

Reactions of $\text{Ru}_5(\mu_5\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}$ with disubstituted alkynes C_2R_2 ($\text{R} = \text{Me}, \text{Ph}$)

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Reaction of the dicarbon-containing complex $\text{Ru}_5(\mu_5\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}$ **1** with diphenylethyne gave as major products $\text{Ru}_5(\mu_5\text{-CCCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}$ **2** and $\text{Ru}_5(\mu_5\text{-CCPhCPh})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ **3**. The only product from the reaction between **1** and but-2-yne was identified as $\text{Ru}_5(\mu_5\text{-CCMeCMe})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ **4**. Pyrolysis of **2** gave **3**. Carbonylation of **3** yields the complex $\text{Ru}_5(\text{CCCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}$ **5**, further heating of which regenerated a mixture of **2** and **3**. The structures of **2** and **3** were determined from single crystal X-ray studies. The Ru_5 clusters in both complexes adopt the open-envelope conformation, the Ru_4 rhombus being planar in **2**, but bent across the $\text{Ru}(3) \cdots \text{Ru}(5)$ diagonal by 39.6° in **3**. The organic ligand is formed by coupling of the C_2 group in **1** with the alkyne and is attached by three of the four carbons in **2** and by all four in **3**, atom C(1) being strongly attached to the Ru_4 rhombus. In **3**, atoms C(1,2,3,4) have an η^4 interaction with $\text{Ru}(4)$.

Introduction

We have described the synthesis of the dicarbon-containing cluster complex $\text{Ru}_5(\mu_5\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}$ (**1**; Scheme 1) by pyrolysis of $\{\text{Ru}_3(\text{CO})_{11}\}_2\{\mu\text{-C}_2(\text{PPh}_2)_2\}$ to give $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$,¹ followed by treatment with Me_2S_2 .² This complex exhibits a wide range of fascinating chemistry, most of which has been summarised earlier.^{3,4} The main features of its reactivity have been rationalised by extended Hückel calculations, the major conclusion being that the electron density on C(2) directs electrophilic attack on the C_2 ligand.⁵ Unlike clusters containing encapsulated carbon atoms, such as $\text{Ru}_5\text{C}(\text{CO})_{15}$ or $\text{Ru}_6\text{C}(\text{CO})_{17}$, in which the carbon atom is relatively unreactive, the exposed situation of the C_2 ligand results in its entering into many reactions, particularly with unsaturated substrates. We have made an extensive study of the reactions of **1** with alkynes, the results of which we now report. This paper will describe several complexes which we have obtained from reactions involving the disubstituted alkynes C_2R_2 ($\text{R} = \text{Me}, \text{Ph}$), two of which have been structurally characterised, amplifying a preliminary communication.⁶

Results

The reaction between **1** and diphenylethyne was carried out in toluene at 100°C for 7 h. Two complexes were isolated from the reaction mixture by preparative TLC. Both formed black crystals which were identified as $\text{Ru}_5(\mu_5\text{-CCCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}$ **2** and $\text{Ru}_5(\mu_5\text{-CCCPhCPh})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ **3** (the faster moving) by single crystal X-ray structure determinations. An independent experiment showed that **2** was converted into **3** on heating in refluxing toluene for 16 h. The IR spectra (Table 1) of both complexes contained only terminal $\nu(\text{CO})$ absorptions. In the ^1H NMR spectrum of **2**, doublet and singlet resonances at δ 1.68 and 2.16, respectively, were assigned to the SMe groups. In the ^{13}C NMR spectrum, singlets at δ 23.62 and 23.72 were also assigned to these groups. The four carbons of the CCCPhCPh chain of the organic ligand were found at δ 325.81, 265.13, 179.52 and 159.97, respectively. The very low field resonance assigned to C(1) is consistent with its having considerable carbidic char-

acter, while the low-field chemical shift of C(2) is similarly the result of shielding by the five metal atoms. In **3**, doublet resonances are found for both SMe groups at δ 1.32 and 2.55 (^1H NMR), with singlets at δ 17.23 and 27.50 in the ^{13}C NMR spectrum showing considerably larger separation than found for **2**, as expected for the μ - and μ_3 -ligands. Resonances at δ 207.80, 180.27, 165.23 and 106.31, respectively, are assigned to the carbons of the CCCPhCPh chain, C(1) showing much lower shielding than found in **2**. The CO ligands gave rise to resonances between δ 193 and 206 in both complexes.

