Cluster Chemistry. Stepwise Hydrogenation of an Acetylide Ligand to Carbon and Methyl on a Ru_5 Cluster. *X*-Ray Structures of [$Ru_5(\mu\text{-}H)(\mu_5\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$] and [$Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$]

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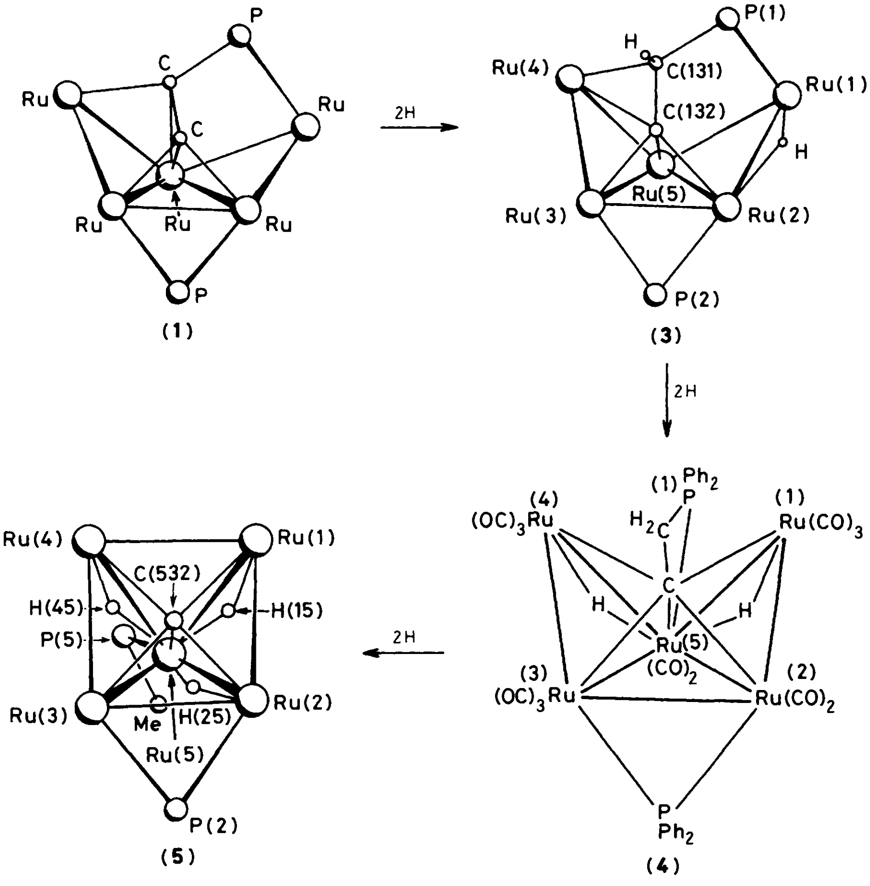
Hydrogenation of [$Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$] proceeds stepwise with absorption of three molecules of H_2 and successive formation of pentanuclear cluster complexes containing μ_5-vinylidene, -methylidyne, and -carbide ligands; the net reaction is an unusual conversion of the $\mu\text{-}C_2PPh_2$ ligand into carbon and $MePPh_2$.

We have recently described the synthesis of the open Ru_5 cluster complex [$Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$] (**1**),[1] and its reaction with CO under mild conditions, which led to cleavage of two Ru–Ru bonds within the Ru_5 cluster,[2] and with H_2 under 10 atm pressure.[3] The latter reaction resulted in elimination of one ruthenium atom and formation of a $P(C_2H)Ph_2$ ligand bonded to the remaining four metal atoms (**2**). We now report the unusual reactions that occur between (**1**) and hydrogen at normal pressure, which eventually result in a novel reduction of the acetylide ligand to carbon and methyl.

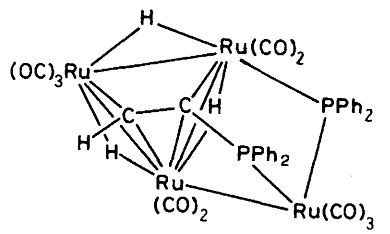
Passage of hydrogen into the black solution of (**1**) in refluxing cyclohexane resulted in a colour change to red. Preparative t.l.c. enabled three major products to be isolated in amounts which depended on the reaction time; trace amounts of [$Ru_4(\mu\text{-}H)_4(CO)_{12}$] and (**2**) were also formed.

$$C{\equiv}CPPh_2 + 3H \longrightarrow C + H_3CPPh_2$$



Scheme 1. *Selected bond distances*: [$Ru_5(\mu\text{-}H)(\mu_5\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$] (**3**): Ru(1)–Ru(2) 3.0729(7), Ru(1)–Ru(5) 2.9680(6), Ru(2)–Ru(3) 2.7805(7), Ru(2)–Ru(5) 2.7695(6), Ru(3)–Ru(4) 2.8139(6), Ru(3)–Ru(5) 2.8705(8), Ru(4)–Ru(5) 2.8397(7), Ru(1)–P(1) 2.388(1), Ru(2)–P(2) 2.326(1), Ru(3)–P(2) 2.284(1), Ru(2)–C(132) 2.175(4), Ru(3)–C(132) 2.014(3), Ru(4)–C(131) 2.175(4), Ru(4)–C(132) 2.187(4), Ru(5)–C(132) 2.162(4), C(131)–C(132) 1.436(5) Å.

