Facile Interconversion of Terminal, Doubly Bridging, and Quadruply Bridging Carbonyl Ligands in Solution: Crystal Structure and Solution Dynamics of the Complexes LWRu$_3$(CO)$_{12}$H, L = C$_5$H$_5$ and C$_5$Me$_5$

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The crystal structures of the tetranuclear mixed-metal complexes LWRu$_3$(CO)$_{12}$H, L = C$_5$H$_5$ and C$_5$Me$_5$, were determined, indicating the presence of a butterfly arrangement with an unusual μ_4-η^2-CO ligand; in solution, these isomers are in equilibrium with other isomers containing only normal σ-bonded CO ligands.

The chemical and structural properties of the π-bonded, quadruply bridging μ_4-CO ligand[1] are interesting because this bonding mode is implicated as a precursor of the cleavage reactions of C–O bonds on metal surfaces.[2] Furthermore, it is of great interest to demonstrate that a σ-bonded CO ligand could undergo reversible reorientation to form the above mentioned bonding, as such a reorientation will strengthen the importance of the μ_4-CO ligand on metal surfaces. There are few reports in the literature on this subject. Klemann has reported the reversible addition of CO to the dinuclear complex Mn$_2$(CO)$_5$(PP)$_2$ (PP = diphenylphosphinoethane), while the π-bonded CO ligands are converted to the normal terminal CO ligands.[3,4] In a polynuclear system, Shriver[5] has described spectroscopic characterization of two isomers of [HFe$_4$(CO)$_{13}$]$^-$, in which the butterfly form with a μ_4-η^2-CO ligand is equilibrated with a proposed tetrahedral Fe$_4$ isomer. In this paper, we report the solid-state structure and the solution dynamics of two complexes incorporating the μ_4-η^2-CO ligand, LWRu$_3$(CO)$_{12}$H, L = C$_5$H$_5$ and C$_5$Me$_5$. More importantly, we have been able to change the bonding mode of the CO ligand, the location of the hydride ligand, and the geometry of the cluster framework by varying the transition metal atoms and the accessory ligand.

An orange crystalline solid of complex (1)‡ having the formula (C$_5$H$_5$)WRu$_3$(CO)$_{12}$H was easily obtained from the reaction of Ru$_3$(CO)$_{12}$ and 3 equiv. of (C$_5$H$_5$)W(CO)$_3$H in refluxing toluene for 45 min;[6] a solution of the orange single crystals was red-brown. The ^{1}H n.m.r. (400 MHz, CD$_2$Cl$_2$, 190 K) spectrum of the isolated compound exhibits three hydride resonance lines at δ −17.03 (1a), −18.67 (J_{W-H} 53 Hz, 1b), and −20.60 (1c), with a relative intensity ratio of 1:1.6:3.2, suggesting the presence of three interconvertible isomers in solution. When the solution was warmed to 305 K, the first two resonance lines broadened and merged into the baseline, behaviour consistent with a facile exchange between the isomers (1a) and (1b). The fluxionality of (1c), on the other hand, was established by the n.m.r. technique of spin-saturation transfer:[7] irradiation of the broad resonance lines at δ −17.03 or −18.67 at 297 K results in a 10% decrease in the intensity of the resonance at δ −20.60; we infer that the structure (1c) also equilibrates within the corresponding isomers **a** and **b**.

The behaviour of the downfield hydride resonances, (1a) and (1b), is associated with that of the analogous osmium complexes LWOs$_3$(CO)$_{12}$H, L = C$_5$H$_5$ (2a[8] and 2b), or C$_5$Me$_5$ (3a and 3b) prepared previously. We have also reported that these WOs$_3$ complexes each exist as two isomers (Scheme 1) and undergo rapid interconversion in solution;[9] therefore, the structure of the isomers (1a) and (1b) can be related to their osmium analogues and easily be differentiated in the light of the J_{W-H} coupling. This assignment is further supported by the solution i.r. spectrum, which shows three absorptions due to the CO stretching modes at 1934vw, 1916w, and 1906w, sh cm^{-1}, suggesting the presence of bridging CO ligands (*vide infra*).