Only one product could be isolated from the reaction between **1** and but-2-yne, namely $\text{Ru}_5(\mu_5\text{-CCMeCMe})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ **4**, which was obtained in 41% yield. Its spectral properties were similar to those of **3**, with the addition of the two inequivalent CMe resonances at δ 2.00 and 2.24 (^1H) and 15.68 and 32.79 (^{13}C) in its NMR spectra. We therefore assign an analogous structure to this complex.

Molecular structures of **2** and **3**

Figs. 1 and 2 show plots of molecules of the two complexes. Significant structural parameters are given in Table 2. Both complexes contain Ru_5 clusters with open envelope conformations, although in **3**, a significant bending of the rhomboidal part occurs about the $\text{Ru}(1) \cdots \text{Ru}(3)$ vector.

(a) $\text{Ru}_5(\mu_5\text{-CCCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}$ **2**. In **2**, the Ru_5 cluster has an open envelope conformation, with the four basal ruthenium atoms $\text{Ru}(1,2,3,4)$ being co-planar [$\chi^2 = 2839$, $\delta(\text{Ru})$ all $\pm 0.032(1)$ Å]. The internal dihedral angle between the basal plane and the flap of the envelope is $118.91(4)^\circ$. The Ru–Ru separations range between 2.697(2) and 2.944(2) Å (average 2.84 Å), the shortest being the $\text{Ru}(4)$ – $\text{Ru}(5)$ vector which is bridged by P(2) and C(2). Atom $\text{Ru}(4)$ is also involved in the two longest bonds to $\text{Ru}(1)$ and $\text{Ru}(3)$, neither of which is bridged by the P or S ligands; the former is the hinge of the envelope flap. Four of the Ru–Ru vectors are alternately bridged by the P and S atoms, the two PPh_2 groups bridging $\text{Ru}(1)$ – $\text{Ru}(2)$ and $\text{Ru}(4)$ – $\text{Ru}(5)$ and the two SMe groups bridging $\text{Ru}(1)$ – $\text{Ru}(5)$ and $\text{Ru}(2)$ – $\text{Ru}(3)$. Each Ru atom carries two terminal CO groups.

