

## $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ : the X-Ray Crystallographic Determination of Two Structural Isomers†

By PETER F. JACKSON, BRIAN F. G. JOHNSON, and JACK LEWIS\*  
(University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW)

and MARY MCPARTLIN and WILLIAM J. H. NELSON  
(Department of Chemistry, The Polytechnic of North London, London N7 8DB)

**Summary** X-Ray analysis has shown the presence of two structural isomers of the  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  anion with metal-hydrogen geometries approximating to  $C_2$  and  $C_{3v}$  symmetry; although the presence of structural isomers has been postulated for several metal carbonyl hydrides, this work presents the first confirmation of their existence in the solid state.

THE i.r. spectrum of  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  indicates only terminal carbonyl groups, and the complexity of the pattern suggests that either a species of low symmetry or that more than one species is present. From the  $^1\text{H}$  n.m.r. spectrum Koepke *et al.*<sup>1</sup> deduce that two structural isomers are present in solution, one having  $C_2$  (or  $C_{2v}$ ) and the other having  $C_{3v}$  symmetry of the metal-hydrogen framework. They also interpret the broad band at  $1442\text{ cm}^{-1}$  in the Raman spectrum to be consistent with bridging hydrogens.

In order to investigate the structure in the solid state orange-red, air stable crystals of  $[(\text{Ph}_3\text{P})_2\text{N}] [\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  (I) were prepared by treating  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  with methanolic potassium hydroxide, precipitating the anion with  $(\text{Ph}_3\text{P})_2\text{NI}$ , and slow recrystallization from  $\text{CH}_2\text{Cl}_2$ -MeOH. The structure was determined by single crystal X-ray diffraction (Figure 1).‡ Three tetrahedron edges Ru(1)-Ru(2),

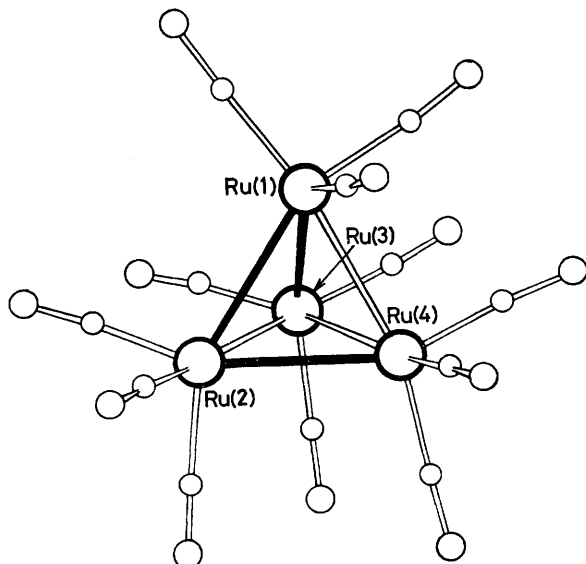


FIGURE 1. Isomer (I) of the anion  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ . The solid Ru-Ru bonds are bridged by the three hydrogen atoms.

Ru(1)-Ru(3), and Ru(2)-Ru(4) are significantly longer [mean  $2.923(1)\text{ \AA}$ ], than the others [mean  $2.803(1)\text{ \AA}$ ] and the carbonyl ligands appear to be pushed back from these edges. This is consistent with the three hydrogens bridging these longer edges.

Since the original crystals diffracted rather poorly, a new crop were grown under apparently identical conditions and a crystal selected for recollection of the data. However this had a triclinic unit cell which Delaunay reduction showed was unrelated to the original, and which was *ca.*  $26\text{ \AA}^3$  smaller. X-Ray analysis of this compound (II) has shown it to be a structural isomer of (I) (Figure 2).‡

