

Journal of Organometallic Chemistry, 384 (1990) 93–103
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20534

Regiospecific coupling of coordinated acetylide and disubstituted alkynes. X-ray structures of $\text{CpWOs}_2(\text{CO})_7[\text{C}(\text{Tol})\text{C}(\text{Tol})\text{CC}^n\text{Bu}]$ and $\text{CpWOs}_2(\text{CO})_7[\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{CCPh}]$

Yun Chi *,

Department of Chemistry, National Tsing Hua University, Hsinchu 30043 (Taiwan)

Gottfried Huttner * and W. Imhof

Anorganisch-Chemisches Institut, der Universität Heidelberg, Im Neuenheimer Feld 270, 6900 Heidelberg 1 (F.R.G.)

(Received August 22nd, 1989)

Abstract

Treatment of the acetylide complexes $\text{CpWOs}_2(\text{CO})_8(\text{C}\equiv\text{CR})$, $\text{Cp} = \text{C}_5\text{H}_5$, $\text{R} = \text{Ph}$, (1) and $\text{R} = ^n\text{Bu}$, (2), with Me_3NO in acetonitrile followed by reaction with various disubstituted alkynes, $\text{C}_2\text{R}'_2$, in refluxing toluene to give two isomeric trinuclear complexes, $\text{CpWOs}_2(\text{CO})_7[\text{C}(\text{R}')\text{C}(\text{R}')\text{CCR}]$, $\text{R} = \text{Ph}$, $\text{R}' = \text{Tol}$, (3); $\text{R} = ^n\text{Bu}$, $\text{R}' = \text{Tol}$, (4); $\text{R} = \text{Ph}$, $\text{R}' = \text{CO}_2\text{Et}$, (5); $\text{R} = ^n\text{Bu}$, $\text{R}' = \text{CO}_2\text{Et}$, (6); $\text{R} = \text{Ph}$, $\text{R}' = \text{CF}_3$, (7) by acetylide-alkyne coupling is described. The structure of each isomeric complex consists of a WOs_2 triangle and a coordinated C_4 hydrocarbyl fragment, established by single-crystal X-ray diffraction studies on 4 and 7. The possible mechanism for the formation of these two coupling products is discussed. Crystal data for 4: space group $P2_1/c$; $a = 14.21(1)$, $b = 10.80(1)$, $c = 21.46(2)$ Å, $\beta = 97.82^\circ$, $Z = 4$; final $R = 0.0541$, $R_w = 0.0469$ and GOF = 2.228. Crystal data for 7: space group $P2_1/c$; $a = 10.446(6)$, $b = 18.08(1)$, $c = 14.437(8)$ Å, $\beta = 105.66(4)^\circ$, $Z = 4$; final $R = 0.0595$, $R_w = 0.0512$ and GOF = 3.307.

Introduction

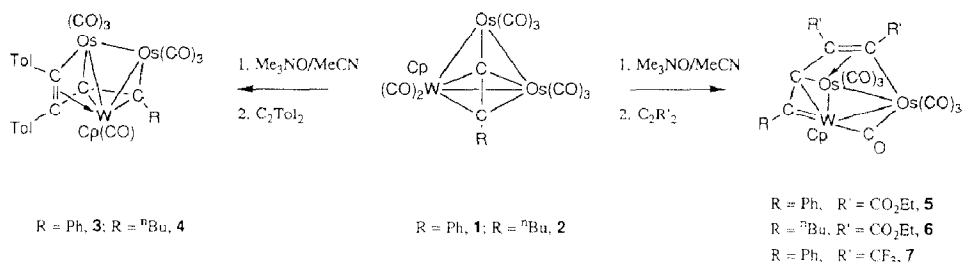
The C_2 hydrocarbons hold a key position in the development of organometallic chemistry. This position is in part attributable to a belief that the chemistry of the C_2 hydrocarbons of the organometallic complexes is analogous to those adsorbed on metal surfaces [1]. Much research activity has been focused on the synthesis of complexes containing C_2 hydrocarbyl ligands, such as alkyne, alkene, vinyl, vinyl-

dene or acetylide [2]. The chemistry of these hydrocarbyl derivatives, particularly the acetylide complexes, has been well developed in recent years. Deeming and coworkers have reported the crystal structure and the reactivities of the acetylide clusters in a triosmium system [3]; Carty and coworkers have also studied the trinuclear and polynuclear ruthenium complexes containing both acetylide and phosphorus bridging ligands [4].

