Organometallics **1994,** *13,* 4167−4169

Isomerization Involving a Quadruply Bridging Carbonyl Ligand: Dynamics and Crystal Structure of (C$_5$Me$_5$)MoRu$_3$(CO)$_{12}$H

Yun Chi,*,† Chi-Jung Su,† Louis J. Farrugia,*,‡ Shie-Ming Peng,§ and Gene-Hsiang Lee§

Departments of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, The University, Glasgow G12 8QQ, Scotland, U.K., and National Taiwan University, Taipei 10764, Taiwan

Received August 4, 1994®

Summary: An X-ray analysis of (C$_5$Me$_5$)MoRu$_3$(CO)$_{12}$H at 110 K showed a butterfly metal framework, on which the oxygen atom of the disordered μ_4-η^2-CO ligand is linked to either the Ru or the Mo atom at two opposite wingtip positions, providing a unique example of isomerism involving the quadruply bridging CO ligand. These two butterfly isomers exist in solution together with a third tetrahedral isomer and undergo slow exchange with this last isomer on the NMR time scale, as demonstrated by ^{1}H and ^{13}C NMR studies.

The chemical and structural properties of the quadruply bridging CO ligand[1] are interesting because this bonding mode is implicated as a precursor for C—O bond cleavage in metal cluster compounds and on surfaces.[2] There are now several reports in the literature relating to the synthesis and structural characterization of cluster molecules containing these μ_4-η^2-CO ligands.[3] Of particular interest are the systematic studies of the Fe$_4$ clusters [Fe$_4$(A)(CO)$_{13}$]$^-$ (A = H, AuPEt$_3$, CuPPh$_3$, HgCH$_3$, HgMo(CO)$_3$Cp, and HgFe(CO)$_2$Cp).[4] For these cluster complexes, Shriver and co-workers have demonstrated that the tetrahedral isomers undergo rapid equilibrium in solution with butterfly forms which possess the μ_4-CO ligand and that the proportion of the latter complexes increases with the increasing Lewis acidity of the substituent A.[5] In this paper, we report structural and NMR studies on the cluster Cp*MoRu$_3$(CO)$_{12}$H, which shows the presence of a disordered μ_4-η^2-CO ligand in the solid state, and the existence of two parallel processes of tetrahedral ↔ butterfly skeletal rearrangements.

The title cluster Cp*MoRu$_3$(CO)$_{12}$H (**1**) is obtained in ca. 65% yield from the reactions of a 1:1 molar ratio of Ru$_3$(CO)$_{12}$ and [Cp*Mo(CO)$_3$][PPh$_4$] in a refluxing THF solution for 2 h, followed by addition of excess CF$_3$CO$_2$H in dichloromethane at room temperature. This modified two-step procedure[6] is better than the method of direct treatment of Ru$_3$(CO)$_{12}$ with LM(CO)$_3$H (M = Mo, W; L = Cp, Cp*), as the latter only offers the desired products LMRu$_3$(CO)$_{12}$H in low yields, in addition to extensive decomposition and formation of the trihydride complexes LMRu$_3$(CO)$_{11}$(μ-H)$_3$.[7]

The IR spectrum of solid **1**[8] contains Ru—CO stretches in the regime 2079-1955 cm^{-1}, two Mo—CO bands at 1910 and 1880 cm^{-1}, and an absorption maximum at 1445 cm^{-1}, which is due to the μ_4-CO ligand. When a crystalline sample of **1** is dissolved in CDCl$_3$ at 295 K, the ^{1}H NMR spectrum exhibits three hydride resonances at δ −13.75 (**1a**), −20.32 (**1b**), and −20.55 (**1c**) with an intensity ratio of 9%:53%:38%, suggesting the presence of three isomers in solution. The ^{1}H NMR integration varies slightly according to the temperature and solvents selected. The observed relative intensities were 8%:51%:41% for **1a**:**1b**:**1c** in toluene-d_8 at 294 K, while in THF-d_8 these ratios are 10%:57%:33%.

Structural characterizations of these three isomers were established. The identification of the isomer **1a** relies on comparison of the ^{1}H NMR data with those for the related cluster Cp*WRu$_3$(CO)$_{12}$H,[7b] which shows a broad hydride signal at δ −15.26 with coupling $J_{\mathrm{W-H}}$ = 51 Hz and two additional signals at δ −20.16 and −20.20. The first signal of **2** and the signal of **1a** are assigned to the tetrahedral isomer, and the proposed structure (see Scheme 1) is related to that already determined for Cp*WOs$_3$(CO)$_{12}$H.[9] The structures of the other two isomers **1b** and **1c** were elucidated from X-ray diffraction studies.[10]

The X-ray analysis performed at 110 K suggests that the molecule contains a MoRu$_3$ butterfly framework with a dihedral angle of 115.07(2)° and a disordered μ_4-η^2-CO ligand, which lies in the cavity of the butterfly

---

† National Tsing Hua University.

