

A High-yield Synthesis of $\text{Ru}_5\text{C}(\text{CO})_{15}$ by the Carbonylation of $\text{Ru}_6\text{C}(\text{CO})_{17}$; the X-Ray Structure Analyses of $\text{Ru}_5\text{C}(\text{CO})_{15}$ and $\text{Ru}_5\text{C}(\text{CO})_{14}\text{PPh}_3$

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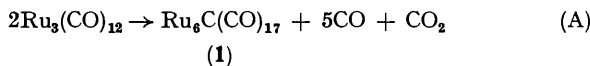
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Summary In reaction with CO at 70 °C and 80 atm the hexanuclear cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$ undergoes carbonylation, ejects $\text{Ru}(\text{CO})_5$ and gives quantitative amounts of $\text{Ru}_5\text{C}(\text{CO})_{15}$ which X-ray analysis has confirmed has a square-pyramidal Ru_5 arrangement with an exposed carido-atom; some reactions of this pentanuclear cluster are reported together with the X-ray structure analysis of its derivative $\text{Ru}_5\text{C}(\text{CO})_{14}\text{PPh}_3$.

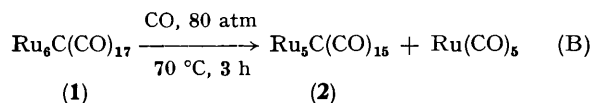
In recent years there has been increasing support¹ for the view that an important step in the Fischer-Tropsch reduction of CO involves C-O bond cleavage and the production of metal-carbido-intermediates. Fundamental to our understanding of the Fischer-Tropsch reaction will be an evaluation of the methods by which such carido-intermediates are produced and also any reactivity that such species exhibit.

Some years ago we reported² the preparation of the hexanuclear carbido-cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**1**) in which the carido atom originated from C-O bond cleavage [reaction (A)]. In this molecule the C atom is completely encapsu-



lated by an octahedron of metal atoms and thus protected from attack by incoming substrates. We now report studies of the carbonylation of this hexanuclear cluster and the high-yield synthesis of $\text{Ru}_5\text{C}(\text{CO})_{15}$ (**2**), a cluster containing an exposed (or surface) carido-atom.

The hexanuclear cluster (**1**) reacts with CO under moderate conditions to produce the pentanuclear cluster (**2**) in quantitative amounts according to equation (B). Pre-



viously (**2**) has only been obtained in 1% yield from the reaction of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with ethylene and it was proposed that it was isostructural with $\text{Fe}_5\text{C}(\text{CO})_{15}$ because of the similarity of their i.r. spectra;³ this has now been verified by X-ray analysis† (Figure 1). The only other product of the

reaction was confirmed as $\text{Ru}(\text{CO})_5$ on the basis of its spectroscopic and physical properties. This may be converted back into $\text{Ru}_3(\text{CO})_{12}$ and re-used to generate (**1**) [see equation (A)].

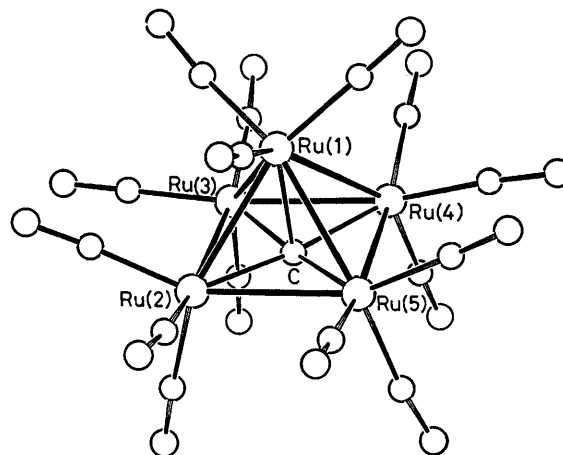
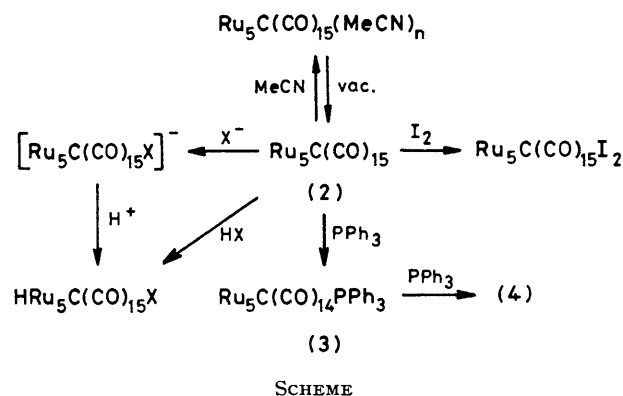