We recently reported that the condensation of $LW(CO)_3(C\equiv CPh)$, $L = C_5H_5$, C_5Me_5 [5], with $Ru_3(CO)_{12}$ or $Os_3(CO)_{10}(NCMe)_2$ in refluxing toluene gives mixed-metal acetylide complexes $LWM_2(CO)_8(C\equiv CPh)$, $M = Os, Ru$ [6]. Our studies have also revealed that the acetylide ligand of $LWRu_2(CO)_8(C\equiv CPh)$ undergoes a rotation of 180° at the face of the WRu_2 triangle in solution [7]. Another goal of our current research is to gain some knowledge of the chemistry and the reactivity of the acetylide ligand in these mixed-metal systems. Thus, carried out the reactions of $CpWOs_2(CO)_8(C\equiv CR)$, $Cp = C_5H_5$, $R = Ph$, (1); $R = {}^nBu$, (2), with various disubstituted alkynes. Two isomeric coupling products were isolated and characterized by structural determination, suggesting that the bonding of the resulting C_4 hydrocarbons was determined by the substituents of the alkyne. Although the coupling between acetylide and alkyne is well established for their homometallic analogues [8], this experiment has produced some unique and interesting features of site selectivity versus the electron properties of the alkynes.

Results and discussion

Treatment of the acetylide complexes $CpWOs_2(CO)_8(C\equiv CR)$, $R = Ph$, (1); $R = {}^nBu$, (2) with 1.2 equivalents of Me_3NO in a mixture of acetonitrile/dichloromethane followed by in situ reaction with ditolylacetylene in refluxing toluene produced a red-orange complex $CpWOs_2(CO)_7[C(Tol)C(Tol)CCR]$, $R = Ph$, (3); $R = {}^nBu$, (4), in moderate yields (Scheme 1). Direct reaction with ditolylacetylene in refluxing toluene (1 h) failed, suggesting that the formation of the "lightly stabilized" acetonitrile substituted precursors [9] is essential for the activation of the acetylide complexes. The formulations of the complexes 3 and 4 were established from microanalytical and spectroscopic data. The solution IR ($\nu(CO)$) spectra suggested the presence of only terminal carbonyl ligands; the 1H NMR spectra and the molecular ion observed in the mass spectra indicated that these complexes might have seven CO ligands and one coordinated ditolylacetylene moiety. As such, it is clear that complexes 3 and 4 are produced by replacement of one CO ligand (2e⁻



Scheme 1

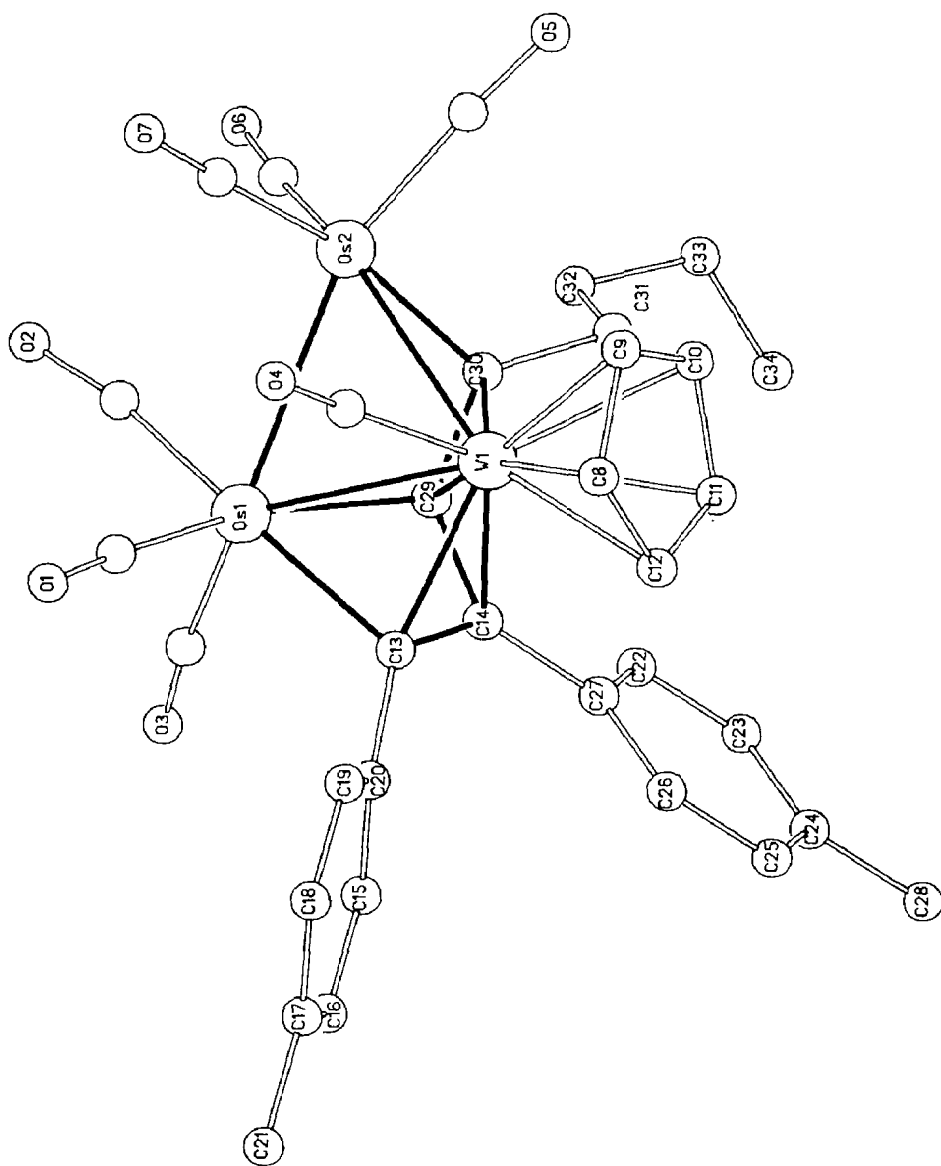


Fig. 1. The structure of CpW(O)₂(CO)₇[C(Tol)C(Tol)C(Tol)CC^tBu] (4) showing the atomic numbering scheme.

