Facile Interconversion of Terminal, Doubly Bridging, and Quadruply Bridging Carbonyl Ligands in Solution: Crystal Structure and Solution Dynamics of the Complexes LWRu3(CO)12H, L = C5H5 and C5Me5

Yun Chi,* Fang-Jy Wu, Bang-Ji Liu, Chwan-Chin Wang, and Sue-Lein Wang†

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

The crystal structures of the tetraneuclear mixed-metal complexes LWRu3(CO)12H, L = C5H5 and C5Me5, were determined, indicating the presence of a butterfly arrangement with an unusual μ4-η2-CO ligand; in solution, these isomers are in equilibrium with other isomers containing only α-bonded CO ligands.

The chemical and structural properties of the α-bonded, quadruply bridging μ4-CO ligand1 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 reorientiation to form the above mentioned bonding, as such a reorientation will strengthen the importance of the μ4-CO ligand on metal surfaces. There are few reports in the literature on this subject. Klemann has mentioned bonding, as such a reorientation will strengthen the importance of the p4-CO ligand on metal surfaces.2 Furthermore, it is also possible that the p4-η2-CO ligand are consistent with those of the related complexes, (C6H5)2Ru2(CO)4(μ4-η2-CO)4(μ4-S) and (C6H5)2Ru2(CO)4(μ4-η2-CO)4(μ4-T).10 Finally, an additional important feature is that the C5H5 ligand of the (C5Me5)3-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 pentamethylecyclopentadienyl complex (4), (C5Me5)WRu3-

---

† For enquiries about the X-ray crystallographic work.
‡ Compound (1): i.r. (C6H6) v(CO) 2088m, 2061s, 2055vs, 2043s, 2038m, 2032m, 1977m, 1957m, 1946m, 1934w, 1916w, and 1906w, sh cm⁻¹; 1H n.m.r. (400 MHz, CD2Cl2, 190 K) spectrum of the isolated compound exhibits three resonance lines at δ = 49.0, 23.0, and 18.67 (Jw,H 53 Hz, Jb), and 20.60 (Jc), 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 behaviour of the downfield hydride resonances, (1a) and (1b), is associated with that of the analogous osmium complexes LWO3(CO)12H, L = C5H5 (2a) and (2b), or C5Me5 (3a and 3b) prepared previously. We have also reported that these WOs3 complexes each exist as two isomers (Scheme 1) and undergo rapid interconversion in solution; 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 Jw,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 C5H5 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 'wingtip' Ru(1)–Ru(1a) vector. The molecule has a unique CO ligand, C10O10(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 C10O10(10) ligand adopts a μ4-η2-bonding mode. The parameters associated with this μ4-η2-CO ligand are consistent with those of the related complexes, (C6H5)2Ru2(CO)4(μ4-η2-CO)4(μ4-S) and (C6H5)2Ru2(CO)4(μ4-η2-CO)4(μ4-T).10 Finally, an additional important feature is that the C5H5 ligand of the (C5Me5)3-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 pentamethylecyclopentadienyl complex (4), (C5Me5)WRu3-

---

§ Crystal data for (1c): C7H10O6W3Ru3, M = 889.29, monoclinic, space group P21/m, a = 7.317(4) Å, b = 15.331(4) Å, c = 9.949(3) Å, β = 102.78(2)°, V = 1008.4(4) Å³, Z = 2, Dc = 2.71 g/cm³, F(000) = 820, μ(Mo-Kα) = 7.446 mm⁻¹, 1747 reflections with I > 3σ(I), R = 3.79%, θmax = 90°, goodness-of-fit = 0.92.

Crystal data for (4d): C6H4O2W3Ru4, M = 595.4, monoclinic, space group P21/c, a = 14.92(5) Å, b = 8.378(1) Å, c = 21.978(5) Å, β = 92.53(2)°, V = 2745.1 Å³, Z = 4, Dc = 2.32 g/cm³, F(000) = 1800, μ(Mo-Kα) = 5.916 mm⁻¹, 3237 reflections with I > 3σ(I), R = 3.49%, ρmax = 5.35%, goodness-of-fit = 1.24. The intensity data were collected on a Nicolet R3mN diffractometer using the θ/2θ scan mode and with graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å; θ scan absorption correction was routinely applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.
(CO)$_3$H,

and studied its crystal structure and solution dynamics. The ORTEP diagram of (4d) 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$_5$Me$_5$ ligand of the (C$_5$Me$_5$)W(CO)$_2$ vertex is now located syn to the μ-η$^2$-CO ligand. It is clear that the structure of (4d) can be generated from isomer c by rotation of the (C$_5$Me$_5$)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$_5$Me$_5$ ligand. Related studies on this topic of rotation of (C$_5$H$_5$)M(CO)$_2$ have already been reported by Stone and co-workers, and by Vahrenkamp.

Complex (4) also displays an interesting isomerization in solution. The $^1$H n.m.r. spectrum (400 MHz, CD$_2$Cl$_2$, room temp.) shows three resonances at -15.26 (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 $^1$H-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$_5$Me$_5$ repulsion in (4a).

In conclusion, in the series of the tetranuclear complexes LWM$_3$(CO)$_3$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, isoelectronic ruthenium and then by using the more bulky C$_5$Me$_5$ 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 n-bonded geometry (as a four-electron donor) to stabilize the cluster electronically. Therefore, the observed preference of isomerization and formation of the μ-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)$_5$(PP)$_2$ to Mn$_2$(CO)$_4$(PP)$_2$, but by a reversible scission of a metal-metal bond.
We thank the National Science Council of the Republic of China for generous financial support of this research. Y. C. also thanks Prof. Dr. John Ogilvie for helpful discussion.

Received, 21st November 1988; Com. 8/04619K

References
5 C. P. Horwitz and D. F. Shriver, Organometallics, 1984, 3, 756.
6 This compound has also been prepared by protonation of the anion (C₅H₅)WRu₃(CO)₁₂⁻ in high yield; however, the structure they proposed for (1) was incorrect, see: M. Cazanoue, N. Lugan, J.-J. Bonnet, and R. Mathieu, Organometallics, 1988, 7, 2480.
13 The average Ru–Ru distance in Ru₃(CO)₁₂ is about 0.0259 Å shorter than the Os–Os distance in Os₃(CO)₁₂; see: M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, Inorg. Chem., 1977, 16, 2655; M. R. Churchill and B. G. DeBoer, ibid., 1977, 16, 878.