COMMUNICATION

ROTATION OF THE ACETYLIDE LIGAND ON THE TRIANGULAR FACE OF TUNGSTEN–DIRUTHENIUM CLUSTERS. CRYSTAL STRUCTURE AND SOLUTION DYNAMICS OF $\text{LWM}_2(\text{CO})_8(\text{CCPh})$, $\text{L} = \text{C}_5\text{H}_5$, C_5Me_5 AND $\text{M} = \text{Os}$, Ru

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Abstract—Reaction of $\text{CpW}(\text{CO})_3\text{—C}\equiv\text{CPh}$ with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ or $\text{Ru}_3(\text{CO})_{12}$ in refluxing toluene gives trinuclear mixed-metal acetylide clusters, $\text{CpWOs}_2(\text{CO})_8(\text{C}\equiv\text{CPh})$ (1) and $\text{CpWRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})$ (3); the acetylide ligands of these two complexes are related to each other by a 120° rotation as indicated by X-ray diffraction studies. In solution, the variable temperature ^1H and ^{13}C NMR spectra suggest that the acetylide ligand of 3 undergoes a 360° rotation on the face of the WRu_2 triangle.

The C_2 hydrocarbyl ligands hold a key position in the development of dinuclear, trinuclear and polynuclear organometallic chemistry. This position is in part due to a belief that the chemistry of the C_2 hydrocarbyl ligands in the organometallic complexes is analogous to those adsorbed on metal surfaces. Among the many interesting properties of the C_2 ligands is their fluxionality and mobility on the coordination sphere of the transition metal complexes. Related studies on the C_2 hydrocarbyl ligands have attracted the attention of many theoretical and synthetic chemists. Schilling and Hoffmann¹ have reported the extended Hückel calculation of some hydrocarbyl ligands on the tri-

angular face of homonuclear transition metal complexes. For the C_2 vinylidene complex, $\text{Co}_3(\text{CO})_9(\text{CCHR})^+$, Norton and co-workers² have reported the disrotatory correlated rotation about the $\text{Co}_3(\text{CO})_9\text{—C}$ vector and C—CHR bond by variable-temperature ^{13}C NMR studies. Stone and co-workers³ and Shapley and co-workers⁴ have both described the so-called “windscreen-wiper” type of motion of a coordinated alkyne ligand on a W_2Os triangular face. For the closely related C_2 acetylide ligand, although the syntheses of many transition metal acetylide clusters have been reported in the literature,⁵ no paper has ever focused on the subject of site selectivity and solution fluxionality. We now report the structural and NMR studies of a series of acetylide complexes, which permit an analysis of the solution dynamics of the acetylide ligand.

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LWM ₂ (CO) ₈ (μ ₃ -η ² -C≡CPh) M	L	Yield
(1)	Os C ₅ H ₅	9%
(2)	Os C ₅ Me ₅	2%
(3)	Ru C ₅ H ₅	50%
(4)	Ru C ₅ Me ₅	57%

Treatment of LW(CO)₃C≡CPh⁶ with the substance Os₃(CO)₁₀(CH₃CN)₂ in refluxing toluene (110°C, 30 min) provided, in addition to a red tetranuclear complex LWOs₃(CO)₁₁(C≡CPh),⁷ a pale yellow trinuclear complex (L = C₅H₅, **1**; L = C₅Me₅, **2**)* in low yield. The ¹³C-{¹H} NMR spectrum of **1** showed two signals at δ 137.5 and 73.8, reminiscent of those reported for the two acetylide carbon nuclei (δ 172.9 and 112.7) in the analogous CpWFe₂(CO)₈(C≡CTol).⁸ The latter is a mixed-metal cluster in which the acetylide ligand

Fig. 1. The ORTEP diagram of **1**. Bond lengths (Å): W—Os(1), 2.8294(19); W—Os(2), 2.9160(18); Os(1)—Os(2), 2.8114(18); W—C(15), 2.20(3); Os(1)—C(15), 2.16(3); Os(2)—C(15), 1.96(3); Os(1)—C(14), 2.17(4); W—C(14), 2.36(4); C(14)—C(15), 1.23(5); C(16)—C(14), 1.47(5). Bond angles (°): Os(2)—C(15)—C(14), 159(3); C(15)—C(14)—C(16), 148(4).