Table 1 Analytical and spectroscopic data

Complex, analysis and MS	IR $\nu(\text{CO})/\text{cm}^{-1}$	NMR, δ (J/Hz)
2 $\text{Ru}_5(\mu_5\text{-CCCPPhCPh})(\mu\text{-SMe})_2\text{-}(\mu\text{-PPh}_2)_2(\text{CO})_{10}$ Found: C, 41.98; H, 2.61. $\text{C}_{52}\text{H}_{36}\text{O}_{10}\text{P}_2\text{Ru}_5\text{S}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 42.19; H, 2.49%; M, 1454 FAB MS: 1454, M^+ ; 1426–1174, $[\text{M} - n\text{CO}]^+$ ($n = 1\text{--}10$)	2046w, 2030vs, 2019s, 2008s, 1997m, 1990w, 1983w, 1966m, 1953w	^1H NMR: 1.68 (3H, d, J_{HP} 0.4, SMe), 2.16 (3H, s, SMe), 6.81–7.97 (30H, m, Ph) ^{13}C NMR: 23.62 (s, SMe), 23.72 (s, SMe), 124.47–133.30 (m, Ph), 140.61 [s, <i>ipso</i> C(CPh)], 140.66 [d, J_{CP} 37.4, <i>ipso</i> C(PPh)], 142.16 [d, J_{CP} 26.8, <i>ipso</i> C(PPh)], 144.42 [d, J_{CP} 26.6, <i>ipso</i> C(PPh)], 145.35 [d, J_{CP} 26.7, <i>ipso</i> C(PPh)], 151.15 [s, <i>ipso</i> C(CPh)], 159.97 (s, CCCPhCPh), 179.52 (s, CCCPhCPh), 186.90 (d, J_{CP} 4.2, CO), 192.96 (d, J_{CP} 7.1, CO), 194.15 (d, J_{CP} 6.8, CO), 194.36 (s, CO), 195.82 (d, J_{CP} 3.7, CO), 197.16 (d, J_{CP} 8.7, CO), 198.76 (s, CO), 206.02 (s, CO), 206.43 (s, CO), 265.13 (s, CCCPhCPh), 325.81 (dd, J_{CP} 9.5, 4.6, CCCPhCPh)
3 $\text{Ru}_5(\mu_5\text{-CCPhCPh})(\mu_3\text{-SMe})\text{-}(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ Found: C, 43.01; H, 2.55. $\text{C}_{51}\text{H}_{36}\text{O}_9\text{P}_2\text{Ru}_5\text{S}_2$ requires C, 43.30; H, 2.34%; M, 1426 FAB MS: 1426, M^+ ; 1398–1174, $[\text{M} - n\text{CO}]^+$ ($n = 1\text{--}9$)	2040w, 2026vs, 2015vs, 2003s, 1980m, 1976m, 1967m, 1938m	^1H NMR: 1.32 (3H, d, J_{HP} 2.6, SMe), 2.55 (3H, d, J_{HP} 1.8, SMe), 6.72–7.86 (30H, m, Ph) ^{13}C NMR: 17.23 (s, SMe), 27.50 (s, SMe), 106.31 (d, J_{CP} 4.7, CCCPhCPh), 126.67–134.09 (m, Ph), 135.50 [d, J_{CP} 27.6, <i>ipso</i> C(PPh)], 140.80 [d, J_{CP} 37.0, <i>ipso</i> C(PPh)], 141.76 [d, J_{CP} 34.2, <i>ipso</i> C(PPh)], 144.59 [d, J_{CP} 34.4, <i>ipso</i> C(PPh)], 148.79 [s, <i>ipso</i> C(CPh)], 165.23 (s, CCCPhCPh), 180.27 (d, J_{CP} 4.5, CCCPhCPh), 193.75 [t (2 overlapping d), J_{CP} 8.1, 2 \times CO], 195.54 (d, J_{CP} 7.0, CO), 196.82 (s, CO), 196.95 (d, J_{CP} 10.0, CO), 201.04 (s, CO), 201.82 (d, J_{CP} 5.4, CO), 202.07 (s, CO), 205.04 (d, J_{CP} 11.1, CO), 207.80 (d, J_{CP} 2.5, CCCPhCPh)
