Journal of Organometallic Chemistry, 378 (1989) 45–56
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20231

Synthesis and characterization of tetranuclear mixed-metal hydride complexes, $LWM_3(CO)_{11}(\mu\text{-}H)_3$, $L = C_5H_5$, C_5Me_5 and M = Ru, Os

Yun Chi *, **Chih-Yi Cheng and Sue-Lein Wang** *

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan (R.O.C.)

(Received June 9th, 1989)

Abstract

Hydrogenation of the tetranuclear mixed-metal clusters $LWM_3(CO)_{12}(\mu\text{-}H)$ ($L = C_5H_5$, M = Os, (**1**); $L = C_5Me_5$, M = Os, (**2**); $L = C_5H_5$, M = Ru, (**3**); $L = C_5Me_5$, M = Ru, (**4**)) in toluene solution has yielded the tetrahedral cluster complexes $LWM_3(CO)_{11}(\mu\text{-}H)_3$ ($L = C_5H_5$, M = Os, (**5**); $L = C_5Me_5$, M = Os, (**6**); $L = C_5H_5$, M = Ru, (**7**); $L = C_5Me_5$, M = Ru, (**8**)). Complex **8** was characterized by single crystal X-ray diffraction. Crystal data for **8**: space group $P2_1/n$; $a = 10.731(4)$, $b = 16.275(4)$, $c = 15.606(4)$ Å, $\beta = 99.76(2)°$, $Z = 4$; $R_F = 0.0255$, $R_w = 0.0245$ and $GOF = 1.19$. Complexes **6** and **8**, which possess a $Cp^*W(CO)_2$ fragment, are present solely as one isomer in solution. The structure of this isomer (denoted **a**) is consistent with the solid state structure of **8** in which the hydride ligands are located on the edges of a WM_2 triangular face. For complexes **5** and **7**, each containing a $CpW(CO)_2$ fragment, variable temperature ^1H NMR studies suggest the presence of two rapidly interconverting isomers (**a** and **b**) in solution. Isomer **b** contains a tetrahedral core similar to isomer **a**, but in **b**, the hydride ligands occupy two M–H–M sites and one W–H–M site, in a zigzag arrangement.

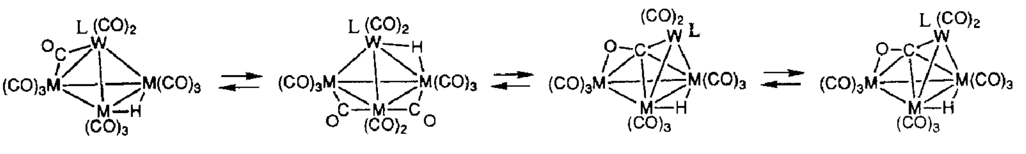
Introduction

The chemistry of mixed-metal clusters of transition-metals has been the subject of considerable research activity [1]. The reason is that the various metals present in mixed-metal clusters can show reactivity patterns and/or structures very different from those of the homometallic analogues. In an effort to prepare and to examine the bonding and the structures of the mixed-metal clusters, we have synthesized and characterized a complete series of the tetranuclear mixed-metal clusters

---

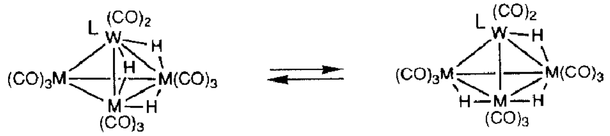
* To whom inquiries concerning the X-ray crystallographic work should be addressed.

0022-328X/89/$03.50



M = Os, L = C_5H_5;	**1a**, 75%	**1b**, 25%		
M = Os, L = C_5Me_5;	**2a**, 32%	**2b**, 68%		
M = Ru, L = C_5H_5;	**3a**, 17%	**3b**, 28%	**3c**, 55%	
M = Ru, L = C_5Me_5;		**4b**, 16%	**4c**, 22%	**4d**, 62%

Scheme 1. The percentage indicated is the proportion of each isomer in solution.



M = Os, L = C_5H_5;	(**5a**), 41%	(**5b**), 59%, in CD_2Cl_2.
	78%	22%, in THF-d_8.
M = Os, L = C_5Me_5;	(**6a**), 100%, in $CDCl_3$.	
M = Ru, L = C_5H_5;	(**7a**), 87%	(**7b**), 13%, in CD_2Cl_2.
M = Ru, L = C_5Me_5;	(**8a**), 100%, in CD_2Cl_2.	

Scheme 2. The percentage indicated is the proportion of each isomer in solution.

$LWM_3(CO)_{12}(\mu\text{-H})$, (L = C_5H_5, M = Os, (**1**); L = C_5Me_5, M = Os, (**2**); L = C_5H_5, M = Ru, (**3**); L = C_5Me_5, M = Ru, (**4**)) [2,3]. In these series of complexes, each individual member adopts a different molecular structure in the solid state and generates two isomers each for (**1**) and (**2**), and three isomers each for (**3**) and (**4**) in solution (Scheme 1). The experiments reported provide for the first time an unambiguous example of a π-bonded CO ligand in equilibrium with regular, σ-bonded CO ligands.

