

Preliminary communication

CLUSTER CHEMISTRY

XXXIV*. REACTIONS OF AN OPEN Ru₅ CLUSTER WITH CO: X-RAY STRUCTURES OF TWO ISOMERS OF [Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₅]

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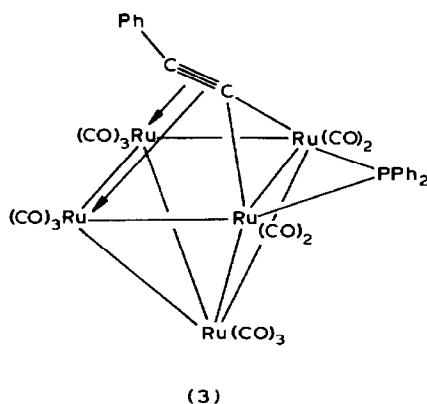
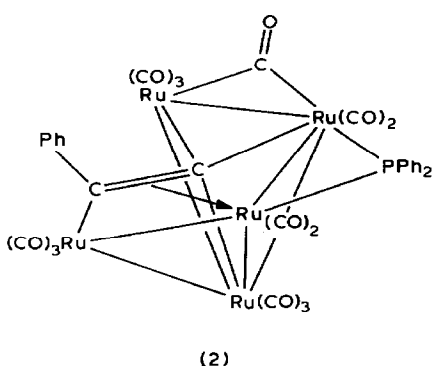
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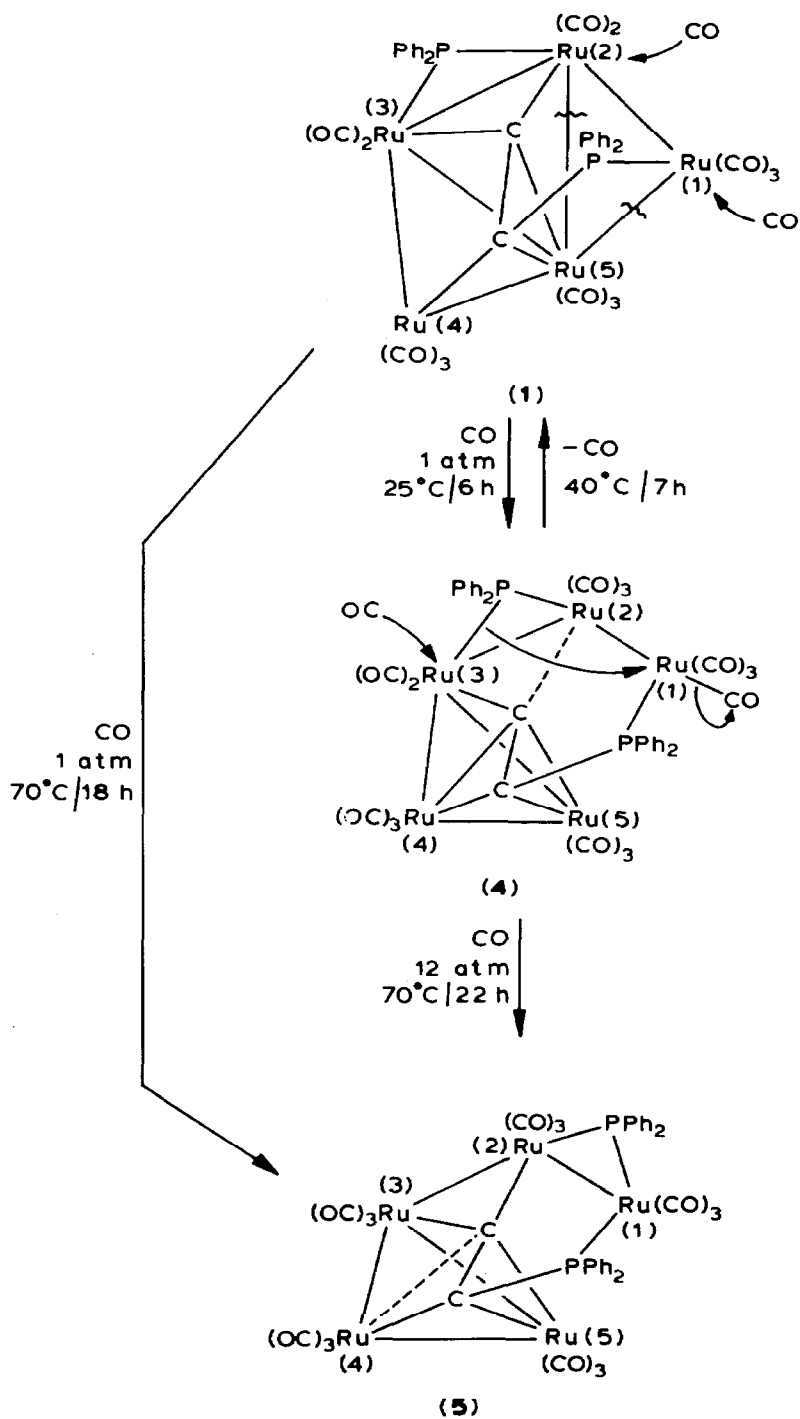
Summary