FIGURE 1. The structure of $\text{Ru}_5\text{C}(\text{CO})_{15}$ (**2**). There are two independent molecules in the asymmetric unit but their overall geometries are essentially the same. Important mean bond lengths (Å) are: Ru(basal)-Ru(basal) 2.85, Ru(apical)-Ru(basal) 2.83, Ru-C(carbido) 2.04, Ru-C(carbonyl) 1.87. Maximum e.s.d.s are: Ru-Ru 0.002, Ru-C(carbido) 0.02, Ru-C(carbonyl) 0.03 Å.

The pentanuclear cluster (**2**) resists further carbonylation (up to 400 atm of CO at 100 °C). On heating (**2**) under argon (ca. 10 atm) the hexanuclear cluster (**1**) is regenerated in high yields (75%). On reaction with H_2 a new hydrido-cluster is obtained. Work is in hand to establish the true identity of this cluster which on heating *in vacuo* regenerates some $\text{Ru}_5\text{C}(\text{CO})_{15}$ (ca. 60%) and which we believe, on the basis of an i.r. study,⁴ to be $\text{H}_2\text{Ru}_5\text{C}(\text{CO})_{15}$.

A feature of the chemistry of $\text{Ru}_5\text{C}(\text{CO})_{15}$ (**2**) (Scheme) is its ability to act as an electron-pair acceptor and, as demonstrated for osmium clusters, adduct formation is apparently facilitated by a flexibility of the metal framework which allows generation of new co-ordination sites by a rearrange-

† Crystal data: (**2**) monoclinic, space group $P2_1/c$, $a = 16.448(3)$, $b = 14.274(2)$, $c = 20.834(4)$ Å, $\beta = 91.36^\circ$, $Z = 8$, $I/\sigma(I) > 3.0$, θ -range 3 – 25° , R -value 0.0514 for 3256 reflections; (**3**), monoclinic, space group Pn , $a = 9.969(2)$, $b = 12.252(2)$, $c = 14.707(3)$ Å, $\beta = 91.238^\circ$, $Z = 2$, $I/\sigma(I) > 3.0$, θ -range 3 – 32° , R -value 0.0434 for 3961 reflections. Data for (**2**) and (**3**) were collected on a Philips PW1100 diffractometer using Mo- K_α radiation. The atomic co-ordinates for (**2**) are available on request from Professor Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. The atomic co-ordinates for (**3**) 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.



ment of the metal polyhedron.⁵ Thus it reacts quickly at room temperature with a variety of solvents and other nucleophilic reagents to produce either adducts or substitution products. For example, (2) reacts reversibly with MeCN to produce adducts of the type $\text{Ru}_5\text{C}(\text{CO})_{15}(\text{MeCN})_n$ ($n = 1$ or 2) which lose MeCN *in vacuo*, and with I_2 to produce $\text{Ru}_5\text{C}(\text{CO})_{15}\text{I}_2$.[‡] With halide anions (2) yields the anionic derivatives $[\text{Ru}_5\text{C}(\text{CO})_{15}\text{X}]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) which may be expected, by analogy with the electronically equivalent $[\text{Os}_5\text{C}(\text{CO})_{15}\text{I}]^-$,⁵ to have *arachno*-pentagonal bipyramidal metal arrangements with the carbido atoms in more exposed positions. I.r. spectroscopy tends to confirm this postulation.⁴ Protonation of these derivatives or direct reaction of (2) with HX yields the neutral hydrido-species $\text{HRu}_5\text{C}(\text{CO})_{15}\text{X}$.