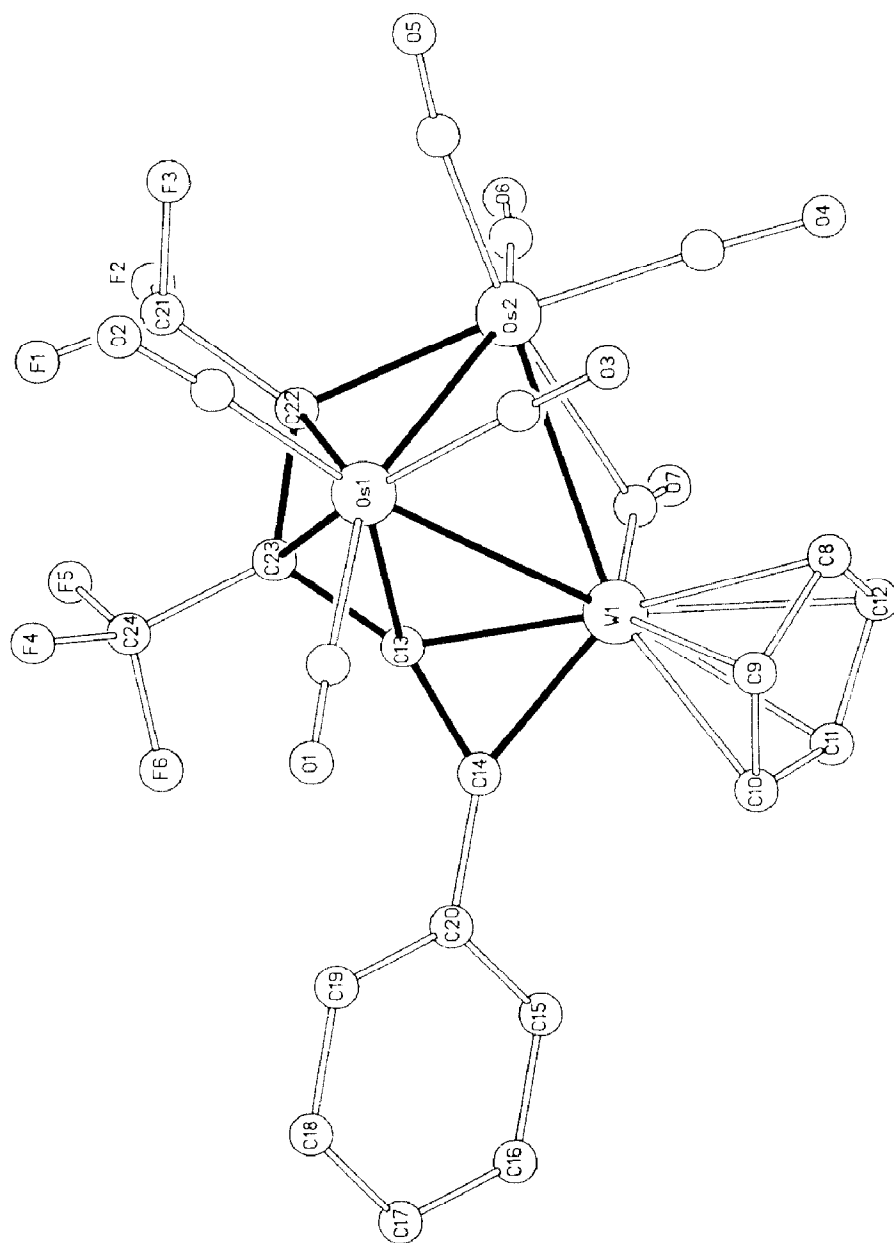


Fig. 2. The structure of $\text{CpW(Os}_2\text{)(CO)}_7\text{[C(CF}_3\text{)C(CF}_3\text{)CCPh]}$ (7) showing the atomic numbering scheme.

donor) by an acetylene ligand ($4e^-$ donor). Therefore, On the basis of the valence electron count we propose that the incoming ditolylacetylene is linked with the coordinated acetylide ligand to give a new C_4 hydrocarbyl moiety. In order to confirm our postulation, an X-ray diffraction study was carried out on **4**.