The title complexes are formed in reactions of Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₃ with CO; the metal skeleton is formed by cleavage of two Ru–Ru bonds. The major differences between the two isomers are the location of the μ-PPh₂ group, and the presence of an unusual Ru→Ru donor bond in the first-formed complex.

We have described the synthesis and structure of the open Ru₅ cluster compound 1 (Scheme 1) [1]. The open cluster geometry (three fused triangles) is apparently preserved by the presence of the tertiary phosphine coordinated to Ru(1); in contrast, the similar complex 2 readily loses CO to form the square-pyramidal complex 3 [2]. It was of interest to examine the reaction of CO with 1 to determine the mode of further cleavage of the Ru₅ cluster.



*For Part XXXIII, see ref. 8.



SCHEME 1

Passage of CO into the black solutions of 1 in cyclohexane under mild conditions (25°C, 1 bar, 6 h) causes precipitation of a dark red complex 4* in 80–85% yield. More vigorous reaction conditions (70°C, 1 bar, 18 h) afforded a red solution, from which a second red complex (5)* was isolated in 35% yield by preparative TLC (silica gel, light petroleum/acetone 85/15). Conversion of 4 to 5 occurs under CO (70°C, 12 bar, 22 h), although loss of CO with regeneration of 1 occurs in refluxing CH₂Cl₂ (7 h, 63% yield). Single-crystal X-ray analyses of 4 and 5 showed them to be isomers of composition Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₅. Suitable crystals of both complexes were obtained from CH₂Cl₂/MeOH under a CO atmosphere. Diffraction data for both complexes were collected on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo-K_α X-rays, λ(Mo-K_α) 0.7107 Å.

Crystal data. 4: C₄₁H₂₀O₁₅P₂Ru₅, *M* = 1319.9, monoclinic, space group *P*2₁/*n*; *a* 11.661(2), *b* 17.312(4), *c* 22.377(2) Å, β 92.56(1)°, *U* 4512.8 Å³; *D*_m 1.92, *D*_c 1.94 g cm⁻³ for *Z* = 4; *F*(000) = 2544, μ(Mo-K_α) 17.07 cm⁻¹.

5: C₄₁H₂₀O₁₅P₂Ru₅, *M* = 1319.9, monoclinic, space group *P*2₁/*c*; *a* 11.496(2), *b* 23.749(4), *c* 16.705(3) Å; β 93.44(2)°, *U* 4552.6 Å³, *D*_m 1.92, *D*_c 1.93 g cm⁻³ for *Z* = 4; *F*(000) = 2544, μ(Mo-K_α) 16.92 cm⁻¹.