* Selected spectroscopic data **1**: IR (C₆H₁₂) ν(CO) 2077(s), 2043(vs), 2005(vs), 1995(s), 1965(s), 1924(m); ¹H NMR (CD₂Cl₂, RT): δ 7.68 (d, 2H), 7.37 (t, 2H), 7.20 (t, 1H), 5.29 (s, 5H); ¹³C-{¹H} NMR (CD₂Cl₂, RT): δ 208.3 (*J*_{W-C} = 165 Hz, W—CO), 204.1 (*J*_{W-C} = 157 Hz, W—CO), 179.4 (Os—CO), 137.5 (CCPh), 73.8 (CCPh, *J*_{W-C} = 16 Hz). **2**: IR (C₆H₁₂) ν(CO) 2076(s), 2041(vs), 2004(vs), 1991(s), 1963(m), 1905(w); ¹H NMR (CDCl₃): δ 7.62 (d, 2H), 7.31 (t, 2H), 7.20 (t, 1H), 1.93 (s, 15H).

† Crystal data for **1**: C₂₁H₁₀O₈W₁Os₂, *M* = 1104.27, monoclinic, space group *P*2₁/*c*, *a* = 8.332(3), *b* = 14.543(4), *c* = 17.819(5) Å, β = 94.46(3)°, *V* = 2152.71 Å³, *Z* = 4, *D*_c = 2.945 g cm⁻³, *F*(000) = 1703.33, Nonius diffractometer with graphite-monochromated Mo-*K*_α radiation, λ = 0.70930 Å, μ(Mo-*K*_α) = 17.28 mm⁻¹. ψ scan absorption correction made, 3777 unique reflections were measured and 2980 reflections with *I* > 2σ(*I*) were used in refinement. Refinement of 42 atoms and 145 parameters converged to *R*_F = 0.068 and *R*_w = 0.090, G.O.F. = 1.768.

‡ Selected spectroscopic data. **3**: IR (C₆H₁₂) ν(CO) 2076(s), 2069(m), 2044(vs), 2033(vs), 2010(vs), 2003(m), 1994(m), 1975(m), 1966(w), 1952(vw), 1930(vw), 1918(vw) cm⁻¹; ¹H NMR (CDCl₃, RT): δ 7.64–7.24 (m, Ph), 5.56 (s, Cp, **3b**), 5.25 (s, Cp, **3a**); ¹³C-{¹H} NMR (d₈-THF, RT): δ 210.8 (*J*_{W-C} = 160 Hz, W—CO, **3a**), 210.7 (*J*_{W-C} = 165 Hz, W—CO, **3a**), 207.6 (*J*_{W-C} = 169 Hz, W—CO, **3b**), 197.0 (Ru—CO, **3b**), 196.6 (Ru—CO, **3a**), 168.9 (CCPh, *J*_{W-C} = 139 Hz, **3b**), 168.6 (CCPh, **3a**), 98.3 (CCPh, *J*_{W-C} = 22 Hz, **3b**), 85.6 (CCPh, *J*_{W-C} = 21 Hz, **3a**). **4**: IR (C₆H₁₂) ν(CO) 2071(m), 2064(vs), 2038(s), 2024(vs), 2005(s), 2001(vs), 1986(m), 1970(w), 1965(w), 1955(w), 1936(vw), 1913(vw) cm⁻¹; ¹H NMR (CD₂Cl₂, 273 K): δ 7.65–7.27 (m, Ph), 2.30 (s, Me, **4b**), 1.93 (s, Me, **4a**); ¹³C-{¹H} NMR (d₈-THF, 226 K): δ 218.5 (W—CO, **4a**), 217.3 (W—CO, **4a**), 214.5 (*J*_{W-C} = 169 Hz, W—CO, **4b**), 175.3 (CCPh, **4b**), 173.0 (CCPh, *J*_{W-C} = 141 Hz, **4a**), 100.1 (CCPh, *J*_{W-C} = 23 Hz, **4b**), 90.2 (CCPh, **4a**).

