeC}_5\text{H}_4\text{W(CO)}_2]_2$ [6], reacted with $\text{Co}_2\text{(CO)}_8$ to give heterobimetallic complexes of the type $\eta^5\text{-RC}_5\text{H}_4\text{(CO)}_3\text{WCo(CO)}_4$ (**2**) without any isolable cluster compound containing an M_2Co_2 cluster core. We describe here the synthesis and characterization of the above two types of complex with general formulae $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_2]_2$ (**1**) and $\eta^5\text{-RC}_5\text{H}_4\text{(CO)}_3\text{WCo(CO)}_4$ (**2**) and the single crystal structure of $[\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{W(CO)}_2]_2$.

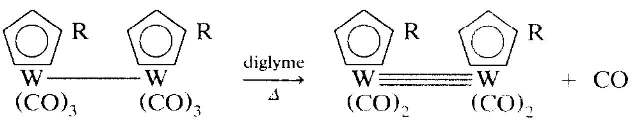
2. Results and discussion

2.1. *Synthesis and characterization of $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_2]_2$ (1a–c)*

Three triply bonded dimers **1a–c**, which are air-stable in the solid state but air-sensitive in solution were prepared by thermal decarbonylation in diglyme at 140°C for 12 h of the corresponding singly bonded complexes $[\eta^5\text{-RC}_5\text{H}_4\text{W(CO)}_3]_2$ (eqn. (1)).

Correspondence to: Dr. L.-C. Song.

0022-328X/93/$6.00



(1)

(1)

Compound 1	**a**	**b**	**c**
R	MeCO	MeO_2C	EtO_2C

The structures of **1a–c** were characterized by C/H analysis, IR, ^{1}H NMR and mass spectroscopies. All show in their IR spectra the absorptions of the coordinating carbonyls in the range 1918–1827 cm^{-1}, besides exhibiting the carbonyl absorptions in the substituents. Such low frequencies for the carbonyls coordinated to the metals in **1a–c**, as compared to typical terminal carbonyl absorption frequencies, can be attributed to their linear semibridging structure (*vide infra*).

The ^{1}H NMR spectra of **1a–c** possess the proton resonance signals of the respective organic groups. For example, signals between δ 5–6 are caused by four hydrogen atoms of each cyclopentadienyl ring. Such four hydrogen atoms of **1a–c** show two sets of apparent triplets. The triplet upfield can be assigned to H^3 and H^4 whereas the triplet downfield is assigned to H^2 and H^5, since the substituents on the ring are electron-withdrawing groups.

The MS spectra of **1a–c** have parent ion peaks and/or the fragment peaks consequent on successive loss of a given number of CO. Furthermore, they also have the fragment peaks arising from the breaking of the metal–metal bond of corresponding species.

2.2. *Crystal structure of 1c*

In order to confirm the structures of **1a–c** we determined the crystal structure of **1c** by X-ray diffraction. The molecular structure of **1c** is given in Fig. 1 and the final positional parameters for the atoms are given in Table 1. The bond lengths and angles are listed in Tables 2 and 3, respectively.

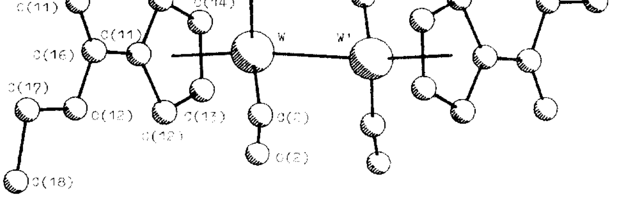


Fig. 1. Perspective view of **1c** showing the atom numbering scheme.

