

Coupling and disproportionation reactions of ethyne on ruthenium carbonyl clusters: molecular structures of $\text{Ru}_5(\mu_4\text{-CHCHCCH}_2)(\text{CO})_{15}$ and $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}^\dagger$

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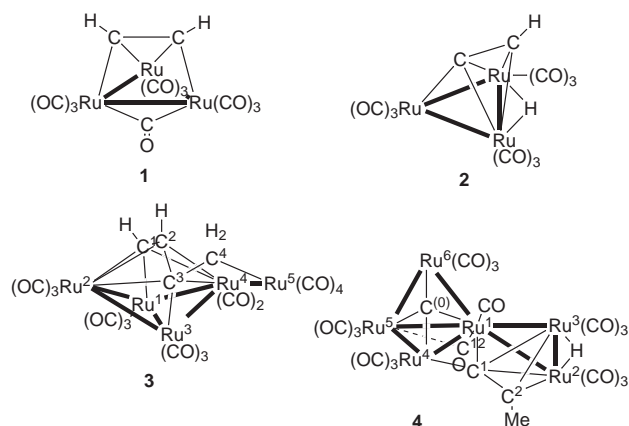
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Received 6th October 1998, Accepted 13th November 1998

Thermolysis of $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1** (50 °C, 6 h) has given $\text{Ru}_5(\mu_4\text{-CHCHCCH}_2)(\text{CO})_{15}$ **3** and $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ **4**, both characterised by X-ray crystallography; in **3**, coupling of two ethyne molecules occurred, likely with prior isomerisation of one to vinylidene, whereas in **4**, two molecules of ethyne disproportionate to carbide and methylethynyl.

Reactions of alkynes with ruthenium cluster carbonyls are rich sources of complexes with unusual structures.^{1,2} Reactions of the simplest alkyne, ethyne, with $\text{Ru}_3(\text{CO})_{12}$ have been known since the 1960s, when the carbonyl was used to catalyse the synthesis of hydroquinone from C_2H_2 , CO and H_2 .³ The complex $\text{Ru}_3(\text{CO})_{11}(\eta\text{-C}_2\text{H}_2)$, prepared from $\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}$ and ethyne at low temperatures,⁴ is converted to $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1** at room temperature. In turn, heating **1** in pen-



tane (bp 36 °C) for 1 h gave $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{H})(\text{CO})_9$ **2** in 91% yield.⁵ We have been interested to find reactions in which further coupling of the cluster-bonded alkyne or alkynyl ligands might occur. With this objective in mind, we examined the thermolysis of **1** in more detail.

When **1** (160 mg, 0.26 mmol) is heated in hexane (50 ml) at 50 °C for 6 h, only 78 mg (50%) of **2** is isolated. Other products, isolated in between 1 and 12% yield, include $\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$, $\text{Ru}_5(\mu_4\text{-CCH}_2)(\text{CO})_{15}$ and $\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\text{CO})_{16}$, containing either ethyne or its tautomer, vinylidene.⁶ The structures of two other complexes have special interest and form the subjects of this work. The complexes can be separated readily by preparative TLC (silica gel, hexane- C_6H_6 4:1). The complexes $\text{Ru}_5(\mu_4\text{-CHCHCCH}_2)(\text{CO})_{15}$ **3**[‡] and $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ **4**[‡] were isolated in 6–8% yields from the fractions with R_f 0.19 and 0.25, respectively. Both complexes were characterised by single-crystal X-ray structure determinations.[§]

Fig. 1 is a plot of a molecule of **3**, selected bond parameters being given in the caption. The cluster core is a C_3Ru_4 pentagonal bipyramid, one carbon of which is linked *via* a CH_2