The structure of **4** is illustrated in Fig. 1. Selected bond distances and angles are given in Table 3. The molecule has a triangular WOs_2 core structure in which the tungsten atom is coordinated to a Cp ring and a CO ligand, and each osmium atom is linked to three, mutually orthogonal, terminal CO ligands. The η^4 - C_4 hydrocarbyl moiety is mainly associated with the Os1–W1 and Os2–W(1) edges of the WOs_2 triangle. If the ditolylacetylene fragment is regarded as a typical organic functional group, the C_4 hydrocarbon can be seen as a coordinated, disubstituted, alkyne ligand in which the alkyne skeleton C29–C30, derived from the acetylide ligand, is bonded to the parallel Os1–Os2 bond by two σ -bonds and to the opposite W1 atom by a π -bond (μ_3 - η^2 -bonding mode) [2a]. Similarly, the ditolylacetylene moiety caps the Os1–C29–W1 triangular face of the M_3C_2 square pyramidal (*nido*) structure by two σ and one π interactions. Finally, by simple electron bookkeeping, the unsaturated C_4 ligand is best described as providing a total of seven electrons to the cluster and giving formal electron counts for the W1, Os1 and Os2 atoms of 19, 18, and 17 e^- , respectively.

In contrast, treatment of the acetylide complexes **1** and **2** with Me_3NO in acetonitrile followed by reaction with an excess of electron-withdrawing alkyne in refluxing toluene, gave a yellowish green complex, $CpWOs_2(CO)_7[C(R')C(R')CCR]$, $R = Ph$, $R' = CO_2Et$, (**5**); $R = ^nBu$, $R' = CO_2Et$, (**6**); $R = Ph$, $R' = CF_3$, (**7**) (Scheme 1). The composition of these complexes, as indicated by mass spectrometry and microanalysis, is closely related to those of the complexes **3** and **4**. However, the color of the solutions as well as the solution IR spectra in the region of CO stretches are completely different, suggesting the presence of a second isomeric form in these WOs_2 complexes that differs in the arrangement of the unsaturated C_4 hydrocarbon.

The structure of complex **7** resembles that of complex **4** in many respects, but there are some marked geometrical differences and more subtle changes in the bonding of the unsaturated C_4 hydrocarbyl chain. Some bond distances and angles are listed in Table 5 and the structure of complex is depicted in Fig. 2. One notable difference from complex **4** is the existence of a semibridging CO ligand [10] which is associated with the longest (W1–Os2) edge. The C_4 hydrocarbon, formed by coupling between the α -carbon of the phenylacetylide ligand and the hexafluoro-2-butyne, spans the two edges not coordinated by the semibridging CO ligand. The hexafluoro-2-butyne fragment can be visualized as being π -bonded to the atom Os1 and σ -bonded to the atoms Os2 and the α -carbon of the acetylide ligand, C13. The α -carbon, C13, of the original acetylide fragment now bridges the W1–Os1 edge, and the β -carbon, C14, is now linked to the atom W1 by a double bond (Scheme 1).

This valence bond description of the hydrocarbon chain in complex **7** is the most concise in terms of maintaining the octet of the carbon atoms, but may not reflect the actual bonding interaction to the metals. The bond lengths C14–C13 (1.38(2) Å) suggest substantial double bond character; the C13–C23 (1.42(2) Å) and C23–C22 (1.44(2) Å) bonds are somewhat longer. Thus, we propose that delocalization takes place within the W1–C13–C14 triangle which provides the C14–C13 bond with some multiple character. This idea is also favored by the long Os1–C13 bond

(2.35(2) Å) compared to values of the C14–W1 bond (2.00(2) Å) and the C13–W1 bond (2.02(25) Å).

Finally, the formation of C₄ hydrocarbon has resulted been elucidated by a study of the ¹³C NMR data of the acetonitrile-substituted precursor, CpWOs₂(CO)₇(CH₃CN)(C≡CPh). Its ¹³C NMR spectrum (room temperature, acetonitrile-*d*₃) in addition to the Os–CO signals, shows four W–CO signals at δ 212.3, 209.0, 208.5 and 205.9 with intensities in the ratio of 1:0.6:1:0.6, suggesting not only the presence of two rapidly interconvertible isomers in solution, but also that the acetonitrile ligand is coordinated to the osmium atom. Based on this observation, we propose that the reaction proceeds by the regiospecific alkyne substitution in the Os(CO)₂(NCMe) center, followed by coupling with the coordinated acetylide and migration of a CO ligand from the tungsten atom to the osmium atom, to give the isolated complexes. However, at this juncture it is still unclear whether the bonding of the C₄ hydrocarbon is determined by the nature of the substituents R' (Tol, CF₃, CO₂Et) or merely by the selectivity to the different acetonitrile isomers, during the initial attack. Studies are in progress to determine the exact structure of the acetonitrile-substituted acetylide derivatives.