For 4, 6002 unique reflections were collected in the range 3 < 2θ < 46°, of which 5406 with *I* > 2.5σ(*I*) were refined to *R* = 0.029, *R*_w = 0.038. For 5, 3879 reflections with *I* > 2.5σ(*I*) out of a total of 4610 unique data collected in the range 2.6 < 2θ < 42° were refined to *R* = 0.037, *R*_w = 0.044. Both structures were solved by direct methods to give the Ru atom positions, with all other non-hydrogen atoms being revealed in subsequent refinement and Fourier difference maps. In the final cycles of the blocked full-matrix least-squares refinement the phenyl rings were included as rigid groups (C–C 1.38 Å) with isotropic thermal parameters, hydrogen atoms were placed in calculated positions (C–H 1.08 Å) with a common thermal parameter and all other atoms were treated anisotropically**.

The molecular structures of 4 and 5 are shown in Fig. 1 and 2, while Fig. 3 shows the heavy atom cores and salient bond distances. It can be seen that the structures are closely related, differing only in the position of the μ-PPh₂ group (bridging Ru(2)–Ru(3) in 4, Ru(1)–Ru(2) in 5), and in the disposition of CO groups on Ru(1), Ru(2) and Ru(3).

Complex 4 is derived from 1, at least formally, by addition of one CO each to Ru(1) and Ru(2), with concomitant cleavage of the bonds from these metal atoms to Ru(5). At the same time, coordination of the alkynyl group has altered so that its interaction with the Ru(3)Ru(4)Ru(5) triangle resembles that found in Ru₃(μ-H)(μ₃-C₂Bu[†])(CO)₉ [3]. However, C(2) asymmetrically bridges the

*Both complexes 4 and 5 were obtained analytically pure (C, H). Complex 4 had m.p. 141–143°C (dec.); infrared (cyclohexane): ν(CO) at 2112m, 2074m, 2060(sh), 2053s, 2044s, 2036(sh), 2018m, 2002s, 1987w, 1965w, 1954w cm⁻¹. Complex 5 had m.p. 160–163°C (dec.); infrared (cyclohexane): ν(CO) at 2100w, 2071m, 2067(sh), 2040s, 2037(sh), 2009w, 1999m, 1990w, 1983w, 1973w, 1966w cm⁻¹.

**The atomic coordinates for complexes described in this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

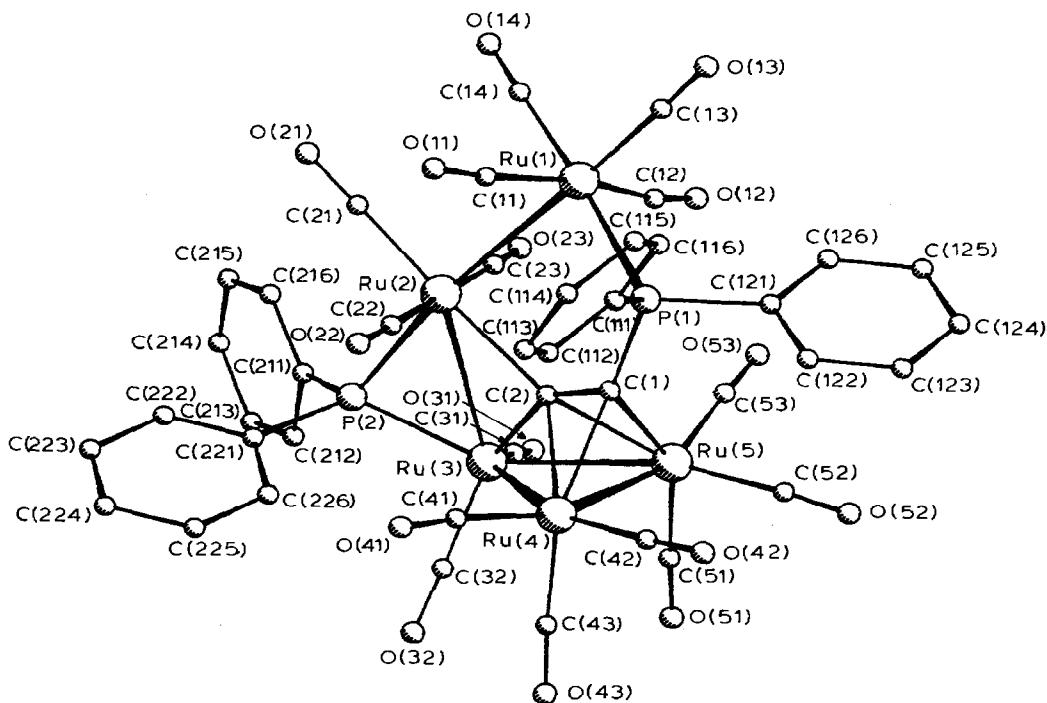


Fig. 1. PLUTO plot of molecular structure of 4, showing atom numbering scheme.