TABLE 1. Fractional coordinates and equivalent isotropic thermal parameters for **1c**

Atom	x	y	z	B_{eq} (Å^2)
W	0.06565(6)	0.47781(4)	0.59091(3)	2.590(7)
C(11)	0.117(1)	0.4472(9)	0.7625(7)	2.7(2)
C(12)	0.193(2)	0.564(1)	0.7457(7)	3.8(2)
C(13)	0.357(2)	0.545(1)	0.6952(8)	4.5(3)
C(14)	0.382(2)	0.423(1)	0.6809(8)	4.2(3)
C(15)	0.236(2)	0.363(1)	0.7227(8)	3.6(2)
C(16)	−0.046(2)	0.4185(9)	0.8158(7)	3.3(2)
O(11)	−0.111(1)	0.3231(6)	0.8225(6)	4.6(2)
O(12)	−0.1113(9)	0.5133(6)	0.8555(5)	3.3(1)
C(17)	−0.264(1)	0.492(1)	0.9170(7)	3.6(2)
C(18)	−0.319(2)	0.615(1)	0.9498(9)	4.9(3)
C(1)	−0.124(2)	0.3499(9)	0.5625(7)	3.3(2)
O(1)	−0.236(1)	0.2740(7)	0.5533(7)	5.6(2)
C(2)	−0.161(2)	0.582(1)	0.5816(8)	4.0(2)
O(2)	−0.293(1)	0.6441(8)	0.5880(6)	5.0(2)

As seen in Fig. 1, the molecule consists of two identical moieties η^5-$EtO_2CC_5H_4W(CO)_2$ dimerized by a bond between two tungsten atoms. The W–W bond length of 2.5064(6) Å is much shorter than those of the metal–metal single bonds in dimers [η^5-C_5H_5-$W(CO)_3]_2$ (3.222 Å) [7], [η^5-$HOOCC_5H_4W(CO)_3]_2$ (3.215 Å) [8], and [η^5-$MeO_2CC_5H_4W(CO)_3]_2$ (3.216 Å) [9], but it is almost the same as that (2.503 Å) in $L_2W_2(CO)_4$ ($L = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$) [10]. On the basis of these facts and the 18-electron rule, a W≡W triple bond should be assigned to the bonding between two tungsten atoms of **1c**. In addition, as required from its space group **P**2$_1$/*c*, **1c** is centrosymmetric and two cyclopentadienyl rings are parallel with respect to each other. For the carbonyls, the average W–C–O angle is 173.5°, which is close to 180° and the average W–W–C bond angle is 76.6°. So the four carbonyls are bent back over the W≡W triple bond, forming a linear semibridging structure. This kind of carbonyl structure is also observed in the chromium [11,12] and molybdenum [13–15] analogues. In fact, these semibridging carbonyls acting as two electron ligands donate their lone electron pairs on carbon

TABLE 2. Bond distances (Å) for **1c**

W–W′	2.5064(6)	C(11)–C(16)	1.480(9)
W–C(11)	2.309(6)	C(12)–C(13)	1.45(1)
W–C(12)	2.329(7)	C(13)–C(14)	1.42(1)
W–C(13)	2.343(8)	C(14)–C(15)	1.42(2)
W–C(14)	2.357(7)	C(16)–O(11)	1.19(2)
W–C(15)	2.344(7)	C(16)–O(12)	1.326(9)
W–*Cp(1)	1.991(8)	O(12)–C(17)	1.478(8)
W–C(1)	1.948(8)	C(17)–C(18)	1.54(2)
W–C(2)	1.946(9)	C(1)–O(1)	1.152(8)
C(11)–C(12)	1.47(1)	C(2)–O(2)	1.164(9)
C(11)–C(15)	1.44(1)		

* Cp(1) is the centre of the five-membered ring composed of C(11)–C(15) atoms; symmetrical transformation: ′ = (−x, 1−y, 1−z).