functions as a five-electron donor, σ-bonded to the tungsten atom, while employing its two orthogonal alkyne π-bonds to bridge the unique Fe—Fe edge. However, since the colour, as well as the IR spectra of these osmium complexes in the region of CO absorption are substantially different from the complex of iron triads, an X-ray diffraction study was carried out on **1**.†

The molecular structure of **1** is shown in Fig. 1, together with some important bond parameters. The molecule has a triangular WOs₂ core structure in which the tungsten atom is coordinated to a Cp ring and two CO ligands, while each of the osmium atoms is linked to three, mutually orthogonal, terminal CO ligands. The most important feature is the orientation of the phenyl acetylide moiety, which is σ-bonded to an osmium atom and at the same time forms a transverse bridge across the second W—Os bond. Therefore, the structure of **1** is related to CpWFe₂(CO)₈(C≡CTol) by a 120° rotation of the acetylide ligand.

In order to further study the preferred orientation of the acetylide ligand over the triangular face of the trinuclear mixed-metal complexes, we have carried out the syntheses and structural determination of the tungsten–diruthenium analogues. Complexes **3** and **4**‡ were similarly obtained in good yield using Ru₃(CO)₁₂ as reagent. Crystals of **3** suitable for X-ray structural determination were obtained by recrystallization from CH₂Cl₂–hexane at room temperature. The structure of **3** is shown in Fig. 2

Fig. 2. The ORTEP diagram of **3**. Bond lengths (Å): W—Ru(1), 2.9976(10); W—Ru(2), 2.9651(10); Ru(1)—Ru(2), 2.6612(11); W—C(15), 1.976(8); Ru(1)—C(15), 2.128(8); Ru(2)—C(15), 2.195(7); Ru(1)—C(14), 2.297(8); Ru(2)—C(14), 2.188(8); C(14)—C(15), 1.314(11); C(16)—C(14), 1.470(11). Bond angles (°): W—C(15)—C(14), 162.5(6); C(15)—C(14)—C(16), 142.5(8).

with selected structural parameters.* The WRu_2 triangle is near-isosceles and the phenyl acetylide moiety is now σ -bonded to the W atom and, quasi-symmetrically, π -bonded to the two ruthenium atoms. Therefore, we conclude that complex **3** is not isostructural with **1** but rather with the iron-containing complexes.

The solution dynamics of these WRu_2 complexes is of particular interest. Both the ^1H NMR and IR spectra in the region of CO absorption suggest the presence of two isomers. Based on the structural information, we proposed that the isomerization is due to a 360° rotation of the acetylide ligand over (**3a**:**3b** = 1 : 1.2) the WRu_2 triangle (Scheme 1). The assignment of each individual isomer is identified by its characteristic ^{13}C NMR data.

The ^{13}C NMR spectrum of **3** at 205 K exhibits three W—CO signals at δ 210.8, 210.5 and 207.3 in the ratio of 1 : 1 : 2.4. Therefore, the first two resonance lines are assigned to the “asymmetric”

Scheme 1.

isomer (**3a**, acetylide C—C bond is orthogonal to the W—Ru bond) and the third one to the “symmetric” isomer (**3b**, acetylide C—C bond is orthogonal to the Ru—Ru bond). This assignment is not unreasonable because the free rotation of the $\text{CpW}(\text{CO})_2$ unit in the asymmetric isomer would be expected to encounter the steric interaction of the phenyl group, whereas in isomer **3b** this process should have a smaller activation energy. Furthermore, five signals at δ 202.5, 200.8, 196.0, 194.2 and 192.4 with an intensity ratio of 1 : 1 : 1 : 1 : 2 can be assigned to the Ru—CO resonances of **3a** to support the assignment; the signal at δ 192.4 is double the intensity of the other four signals and therefore corresponds to two coincident signals.