In the present study we have explored the action of dihydrogen on the complexes **1** to **4** which produce the trihydride complexes $LWM_3(CO)_{11}(\mu\text{-H})_3$ (L = C_5H_5, M = Os, (**5**); L = C_5Me_5, M = Os, (**6**); L = C_5H_5, M = Ru, (**7**); L = C_5Me_5, M = Ru, (**8**)) in high yields. The crystal structure of complex **5** has been determined [4], but up to now the existence of a second isomer in solution has not yet been reported. As part of our study on the solution dynamics of the mixed-metal cluster complexes, we have fully characterized the unknown isomer in solution. We report here the preparation of the hydride clusters, the crystal structure of **8**, and variable temperature NMR studies of the hydride exchange and the intramolecular tautomerization (Scheme 2).

Results and discussion

Preparation of the trihydride complexes $LWM_3(CO)_{11}(\mu\text{-H})_3$

In general, the tetranuclear hydride complexes, $LWM_3(CO)_{11}(\mu\text{-H})_3$, have been isolated in low yield from the reactions of tungsten hydride, $LW(CO)_3H$, with group 8 trinuclear carbonyl complexes, $Os_3(CO)_{10}(CH_3CN)_2$ or $Ru_3(CO)_{12}$, in addition to the major product of the tetranuclear mixed-metal cluster, $LWM_3(CO)_{12}(\mu\text{-H})$.

Hydrogenation of the complexes $LWM_3(CO)_{12}(\mu\text{-}H)$ in toluene has served as an alternative path to generate the required complexes; however, the conditions of the reaction differ slightly. The hydrogenation of the relevant W/Os_3 complexes was carried out under pressure (50 psig) to ensure complete and clean conversion to the trihydride complexes. The inertness of the W/Os_3 complexes is consistent with the general belief that the osmium compounds are kinetically much more stable than the related ruthenium complexes. This difference has been reported previously in the literature: reaction of $Ru_3(CO)_{12}$ with hydrogen (1 atm) in refluxing octane yielded the tetranuclear complex $Ru_4(CO)_{12}(\mu\text{-}H)_4$ [5]; however, the analogous $Os_4(CO)_{12}(\mu\text{-}H)_4$ was prepared from the reaction of $Os_3(CO)_{12}$ with hydrogen under pressure (120 atm) at 100 ° C [6].

*Crystal structure of $Cp^{\star}WRu_3(CO)_{11}(\mu\text{-}H)_3$ (**8**)*

The molecular structure of complex **8** was determined from a single-crystal X-ray diffraction study. The molecular geometry and the scheme used for labeling the atoms are shown in Fig. 1. The bond distances and the bond angles are listed in Tables 1 and 2, respectively. The tungsten atom and the three ruthenium atoms form the tetrahedral core which is associated with the expected 60 outer valence electrons. The tungsten atom is coordinated to a Cp* ligand and two terminal CO

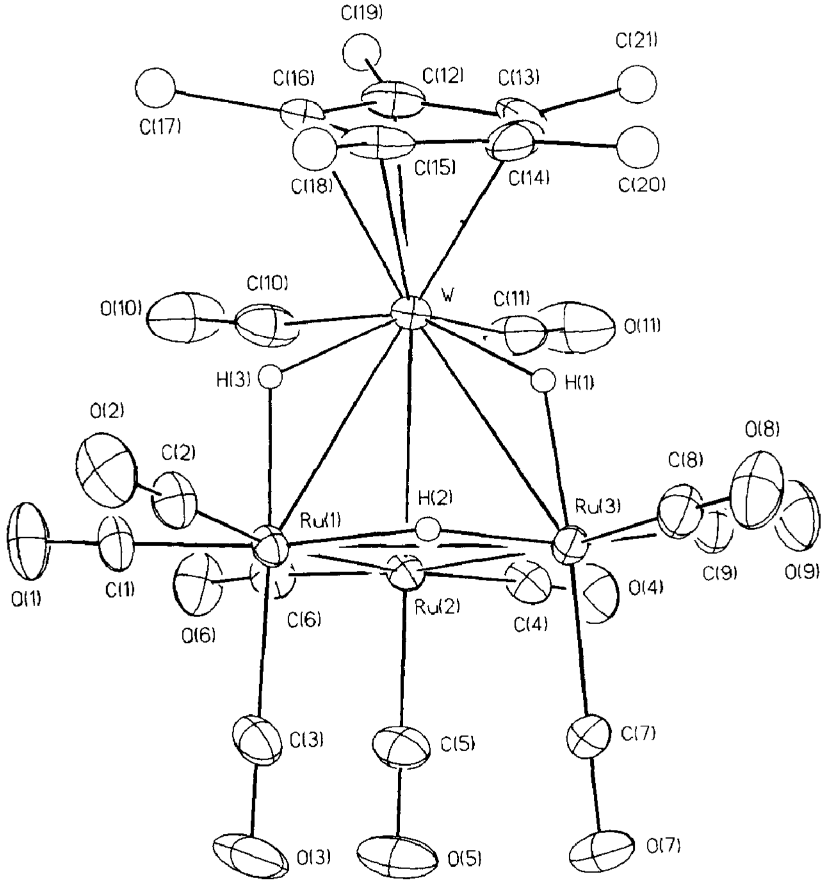


Fig. 1. The molecular structure of $Cp^{\star}WOs_3(CO)_{11}(\mu\text{-}H)_3$ (**8**) showing the atomic numbering scheme.