‡ University of Glasgow.

§ National Taiwan University.

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

[1] (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

[2] (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Power, H. R. *J. Chem. Soc., Chem. Commun.* **1989**, 442. (c) Bailey, P. J.; Duer, M. J.; Johnson, B. F. G.; Lewis, J.; Conole, C.; McPartlin, M.; Powell, H. R.; Anson, C. E. *J. Organomet. Chem.* **1990**, *383*, 441.

[3] (a) Field, J. S.; Haines, R. J.; Jay, J. A. *J. Organomet. Chem.* **1989**, *377*, C35. (b) Gibson, C. P.; Dahl, L. F. *Organometallics* **1988**, *7*, 535. (c) Brun, L. P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926. (d) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Pearsall, M.-A.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1089. (e) Adams, R. D.; Alexander, M. S.; Arafa, I.; Wu, W. *Inorg. Chem.* **1991**, *30*, 4717. (f) Adams, R. D.; Li, Z.; Lii, J.-C.; Wu, W. *Organometallics* **1992**, *11*, 4001.

[4] (a) Wang, J.; Sabat, M.; Horwitz, C. P.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 552. (b) Horwitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8136.

[5] (a) Horwitz, C. P.; Shriver, D. F. *Organometallics* **1984**, *3*, 756. (b) Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147.

[6] Cazanoue, M.; Lugan, N.; Bonnet, J.-J.; Mathieu, R. *Organometallics* **1988**, *7*, 2480.

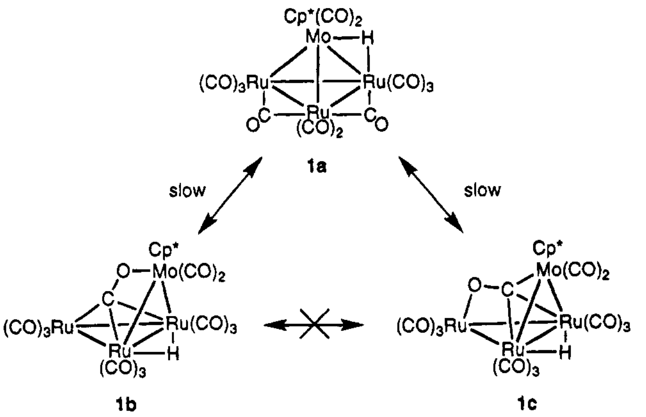
[7] (a) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534. (b) Chi, Y.; Wu, F.-J.; Liu, B.-J.; Wang, C.-C.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 873. (c) Chi, Y.; Cheng, C.-Y.; Wang, S.-L. *J. Organomet. Chem.* **1989**, *378*, 45.

[8] Selected data for **1** are as follows. IR (C$_6$H$_{12}$, ν(CO)): 2084 (m), 2051 (vs), 2037 (s), 2033 (s), 2015 (m), 2009 (s), 1995 (m), 1988 (w), 1979 (w), 1959 (vw), 1922 (w), 1896 (w) cm^{-1}. Anal. Calcd for C$_{22}$H$_{16}$O$_{12}$MoRu$_3$: C, 30.32; H, 1.85. Found: C, 30.23; H, 1.88.

[9] Peng, S.-M.; Lee, G.-H.; Chi, Y.; Peng, C.-L.; Hwang, L.-S. *J. Organomet. Chem.* **1989**, *371*, 197.