The identity of the third isomer (1c) has been determined by a single crystal X-ray diffraction.§ The molecular structure is shown in Figure 1 together with some important structural parameters. Three terminal CO ligands are associated with each of the three Ru atoms, whereas a C$_5$H$_5$ ligand and two terminal CO ligands are linked to the W atom; the core structure constitutes a butterfly arrangement with a dihedral angle of 118.6° and we propose that the missing bridging hydride ligand is associated with the 'hinge' Ru(1)–Ru(1a) vector. The molecule has a unique CO ligand, C(10)O(10), and a crystallographically imposed plane of symmetry that passes through this CO ligand and the 'wingtip' W and Ru(2) atoms. The carbon atom C(10) resides within bonding distance of all the transition metal atoms and the oxygen atom O(10) is tilted and co-ordinated to the Ru(2) atom; we therefore consider that this unique C(10)O(10) ligand adopts a μ_4-η^2-bonding mode. The parameters associated with this μ_4-η^2-CO ligand are consistent with those of the related complexes, (C$_5$H$_5$)$_2$Mo$_2$Ru$_4$(CO)$_{13}$(μ_4-CO)(μ_4-S) and (C$_5$H$_5$)$_2$Mo$_2$Ru$_5$(CO)$_{14}$(μ_4-CO)$_2$(μ_4-S).[10] Finally, an additional important feature is that the C$_5$H$_5$ ligand of the (C$_5$H$_5$)W(CO)$_2$ vertex is located *anti* to the π bonded CO ligands.

In order to extend the scope of this reaction and to investigate further the effect of the steric bulk of the surrounding ligand, we have also prepared the analogous pentamethylcyclopentadienyl complex (4), (C$_5$Me$_5$)WRu$_3$-

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‡ Compound (1): i.r. (C$_6$H$_{12}$) ν(CO) 2088m, 2061s, 2055vs, 2043s, 2038m, 2032m, 2017m, 2012s, 1997m, 1987w, 1971vw, 1964w, 1934vw, 1916w, and 1906w, sh cm^{-1}; ^{1}H n.m.r. (400 MHz, CD$_2$Cl$_2$, 190 K) δ 5.17 (s, C$_5$H$_5$), 5.15 (s, C$_5$H$_5$), 4.94 (s, C$_5$H$_5$), −17.02 (s, Ru–H–Ru), −18.67 (s, J_{W-H} 53 Hz, W–H–Ru), −20.60 (s, Ru–H–Ru). Compound (4): i.r. (C$_6$H$_{12}$) ν(CO) 2084m, 2050vs, 2037s, 2034s, 2010s, 1994m, 1980w, 1958vw, and 1918w cm^{-1}; ^{1}H n.m.r. (400 MHz, CD$_2$Cl$_2$, room temp.) δ 2.11 (s, C$_5$Me$_5$), 2.08 (s, C$_5$Me$_5$), 2.07 (s, C$_5$Me$_5$), −15.26 (s, J_{W-H} 51 Hz, W–H–Ru), −20.16 (s, Ru–H–Ru), −20.20 (s, Ru–H–Ru); m/z (electron impact, ^{102}Ru, ^{186}W) 964 (M^+). Satisfactory elemental analyses were obtained for both complexes.
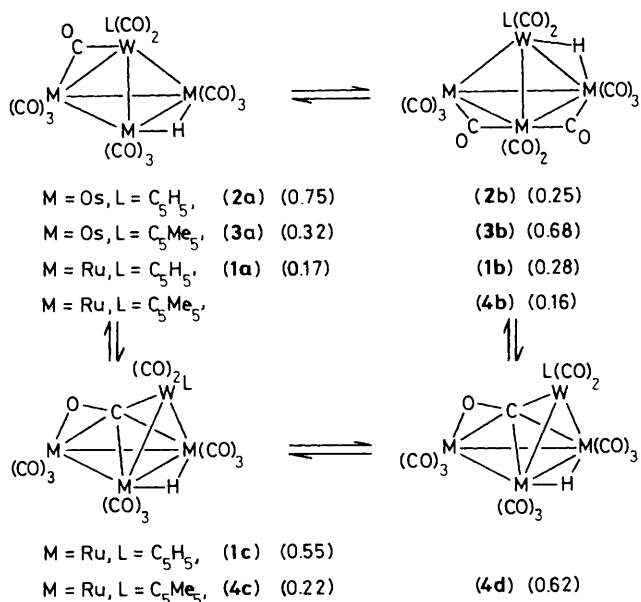
M = Os, L = C_5H_5,   (2a) (0.75)   (2b) (0.25)