Table 1

Selected interatomic distances (Å) of complex **8** (esd's in parentheses)

(A) Metal–metal distances			
Ru(1)–Ru(2)	2.793(1)	Ru(1)–Ru(3)	2.917(1)
Ru(2)–Ru(3)	2.791(1)	W–Ru(1)	3.077(1)
W–Ru(2)	2.903(1)	W–Ru(3)	3.079(1)
(B) Metal–carbonyl distances			
Ru(1)–C(1)	1.907(7)	Ru(1)–C(2)	1.921(7)
Ru(1)–C(3)	1.920(9)	Ru(2)–C(4)	1.898(7)
Ru(2)–C(5)	1.861(9)	Ru(2)–C(6)	1.877(7)
Ru(3)–C(7)	1.902(10)	Ru(3)–C(8)	1.916(7)
Ru(3)–C(9)	1.880(7)	W–C(10)	1.994(9)
W–C(11)	1.975(9)		
(C) Carbon–oxygen distances			
C(1)–O(1)	1.124(9)	C(20–O(2)	1.130(9)
C(3)–O(3)	1.121(12)	C(4)–O(4)	1.137(9)
C(5)–O(5)	1.148(1)	C(6)–O(6)	1.145(9)
C(7)–O(7)	1.133(13)	C(8)–O(8)	1.133(9)
C(9)–O(9)	1.139(10)	C(10)–C(10)	1.165(1)
C(11)–O(11)	1.145(11)		
(D) Distances involving the η^5-C_5Me_5 ligands			
W–C(12)	2.291(9)	W–C(13)	2.299(14)
W–C(14)	2.363(9)	W–C(15)	2.360(8)
W–C(16)	2.325(8)	C(12)–C(13)	1.403(14)
C(13)–C(14)	1.373(18)	C(14)–C(15)	1.358(15)
C(15)–C(16)	1.400(1)	C(12)–C(16)	1.395(12)
(E) Metal–hydride distances			
W–H(1)	1.916	Ru(3)–H(1)	1.651
Ru(1)–H(2)	1.712	Ru(3)–H(2)	1.692
W–H(3)	1.929	Ru(1)–H(3)	1.688

ligands, and each of the three basal ruthenium atoms is associated with three terminal CO ligands. The local environment of the basal ruthenium atom corresponds to a pseudo-octahedral arrangement.

Three hydride-ligand bridges W–Ru(1), W–Ru(3) and Ru(1)–Ru(3) were located on the difference Fourier map, and their positions are consistent with the ^{1}H NMR data (vide infra). There are many structural characteristics which are consistent with the location of the bridging hydride ligands. The W–Ru(1) and W–Ru(3) (3.077(1) Å and 3.079(1) Å) distances are longer than the third, unbridged, W–Ru(2) distance (2.903(1) Å); the Ru(1)–Ru(3) bond (2.977(1) Å), which is associated with the hydride H(2), is longer than the other two, Ru(1)–Ru(2) (2.793(1) Å) and Ru(2)–Ru(3) (2.791(1) Å). This variation in the metal–metal distances is in agreement with the results that the bridging hydrides are coordinated to the long metal–metal bonds. Furthermore, the expected, abnormally large M–M–C angles for CO ligands adjacent to, and in the same plane as, the bridging hydride are also observed. These large M–M–C angles are in the range 116–118°, in contrast to usual M–M–C angles of 70–95°. The out-of-plane displacement of the methyl groups reflects the steric crowding around the Cp* ring. The methyl groups of the Cp* ring have been pushed away from the WRu_3 core. The largest deviations are

Table 2

Selected bond angles (deg) of complex **8** (esd's in parentheses)

(A) Intermetallic angles			
W-Ru(1)-Ru(2)	59.0(1)	W-Ru(2)-Ru(1)	65.4(1)
Ru(1)-W-Ru(2)	55.6(1)	W-Ru(1)-Ru(3)	61.8(1)
W-Ru(3)-Ru(1)	61.7(1)	Ru(1)-W-Ru(3)	56.6(1)
W-Ru(2)-Ru(3)	65.4(1)	W-Ru(3)-Ru(2)	59.0(1)
Ru(2)-W-Ru(3)	55.5(1)	Ru(1)-Ru(2)-Ru(3)	63.0(1)
Ru(2)-Ru(3)-Ru(1)	58.5(1)	Ru(3)-Ru(1)-Ru(2)	58.5(1)
(B) Metal-carbon-oxygen angles			
Ru(1)-C(1)-O(1)	179.5(7)	Ru(1)-C(2)-O(2)	176.9(6)
Ru(1)-C(3)-O(3)	178.2(7)	Ru(2)-C(4)-O(4)	176.0(7)
Ru(2)-C(5)-O(5)	176.1(7)	Ru(2)-C(6)-O(6)	175.7(7)
Ru(30-C(7)-O(7)	176.9(7)	Ru(3)-C(8)-O(8)	177.2(6)
Ru(3)-C(9)-O(9)	177.8(7)	W-C(10)-O(10)	171.5(8)
W-C(11)-O(11)	169.0(9)		
(C) Metal-metal-carbon angles			
Ru(1)-Ru(3)-C(8)	115.6(2)	Ru(3)-Ru(1)-C(2)	118.1(2)
Ru(1)-Ru(2)-C(6)	102.0(2)	Ru(2)-Ru(1)-C(1)	84.6(2)
Ru(2)-Ru(3)-C(9)	88.2(2)	Ru(3)-Ru(2)-C(4)	100.8(2)
W-Ru(1)-C(1)	96.7(3)	W-Ru(1)-C(2)	113.3(2)
W-Ru(2)-C(4)	108.6(2)	W-Ru(20-C(6)	106.3(2)
W-Ru(3)-C(8)	115.9(2)	W-Ru(3)-C(9)	95.3(3)
(D) Metal-hydride-metal angles			
W-H(1)-Ru(3)	119.2	Ru(1)-H(2)-Ru(3)	117.9
W-H(3)-Ru(1)	116.4		

0.25 Å for C(21), which is closest to O(11) (C(21) ··· O(11) = 3.19 Å), and 0.24 Å for C(19), which is precisely eclipsed by the carbonyls, C(10)O(10) and C(11)O(11); the smallest deviation is 0.17 Å for C(18), which lies almost above the bridging hydrides.