[$Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$] (**5**): Ru(1)–Ru(2) 2.9170(6), Ru(1)–Ru(4) 2.9014(7), Ru(1)–Ru(5) 2.8934(6), Ru(2)–Ru(3) 2.7705(6), Ru(2)–Ru(5) 2.8347(5), Ru(3)–Ru(4) 2.8948(7), Ru(3)–Ru(5) 2.8820(6), Ru(4)–Ru(5) 2.8391(6), Ru(2)–P(2) 2.3094(10), Ru(3)–P(2) 2.3040(8), Ru(5)–P(5) 2.3408(8), Ru(1)–C(532) 2.022(3), Ru(2)–C(532) 2.065(2), Ru(3)–C(532) 1.971(3), Ru(4)–C(532) 2.060(2), Ru(5)–C(532) 2.075(2), Ru(1)–H(15) 1.79(3), Ru(2)–H(25) 1.88(3), Ru(4)–H(45) 1.92(3), Ru(5)–H(15) 1.77(5), Ru(5)–H(25) 1.73(3), Ru(5)–H(45) 1.72(3) Å.



(2)

Black $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ (**3**), dark red $[Ru_5(\mu\text{-}H)_2(\mu_5\text{-}CCH_2PPh_2)(CO)_{13}]$ (**4**), and orange $[Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)]$ (**5**) were isolated;† complex (**3**) was also made by successive addition of H^- ($K[HBBu^s_3]$) and H^+ (H_3PO_4) to (**1**), while (**5**) was also obtained by addition of hydrogen to (**3**) or (**4**). Complexes (**3**) and (**5**) have been fully characterised by single-crystal *X*-ray studies.‡

Complexes (**3**), (**4**), and (**5**) result from the successive addition of three molecules of dihydrogen to (**1**). Scheme 1 shows the heavy atom cores of (**1**), (**3**), and (**5**), together with the proposed structure of (**4**). It can be seen that little change has occurred in the metal cores of (**1**) and (**3**); of the added hydrogen atoms, one bridges the Ru(1)–Ru(2) bond, and the other is attached to C(131), thus converting the acetylide ligand in (**1**) into the unusual diphenylphosphinovinylidene ligand in (**3**). The vinylidene interacts in an η^2 fashion with Ru(4), while C(132) is within bonding distance of Ru(2), Ru(3), and Ru(5); P(1) is bonded to Ru(1) by a normal 2e covalent donor bond.

The metal skeleton in (**5**), on the other hand, forms a distorted square pyramid, which contains a carbido carbon, C(532), in the square base. It is thus a derivative of the well known $[Ru_5C(CO)_{15}]$. This carbon is the α-carbon of the acetylide ligand in (**1**), closure of the Ru_5 cluster resulting in cleavage of the C–C bond. The β-carbon is found as the methyl group of the $PMePh_2$ ligand attached to Ru(5). Co-ordination about the five ruthenium atoms is completed by the μ-PPh_2 group which bridges the Ru(2)–Ru(3) bond, the eleven CO ligands, and three metal-bonded hydrogen atoms, H(15,25,45), which bridge three of the apical Ru–basal Ru bonds.

The illustrated structure for (**4**) is consistent with the n.m.r. data;† a second hydrogen has added to the β-carbon of the acetylide to give a methylene group, while the two cluster-bound hydrogens are in similar environments. The cluster contains a diphenylphosphinomethylmethylidyne ligand, and resembles to a degree the functional methylidyne ligands in tetranuclear iron clusters.[5]

The successive transformations of (**1**) to (**3**), (**4**), and (**5**) are readily appreciated by reference to Scheme 1, which illustrates the pincer movement of the outer Ru atoms of the swallow Ru_5 cluster as they close and cleave the C–C unit of the μ-phosphinoacetylide ligand.

The normal course of hydrogenation of a C≡C bond is initial *cis*-addition, with eventual formation of the corresponding alkane. To our knowledge, two examples of similar reactions of cluster-bound acetylides have been reported: addition of H_2 to $HRu_3(\mu_3\text{-}C_2R)(CO)_9$ (R = Bu^t),[6] and the reaction of $Ru_5(\mu_4\text{-}C_2R)(\mu\text{-}PPh_2)(CO)_{13}$ (R = $CHMe_2$) with PH_2Ph,[7] both of which give complexes containing μ_3-CCH_2R ligands. Further reduction of the alkylidyne complexes afforded the alkane CH_3CH_2R in which the C_2 unit present in the original acetylide is preserved.