M = Os, L = C_5Me_5,   (3a) (0.32)   (3b) (0.68)

M = Ru, L = C_5H_5,   (1a) (0.17)   (1b) (0.28)

M = Ru, L = C_5Me_5,   (4b) (0.16)

M = Ru, L = C_5H_5,   (1c) (0.55)

M = Ru, L = C_5Me_5,   (4c) (0.22)   (4d) (0.62)

Scheme 1. The numbers in parentheses are the relative ratios in solution.

Figure 2. ORTEP view of the molecular structure of (**4d**). Bond lengths (Å): W–Ru(1), 3.020(1); Ru(1)–Ru(2), 2.818(1); Ru(1)–Ru(3), 2.848(1); Ru(2)–Ru(3), 2.812(1); W–Ru(2), 2.983(1); Ru(1)–C(12), 2.377(10); Ru(2)–C(12), 2.357(10); Ru(3)–C(12), 2.418(10); W–C(12), 1.986(10); C(12)–O(12), 1.190(13); Ru(3)–O(12), 2.151(7). Bond angles (°): W–C(12)–Ru(3), 153.9(6); W–C(12)–O(12), 143.3(8); Ru(1)–Ru(2)–C(4), 104.4(4); Ru(1)–Ru(2)–C(6), 115.0(3); Ru(2)–Ru(1)–C(1), 101.8(4); Ru(2)–Ru(1)–C(3), 117.8(4).
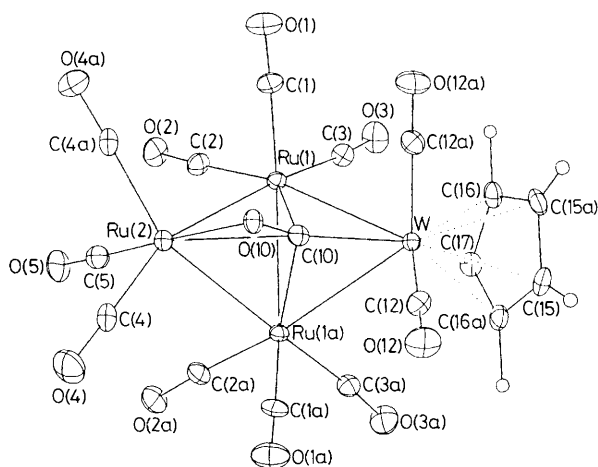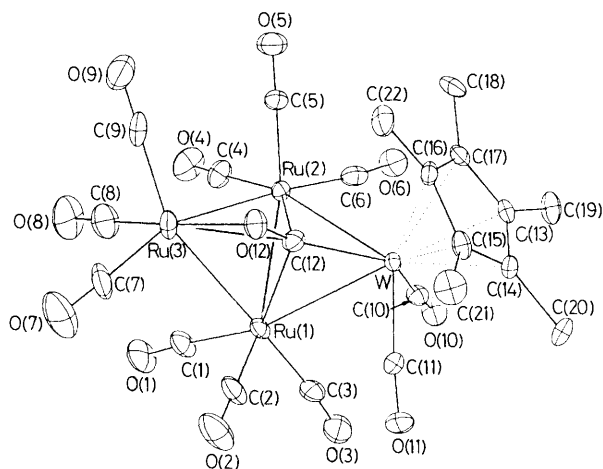