Experimental

Infrared spectra were recorded by Perkin–Elmer 580 spectrometer calibrated from the absorption of cyclohexane at 2138.5 cm⁻¹ and the absorption of polystyrene film at 1944.5 cm⁻¹. ¹H and ¹⁹F NMR spectra were recorded by Bruker AM-400 (400.13 MHz) instrument. Mass spectra were obtained on JEOL-HX110 instrument operating in electron impact, field desorption, or fast atom bombardment modes; mass spectral data were calculated by using ¹⁸⁴W and ¹⁹²Os. All reactions were performed under nitrogen in deoxygenated solvents dried with the appropriate agent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F₂₅₄, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F₂₅₄, E. Merck). Elemental analyses were performed by the staff of the Southern Regional Instrument Center at National Cheng Kung University, Tainan (Taiwan). The mixed-metal acetylide complexes CpWOs₂(CO)₈(C≡CR), R = Ph, (1); ⁿBu, (2), were prepared by published procedures [6,7].

Preparation of CpWOs₂(CO)₇[C(Tol)C(Tol)CCPh] (3). The reactions of the acetylide complexes, CpWOs₂(CO)₈(C≡CR), with disubstituted acetylenes were all performed under similar reaction conditions, thus the experimental details of only one reaction are reported here. The acetylide complex CpWOs₂(CO)₈(C≡CPh) (37 mg, 0.039 mmol), in a 50-ml round bottom reaction flask, was treated with sublimed Me₃NO (3.5 mg, 0.047 mmol) in a mixture of dichloromethane (15 ml) and acetonitrile (10 ml) at ambient temperature for 30 min. Then, the solvent was evaporated off (in vacuo), ditolylacetylene (12 mg, 0.058 mmol) was added, the reaction mixture was dissolved in toluene (30 ml), and refluxed for 20 min. The solvent was evaporated off, and the residue was separated by thin layer chromatography (silica gel, dichloromethane:hexane = 1:1), to give 20 mg of the coupling product CpWOs₂(CO)₇[C(Tol)C(Tol)CCPh] as a red-orange material (0.018 mmol, 46%). Crystals of complex 3 were isolated by recrystallization from a mixture of dichloromethane/methanol. Selected spectroscopic data: FAB mass spectrum: *m/z*

1136 (M^+). IR(C_6H_{12}): $\nu(CO)$ 2069(s), 2043(s), 2001(vs), 1987(m), 1967(s), 19505(vw) cm^{-1} . 1H NMR ($CDCl_3$, 294 K) δ 7.09–6.68 (m, 13H), 5.08 (s, 5H), 2.37 (s, 3H), 2.28 (s, 3H). Elemental analysis: Found: C, 37.49; H, 2.17. $WOs_2C_{36}H_{24}O_7$ calcd.: C, 38.03; H, 2.13%.

$CpWOs_2(CO)_7[C(Tol)C(Tol)CC^iBu]$ (**4**). Crystals suitable for the X-ray diffraction study were obtained from a layered solution of dichloromethane/methanol at ambient temperature. Yield: 30%. Selected spectroscopic data: FAB mass spectrum: m/z 1116 (M^+). IR(C_6H_{12}): $\nu(CO)$ 2069(vs), 2042(vs), 1999(vs), 1984(s), 1965(s), 1945(w) cm^{-1} . 1H NMR ($CDCl_3$, 294 K) δ 7.17–7.03 (m, 8H), 5.08 (s, 5H), 2.45 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 1.93 (m, 1H), 1.81 (m, 1H), 1.42 (h, 2H), 0.99 (t, 3H). Elemental analysis: Found: C, 36.56; H, 2.53. $WOs_2C_{34}H_{28}O_7$ calcd.: C, 36.70; H, 2.54%.

$CpWOs_2(CO)_7[C(CO_2Et)C(CO_2Et)CCPh]$ (**5**). Dark-green crystals of complex **5** were recrystallized from dichloromethane/water/methanol mixture at ambient temperature. Yield: 46%. Selected spectroscopic data: FAB mass spectrum: m/z 1100 (M^+). IR(CCl_4): $\nu(CO)$ 2076(s), 2049(vs), 2004(s,br), 1996(s), 1984(s), 1726(w) cm^{-1} . 1H NMR ($CDCl_3$, 294 K) δ 7.63 (m, 2H), 7.45 (m, 3H), 5.85 (s, 5H), 4.37–4.18 (m, 4H), 1.29 (t, 3H), 1.21 (t, 3H). Elemental analysis: Found: C, 31.01; H, 2.10. $WOs_2C_{28}H_{20}O_{11}$ calcd.: C, 30.67, H, 1.84%.

$CpWOs_2(CO)_7[C(CO_2Et)CC^iBu]$ (**6**). Dark-green crystals of complex **6** were recrystallized from a dichloromethane/water/methanol mixture at ambient temperature. Yield: 36%. Selected spectroscopic data: FAB mass spectrum: m/z 1080 (M^+). IR(C_6H_{12}): $\nu(CO)$ 2076(s), 2050(vs), 2005(s), 1995(s), 1991(m,sh), 1984(s), 1725(w,br) cm^{-1} . 1H NMR ($CDCl_3$, 294 K) δ 5.77 (s, 5H), 4.36 (m, 3H), 4.20 (m,

Table 1

Experimental data from the X-ray diffraction studies for complexes **4** and **7**