4 $\text{Ru}_5(\mu_5\text{-CCMeCMe})(\mu_3\text{-SMe})\text{-}(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$ Found: C, 37.88; H, 2.48. $\text{C}_{41}\text{H}_{32}\text{O}_9\text{P}_2\text{Ru}_5\text{S}_2$ requires C, 37.86; H, 2.47%; M, 1301 FAB MS: 1301, M^+ ; 1273–1049, $[\text{M} - n\text{CO}]^+$ ($n = 1\text{--}9$)		^1H NMR: 1.37 (3H, d, J_{HP} 3.0, SMe), 2.00 [3H, s(br), CMe], 2.24 [3H, s(br), CMe], 2.40 (3H, d, J_{HP} 2.3, SMe), 7.12–7.76 (20H, m, Ph) ^{13}C NMR: 15.68 (s, CMe), 17.65 (s, SMe), 27.67 (s, SMe), 32.79 (s, CMe), 99.32 (d, J_{CP} 5.1, CCMcCMe), 127.43–134.53 (m, Ph), 136.51 (d, J_{CP} 28.5, <i>ipso</i> C), 140.36 (d, J_{CP} 35.6, <i>ipso</i> C), 142.82 (d, J_{CP} 33.4, <i>ipso</i> C), 145.33 (d, J_{CP} 33.5, <i>ipso</i> C), 163.17 (s, CCMcCMe), 180.63 (d, J_{CP} 4.8, CCMcCMe), 192.72 (d, J_{CP} 8.1, CO), 193.61 (d, J_{CP} 8.2, CO), 195.80 (d, J_{CP} 7.5, CO), 196.39 (s, CO), 197.41 (d, J_{CP} 8.4, CO), 201.49 (s, CO), 202.66 (d, J_{CP} 5.0, CO), 203.13 (s, CO), 205.28 (d, J_{CP} 9.7, CO), 206.34 (d, J_{CP} 4.5, CCMcCMe)
5 $\text{Ru}_5(\text{CCCPhCPh})(\mu\text{-SMe})_2\text{-}(\mu\text{-PPh}_2)_2(\text{CO})_{11}$ Found: C, 43.00; H, 2.45. $\text{C}_{35}\text{H}_{36}\text{O}_{11}\text{P}_2\text{Ru}_5\text{S}_2$ requires C, 42.93; H, 2.46%; M, 1482 FAB MS: 1482, M^+	2088m, 2039vs, 2022vs, 2005s, 1997m, 1972m, 1965m, 1948m, 1937vw, 1923w	^1H NMR: 1.36 (3H, s, SMe), 2.26 (3H, d, J_{HP} 3.0, SMe), 5.24 (1.4H, s, 0.7 CH_2Cl_2), 6.97–7.94 (30H, m, Ph) ^{13}C NMR: 21.74 (t, J_{CP} 3.3, SMe), 26.35 (s, SMe), 125.50–135.21 (m, Ph), 133.35 [s(br), CCCPhCPh], 137.47 [s, <i>ipso</i> C(CPh)], 139.34 [d, J_{CP} 17.0, <i>ipso</i> C(PPh)], 141.25 [d, J_{CP} 37.9, <i>ipso</i> C(PPh)], 141.62 [d, J_{CP} 17.0, <i>ipso</i> C(PPh)], 147.13 [d, J_{CP} 16.9, <i>ipso</i> C(PPh)], 151.44 (s, CCCPhCPh), 178.48 (d, J_{CP} 11.2, CO), 179.25 (d, J_{CP} 3.3, CCCPhCPh), 187.72 (s, CO), 188.80 (s, CO), 189.85 (d, J_{CP} 7.9, CO), 190.09 (d, J_{CP} 7.6, CO), 190.48 (d, J_{CP} 10.2, CO), 194.99 (s, CO), 197.39 (d, J_{CP} , CO), 199.36 (s, CO), 199.71 (d, J_{CP} 5.9, CO), 203.52 (s, CO), 203.98 (d, J_{CP} 9.7, CO), 207.64 (t, J_{CP} 6.8, CO), 343.75 (d, J_{CP} 8.3, CCCPhCPh)