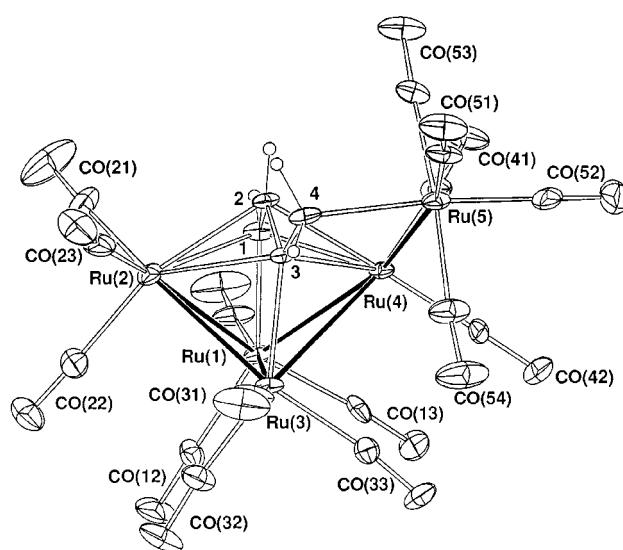


Fig. 1 Plot of a molecule of $\text{Ru}_5(\mu_4\text{-CHCHCCH}_2)(\text{CO})_{15}$ **3** showing atom numbering scheme. Bond lengths: Ru(1)–Ru(2) 2.834(3), Ru(1)–Ru(3) 2.807(3), Ru(1)–Ru(4) 2.849(2), Ru(2)–Ru(3) 2.782(3), Ru(3)–Ru(4) 2.874(2), Ru(4)–Ru(5) 2.815(2), Ru(1)–C(1) 2.09(1), Ru(2)–C(1,2,3) 2.24(2), 2.20(2), 2.45(2), Ru(3)–C(3) 2.13(1), Ru(4)–C(1,2,3) 2.25(2), 2.23(2), 2.24(2), Ru(5)–C(4) 2.17(2), C(1)–C(2) 1.43(2), C(2)–C(3) 1.43(2), C(3)–C(4) 1.47(2) Å. Bond angles: C(1)–C(2)–C(3) 121(1), C(2)–C(3)–C(4) 117(1), Ru(5)–C(4)–C(3) 98(1), Ru(4)–Ru(5)–C(4) 78.7(4)°.

group to the fifth Ru atom, which is also bonded to Ru(4). Atoms Ru(1,2,3) each have three terminal CO ligands; the $\text{Ru}(5)(\text{CO})_4$ group takes the place of the third CO group on Ru(4) [angles Ru(3)–Ru(4)–Ru(5) 94.42(8), Ru(1)–Ru(4)–C(41) 112.6(6)°]. Atoms Ru(1,3) are σ -bonded to C(1) and C(3), respectively; the strain inherent in the four-membered C(3)–C(4)–Ru(5)–Ru(4) ring is evidenced by the internal angle at C(4) being only 98(1)°. Three carbons C(1,2,3) of the organic ligand are coplanar with Ru(1) and Ru(3) and interact equally with Ru(2) and Ru(4) in a π -type bond. This cluster is best described as an Ru-spiked Ru_4C_3 system with 76 cluster valence electrons (c.v.e.).

A plot of **4** is given in Fig. 2, the caption containing selected bond parameters. In this hexanuclear cluster, the Ru_6 core can be described as a butterfly, to a hinge atom of which an Ru_2 unit is attached. The cleft of the butterfly carries a carbon atom and the hinge vector is bridged by a CO ligand. This structural feature has been described previously in $\text{Ru}_4\text{C}(\mu\text{-CO})(\text{CO})_{12}$ ⁷ and comparable structural parameters are similar. Apart from Ru(1), which has only one CO, all Ru atoms carry three terminal CO ligands. The Ru(2)–Ru(3) vector is bridged by a hydrogen atom, but as found in other hydrido-alkynyl Ru_3 complexes, is not particularly lengthened as a result. The $\mu_4\text{-CCMe}$ is bonded to Ru(1) and Ru(4) *via* C(1) and to Ru(2,3) *via* both carbons. As judged by the C(1)–C(2) separation of