<i>(a) Complex 4</i>	
Formula: $W_1Os_2C_{34}H_{28}O_7$	mol. wt.: 1112.8
$a = 14.21(1) \text{ \AA}$	monoclinic, space group $P2_1/c$
$b = 10.80(1) \text{ \AA}$	$Z = 4$
$c = 21.46(2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$\beta = 97.82(8)^\circ$	$F(000) = 2056$
$V = 3263(5) \text{ \AA}^3$	$\mu = 11.42 \text{ mm}^{-1}$
no. of unique data, total with $I > 3\sigma(I)$	5770, 4377
no. of atoms and parameters refined	74, 368
R, R_w : 0.0541, 0.0469	GOF: 2.228
<i>(b) Complex 7</i>	
Formula: $W_1Os_2C_{24}H_{10}F_6O_7$	mol. wt.: 1088.6
$a = 10.4476(6) \text{ \AA}$	monoclinic, space group $P2_1/c$
$b = 18.08(1) \text{ \AA}$	$Z = 4$
$c = 14.437(8) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$\beta = 105.66(4)^\circ$	$F(000) = 1960$
$V = 2624.8 \text{ \AA}^3$	$\mu = 14.22 \text{ mm}^{-1}$
no. of unique data, total with $I > 3\sigma(I)$	5457, 4284
no. of atoms and parameters refined	50, 342
R, R_w : 0.0595, 0.0512	GOF: 3.307

1H), 3.38 (m, 1H), 3.20 (m, 1H), 1.74 (m, 1H), 1.61 (m, 1H), 1.39 (m, 2H), 1.36 (t, 3H), 1.30 (t, 3H), 0.94 (t, 3H). Elemental analysis: Found: C, 28.90; H, 2.26. $WOs_2C_{26}H_{24}O_{11}$ calcd.: C, 29.0; H, 2.25%.

$CpWOs_2(CO)_7[C(CF_3)C(CF_3)CCPh]$ (7). Dark-green crystals of 7 suitable for the X-ray diffraction study were obtained from a layered solution of dichloro-

Table 2

Positions and thermal parameters for complex 4

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Os1	0.20853(5)	0.24970(6)	0.17607(3)	0.0361(2)
Os2	0.26367(5)	0.46812(6)	0.25101(3)	0.0415(2)
W1	0.34458(5)	0.40980(6)	0.14119(3)	0.0346(2)
C1	0.273(1)	0.095(2)	0.2064(8)	0.051(6)
O1	0.311(1)	0.005(1)	0.2208(7)	0.083(6)
C2	0.138(1)	0.260(1)	0.245(1)	0.063(8)
O2	0.091(1)	0.248(1)	0.2862(7)	0.079(6)
C3	0.098(1)	0.179(1)	0.1281(8)	0.045(6)
O3	0.0314(9)	0.147(1)	0.0967(6)	0.065(5)
C4	0.400(1)	0.303(2)	0.2101(7)	0.047(6)
O4	0.4461(9)	0.241(1)	0.2472(6)	0.075(5)
C5	0.324(2)	0.618(2)	0.2742(8)	0.069(8)
O5	0.359(1)	0.716(1)	0.2843(8)	0.102(7)
C6	0.158(1)	0.512(2)	0.2839(8)	0.056(7)
O6	0.089(1)	0.547(1)	0.3043(6)	0.086(6)
C7	0.329(1)	0.379(2)	0.3244(8)	0.063(7)
O7	0.366(1)	0.330(1)	0.3670(6)	0.094(7)
C8	0.5032(8)	0.4087(9)	0.1238(6)	0.044(6)
C9	0.4909(8)	0.5117(9)	0.1630(6)	0.057(7)
C10	0.4260(8)	0.5944(9)	0.1285(6)	0.074(9)
C11	0.3983(8)	0.5424(9)	0.0679(6)	0.070(8)
C12	0.4460(8)	0.4276(9)	0.0650(6)	0.061(7)
C13	0.267(1)	0.259(1)	0.0879(7)	0.043(5)
C14	0.215(1)	0.372(1)	1.0660(7)	0.034(5)
C15	0.2233(7)	0.103(1)	0.0006(5)	0.053(6)
C16	0.2422(7)	-0.006(1)	-0.0308(5)	0.070(8)
C17	0.3268(7)	-0.070(1)	-0.0131(5)	0.072(9)
C18	0.3927(7)	-0.025(1)	0.0360(5)	0.069(8)
C19	0.3739(7)	0.084(1)	0.0674(5)	0.063(7)
C20	0.2892(7)	0.147(1)	0.0497(5)	0.046(6)
C21	0.341(2)	-0.187(2)	0.049(1)	0.13(1)
C22	0.1227(7)	0.5102(9)	-0.0090(4)	0.043(6)
C23	0.0995(7)	0.5640(9)	-0.0681(4)	0.058(7)
C24	0.1501(7)	0.5333(9)	-0.1169(4)	0.059(7)
C25	0.2256(7)	0.4490(9)	-0.1065(4)	0.056(7)
C26	0.2488(7)	0.3952(9)	-0.0474(4)	0.051(6)
C27	0.1973(7)	0.4258(9)	0.0014(4)	0.034(5)
C28	0.128(2)	0.589(2)	0.049(1)	0.13(1)
C29	0.193(1)	0.417(1)	0.1237(8)	0.045(6)
C30	0.218(1)	0.523(1)	0.1590(7)	0.042(6)
C31	0.202(1)	0.659(1)	0.1331(8)	0.045(6)
C32	0.105(1)	0.704(2)	0.149(1)	0.074(8)
C33	0.082(1)	0.833(2)	0.119(1)	0.078(9)
C34	0.056(2)	0.833(2)	0.052(1)	0.11(1)