Table 2 Selected bond distances (Å) and angles (°) for **2** and **3**

	2	3		2	3
Ru(1)–Ru(2)	2.883(1)	3.113(2)	Ru(5)–P(2)	2.347(3)	2.218(4)
Ru(1)–Ru(4)	2.944(2)		Ru(1)–C(1)	2.218(8)	2.43(1)
Ru(1)–Ru(5)	2.833(1)	3.149(2)	Ru(1)–C(2)		2.10(1)
Ru(2)–Ru(3)	2.780(2)	2.908(2)	Ru(2)–C(1)	2.134(8)	2.14(1)
Ru(2)–Ru(5)	2.975(2)	2.975(2)	Ru(3)–C(1)	2.123(9)	2.13(1)
Ru(3)–Ru(4)	2.928(1)	2.773(2)	Ru(3)–C(4)	2.117(8)	2.10(1)
Ru(4)–Ru(5)	2.697(2)	2.907(1)	Ru(4)–C(1)	2.129(8)	2.30(1)
Ru(1)–S(1)	2.418(3)	2.413(4)	Ru(4)–C(2)	2.203(9)	2.35(1)
Ru(2)–S(2)	2.418(3)	2.388(4)	Ru(4)–C(3)		2.35(1)
Ru(3)–S(2)	2.454(3)	2.452(3)	Ru(4)–C(4)		2.33(1)
Ru(5)–S(1)	2.393(3)	2.397(3)	Ru(5)–C(1)		2.21(1)
Ru(5)–S(2)		2.368(4)	Ru(5)–C(2)	2.108(7)	
Ru(1)–P(1)	2.335(3)	2.317(4)	C(1)–C(2)	1.42(1)	1.35(1)
Ru(2)–P(1)	2.266(3)	2.351(4)	C(2)–C(3)	1.48(1)	1.45(1)
Ru(4)–P(2)	2.289(2)	2.354(3)	C(3)–C(4)	1.36(1)	1.44(2)
C(1)–Ru(3)–C(4)	79.2(3)	76.0(4)	Ru(3)–C(1)–C(2)	106.9(6)	118.0(8)
Ru(1)–C(1)–Ru(3)	141.1(4)		Ru(4)–C(1)–C(2)	73.7(5)	75.1(7)
Ru(2)–C(1)–Ru(4)	144.4(4)	154.2(6)	Ru(5)–C(1)–C(2)		120.6(9)
Ru(3)–C(1)–Ru(5)		107.6(5)	Ru(5)–C(2)–C(1)	109.7(5)	
Ru(1)–C(1)–C(2)	107.3(5)	59.4(6)	C(1)–C(2)–C(3)	117.2(7)	115(1)
Ru(1)–C(2)–C(1)		87.0(7)	C(2)–C(3)–C(4)	112.7(7)	113.6(9)
Ru(2)–C(1)–C(2)	142.0(6)	130.6(9)	C(3)–C(4)–Ru(3)	115.1(6)	116.3(7)
Internal interplanar angles:					
For 2 : Ru(1,2,3,4)/Ru(1,4,5)		118.91(4)			
For 3 : Ru(1,2,5)/Ru(2,3,5)		107.93(4)			
		Ru(2,3,5)/Ru(3,4,5)			140.40(4)