Ru(2)—Ru(3) vector (Ru(2)—C(2), 2.324(4); Ru(3)—C(2), 1.992(4) Å). A similar situation was found in $\text{Co}_2\text{FeRu}(\mu_4\text{-C}_2\text{Ph})(\mu\text{-CO})(\text{CO})_9(\eta\text{-C}_5\text{H}_5)$ [4].

The most unusual feature of the structure of 4 is the coordination about Ru(1). This metal is approximately octahedrally coordinated by four CO ligands, P(1) and Ru(2). Since the P(1)→Ru(1) bond (2.406(1) Å) is a normal two-electron donor link, the metal atom achieves an 18e count from this tertiary phosphine and the four CO ligands. Consequently, the Ru(1)—Ru(2) bond (3.009(1) Å) must be considered to be another example of an unsupported donor bond, the first of which was observed in the complex $(\text{OC})_5\text{Os}\rightarrow\text{OsCl}(\text{GeCl}_3)(\text{CO})_3$ [5]. In both instances, the metal atom separation is considerably longer than those found in the analogous $\text{M}_3(\text{CO})_{12}$ (M = Ru or Os) complexes.

Conversion of 4 into 5 can be achieved by attack of CO on Ru(3), displacing P(2) which pivots on Ru(2) to displace in turn a CO from Ru(1). This has the expected shortening effect on Ru(1)—Ru(2) (now 2.887(1) Å), although Ru(2)—Ru(3) is slightly longer, at 2.965(1) Å. The interaction of Ru(2) with C(2) is also strengthened (Ru(2)—C(2) 2.261(7), Ru(3)—C(2) 2.027(7) Å), while the alkynyl group is more symmetrically bonded in 5 than it is in 4, where the C(1)—C(2) vector is slewed across the Ru_3 triangle; in the latter complex, Ru(3)—Ru(4) is ca. 0.1 Å longer than Ru(3)—Ru(5), whereas these distances are almost equal in 5. In both complexes, the Ru(4)—Ru(5) separation is short (2.670(1), 2.675(1) Å, respectively), but there is no obvious explanation. None of the metal—metal bonds in 5 are of the type found between Ru(1) and Ru(2) in 4, and the net effect of the isomerisation is to give a more equitable distribution of electron density over the cluster.