The structure of **8** is slightly different from that of the structurally characterized complex **5**, which exhibits the presence of at least one semibridging CO ligand located on the unique W-Os bond [7]. The W-C(10)-O(10) and W-C(11)-O(11) angles (171.5(8) and 169.0(9)°) of complex **8** are almost linear, suggesting that the semibridging interaction is extremely weak. This observation can be understood in terms of the semibridging CO-Cp* repulsion, because the formation of semibridging CO ligands reduces the distance and thus increase the nonbonding interaction between the oxygen atom of the CO ligand and the methyl groups of the Cp* ring. A similar argument has been applied successfully to account for the decrease in the isomer ratio of **2a** : **2b** with respect to that of **1a** : **1b** in solution [2].

Finally, as there are no semibridging CO ligands [8] to distribute electron density more evenly around the cluster complex, the formal electron count for each metal vertex, if the metal atoms and ligands are neutral, is 19 outer valence electrons for W atom, 18 electrons for the Ru(1) and Ru(3) atoms and 17 electrons for Ru(2).

Hydride exchange and intramolecular isomerization

The ^1H NMR spectrum of the triosmium complex **6** in $CDCl_3$ solution at room temperature shows two signals at δ −19.86 (J(W-H) = 43 Hz) and −21.43 of which the areas are in the ratio of 2 : 1. This feature suggests that complex **6** adopts the structure established for the analogous triruthenium complex **8**. On warming to 353 K in toluene-d_8 solution, both signals broaden slightly, indicating that the rate of hydride exchange is slow.

In contrast, hydride exchange is much more facile for the related triruthenium complex **8** on the NMR time scale. The ^{1}H NMR spectrum of **8** at room temperature is a broad and featureless hydride signal at δ −18.46. However, as the temperature is decreased to 235 K, the broad signal splits into two sharp signals at δ −18.34 (J(W–H) = 47 Hz) and −18.69 in the ratio of 2 : 1. The former is assigned to the hydrides associated with the W–Ru bonds, and the latter to the hydride linked to the Ru–Ru bond, from the presence of the tungsten satellites. On the other hand the ^{1}H NMR spectrum (toluene-d_8) at 348 K displays a sharp hydride signal at δ −17.83, which suggests that the exchange of hydrides is very rapid under this condition; the J(W–H) coupling constant of 32 Hz is equivalent to the arithmetic mean of those of the W–H–Ru and Ru–H–Ru hydrides. Finally, the Gibb's energy of activation $\Delta G^\ddagger$ (57 kJ/mol) has also been calculated from the data of the chemical shift difference between the hydride signals (140 Hz) and the coalescence temperature (T_c = 290 K).

The hydride exchange in complexes **5** and **7**, which both contain a $CpW(CO)_2$ fragment, is much more complex in solution. The limiting ^{1}H NMR spectrum of **5** at 211 K in CD_2Cl_2 is shown in Fig. 2. Five signals at δ −19.42, −20.90 (J(W–H) = 44 Hz), −21.06, −21.13 (J(W–H) = 42 Hz), and −21.51, which are in the region expected for edge-bridging hydrides, were observed in the ratio 1 : 1 : 0.7 : 1.4 : 1. The nonintegral ratio of these hydride signals provided the first evidence of the presence of two isomeric species (in the ratio of 0.7 : 1. Consequently, the signals at δ −21.06 and −21.13 in the ratio of 0.7 : 1.4 are assigned to the hydrides of the isomer **5a** and the other three signals of equal intensity at δ −19.42, −20.90 and −21.51, to the hydrides of the isomer **5b** (Scheme 2). The structure of isomer **b** is proposed on the basis of the crystal structure of the analogous Mo/Os_3 complex, $CpMoOs_3(CO)_{11}(\mu\text{-}H)_3$, reported by Shore and coworkers [9] and the structural isomerization of the hydrido-metal cluster anion, $Ru_4(CO)_{12}(\mu\text{-}H)_3^-$, reported by Kaesz and coworkers [10]. Furthermore, the characteristic tungsten satellites of the hydride signal at δ −20.90 provide additional support for the postulated structure of isomer **b**.

As the temperature was raised to 233 K, we clearly saw that the unique Os–H–Os hydride of **5a** began to undergo rapid exchange with the W–H–Os hydrides of the same molecule, whereas only one of the Os–H–Os hydrides of **5b** underwent exchange with the characteristic W–H–Os hydride. This observation is reflected in the hydride signals, except for the signal at δ −19.42, broadens and coalesces substantially within the range 233–253 K. While the temperature was being raised to 303 K, only one broad signal, at −20.55, was observed, which suggests that both hydride scrambling and rapid intramolecular tautomerism were occurring.