Table 3

Selected bond lengths (Å) and angles (deg) for complex 4

W1–Os1	2.769(3)	W1–Os2	2.830(3)
Os1–Os2	2.898(3)	W1–C13	2.20(2)
W1–C14	2.31(1)	W1–C29	2.14(2)
W1–C30	2.26(2)	Os1–C13	2.17(2)
Os1–C29	2.13(2)	Os2–C30	2.08(2)
C13–C14	1.47(2)	C14–C29	1.41(2)
C29–C30	1.39(2)		
Os1–W1–Os2	62.3(1)	W1–Os1–Os2	59.9(1)
W1–Os2–Os1	57.8(1)	W1–C29–Os1	81.0(5)
W1–C30–Os2	81.4(5)	W1–C13–Os1	78.7(5)
C13–C14–C29	100(1)	C15–C29–C30	134(2)

Table 4

Positions and thermal parameters for complex 7

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Os1	0.02024(6)	0.18512(4)	0.42846(4)	0.0318(2)
Os2	0.01512(7)	0.32577(4)	0.34679(4)	0.0342(2)
W1	0.26820(6)	0.24386(4)	0.39786(4)	0.0332(2)
C1	0.094(2)	0.095(1)	0.491(1)	0.044(7)
O1	0.145(2)	0.0431(8)	0.5282(9)	0.069(7)
C2	−0.150(2)	0.160(1)	0.449(1)	0.044(7)
O2	−0.246(1)	0.1430(9)	0.461(1)	0.069(6)
C3	0.070(2)	0.249(1)	0.536(1)	0.056(8)
O3	0.102(1)	0.2832(8)	0.6074(8)	0.063(6)
C4	0.108(2)	0.405(1)	0.429(1)	0.052(7)
O4	0.167(2)	0.4522(9)	0.475(1)	0.085(7)
C5	−0.143(2)	0.357(1)	0.381(1)	0.060(8)
O5	−0.226(1)	0.3796(9)	0.408(1)	0.073(6)
C6	−0.024(2)	0.382(1)	0.231(1)	0.047(7)
O6	−0.049(1)	0.4116(7)	0.1588(8)	0.058(5)
C7	0.223(2)	0.317(1)	0.291(1)	0.049(7)
O7	0.237(1)	0.3518(8)	0.2244(9)	0.058(5)
C8	0.33(1)	0.3137(9)	0.538(1)	0.071(9)
C9	0.395(1)	0.2373(9)	0.559(1)	0.069(9)
C10	0.473(1)	0.2089(9)	0.500(1)	0.07(1)
C11	0.498(1)	0.2677(9)	0.442(1)	0.07(1)
C12	0.436(1)	0.3324(9)	0.465(1)	0.08(1)
C13	0.145(2)	0.1685(9)	0.317(1)	0.034(6)
C14	0.276(1)	0.1456(9)	1.336(1)	0.032(5)
C15	0.470(1)	0.0892(6)	0.298(1)	0.058(8)
C16	0.543(1)	0.0267(6)	0.288(1)	0.09(1)
C17	0.500(1)	−0.0435(6)	0.306(1)	0.09(1)
C18	0.382(1)	−0.0511(6)	0.333(1)	0.062(9)
C19	0.309(1)	0.0113(6)	0.343(1)	0.050(7)
C20	0.352(1)	0.0815(6)	0.325(1)	0.039(6)
C21	−0.217(1)	0.222(1)	0.231(1)	0.039(6)
C22	−0.071(1)	0.2257(8)	0.280(1)	0.028(5)
C23	0.007(2)	0.1621(9)	0.271(1)	0.037(6)
C24	−0.043(2)	0.095(1)	0.208(1)	0.051(7)
F1	−0.274(1)	0.1569(6)	0.2241(8)	0.060(5)
F2	−0.236(1)	0.2496(7)	0.1405(7)	0.072(5)
F3	−0.295(1)	0.2654(7)	0.2714(8)	0.070(5)
F4	−0.107(1)	0.0453(6)	0.2462(8)	0.060(5)
F5	−0.118(1)	0.1113(6)	0.1217(7)	0.060(4)
F6	0.062(1)	0.0579(6)	0.1923(8)	0.064(5)