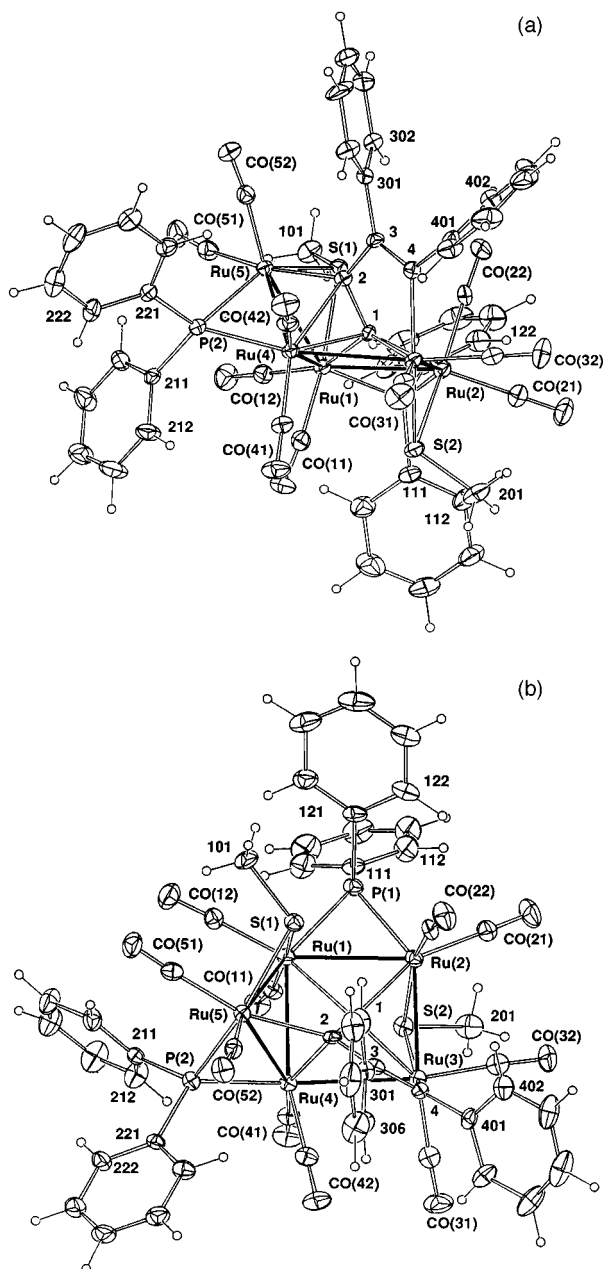


Fig. 1 Plots of a molecule of $\text{Ru}_5(\mu_5\text{-CCPhCPh})(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}$, **2**, (a) oblique to and (b) normal to the Ru_4 plane, showing the atom numbering scheme. In this and Fig. 2, non-hydrogen atoms are shown as 20% thermal ellipsoids, hydrogen atoms have arbitrary radii of 0.1 Å.

The organic ligand has been formed by coupling of the alkyne with the C_2 ligand, forming new C(2)–C(3) and C(4)–Ru(3) bonds, to generate a five-membered metallacycle. Of the four carbons, C(1) is tightly bound to the four basal Ru atoms [Ru(1,2,3,4)–C(1) 2.218(8), 2.134(8), 2.123(9), 2.129(8) Å] and C(2) bridges the Ru(4)–Ru(5) vector [Ru(4,5)–C(2) 2.203(9), 2.108(7) Å]. Atoms C(1)–C(2) are thus asymmetrically bonded to Ru(4). Atoms C(3) and C(4) form a C=C double bond [1.36(1) Å] which is not co-ordinated to the cluster and there is a σ -bond between Ru(3) and C(4) [2.117(8) Å]. The short C(1)–C(2) separation [1.42(1) Å] suggests some degree of multiple bond character here also.

The cluster valence electron (c.v.e.) count is 78 [5Ru (40) + 10CO (20) + 2SMe (6) + 2PPh₂ (6) + the organic ligand (6)], as expected for an M_5 cluster with six M–M bonds.⁷

(b) $\text{Ru}_5(\mu_5\text{-CCPhCPh})(\mu_3\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$, **3.** In **3**, the Ru_4 rhomboid is bent about the Ru(3)⋯Ru(5) diagonal