The effect of solvent on the ratio **5a** : **5b** has also been investigated. Dissolution of **5** in THF-d_8 gives an **a** : **b** ratio of 3.5 : 1. This observation not only supports the suggestion that two isomers are present in solution but it also indicates that isomer **5a** is more polar than isomer **5b**. Attempts to study the equilibria established in solvents of differing dielectronic constants, such as acetone-d_6 or acetonitrile-d_3, were hampered by the poor solubility of the complex.

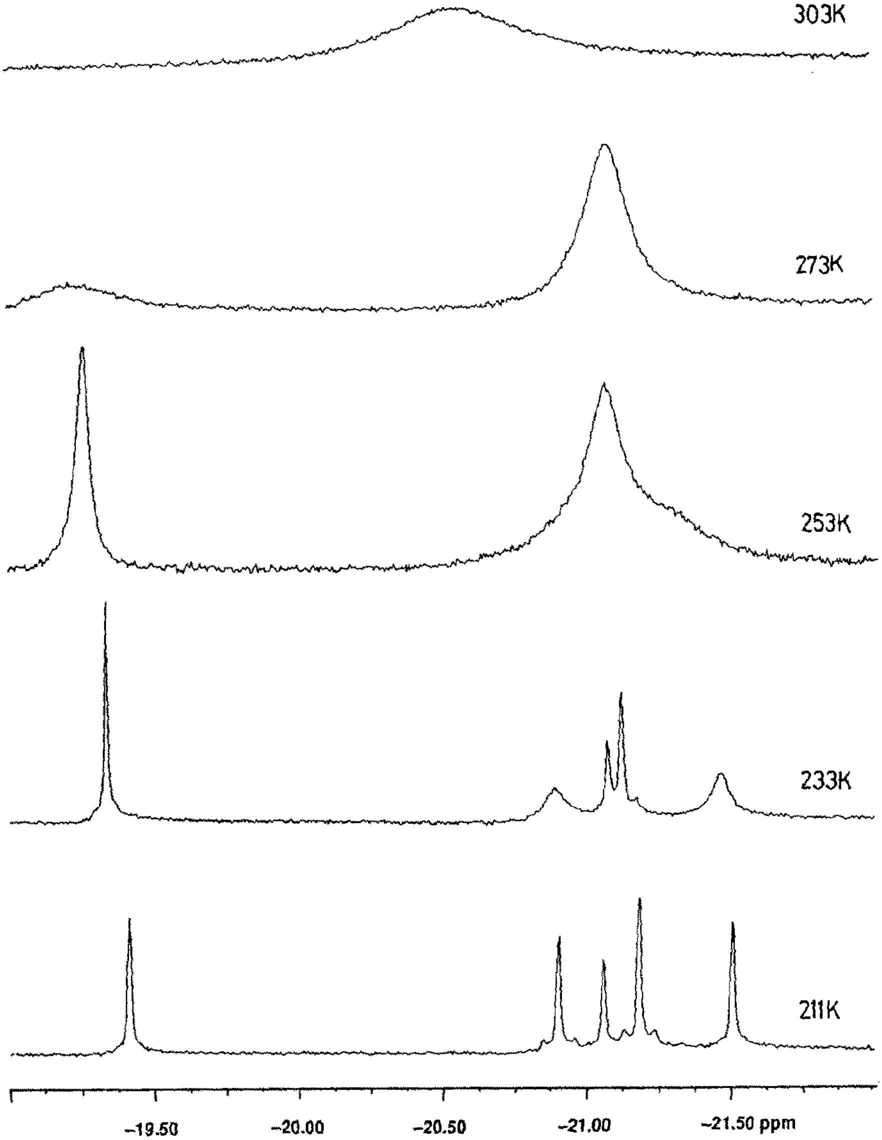


Fig. 2. The variable temperature ^{1}H NMR spectra (CD_2Cl_2) of $CpWOs_3(CO)_{11}(\mu\text{-}H)_3$ (5) in the region of the hydride resonances.

The related W/Ru_3 complex (7) exhibits similar intermolecular tautomerization (Scheme 2). The ^{1}H NMR spectrum of 7 at room temperature shows a sharp signal at δ -17.95 (J(W–H) = 24 Hz) corresponding to three bridging hydrides which undergo rapid scrambling (Fig. 3). However, while the temperature was being decreased to 185 K, the hydride signal broadened and split into five signals at δ -17.24, -17.33, -18.53, -18.98, and -19.65 (J(W–H) = 45 Hz) in the ratio 1 : 1 : 6.7 : 1 : 13.3. Therefore, the signals at δ -18.53 and -19.65 in the ratio 6.7 : 13.3 are assigned to the hydrides of the major, symmetrical isomer **7a** and the other three signals at δ -17.24, -17.33 and -18.98, to the hydrides of isomer **7b**.