0276-7333/94/2313-4167$04.50/0

Scheme 1



skeleton. Two molecular drawings are presented (Figure 1) which emphasize the interaction between the disordered μ_4-η^2-CO ligand C(1)O(1) and C(1′)O(1′) and the metal core. As indicated in Figure 1, the cluster core is essentially identical with that found for the WRu_3 derivative, showing three CO ligands on each Ru atom and two CO ligands on the Mo atom. The butterfly wingtips comprise the Mo and one Ru atom, and the hydride ligand bridges the hinge Ru—Ru vector. The refined occupancies of C(1)O(1) and C(1′)O(1′) were 65% and 35%, respectively. This ratio differs from that observed in solution (*vide infra*). The carbon atom C(1) is coordinated to the metal atoms Mo, Ru(1), and Ru(3), while the oxygen atom O(1) is tilted toward the Ru(2) atom with the angle Mo—C(1)—O(1) being 138.5(7)°. The minor component C(1′) atom is associated with all three Ru atoms, and the O(1′) atom is bonded to the Mo atoms, with an angle Ru(2)—C(1′)—O(1′) of 137(2)°. The metric parameters of the μ_4-CO ligand in both isomers are consistent with those of the tetrairon complexes $[Fe_4(A)(CO)_{13}]^-$ discussed earlier[4,5] and the pentanuclear heterometallic clusters $Cp^*{}_2W_2Ru_4(CO)_{12}(\mu$-$PPh)_2$[11] and $Cp_2Mo_2Ru_4(CO)_{13}(\mu_4$-$CO)(\mu_4$-$S)$.[12]

This interpretation of the disorder is fully consistent with a solid-state ^{13}C CPMAS spectrum of a highly crystalline sample of **1**, which shows two signals in the μ_4-CO region at δ 274.5 and 256.3 with intensity ratio 2:1. These signals can thus be unambiguously assigned to the carbon atoms C(1) and C(1′), respectively. The ^{13}C NMR spectrum in CD_2Cl_2 solution at 175 K shows two signals with very similar shifts at δ 272.6 (**1c**) and 255.0 ($^2J_{C-C}$ = 21 Hz) (**1b**), but their relative intensities are reversed (1:2) (see Figure 2). We suggest that the μ_4-CO ligand in **1c** is more downfield than that in **1b** because this carbon atom bridges the $MoRu_2$ triangle rather than the Ru_3 triangle. The small ^{13}C—^{13}C coupling on the signal at δ 255.0 is described as the coupling between C(1′) and the trans carbonyl C(8)O(8) at δ 203.4 on the Ru(2) atom.