The Ru—CO signals of **3b** were not observed in this spectrum. However, while the temperature was decreasing to 190 K, its W—CO signal broadened and collapsed, suggesting the slow-down of the $\text{CpW}(\text{CO})_2$ rotation, and three very broad Ru—CO signals at δ 203, 198.5 and 189 appeared in the spectrum, consistent with the symmetric nature of **3b**, as suggested by the solid-state structural studies. Interpretation of the ^{13}C NMR data for **4** followed similar studies. From the relative intensities of the methyl signals in the ^1H NMR spectrum at room temperature, it is deduced that an isomer ratio **4a**:**4b** of 1 : 5.5 prevails.

The kinetic parameters of the acetylide ligand rotation have also been calculated from the data of the variable-temperature ^{13}C and ^1H NMR spectroscopies. The racemization process of **3a** consists of a simultaneous correlated rotation of the $\text{CpW}(\text{CO})_2$ moiety around an axis through tungsten and a 120° rotation of the acetylide ligand over the tungsten atom (step A, **3a** $\leftrightarrow$ **3a'**, Scheme 1). Therefore, the coalescence of the two W—CO resonances, as well as the coalescence of the six

* Crystal data for **3**: $\text{C}_{21}\text{H}_{10}\text{O}_8\text{W}_1\text{Ru}_2$, $M = 776.29$, monoclinic, space group $P2_1/n$, $a = 12.4756(13)$, $b = 13.216(4)$, $c = 13.395(4)$ Å, $\beta = 97.993(17)^\circ$, $V = 2186.95$ Å³, $Z = 4$, $D_c = 2.358$ g cm⁻³, $F(000) = 1447.68$, Nonius diffractometer with graphite-monochromated Mo- K_α radiation, $\lambda = 0.70930$ Å, $\mu(\text{Mo-}K_\alpha) = 6.74$ mm⁻¹. ψ scan absorption correction made, 3840 unique reflections were measured and 2851 reflections with $I > 2\sigma(I)$ were used in refinement. Refinement of 42 atoms and 290 parameters converged to $R_F = 0.029$ and $R_w = 0.027$, G.O.F. = 1.583.

Ru—CO resonances in **3a**, would provide the appropriate kinetic data for step A. In fact, both the W—CO and the Ru—CO resonance lines have broadened and merged into single lines during the temperature rise to 300 K. A free energy of activation ($\Delta G^\ddagger$), calculated from the dynamic behaviour of the W—CO resonance lines, is estimated to be 62 kJ mol⁻¹.*

In contrast to the racemization of **3a**, isomerization between **3a** and **3b** is consistent with a 120° rotation from a W—Ru edge to the Ru—Ru edge (steps B, **3a** ↔ **3b** or **3a'** ↔ **3b**). Because only two Cp signals were observed in the ¹H NMR spectrum at 300 K, we conclude that the energy barrier of rotation of the CpW(CO)₂ unit is much too small to affect the energy barrier of steps B. The free energy of activation ($\Delta G^\ddagger$), calculated from the coalescence of the Cp signals, is 67 kJ mol⁻¹ at 338 K, providing an estimate of the energy barrier of steps B.

Interestingly, the acetylide ligand of the WOs₂ complexes is static on the time scale of ¹³C NMR spectroscopy. The ¹³C NMR spectrum of **1** at 295 K (d₈-toluene) exhibits two W—CO signals at δ 208.6 and 204.0, a sharp Os(CO)₃ line at δ 179.7, and two very broad Os—CO signals at δ 178.8 and 173.4. The exchange of the Os—CO resonances is not due to the rotation of the acetylide ligand, but to a localized Os(CO)₃ rotation around an axis through the two different osmium atoms. When the temperature is increased to 350 K, the sharp Os(CO)₃ signal remained unchanged and the broad

Os—CO signals became a relatively sharp signal at δ 176.5, confirming that the racemization of **1** has not occurred at this temperature.

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* The free energy of activation $\Delta G^\ddagger$ calculated from the ¹³C NMR data recorded on d₈-toluene solution is 70 KJ mol⁻¹. This data suggests that the rotation of the acetylide ligand possibly involves a transition state in which the acetylide C—C bond is perpendicular to the WRu₂ triangle.