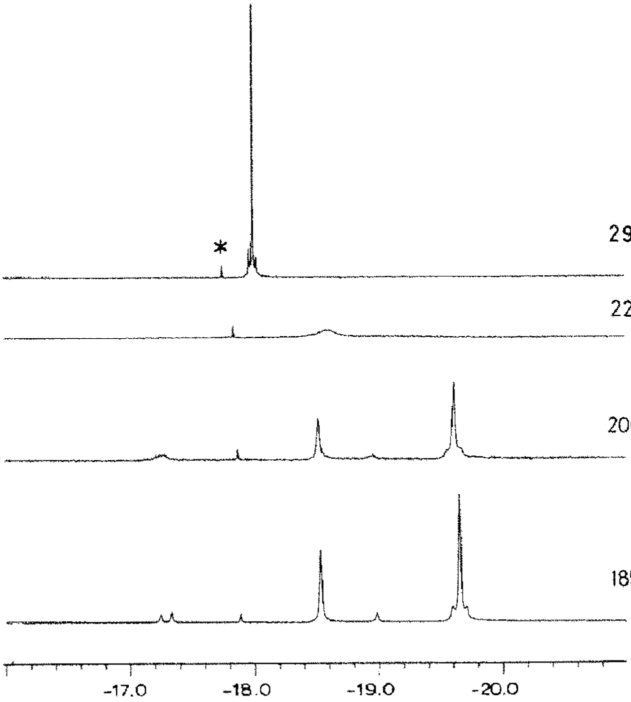


Fig. 3. The variable temperature ^{1}H NMR spectra (CD_2Cl_2) of $CpWRu_3(CO)_{11}(\mu\text{-}H)_3$ (7) in the region of the hydride resonances; the signal marked with an asterisk is from an unknown impurity.

The tungsten satellites of the signal attributable to the unique W–H–Ru hydride of **7b** were not observed because of the relatively small proportion of **7b**; however, we have assigned the signal at δ −17.24 to the W–H–Ru hydride from the observation that its peak height is the weakest of the three hydride signals.

Summary

We have shown that the Cp* substituted complexes **6** and **8** are present only as isomer **a** in solution and in the solid state; isomer **a** possesses tetrahedral geometry in which the hydride ligands are located on the three edges of a WM_2 triangular face. However, for the complexes **5** and **7**, which both contain a Cp substituent, ^{1}H NMR studies indicate the presence of two rapidly interconverting isomers (**a** and **b**) in solution. The minor component, isomer **b**, has a tetrahedral cluster core similar to that in isomer **a**, but in **b** the hydride ligand occupy two M–H–M sites and one W–H–M site in a zigzag arrangement. Furthermore, since both Cp* complexes show only one isomer in solution, we speculate that in this system the influences of the ligand, rather than the influences of the transition metals, are the major factors determining the stability of the isomers.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 580 spectrometer calibrated from the absorptions of cyclohexane at 2138.5 cm^{-1}, and of polystyrene film at 1944.5 cm^{-1}. Proton NMR spectra were recorded by use of a Bruker AM-400

(400.13 MHz) instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in electron impact, field desorption, or fast atom bombardment modes. All reactions were performed under nitrogen in deoxygenated solvents dried with the appropriate reagent. The progress of the reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, 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 complexes $CpWOs_3(CO)_{12}(\mu\text{-}H)$ [4], $Cp^{\star}WOs_3(CO)_{12}(\mu\text{-}H)$ [2], $CpWRu_3(CO)_{12}(\mu\text{-}H)$ and $Cp^{\star}WRu_3(CO)_{12}(\mu\text{-}H)$ [3] were prepared by published procedures.

Hydrogenation of $C_5H_5WOs_3(CO)_{12}(\mu\text{-}H)$. A toluene solution (30 ml) of $CpWOs_3(CO)_{12}(\mu\text{-}H)$ (50 mg, 0.043 mmol) was placed in a 250 ml pressure bottle. A partial vacuum was drawn over the toluene solution, and the bottle was charged with hydrogen gas to a pressure of 50 psig. The solution was heated in an oil bath at 120 °C for 6 h, the solvent was evaporated under vacuum, and the residue was separated by preparative TLC (hexane/dichloromethane, 2 : 3), to give the trihydride complex $CpWOs_3(CO)_{11}(\mu\text{-}H)_3$ (43 mg, 0.038 mmol (86%)) as an orange-red crystalline solid after recrystallization from dichloromethane/methanol at room temperature.

Spectroscopic data: MS (FD, ^{192}Os, ^{184}W), m/z 1136(M^+); IR(C_6H_{12}) ν(CO) 2093(m), 2063(s), 2053(vs), 2015(s), 2005(m), 1993(sh,w), 1988(s) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 294 K) δ 5.39 (s, 5H), −20.76 (very broad, 3H). Elemental analysis: Found: C, 16.94; H, 0.74. $C_{16}H_8O_{11}W_1Os_3$ calcd.: C, 16.99; H, 0.71%.

Hydrogenation of $C_5Me_5WOs_3(CO)_{12}(\mu\text{-}H)$. A toluene solution (35 ml) of $Cp^{\star}WOs_3(CO)_{12}(\mu\text{-}H)$ (40 mg, 0.033 mmol) was placed in a 250 ml pressure bottle. A partial vacuum was drawn over the toluene solution, and the bottle was charged with hydrogen gas to a pressure of 50 psig. The solution was heated in a silicone oil bath at 120 °C for 5 h, the solvent was evaporated under vacuum, and the residue was separated by preparative TLC (eluant: hexane/dichloromethane, 3 : 2), to give the trihydride complex $Cp^{\star}WOs_3(CO)_{11}(\mu\text{-}H)_3$ (35 mg, 0.029 mmol (88%)) as an orange crystalline solid after recrystallization from dichloromethane-methanol.

Spectroscopic data: MS (FAB, ^{192}Os, ^{184}W), m/z 1206(M^+); IR(CCl_4) ν(CO) 2089(s), 2060(vs), 2033(vs), 2014(s), 2000(m), 1985(s), 1963(w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 2.07 (s, 15H), −19.86 (s, 2H, $J(W\text{-}H) = 43$ Hz), −21.43 (s, 1H). Elemental analysis: Found: C, 20.95; H, 1.50. $C_{21}H_{18}O_{11}W_1Os_3$ calcd.: C, 20.90; H, 1.51%.