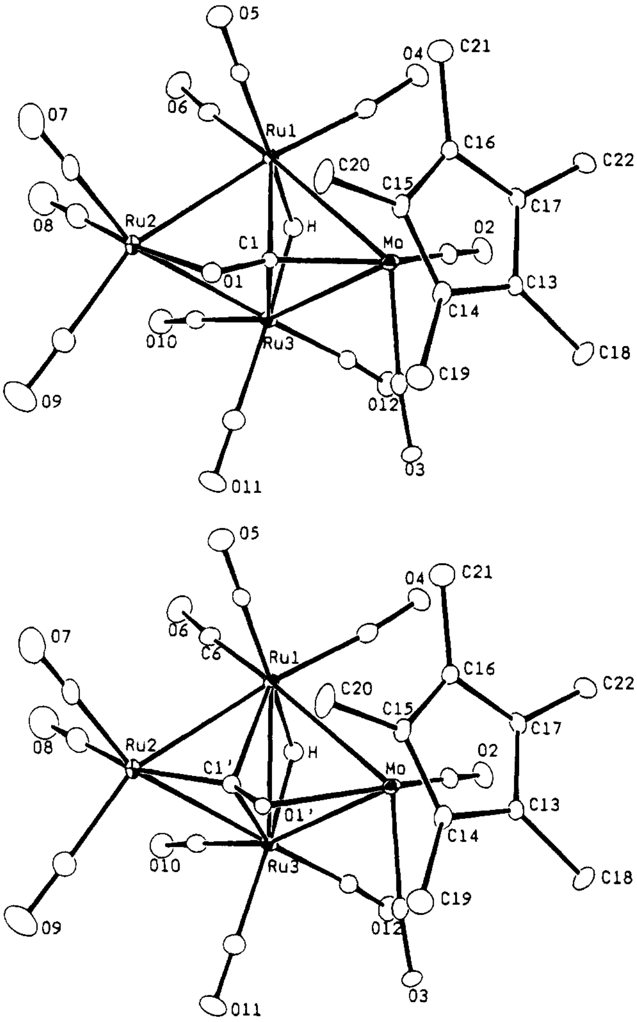


Figure 1. Two molecular drawings of **1**, giving special emphasis to the interaction between the disordered μ_4-CO ligand and the metal core. The top and the bottom figures illustrate the structures of isomers **1c** (65%) and **1b** (35%), respectively. Thermal ellipsoids are shown at the 30% level. Metal—metal bond lengths (Å): Mo—Ru(1) = 2.962(1), Mo—Ru(3) = 2.997(1), Ru(1)—Ru(2) = 2.801(1), Ru(1)—Ru(3) = 2.821(1), Ru(2)—Ru(3) = 2.843(1). Metal—CO distances for **1c** (Å): Mo—C(1) = 1.948(9), Ru(1)—C(1) = 2.290(9), Ru(2)—C(1) = 2.423(9), Ru(3)—C(1) = 2.346(9), Ru(2)—O(1) = 2.216(7), C(1)—O(1) = 1.24(1). Metal—CO distances for **1b** (Å): Mo—C(1′) = 2.57(2), Ru(1)—C(1′) = 2.27(2), Ru(2)—C(1′) = 1.78(2), Ru(3)—C(1′) = 2.25(2), Mo—O(1′) = 2.32(1), C(1′)—O(1′) = 1.26(2).

The Mo—CO ligands of **1b** resonante at δ 239.2 and 228.5, while those of **1c** are seen as broad signals at δ 226.0 and 222.1. It is likely that the Mo—CO ligands of **1b** occur at high frequency and undergo a slower pairwise exchange with respect to those of **1c** because the electronegative oxygen atom bonded to the Mo center effectively "locks" the oscillation of the Cp*Mo(CO)$_2$ fragment and raises the barrier to this normally low energy process. We estimate a rate constant of 0.22(±0.04) s^{-1} at 223 K for this vertex oscillation in **1b**, from a ^{13}C EXSY spectrum (mixing time 0.2 s), which corresponds to a barrier $\Delta G^‡$ of 56.9(±0.6) kJ mol^{-1}. A crude estimate of 34(±1) kJ mol^{-1} for $\Delta G^‡$ of the same process in isomer **1c** is obtained from the coalescence temperature. The Mo—CO resonances of **1a** are not observed, since they are in rapid exchange with other Ru—CO ligands, but an average signal for all carbonyls

---

(10) The single crystals were grown by solvent diffusion of CH_3OH into CH_2Cl_2 solution at room temperature. Selected crystal data: $C_{22}H_{16}O_{12}MoRu_3$, M_r = 871.5, monoclinic, space group $P2_1/c$, a = 14.663(5) Å, b = 8.282(2) Å, c = 21.923(4) Å, β = 93.04(3)°, V = 2659(1) Å^3, Z = 4, D_c = 2.17 g/cm^3, $F(000)$ = 1648, μ(Mo Kα) = 21.5 cm^{-1}, 4150 reflections with $I \geq 2\sigma(I)$, R = 3.5%, R_w = 3.6%, GOF = 4.61. The intensity data were collected on a Nonius CAD4 diffractometer at 110 K with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å); a ψ-scan absorption correction was routinely applied.

(11) Wang, J.-C.; Lin, R.-C.; Chi, Y.; Peng, S.-H.; Lee, G.-H. *Organometallics* **1993**, *12*, 4061.

(12) Adams, R. D.; Babin, J. E.; Tasi, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 685.