Table 5

Selected bond lengths (Å) and angles (deg) for complex **7**

W1–Os1	2.941(2)	W1–Os2	2.945(2)
Os1–Os2	2.797(2)	W1–C14	2.00(2)
W1–C13	2.02(2)	Os1–C13	2.35(2)
Os1–C23	2.27(2)	Os1–C22	2.22(1)
Os2–C22	2.13(2)	C13–C14	1.38(2)
C13–C23	1.42(2)	C22–C23	1.44(2)
W1–C7	1.99(2)	Os2–C7	2.53(2)
W1–Os1–Os2	61.7(1)	W1–Os2–Os1	61.6(1)
W1–C13–C14	69.1(9)	W1–C14–C13	70.6(9)
Os1–W1–Os2	56.7(1)	C13–W1–C14	40.3(6)
C14–C13–C23	154(2)	C13–C23–C22	115(1)
W1–C7–O7	158(26)	Os2–C7–O7	122(2)

methane/water/methanol at ambient temperature. Yield: 42%. Selected spectroscopic data: FAB mass spectrum: m/z 1092 (M^+). IR(C_6H_{12}) $\nu(CO)$ 2082(s), 2054(vs), 2015(m), 2006(m), 1987(s) cm^{-1} . 1H NMR ($CDCl_3$, 294 K) δ 7.49–7.45 (m, 5H), 5.88 (s, 5H). ^{19}F NMR ($CDCl_3$, 294 K) δ –46.96 (q, 3F, $^5J_{F-F}$ = 15 Hz), –50.04 (q, 3F, $^5J_{F-F}$ = 15 Hz). Elemental analysis: Found: C, 26.25; H, 0.92. $WOs_2C_{24}H_{10}F_6O_7$ calcd.: C, 26.48; H, 0.93%.

X-ray Crystallography. The structures were solved by direct methods by use of the SHELXTL PLUS program and refined by full-matrix least squares. The data collection and refinement parameters for **4** and **7** are given in Table 1. Atomic positional parameters for **4** are listed in Table 2, and selected bond angles and lengths are listed in Table 3. The corresponding parameters for **7** are listed in Tables 4 and 5, respectively. Further details of the crystal structure study may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-53875, the names of the authors, and the journal citation.

Acknowledgements

This work was supported by the National Science Council of the Republic of China.

References

- 1 E.L. Muetterties and J. Stein, *Chem. Rev.*, 79 (1979) 479.
- 2 (a) E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 83 (1983) 203. (b) M.I. Bruce and A.G. Swincer, *Adv. Organomet. Chem.*, 22 (1983) 59. (c) S. Aime and A.J. Deeming, *J. Chem. Soc., Dalton Trans.*, (1983) 1807. (d) H.D. Kaesz and A.P. Humphries, *Prog. Inorg. Chem.*, 25 (1979) 146. (e) E. Rosenberg, *Polyhedron*, 8 (1989) 383. (f) P.N. Nickias, J.P. Selegue and B.A. Young, *Organometallics*, 7 (1988) 2248.
- 3 (a) E. Boyar, A.J. Deeming, M.S.B. Felix, S.E. Kabir, T. Adatia, R. Bhusate, M. McPartlin and H.R. Powell, *J. Chem. Soc., Dalton Trans.*, (1989) 5. (b) A.J. Deeming, M.S.B. Felix, P.A. Bates and M.B. Hursthouse, *J. Chem. Soc., Chem. Comm.*, (1987) 461.
- 4 (a) D. Nucciarone, S.A. MacLaughlin, N.J. Taylor and A.J. Carty, *Organometallics*, 7 (1988) 106. (b) D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics*, 7 (1988) 127. (c) S.A. MacLaughlin, J.P. Johnson, N.J. Taylor, A.J. Carty and E. Sappa, *Organometallics*, 2 (1983) 352.

- 5 M.I. Bruce, M.G. Humphrey, J.G. Matison, S.K. Roy and A.G. Swincer, *Aust. J. Chem.*, 37 (1984) 1955.
- 6 Y. Chi, G.-H. Lee, S.-M. Peng and C.-H. Wu, *Organometallics*, 8 (1989) 1574.
- 7 Y. Chi, S.-M. Peng, G.-H. Lee and B.-J. Liu, *Polyhedron*, 8 (1989) 2003.
- 8 (a) E. Sappa, G. Pasquinelli, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1989) 601. (b) E. Sappa, A.M. Manotti Lanfredi, G. Predieri and A. Tiripicchio, *Inorg. Chim. Acta*, 61 (1982) 217.
- 9 (a) B.F.G. Johnson, J. Lewis and D.A. Pippard, *J. Chem. Soc., Dalton Trans.*, (1981) 409. (b) M. Tachicawa and J.R. Shapley, *J. Organomet. Chem.*, 124 (1977) C19.
- 10 (a) C.P. Horwitz and D.F. Shriver, *Adv. Organomet. Chem.*, 219 (1984) 23. (b) R. Colton and J.M. McCormick, *Coord. Chem. Rev.*, 31 (1980) 1. (c) F.A. Cotton, *Prog. Inorg. Chem.*, 21 (1976) 1.