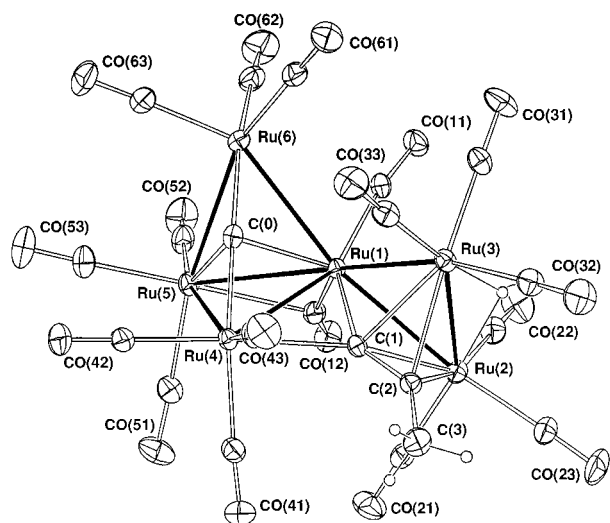


Fig. 2 Plot of a molecule of $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_3\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ **4** showing atom numbering scheme. Bond lengths: Ru(1)–Ru(2) 2.8303(8), Ru(1)–Ru(3) 2.8076(8), Ru(1)–Ru(4) 2.8341(7), Ru(1)–Ru(5) 2.7543(7), Ru(1)–Ru(6) 2.8272(7), Ru(2)–Ru(3) 2.7819(9), Ru(4)–Ru(5) 2.8373(8), Ru(5)–Ru(6) 2.8258(8), Ru(1)–C(0) 2.123(4), Ru(4)–C(0) 1.955(4), Ru(5)–C(0) 2.144(5), Ru(6)–C(0) 1.911(4), Ru(1)–C(1) 2.027(4), Ru(2)–C(1) 2.304(5), Ru(2)–C(2) 2.143(5), Ru(3)–C(1) 2.251(5), Ru(3)–C(2) 2.247(5), Ru(4)–C(1) 2.297(4), C(1)–C(2) 1.308(6) Å. Bond angles: Ru(1)–C(0)–Ru(5) 80.4(2), Ru(4)–C(0)–Ru(6) 174.9(3), Ru(4)–C(1)–C(2) 135.5(4), C(1)–C(2)–C(3) 136.6(5)°.

1.308(6) Å and the angle C(1)–C(2)–C(3) of 136.6(5)°, this ligand is a μ_4 -alkynyl group, similar to that found in $\text{Ru}_3\text{Pt}(\mu\text{-H})(\mu_4\text{-C}_2\text{Bu}^t)(\text{CO})_9(\text{dppe})$, for example.⁸ The c.v.e. count is 90.

The spectroscopic properties of **3** and **4** are consistent with their solid-state structures. Their IR $\nu(\text{CO})$ spectra contain respectively ten and eleven terminal CO absorptions, while a band at 1887 cm^{-1} in the spectrum of **4** is assigned to the bridging CO ligand. In the ^1H NMR spectrum of **3**, no high-field signals were detected; signals at δ 5.84, 9.64 and at 3.01 and 4.12 were assigned to protons in C(1) and C(2) and to the CH_2 group, respectively. For **4**, the Me resonance is at δ 1.65, while a singlet at δ –19.3 confirms the presence of the cluster-bound hydride.

The organic ligands in **3** and **4** are formed by coupling of two C_2H_2 ligands of the original complex **1**, with concomitant cluster expansion and hydrogen migration from C(3) to C(4). In **3**, the latter process is reminiscent of the common alkyne to vinylidene isomerisation that is widespread in mononuclear and cluster chemistry. For example, conversion of ethyne to vinylidene on an Os_3 cluster has been described by Deeming.⁹ Subsequent cluster-mediated coupling of the vinylidene with ethyne would give the C_4 ligand. The course of this reaction is not obvious, dimerisation of the Ru_3 cluster being accompanied by considerable rearrangement and loss of one ruthenium atom. The formation of **4** requires a more fundamental change, three of the four hydrogens of two ethyne molecules ending up on the same carbon atom [C(3)], while the fourth is attached to the cluster. Further, disproportionation of the two alkynes, an uncommon process on Group 8 carbonyl clusters, results in formation of the novel carbido cluster. This reaction may be related to the cleavage of alkynes by $\text{Co}_3(\mu_3\text{-CO})_2\text{Cp}_3$, for example.¹⁰

In conclusion, we have demonstrated the occurrence of two novel reactions of ethyne on an Ru_3 cluster leading to com-

plexes containing acyclic C_4 (in **3**) or carbide and methylethynyl ligands (in **4**) which do not have counterparts in the chemistry of mono- or di-substituted alkynes on Group 8 metal carbonyl clusters.