Hydrogenation of $C_5H_5WRu_3(CO)_{12}(\mu\text{-}H)$. A toluene solution (20 ml) of $CpWRu_3(CO)_{12}(\mu\text{-}H)$ (34 mg, 0.038 mmol) was heated at reflux under 1 atm of hydrogen. The color turned rapidly from red-orange to orange. After refluxing for 3 min, the solvent was evaporated under vacuum and the residue was separated by preparative TLC (eluant: hexane/dichloromethane, 3 : 2), to give the trihydride complex $CpWRu_3(CO)_{11}(\mu\text{-}H)_3$ (14 mg, 0.016 mmol (42%)) as a red-orange crystalline solid after recrystallization from dichloromethane-methanol. The low yield is attributed to the poor stability of this complex in solution.

Spectroscopic data: MS (FAB, ^{102}Ru, ^{184}W), m/z 866(M^+); IR(CCl_4) ν(CO) 2090(m), 2087(sh,m), 2060(vs), 2057(vs), 2035(s), 2019(s), 2010(s), 1998(s), 1942(vw) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 294 K) δ 5.36 (s, 5H), −18.00 (s, 3H,

J(W–H) = 23 Hz). Elemental analysis: Found: C, 22.13; H, 0.91. $C_{16}H_8O_{11}W_1Ru_3$ calcd.: C, 22.18; H, 0.93%.

Hydrogenation of $C_5Me_5WRu_3(CO)_{12}(\mu\text{-}H)$. A toluene solution (20 ml) of $Cp^{\star}WRu_3(CO)_{12}(\mu\text{-H})$ (17 mg, 0.018 mmol) was heated at reflux under 1 atm of hydrogen. The color turned rapidly from red-orange to orange. After refluxing for 10 min, the solvent was evaporated under vacuum and the residue was separated by preparative TLC (eluant: hexane/dichloromethane, 3:2), to give the trihydride complex $Cp^{\star}WRu_3(CO)_{11}(\mu\text{-H})_3$ (15 mg, 0.016 mmol (89%)) as red-orange needles after recrystallization from dichloromethane/methanol.

Spectroscopic data: MS (FAB, ^{102}Ru, ^{184}W), m/z 936(M^+); IR(C_6H_{12}) ν(CO) 2085(s), 2055(vs), 2051(sh,w), 2032(vs), 2014(s), 2001(w), 1992(s), 1974(w) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 235 K) δ 2.03 (s, 15H), −18.34 (s, 2H, J(W–H) = 47 Hz), −18.69 (s, 1H). Elemental analysis: Found: C, 26.48; H, 1.95. $C_{21}H_{18}O_{11}W_1Ru_3$ calcd.: C, 26.93; H, 1.94%.

Structural determination of $C_5Me_5WRu_3(CO)_{12}(\mu\text{-}H)_3$. Crystals suitable for diffraction analysis were obtained from dichloromethane/methanol solution at −20 °C. A crystal was mounted on a Nicolet R3m/V diffractrometer controlled by a MicroVAX II computer. Lattice constants were obtained from 15 reflections with $10.66 \leq 2\theta \leq 30.58°$. The space group is $P2_1/n$, $\theta/2\theta$ scan data were collected at room temperature for two octants of the sphere ($0 \leq h \leq 12$, $-19 \leq k \leq 0$, $-18 \leq l \leq 18$) outside the 2θ limit of 50.0°. The intensity data were corrected for absorp-

Table 3

Experimental data for the X-ray diffraction study of complex **8**

(A) Crystal Data			
a (Å)	10.731(4)	Crystal system	monoclinic
b (Å)	16.275(4)	Space group	$P2_1/n$
c (Å)	15.606(4)	Z	4
β (°)	99.76(2)	V	2686(1) Å^3
Formula	$C_{21}H_{18}O_{11}W_1Ru_3$	Mol. wt.	933.4
Density (calcd) (g cm^{-3})	2.308	F(000)	1743
Temperature (K)	297		

(B) Data Collection, Reduction, Solution and Refinement	
Data collection instrument	Nicolet R3m/V
Radiation (monochromated in incident beam)	Mo-K_α (λ = 0.71073 Å)
Scan method	$2\theta-\theta$ scan mode
Scan range (°)	1.05 plus K_α separation
Scan speed (°/min)	variable; 4.19 to 14.65
Crystal size (mm)	0.18×0.20×0.50
Linear absorption coefficient (mm^{-1})	6.04 mm^{-1}
Transmission factors: max, min.	0.99, 0.35
No. of unique data, total with $I > 3\sigma(I)$	4758, 3526
No. of atoms and parameters refined	36, 326
Largest and mean Δ/σ	0.191, 0.001
R; R_w [a]	2.55%; 2.45%
GOF [b]	1.19
Residual electron density, e Å^{-3}: max./min.	0.93/−0.42

[a] $w^{-1} = \sigma^2(F) + 0.0002F^2$. [b] $S = [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ N_o = number of observations; N_v = number of variables).