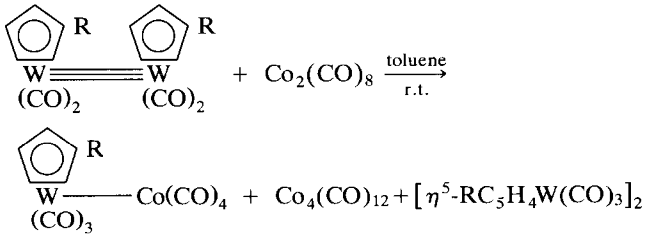
TABLE 3. Bond angles (°) for **1c**

W′–W–*Cp(1)	159.1(2)	C(12)–C(13)–C(14)	109.7(7)
W′–W–C(1)	81.9(2)	C(13)–C(14)–C(15)	108.4(7)
W′–W–C(2)	71.3(2)	C(11)–C(15)–C(14)	108.2(7)
*Cp(1)–W–C(1)	115.7(2)	C(11)–C(16)–O(11)	124.5(6)
*Cp(1)–W–C(2)	118.2(3)	C(11)–C(16)–O(12)	111.0(6)
C(1)–W–C(2)	87.6(4)	O(11)–C(16)–O(12)	124.5(6)
C(12)–C(11)–C(15)	108.4(6)	C(16)–O(12)–C(17)	115.1(5)
C(12)–C(11)–C(16)	126.9(6)	O(12)–C(17)–C(18)	104.7(5)
C(15)–C(11)–C(16)	124.6(6)	W–C(1)–O(1)	174.9(6)
C(11)–C(12)–C(13)	105.6(7)	W–C(2)–O(2)	172.2(6)

atoms to the nearby metal and concurrently use their π^*-orbitals to accept π-electrons from M≡M [14]. The asymmetric parameter α of this semibridge equals 0.31, which is greater than those of $Cp_2Cr_2(CO)_4$ and $Cp_2Mo_2(CO)_4$ [12,13]. It is interesting to note that the angle of η^5-$RC_5H_{4_{centre}}$–W–W of **1c** is 159.1°, which indicates that its configuration is bent, this being contrary to that of Cp_{centre}–Mo–Mo in $Cp_2Mo_2(CO)_4$ [13] and the same as those of $Cp^\star_{centre}$–Cr–Cr in $Cp^\star_2Cr_2(CO)_4$ ($Cp^\star$ = Cp, η^5-C_5Me_5) [11,12] and of $Cp^\star_{centre}$–Mo–Mo in $Cp^\star_2Mo_2(CO)_4$ ($Cp^\star$ = η^5-C_5Me_5) [15]. For the bent and linear configurations in corresponding Cr and Mo complexes Curtis and Hall proposed two explanations on the basis of either electronic [13] or steric factors [14]. Obviously, in terms of the steric factor suggested by Hall the bent configuration of η^5-$RC_5H_{4_{centre}}$–W–W in **1c** cannot be explained according to the magnitude of the metal atom, since the tungsten atom is larger than the molybdenum atom. In such a case we believe that both electronic and steric factors of the functionally substituent EtO_2C would play an important role in deciding the configuration of η^5-$RC_5H_{4_{centre}}$–W–W in **1c**.

2.3. *Reaction of [η^5-$RC_5H_4W(CO)_2]_2$ **1a** or **1b** with $Co_2(CO)_8$*

1a and **1b** reacted with $Co_2(CO)_8$ in toluene at room temperature for 4 h to give the new heterobimetallic compounds **2a** and **2b** as well as $Co_4(CO)_{12}$ and [η^5-$RC_5H_4W(CO)_3]_2$ [5] (eqn. (2)). This result is apparently similar to that of the reaction between $[CpMo(CO)_2]_2$ and $Co_2(CO)_8$ reported by Curtis and Klingler [16], but quite different from Chetcuti's result [6] which showed the reaction of [η^5-$MeC_5H_4W(CO)_2]_2$ with $Co_2(CO)_8$ to give not only the heterobimetallic complexes of type **2** but also the cluster compound with a W_2Co_2 cluster core. From these results it appears that Curtis's mechanism involving an M_2Co_2 tetrahedral core intermediate is quite plausible for this kind of reaction. However, it might not explain why the electron-releasing methyl substituent on the cyclopentadienyl ring may stabilize the W_2Co_2 intermediate to make it isolable, while it may not if the electron-withdrawing MeCO and MeO_2C or the hydrogen atom in the case of parent cyclopentadienyl are on the ring. So the detailed mechanism still needs further study. It is worth pointing out that the carbonyls of **2a** and **2b**, in contrast to those semibridging carbonyls of **1a–c** (*vide supra*), are typical terminal carbonyls due to their much higher frequencies of 2082–1909 cm^{-1}. However, the ^1H NMR and MS behaviours of **2a** and **2b** are similar to those of **1a–c**. For instance, the four hydrogen atoms on the cyclopentadienyl ring exhibit two sets of peaks, one upfield attributed to H^3 and H^4, and the other downfield (H^2 and H^5). The MS data of **2a** and **2b** indicated the presence of the fragment ions by the successive losses of CO from parent ions and by breaking the metal–metal bond of the corresponding intermediate ions.