Figure 1. ORTEP view of the molecular structure of (**1c**). Bond lengths (Å): W–Ru(1), 2.965(2); Ru(1)–Ru(2), 2.798(2); Ru(1)–Ru(1a), 2.824(2); W–C(10), 2.045(10); Ru(1)–C(10), 2.265(10); Ru(2)–C(10), 2.376(10); C(10)–O(10), 1.267(13); Ru(2)–O(10), 2.114(7). Bond angles (°): W–C(10)–Ru(2), 155.4(6); W–C(10)–O(10), 142.1(9); Ru(1a)–Ru(1)–C(3), 114.9(3); Ru(1a)–Ru(1)–C(2), 108.0(3).

$(CO)_{12}H$,‡ and studied its crystal structure and solution dynamics. The ORTEP diagram of (**4**) is presented in Figure 2. Basically, the solid state structure (denoted as **4d**), being very similar to that of (**3c**), indicates that the WRu$_3$ core adopts a butterfly geometry with a dihedral angle of 114.4° and suggests that the undetermined hydride ligand is associated with the 'hinge' Ru–Ru vector. However, one important difference between the structure of (**4d**) and that of (**3c**) is that the C_5Me_5 ligand of the $(C_5Me_5)W(CO)_2$ vertex is now located *syn* to the μ_4-CO ligand. It is clear that the structure of

(**4d**) can be generated from isomer **c** by rotation of the $(C_5Me_5)W(CO)_2$ vertex, which would avoid the large repulsion between the CO ligands, C(6)–O(6) and C(3)–O(3), and the C_5Me_5 ligand. Related studies on this topic of rotation of $(C_5H_5)M(CO)_2$ have already been reported by Stone and co-workers,[11] and by Vahrenkamp.[12]

Complex (**4**) also displays an interesting isomerization in solution. The ^1H n.m.r. spectrum (400 MHz, CD$_2$Cl$_2$, room temp.) shows three resonances at δ -15.26 (J_{W-H} 51 Hz, **4b**), -20.16 (**4c**), and -20.20 (**4d**), with an intensity ratio $1:1.4:4$. The assignments were made on the basis of the characteristic J_{W-H} coupling, and the minute chemical shift difference of the two highfield hydride resonances which is expected for isomers **c** and **d**. It is of interest that isomer **a** was not observed in solution; we attribute this to the extremely unfavourable bridging CO–C_5Me_5 repulsion in (**4a**).

In conclusion, in the series of the tetranuclear complexes $LWM_3(CO)_{12}H$, there are several isomers that exist in both the solid and the solution state. We are able to shift the equilibrium from a WM$_3$ tetrahedron to a butterfly arrangement by replacing osmium with the slightly smaller,[13] isoelectronic ruthenium and then by using the more bulky C_5Me_5 ligand (Scheme 1). The smaller WRu$_3$ core prefers to adopt the butterfly arrangement because this geometry would create more space for the co-ordinated CO ligands; at the same time, a CO ligand adopts the π-bonded geometry (as a four-electron donor) to stabilize the cluster electronically. Therefore, the observed preference of isomerization and formation of the μ_4-η^2-CO ligand can be understood in terms of a synergism of steric and electronic effects. However, more than two isomers of different molecular geometry were observed in the solution state, indicating that the overall influence of the steric and electronic effects is relatively weak.

Finally, and most importantly, these experiments have provided a unique cluster model of CO reorientation from terminal to π bonding. The necessary unsaturation is not generated by a prior CO elimination, as indicated in the transformation from $Mn_2(CO)_6(PP)_2$ to $Mn_2(CO)_5(PP)_2$,[3] but by a reversible scission of a metal–metal bond.

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