tion, Lorentz, and polarization effects. Corrections for absorption effects were by ψ-scans of a few suitable reflections with χ values close to 90°. The structure was solved by direct methods with the SHELXTL PLUS program [11] and refined by full-matrix least-squares method. Anomalous dispersion corrections were applied to atoms with atomic numbers of more than 16. Scattering factors were taken from the International Tables for X-ray Crystallography, 1974. All non-hydrogen atoms were located from an electron density map and were refined with anisotropic thermal parameters. The hydrogen atoms of the methyl groups were added at idealized

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å $\times 10^3$) for complex **8**

Atom	*x*	*y*	*z*	*U*(eq) [a]
W	394(1)	7770(1)	1888(1)	37(1)
Ru(1)	−2151(1)	7293(1)	2408(1)	38(1)
Ru(2)	−484(1)	8354(1)	3440(1)	39(1)
Ru(3)	−1803(1)	8987(1)	1885(1)	40(1)
O(1)	−1117(6)	6001(3)	3739(4)	91(3)
O(2)	−3717(5)	6126(3)	1125(3)	78(2)
O(3)	−4305(6)	7722(4)	3366(4)	99(3)
O(4)	1068(6)	9827(3)	4181(4)	86(3)
O(5)	−2456(6)	8848(5)	4498(4)	104(3)
O(6)	650(6)	7266(3)	4938(4)	86(3)
O(7)	−3818(7)	9691(4)	2822(5)	121(4)
O(8)	−3224(7)	9507(3)	108(4)	88(3)
O(9)	−146(7)	10496(3)	2152(4)	99(3)
O(10)	1703(7)	6564(5)	3348(4)	117(3)
O(11)	2358(6)	9041(5)	2774(5)	132(4)
C(1)	−1497(8)	6483(4)	3248(5)	58(3)
C(2)	−3149(7)	6576(4)	1585(5)	54(3)
C(3)	−3499(9)	7562(5)	3026(5)	62(3)
C(4)	499(7)	9280(5)	3875(4)	54(3)
C(5)	−1736(8)	8660(5)	4069(5)	65(3)
C(6)	245(8)	7661(5)	4349(5)	58(3)
C(7)	−3043(9)	9429(5)	2494(6)	71(3)
C(8)	−2704(8)	9293(4)	763(5)	58(3)
C(9)	−772(8)	9927(4)	2068(5)	58(3)
C(10)	1176(9)	7040(6)	2859(5)	80(4)
C(11)	1557(8)	8599(6)	2505(6)	78(4)
C(12)	2032(7)	7283(6)	1263(5)	67(3)
C(13)	1627(14)	8024(6)	848(8)	97(5)
C(14)	436(13)	7896(7)	385(6)	92(5)
C(15)	66(7)	7116(6)	519(5)	65(3)
C(16)	1051(8)	6715(4)	1064(5)	55(3)
C(17)	1118(13)	5826(5)	1270(7)	147(7)
C(18)	−1083(10)	6697(10)	61(7)	208(10)
C(19)	3337(9)	7087(10)	1703(8)	192(10)
C(20)	−251(18)	8483(9)	−240(7)	302(15)
C(21)	2508(17)	8715(8)	781(10)	287(15)
H(1)	−839	8528	1317	80
H(2)	−2483	8058	1650	80
H(3)	−971	6998	1885	80

[a] Equivalent isotropic *U*(eq) defined as one third of the trace of the orthogonalized U_{ij} tensor.

positions and the hydride hydrogen was located on the difference electron density map; all the hydrogen atoms were included in the structure factor calculations. The data collection parameters and the atomic coordinates are listed in Table 3 and 4. Tables of anisotropic thermal parameters, structure factor amplitudes, and non-essential bond distance and angle parameters are available from the author (S.-L.W.).

Acknowledgement

This work was supported by the National Science Council of the Republic of China. Y.C. thanks Prof. Dr. John Ogilvie for helpful discussions.

References

1 W.L. Galdfelter and G.L. Geoffery, Adv. Organomet. Chem., 18 (1980) 207.
2 S.-M. Peng, G.-H. Lee, Y. Chi, C.-L. Peng and L.-S. Hwang, J. Organomet. Chem., 371 (1989) 197.
3 Y. Chi, F.-J. Wu, B.-J. Liu, C.-C. Wang and S.-L. Wang, J. Chem. Soc., Chem. Commun., (1989) 873.
4 M.R. Churchill, F.J. Hollander, J.R. Shapley and D.S. Foose, J. Chem. Soc., Chem. Commun., (1978) 534.
5 S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, J. Am. Chem. Soc., 97, (1975) 3942.
6 B.F.G. Johnson, J. Lewis, P.R. Raithby, G.M. Sheldrick and K. Wong, J. Chem. Soc., Dalton Trans., (1978), 673.
7 M.R. Churchill, F.J. Hollander, Inorg. Chem., 18 (1979) 161.
8 (a) F.A. Cotton, Prog. Inorg. Chem., 21 (1976) 1. (b) R. Colton and J.M. McCormick, Coord. Chem. Rev., 31 (1980) 1. (c) C.P. Horwitz and D.F. Shriver, Adv. Organomet. Chem., 23 (1984) 219.
9 L.Y. Hsu, W.L. Hsu, D.Y. Jan and S.G. Shore, Organometallics, 3 (1986) 1041.
10 J.W. Koepke, J.R. Johnson, S.A.R. Knox and H.D. Kaesz, J. Am. Chem. Soc., 97 (1975) 3947.
11 G.M. Sheldrick, (1986), SHELXTL PLUS User Manual. Nicolet XRD Corporation. Madison, Wisconsin, U.S.A.