(2)

(2)

Compound 2	a	b
R	MeCO	MeO_2C

3. Experimental section

All reactions and manipulations were carried out under highly prepurified N_2 using Schlenk or vacuum-line techniques. Diglyme and toluene were vigorously dried by distillation from Na/benzophenone ketyl. Chromatographic silica gel was about 300–400 mesh. Petroleum ether and CH_2Cl_2 were deoxygenated by bubbling N_2 for about 15 min prior to use. $Co_2(CO)_8$ was purchased from Strem. [η^5-$RC_5H_4W(CO)_3]_2$ (R = MeCO, MeO_2C, EtO_2C) were prepared by published procedures [5]. The IR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer and the ^1H NMR spectra on a Jeol JNM-PMX 60SI NMR spectrometer. Elemental analysis, MS and melting point determinations were performed with a Perkin-Elmer model 240C analyzer, an HP5988A spectrometer and a Yanako MP-500 Apparatus, respectively.

3.1. *Preparation of [η^5-$MeCOC_5H_4W(CO)_2]_2$ (**1a**)*

A 100 ml two-necked flask equipped with a magnetic stir-bar, an air-tight septum and a reflux condenser fitted with a N_2 inlet was charged with 0.6 g (0.8 mmol) of [η^5-$MeCOC_5H_4W(CO)_3]_2$ and 25 ml of diglyme. The solution was stirred and heated at 140°C for 12 h. Solvent was removed under vacuum and the residue dissolved in 5 ml CH_2Cl_2 which was subjected to chromatographic separation on an air-free silica gel column with CH_2Cl_2 as eluent. The first red band consisted of recovered starting material. The second brown band, after removal of solvent and drying under vacuum, gave 0.126 g (23%) of $[\eta^5\text{-MeCOC}_5H_4W(CO)_2]_2$ (**1a**) as a brown solid, m.p. 207–210°C (dec.). Anal. Found: C, 31.13; H, 1.88. Calc. for $C_{18}H_{14}O_6W_2$: C, 31.15; H, 2.03%. IR (KBr disc): ν(C≡O), 1892.8s, 1868.4s cm^{-1}; ν(C=O), 1671.5s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 2.30 [s, 6H, $2(CH_3)$], 5.56 [t, 4H, $2(H^3, H^4)$], 5.86 [t, 4H, $2(H^2, H^5)$]. Mass spectrum (EI), *m/z* (relative intensity): 638 ($M^+ - 2CO$, 24.7), 610 ($M^+ - 3CO$, 19.6), 582 ($M^+ - 4CO$, 72.9), 291 ($MeCOC_5H_4W^+$, 60.5), 248 ($C_5H_4W^+$, 22.3).

3.2. *Preparation of $[\eta^5\text{-MeO}_2CC_5H_4W(CO)_2]_2$ (1b) and $[\eta^5\text{-EtO}_2CC_5H_4W(CO)_2]_2$ (1c)*

1b and **1c** were prepared similarly, using 0.626 g (0.8 mmol) of $[\eta^5\text{-MeO}_2CC_5H_4W(CO)_3]_2$ and 0.648 g (0.8 mmol) of $[\eta^5\text{-EtO}_2CC_5H_4W(CO)_3]_2$, respectively. They are all brown solids.