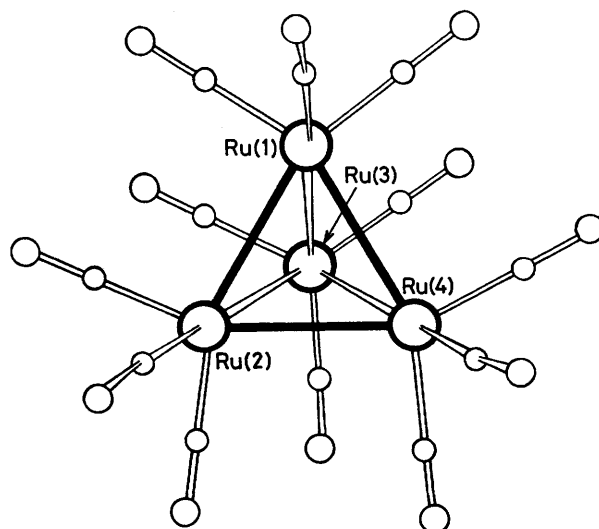


FIGURE 2. Isomer (II) of the anion  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ . The three hydrogen atoms bridge the edges of the triangular face Ru(1), Ru(2), Ru(4).

The anion in (II) has three Ru-Ru bonds, in this case forming the triangular face Ru(1), Ru(2), Ru(4), which are significantly longer [mean  $2.937(1)\text{ \AA}$ ] than the others [mean  $2.787(1)\text{ \AA}$ ]. The carbonyl ligands appear to be pushed back from these edges indicating that they are bridged by the three hydrogens. Thus the metal-hydrogen geometry in the two isomeric forms of the  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  anion has symmetry approximating to  $C_2$  in (I) and  $C_{3v}$  in (II). Although evidence in favour of such isomers has appeared for several metal carbonyl hydrides,<sup>1,2</sup> this work apparently presents the first confirmation of their existence

† No reprints available.

‡ *Crystal data*: (I), triclinic, space group  $P\bar{1}$ ,  $a = 17.361$ ,  $b = 11.735$ ,  $c = 12.321\text{ \AA}$ ,  $\alpha = 94.61^\circ$ ,  $\beta = 98.44^\circ$ ,  $\gamma = 88.52^\circ$ ,  $Z = 2$ ,  $I/\sigma(I) > 3.0$ ,  $2\theta = 3-30^\circ$ , present  $R$ -value =  $0.0545$  for 6050 reflections; (II), triclinic, space group  $P\bar{1}$ ,  $a = 15.608$ ,  $b = 15.370$ ,  $c = 11.219\text{ \AA}$ ,  $\alpha = 99.26^\circ$ ,  $\beta = 103.27^\circ$ ,  $\gamma = 105.72^\circ$ ,  $Z = 2$ ,  $I/\sigma(I) > 3.0$ ,  $2\theta = 3-32^\circ$ , present  $R$ -value =  $0.0432$  for 10945 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

in the solid state. In both isomers, the lengths of the hydrogen bridged Ru–Ru bonds are in good agreement with those determined for  $\alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13}$ <sup>3</sup> [mean 2.930(12) Å] which has two  $\mu_2$  hydrogen ligands.

A better crystal of (I) was obtained from a later recrystallisation and the recollected data used in the final refinement. Koepke *et al.* found that the equilibrium in solution,  $C_2 \rightleftharpoons C_{3v}$ , is influenced by the polarity of the solvent system, the more polar  $C_{3v}$  isomer being favoured in solvents of increasing polarity. This suggests that the crystals of the two isomers separated from solution under differing conditions of solvent polarity. Further, their occurrence in solution and in the solid state indicates relatively little energy difference between the possible hydrogen bridging positions, as shown by Hoffmann *et al.*<sup>4</sup> using extended Hückel calculations on  $\text{H}_4\text{Fe}_4(\text{CO})_{12}$ .

This work draws attention to the fact that the determination of structure by single crystal analysis does not necessarily give the unique solid state geometry. Where there is the possibility of more than one isomer existing, it may be necessary not only to examine several crystals, but to repeat the recrystallization under different conditions.

In this connection it is interesting to note the work of Bau<sup>5</sup> and Churchill<sup>6</sup> who have shown that in the structures of  $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2$  and  $\text{H}_4\text{Ru}_4(\text{CO})_{10}\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  the bridging H-atoms adopt different bridging arrangements.

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