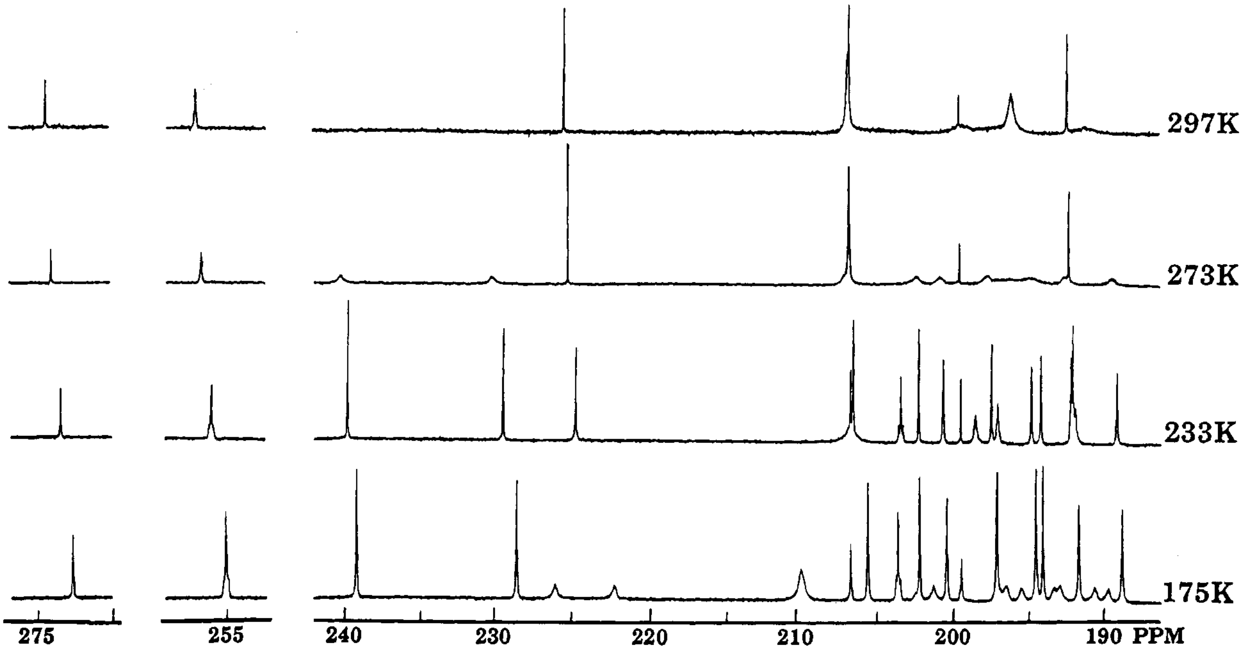


Figure 2. Variable-temperature ^{13}C NMR spectra of **1** in CD_2Cl_2 solution in the region of CO resonances.

of **1a** is observed at δ ~206 at room temperature. The assignment and exchange behavior of the Ru-bound carbonyls in isomer **1b** and **1c** will be discussed in a later paper.

The *interisomer* exchange process has been examined. When the hydride due to **1a** (toluene-d_8, 294 K) was saturated, we observed a decrease in intensities in the corresponding signals for **1b** and **1c**, indicating a slow exchange between isomers. Preliminary quantitative studies using a DANTE pulse train[13] to selectively invert the three hydride resonances in turn revealed that there is a slow exchange between isomers **1a** and **1b** (ca. 1 s^{-1} at 298 K and ca. 28 s^{-1} at 334 K) and a slightly slower exchange between **1a** and **1c** (ca. 0.25 s^{-1} at 298 K and ca. 5 s^{-1} at 334 K). However, in all our ^1H and ^{13}C EXSY and DANTE studies, we were unable to obtain evidence for any *direct* exchange between the two butterfly isomers **1b** and **1c** by "flipping" of the oxygen atom of the μ_4-CO ligand between the wingtip metal atoms. These experimental observations are also consistent with our theoretical studies, since extended Hückel calculations using the CACAO package[14] on the model complex $(Cp)MoRu_3(CO)_{12}H$ indicate that there is a substantial barrier of ca. 190 kJ mol^{-1} for the direct interconversion of **1b** and **1c** via a transition state with a μ_4-η^1-CO ligand. Such a ligand has been observed by Curtis and co-workers[15] in the complex $Cp_4Mo_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}\eta^1\text{-}CO)$, but it does not appear to play a significant role in the interisomer exchange process of cluster **1**.

In conclusion, compound **1** is the first butterfly cluster with a disordered μ_4-CO ligand to receive thorough structural characterization. The isomerism between **1b** and **1c** is not caused by rotation of the $Cp^*Mo(CO)_2$ vertex as we originally proposed,[7b] although it has been established in other cluster systems.[16] The most probable mechanism for interconversion of these isomers with Mo—O- and Ru—O-bound isocarbonyl ligands is an indirect pathway involving a tetrahedral isomer with "normal" terminal or bridging CO ligands.

Acknowledgment. We thank the National Science Council of the Republic of China (Grant No. NSC 83-0208-M007-43) and the SERC (U.K.) for support and Carlo Mealli for supplying the extended Hückel package CACAO.

Supplementary Material Available: Tables of crystal data, bond distances and angles, atomic coordinates, and anisotropic thermal parameters for **1** (6 pages). Ordering information is given on any current masthead page.

OM9406198

---

[13] (a) Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433. (b) Grassi, M.; Mann, B. E.; Pickup, B. T.; Spencer, C. M. *J. Magn. Reson.* **1986**, *69*, 92.

[14] (a) Mealli, C.; Proserpio, D. M. CACAO Version 4.0; July 1994, Firenze, Italy. (b) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

[15] Li, P.; Curtis, M. D. *J. Am. Chem. Soc.* **1989**, *111*, 8279.

[16] (a) Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 863. (b) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101. (c) Sutin, K. A.; Li, L.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1991**, *10*, 2362.