$[\eta^2\text{-MeO}_2CC_5H_4W(CO)_2]_2$ (**1b**), 0.199 g (34%), m.p. 136–138°C. Anal. Found: C, 29.79; H, 1.82. Calc. for $C_{18}H_{14}O_8W_2$: C, 29.78; H, 1.94%. IR (KBr disc): ν(C≡O), 1917.6s, 1827.3s, cm^{-1}; ν(C=O), 1720.7s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 3.83 [s, 6H, $2(CH_3)$], 5.50 [t, 4H, $2(H^3, H^4)$], 5.89 [t, 4H, $2(H^2, H^5)$]. Mass spectrum (EI), *m/z* (relative intensity): 726 (M^+, 9), 670 ($M^+ - 2CO$, 7), 642 ($M^+ - 3CO$, 10), 614 ($M^+ - 4CO$, 9), 639 ($M^+ - CO - MeO_2C$, 4), 611 ($M^+ - 2CO - MeO_2C$, 4), 583 ($M^+ - 3CO - MeO_2C$, 6), 555 ($M^+ - 4CO - MeO_2C$, 13), 552 ($M^+ - 2CO - 2MeO_2C$, 11), 524 ($M^+ - 3CO - 2MeO_2C$, 12), 496 [$(C_5H_4W)_2^+$, 8], 363 ($1/2M^+$, 12), 335 ($1/2M^+ - CO$, 75), 307 ($1/2M^+ - 2CO$, 58), 304 ($1/2M^+ - MeO_2C$, 8), 276 ($1/2M^+ - CO - MeO_2C$, 58), 248 ($C_5H_4W^+$, 41), 184 (W^+, 3), 64 ($C_5H_4^+$, 1).

$[\eta^5\text{-EtO}_2CC_5H_4W(CO)_2]_2$ (**1c**), 0.137 g (23%), m.p. 95°C. Anal. Found: C, 31.79; H, 2.38. Calc. for $C_{20}H_{18}O_8W_2$: C, 31.86; H, 2.41%. IR (KBr disc): ν(C≡O), 1909.4s; 1851.9s cm^{-1}; ν(C=O), 1712.5s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 1.33 [t, 6H, $2(CH_3)$], 4.30 [q, 4H, $2(CH_2)$], 5.50 [br s, 4H $2(H^3, H^4)$], 5.89 [br s, 4H, $2(H^2, H^5)$]. Mass spectrum (EI), *m/z* (relative intensity): 754 (M^+, 17), 726 ($M^+ - CO$, 3), 698 ($M^+ - 2CO$, 8), 670 ($M^+ - 3CO$, 18), 642 ($M^+ - 4CO$, 33), 625 ($M^+ - 2CO - EtO_2C$, 3), 608 ($M^+ - 2EtO_2C$, 2), 597 ($M^+ - 3CO - EtO_2C$, 6), 569 ($M^+ - 4CO - EtO_2C$, 17), 496 [$(C_5H_4W)_2^+$, 19], 349 [$EtO_2CC_5H_4W(CO)^+$, 11], 321 ($EtO_2CC_5H_4W^+$, 10), 304 [$C_5H_4W(CO)_2^+$, 3], 276 [$C_5H_4W(CO)^+$, 3], 248 ($C_5H_4W^+$. 15), 184 (W^+, 1), 64 ($C_5H_4^+$, 6).