In contrast the conversion of (**4**) into (**5**), *which occurs with cleavage of the C–C bond*, is therefore unprecedented. It results from concomitant formation of strong metal–metal bonds and a stable carbido cluster complex. We recall that pyrolysis of $[Ru_5(\mu_5\text{-}CNBu^t)(CO)_{14}(CNBu^t)]$, which has the same metal core as (**1**),[8] afforded $[Ru_6C(CO)_{16}(CNBu^t)]$ by cleavage of the C–N bond in the bridging isocyanide ligand;[9] the well known formation of $[Ru_6C(CO)_{17}]$ from $[Ru_3(CO)_{12}]$ at 170 °C[10] is another example of this type of reaction.

We thank the Australian Research Grants Scheme for support of this work, undertaken when M.L.W. was a recipient of a Commonwealth Post-graduate Research Award.

Received, 29th January 1985; Com. 140

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† *Spectroscopic data:* (**3**) ν(CO) 2084m, 2064s, 2029s, 2016s, 2002m, 1992vw, 1979m, 1965w, and 1952w cm^{-1}; ^{1}H n.m.r.: δ ($CDCl_3$) 7.42 (m, 20H, Ph), 5.86 (d, J_{HP} 6.0 Hz, 1H, =CH), and −13.11 (dd, J_{HP} 13.8 and 21.5 Hz, 1H, RuH); (**4**) ν(CO) 2082m, 2058w, 2041m, 2028s, 2014(sh), 2004w, 1984m, and 1977m cm^{-1}; ^{1}H n.m.r.: δ ($CDCl_3$) 7.39 (m, 20H, Ph), 5.04 (m, 2H, CH_2), and −20.19 (dd, J_{HP} 6.9 and 12.0 Hz, 2H, RuH); (**5**) ν(CO) 2085s, 2055vs, 2032vs, 2020vs, 2002m, 1994w, 1989w, 1978m, and 1945w cm^{-1}; ^{1}H n.m.r.: δ ($CDCl_3$) 7.27 (m, 20H, Ph), 1.88 (d, J_{HP} 7.7 Hz, 3H, Me), −19.97 (m, 2H, RuH), and −22.50 (dq, J_{HH} 2.5 Hz, J_{HP} 17.9 Hz, 1H, RuH).

‡ *Crystal data:* (**3**), $[HRu_5(CCHPPh_2)(PPh_2)(CO)_{13}] \equiv C_{39}H_{22}O_{13}P_2Ru_5$, $M = 1265.9$, monoclinic, space group $P2_1/n$ (variant of $P2_1/c$, C^5_{2h}, No. 14), $a = 25.115(6)$, $b = 10.126(2)$, $c = 17.373(4)$ Å, $\beta = 109.88(2)°$, $U = 4155(2)$ Å^3, D_c ($Z = 4$) = 2.02 g cm^{-3}. Monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 17.6$ cm^{-1}. Specimen: 0.29 × 0.21 × 0.40 mm. $T = 295$ K. R 0.038 (R' 0.032) for 9411 unique 'observed' reflections [2θ–θ scan mode, $2\theta < 65°$, $I > 3\sigma(I)$, Syntex $P\bar{1}$ diffractometer]. Refinement was by 9 × 9 block-diagonal least-squares after Gaussian absorption correction and solution of structure by direct methods. All non-hydrogen atoms were given anisotropic thermal parameters; neutral complex scattering factors were used.[4]

(**5**), $[H_3Ru_5C(PPh_2)(CO)_{11}(P\underline{M}ePh_2)] \equiv C_{37}H_{26}O_{11}P_2Ru_5$, $M = 1213.9$, triclinic, space group $P1$ (C^1_i, No. 2), $a = 18.658(4)$, $b = 12.483(3)$, $c = 9.678(2)$ Å, $\alpha = 69.13(2)$, $\beta = 78.21(2)$, $\gamma = 73.19(2)°$, $U = 2003.8(8)$ Å^3, D_c ($Z = 2$) = 2.01 g cm^{-3}, $F(000) = 1172$. Monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 18.2$ cm^{-1}. Specimen: 0.06 × 0.30 × 0.30 mm. $T = 295$ K. R 0.026 (R' 0.029) for 10 214 unique 'observed' reflections (2θ–θ scan mode, $2\theta < 65°$, $I > 3\sigma(I)$, Syntex $P2_1$ diffractometer]. Refinement was carried out as for (**3**).

The atomic co-ordinates for 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.

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