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey plc, Reading, for a generous loan of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$.

Notes and references

† Dedicated to Warren Roper on the occasion of his 60th birthday, in recognition of his outstanding contributions to organometallic chemistry.

‡ Selected spectroscopic data. For **3**. IR (cyclohexane): $\nu(\text{CO})$ 2116w, 2079m, 2057m, 2049s, 2041s, 2033s, 2017m, 2010m, 1986w (br), 1953w cm^{-1} . ^1H NMR (CDCl_3): δ 3.01 [d, 1H, $J(\text{HH})$ 7, CH_2], 4.12 [d, 1H, $J(\text{HH})$ 7, CH_2], 5.84 [d, 1H, $J(\text{HH})$ 5.4 Hz, CH], 9.64 (d, 1H, CH). For **4**. IR (cyclohexane): $\nu(\text{CO})$ 2081s, 2077s, 2072m, 2062vs, 2047m, 2036m, 2027m, 2019m, 1992w, 1985w, 1945w (br), 1887w (br) cm^{-1} . ^1H NMR (CDCl_3): δ –19.3 (s, 1H, RuH), 1.65 (s, 3H, Me).

§ Crystal data for **3**: red crystal, $\text{Ru}_5(\mu_4\text{-CHCHCCH}_2)(\text{CO})_{15}$ **3** \equiv $\text{C}_{15}\text{H}_4\text{O}_{15}\text{P}_2\text{Ru}_5$, $M = 977.6$, monoclinic, space group $P2_1/c$, $a = 11.517(8)$, $b = 14.792(11)$, $c = 16.503(18)$ Å, $\beta = 113.41(7)^\circ$, $V = 2580$ Å³, $Z = 4$, $\rho_c = 2.516$ g cm^{-3} , $F(000) = 1832$. Crystal dimensions: $0.05 \times 0.24 \times 0.32$ mm, $\mu(\text{Mo-K}\alpha) = 29.3$ cm^{-1} , A^* (min, max) = 1.15, 1.96. $N = 4511$, N_o [$I > 3\sigma(I)$] = 3179; $R = 0.061$, $R_w = 0.067$.

For **4**: dark red crystal, $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ (**4**) \equiv $\text{C}_{21}\text{H}_4\text{O}_{17}\text{Ru}_6$, $M = 1134.7$, monoclinic, space group $C2/c$, $a = 34.595(9)$, $b = 9.534(2)$, $c = 19.461(4)$ Å, $\beta = 108.97(2)^\circ$, $V = 6070$ Å³, $Z = 8$, $\rho_c = 2.483$ g cm^{-3} , $F(000) = 4240$. Crystal dimensions: $0.08 \times 0.58 \times 0.23$ mm, $\mu(\text{Mo-K}\alpha) = 29.8$ cm^{-1} , A^* (min, max) = 1.26, 1.81. $N = 5329$, N_o [$I > 3\sigma(I)$] = 4521; $R = 0.027$, $R_w = 0.031$.

Unique diffractometer data sets were measured at ca. 295 K to $2\theta_{\text{max}} = 50^\circ$ (CAD4 diffractometer, 2θ – θ scan mode; monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å); N independent reflections were obtained N_o being considered 'observed' and used in the full-matrix least squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x , y , z , $U_{\text{iso}}(\text{H})$) were included constrained at estimated values for **3** and refined in **4**. The precision of the determination for **3** was adversely affected by the use of a split crystal. CCDC reference number 186/1245. See <http://www.rsc.org/suppdata/dt/1999/13/> for crystallographic files in .cif format.

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Communication 8/077811