Interestingly with triphenylphosphine two products (3) and (4) are obtained. Product (3) is unstable in the presence of excess of PPh_3 , being slowly converted into (4). X-Ray analysis[†] has established that (3) is $\text{Ru}_5\text{C}(\text{CO})_{14}\text{PPh}_3$, with a structure related to that of (2) by replacement of a basal CO ligand by PPh_3 (Figure 2). In the molecules of both (2) and (3) the carbido-atom lies slightly below the square base of metal atoms [0.11 \AA for (2) and 0.19 \AA for (3)] as has previously been observed in the square-pyramidal structures of $\text{Fe}_5\text{C}(\text{CO})_{15}$,⁶ $\text{Os}_5\text{C}(\text{CO})_{15}$,⁵ and $[\text{RhFe}_4\text{C}(\text{CO})_{14}]^-$.⁷

[‡] $\text{Ru}_5\text{C}(\text{CO})_{15}\text{I}_2$ has been characterised on the basis of elemental analysis, mass spectrometry, and i.r. spectroscopy.

¹ R. Pettit, 2nd International Symposium on Homogeneous Catalysis, Dusseldorf, 1980.

² B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 1970, 901; C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.

³ C. R. Eady, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Organomet. Chem.*, 1973, 57, C82.

⁴ I. Oxtan, personal communication.

⁵ P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 564.

⁶ E. H. Braye, L. F. Dahl, W. Hubel, and D. L. Wampler, *J. Am. Chem. Soc.*, 1962, 84, 4633.

⁷ M. Tachikawa, A. C. Sievert, E. L. Muetterties, M. R. Thompson, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1980, 102, 1726.

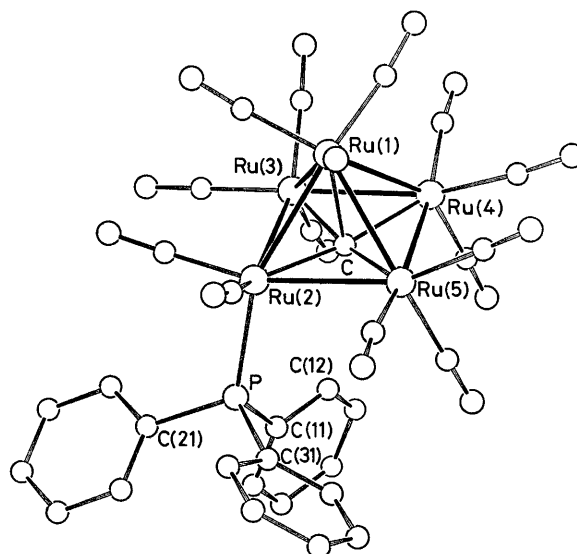


FIGURE 2. The structure of $\text{Ru}_5\text{C}(\text{CO})_{14}(\text{PPh}_3)$ (3). Important bond lengths (\AA) are: Ru(1)–Ru(2) 2.817, Ru(1)–Ru(3) 2.799, Ru(1)–Ru(4) 2.831, Ru(1)–Ru(5) 2.825, Ru(2)–Ru(3) 2.940, Ru(2)–Ru(5) 2.897, Ru(3)–Ru(4) 2.835, Ru(4)–Ru(5) 2.815, Ru(2)–P 2.376, Ru–C(carbido) 2.06 (mean), Ru–C(carbonyl) 1.89 (mean). Maximum e.s.d.s are: Ru–Ru 0.002, Ru–P 0.003, Ru–C 0.02 \AA . There is a short contact between a phenyl hydrogen atom and the carbido-atom, H(12)–C(carbido) 2.42 \AA .

Finally we note that $\text{Ru}_5\text{C}(\text{CO})_{15}$ does not undergo reaction with electrophilic reagents such as Me^+ , but does react with H^+ to generate $[\text{HRu}_5\text{C}(\text{CO})_{15}]^+$, in which the H^+ ion is associated with the metallic cluster rather than the carbido carbon atom which would appear to be carbo-cationic.

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