3.3. *Reaction of 1a or 1b with $Co_2(CO)_8$*

A 100 ml two-necked flask equipped with a magnetic stir-bar and an air-tight septum was charged with 25 ml toluene, 0.383 g (0.552 mmol) $[\eta^5\text{-MeCOC}_5H_4W(CO)_2]_2$ (**1a**) and 0.378 g (1.105 mmol) $Co_2(CO)_8$ or 0.200 g (0.276 mmol) $[\eta^5\text{-MeO}_2CC_5H_4W(CO)_2]_2$ (**1b**) and 0.150 g (0.439 mmol) $Co_2(CO)_8$. The reaction mixture was stirred for about 5 h at room temperature until TLC showed that no starting material remained. Solvent was removed under reduced pressure and the residue dissolved in 10 ml CH_2Cl_2, which was subjected to chromatography on air free silica gel column. Three bands were observed on the column using petroleum ether/CH_2Cl_2 (v/v = 2/3) as eluent. The first black band is $Co_4(CO)_{12}$ and the third red band is singly bonded dimer $[\eta^5\text{-RC}_5H_4W(CO)_3]_2$ (R = MeCO, MeO_2C), which are confirmed by IR spectrum. The second pink band, after removal of solvent and drying under vacuum, gave **2a** or **2b**.

$[\eta^5\text{-MeCOC}_5H_4(CO)_3W\text{-}Co(CO)_4]$ (**2a**), 0.152 g, 50% yield, m.p. 91–92°C. Anal. Found: C, 30.40; H, 1.25. Calc. for $C_{14}H_7CoO_8W$: C, 30.80; H, 1.29%. IR (KBr disc): ν(C≡O), 2073.4s, 2007.8s, 1975.0vs, 1934.0vs, 1909vs cm^{-1}; ν(C=O), 1687.9s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 2.33 (s, 3H, CH_3), 5.83 (br s, 2H, H^3, H^4), 5.97 (br s, 2H, H^2, H^5). Mass spectrum (EI), *m/z* (relative intensity): 490 ($M^+ - 2CO$, 0.4), 462 ($M^+ - 3CO$, 0.5), 434 ($M^+ - 4CO$, 1.6), 406 ($M^+ - 5CO$, 1.3), 378 ($M^+ - 6CO$, 1.7), 350 ($M^+ - 7CO$, 3.7), 375 [$MeCOC_5H_4W(CO)_3^+$, 1.1], 347 [$MeCOC_5H_4W(CO)_2^+$, 3.1], 319 [$MeCOC_5H_4W(CO)^+$, 0.8], 291 ($MeCOC_5H_4W^+$, 6.3), 248 ($C_5H_4W^+$, 1.1), 184 (W^+, 0.5), 64 ($C_5H_4^+$, 0.2), 171 [$Co(CO)_4^+$, 10.5], 143 [$Co(CO)_3^+$, 33.9], 115 [$Co(CO)_2^+$, 27.8], 87 [$Co(CO)^+$, 61.7], 59 (Co^+, 100).

$[\eta^5\text{-MeO}_2CC_5H_4(CO)_3W\text{-}Co(CO)_4]$ (**2b**), 0.062 g, 40% yield, m.p. 87–88°C. Anal. Found: C, 29.76; H, 1.44. Calc. for $C_{14}H_7CoO_9W$: C, 29.92; H, 1.26%. IR (KBr disc): ν(C≡O), 2081.6s, 2032.4s, 1983.2vs, 1917.6vs cm^{-1}, ν(C=O), 1728.9s cm^{-1}, ^1H NMR ($CDCl_3$, δ, ppm): 3.79 (s, 3H, CH_3), 5.69 (br s, 2H, H^3, H^4), 5.96 (br s, 2H, H^2, H^5). Mass spectrum (EI), *m/z* (relative intensity): 506 ($M^+ - 2CO$, 11.7), 478 ($M^+ - 3CO$, 6.6), 450 ($M^+ - 4CO$. 26.2), 422 ($M^+ - 5CO$, 10.2), 394 ($M^+ - 6CO$, 22.4), 366 ($M^+ - 7CO$. 16.0), 391 [$MeO_2CC_5H_4W(CO)_3^+$, 7.9], 363 [$MeO_2CC_5H_4W(CO)_2^+$, 2.8], 335 [$MeO_2CC_5H_4W(CO)^+$, 13.5], 307 ($MeO_2CC_5H_4W^+$, 14.6), 248 ($C_5H_4W^+$, 4.6), 171 [$Co(CO)_4^+$, 1.8], 143 [$Co(CO)_3^+$, 6.0]. 115 [$Co(CO)_2^+$. 11.9], 87 [$Co(CO)^+$, 10.0], 59 (Co^+, 12.2).