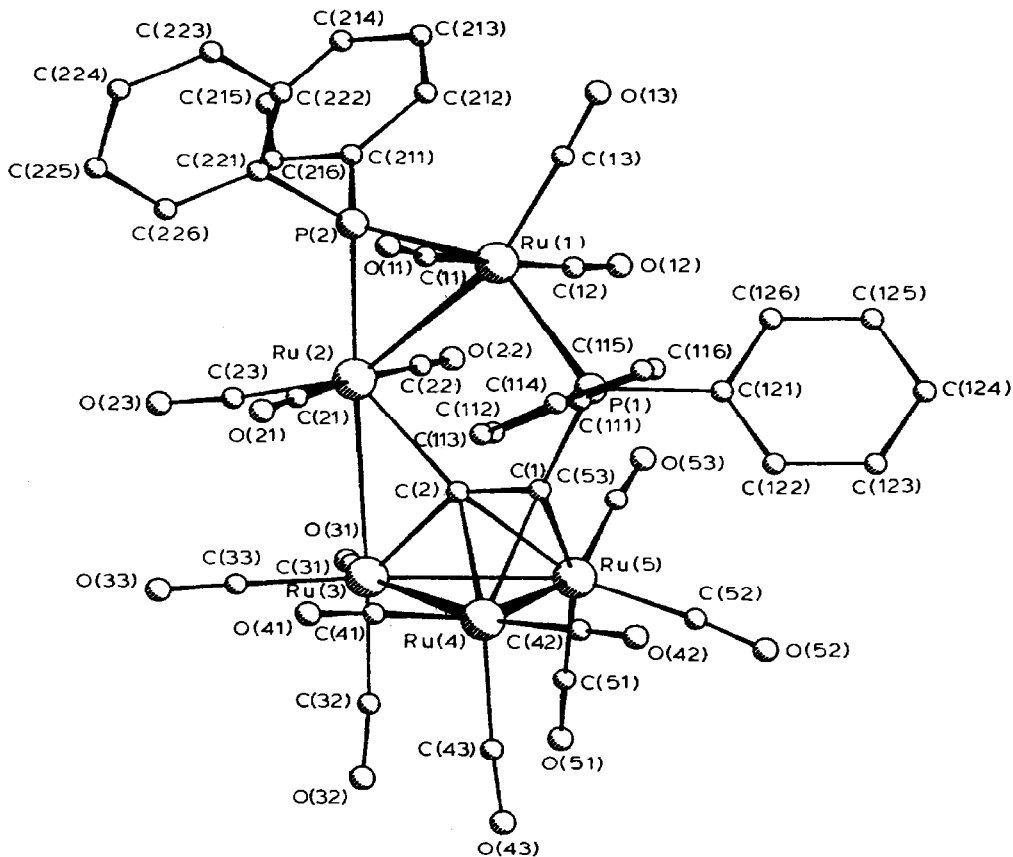


Fig. 2. PLUTO plot of molecular structure of 5, showing atom numbering scheme.

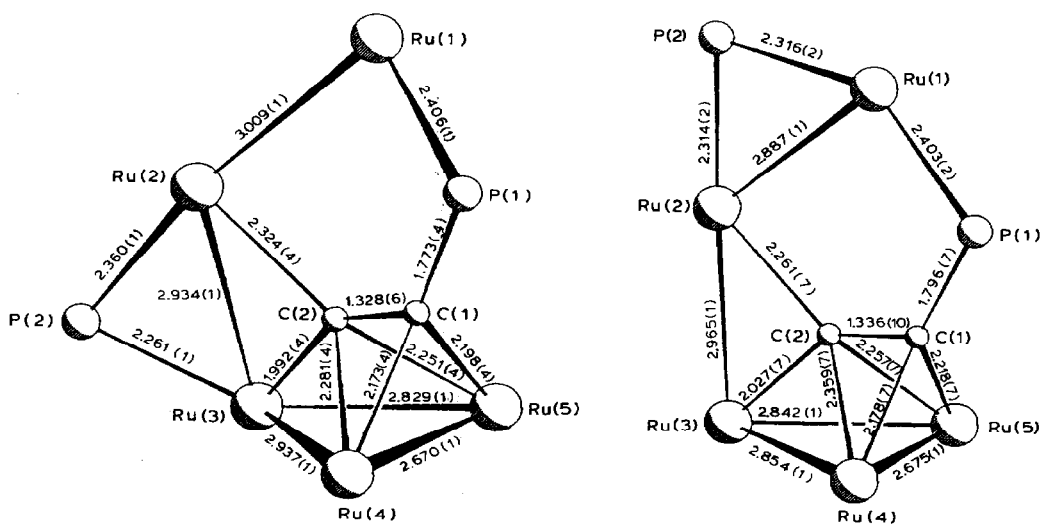


Fig. 3. Heavy atom skeletons of 4 (left) and 5 (right), with important bond distances.

The conversion of 1 to 4 and subsequent isomerisation to 5 are depicted formally in Scheme 1, although the ready mobility of ligands such as CO on cluster complexes makes the detailed course of these novel reactions uncertain. The oft-expressed proposition [5] that bridging PR_2 groups may hold clusters intact during their reactions is again called into question [6,7] by the results described above: while the metal skeleton is essentially unaltered, the PPh_2 group migrates to a second site, remaining bonded to Ru(2) during this process. Such reactions, in which opening of the Ru_2P group generates a further coordination site, may have implications for the role of such groups in cluster-catalysed reactions.

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