3.4. *Single-crystal structure determination of 1c*

Crystals of **1c** suitable for X-ray diffraction were obtained by recrystallization from mixed solvents of CH_2Cl_2/petroleum ether at −20°C. A red crystal measuring 0.1 × 0.2 × 0.2 mm was mounted on a glass fibre and placed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 1614 independent reflections was collected at room temperature, with Mo Kα ($\lambda = 0.71073$ Å) by ω-2θ scan mode and in the range of $2° \leq \theta \leq 23°$. Of the total reflections, 1344 with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinement. Data were corrected for Lorentz and polarization effects, and an empirical absorption was applied on the intensities. The crystal is monoclinic, of space group $P2_1/c$, with $a = 6.847(1)$, $b = 11.644(2)$, $c = 13.541(4)$ Å, $\beta = 101.02(2)°$, $V = 1043.4$ Å^3, $M_r = 750.03$, $Z = 2$, $D_x = 2.38$ g/cm^3, $\mu = 113$ cm^{-1}, $F(000) = 692$. The structure was solved by the heavy atom method and the position of the tungsten atom was located by Patterson analysis. Remaining non-hydrogen atoms were found in succeeding difference Fourier syntheses. The final refinement by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged to unweighted and weighted agreement factors of 0.025 and 0.029. The highest peak on the final difference Fourier map had a height of 0.65 e/Å^3. All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Acknowledgement

We are grateful to the National Science Foundation of China for financial support of this work.

References

1 R. Davis and L.A.P. Kane-Maguire, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, New York, 1982, Vol. 3, pp. 961–1077, 1176–1253, 1331–1384.

2 D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, New York, 1982, Vol. 6, pp. 763–877.

3 F.A. Cotton and R.A. Walton, *Multiple Bonds between Metal Atoms*, Wiley-Interscience, New York, 1982, Chap. 5, pp. 183–264.

4 M.D. Curtis, *Polyhedron, 6* (1987) 759.

5 L.-C. Song and J.-Y. Shen, *Chem. J. Chin. Univ., 13* (1992) 1227.

6 M.J. Chetcuti, J.C. Gordon and P.E. Fanwick, *Inorg. Chem., 29* (1990) 3781.

7 R.A. Adams, D.M. Collins and F.A. Cotton, *Inorg. Chem., 13* (1974) 1086.

8 A. Avey, S.C. Tenhaeff, T.J.R. Weakley and D.R. Tyler, *Organometallics, 10* (1991) 3607.

9 T.J.R. Weakley, A.A. Avey, Jr. and D.R. Tyler, *Acta Crystallogr., Sect. C, 48* (1992) 154.

10 W. Kläul, A. Müller, R. Herbst and E. Egert, *Organometallics, 6* (1987) 1824.

11 J. Potenza, P. Giordano, D. Mastropaolo and A. Efraty, *Inorg. Chem., 13* (1974) 2540.

12 M.D. Curtis and W.M. Butler, *J. Organomet. Chem., 155* (1978) 131.

13 R.J. Klingler, W.M. Butler and M.D. Curtis, *J. Am. Chem. Soc., 100* (1978) 5034.

14 B.J. Morris-Sherwood, C.B. Powell and M.B. Hall, *J. Am. Chem. Soc., 106* (1984) 5079.

15 J.-S. Huang and L.F. Dahl, *J. Organomet. Chem., 243* (1983) 57.

16 M.D. Curtis and R.J. Klingler, *J. Organomet. Chem., 161* (1978) 23.