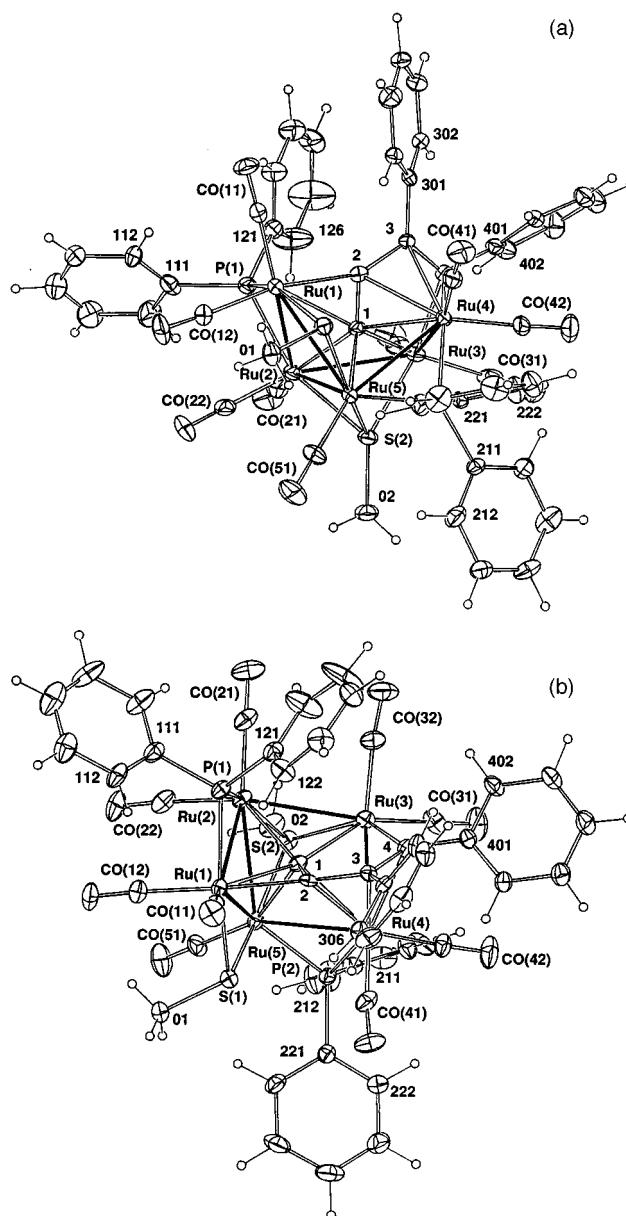
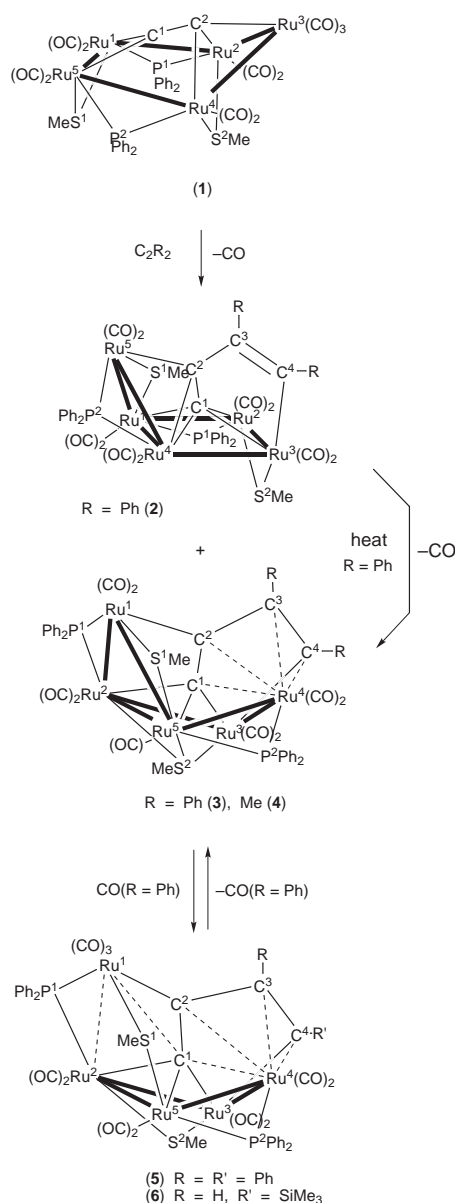


Fig. 2 Plots of a molecule of $\text{Ru}_5(\mu_5\text{-CCPhCPh})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_9$, **3**, (a) oblique to and (b) normal to the Ru_4 planes, showing the atom numbering scheme.

[internal interplanar angle Ru(2,3,5)/Ru(3,4,5) 140.40(4)°, while the flap is open by 107.93(4)°. The Ru–Ru separations are between 2.773(2) and 3.149(2) Å (average 2.971 Å, *ca.* 0.13 Å longer than in **2**). Two bonds are longer than 3.0 Å, namely those from Ru(1) to Ru(2) and Ru(5) forming the flap of the envelope, while the shortest is Ru(3)–Ru(4). The two PPh₂ groups bridge Ru(1)–Ru(2) and Ru(4)–Ru(5) and a $\mu\text{-SMe}$ group bridges Ru(1)–Ru(5). In contrast to **2**, the second SMe group adopts a μ_3 bridging mode, being attached to atoms Ru(2), Ru(3) and Ru(5). Comparison of the bridging PPh₂ and SMe ligands in **2** and **3** shows that the common asymmetry of the former bridges is reversed: the shorter Ru–P bonds are Ru(2)–P(1), Ru(4)–P(2) in **2** and Ru(1)–P(1), Ru(5)–P(2) in **3**. However, the direction of the S(1)Me bridge is the same in both complexes.

All four carbons of the organic ligand have an η^4 π -type interaction with Ru(4) [Ru(4)–C(1,2,3,4) 2.30–2.35(1) Å]. Atom C(1) also bonds to the three other Ru atoms of the Ru_4 rhombus [Ru(2,3,5)–C(1) 2.14, 2.13, 2.21(1) Å], with possibly a very weak interaction with Ru(1) [2.43(1) Å]. The C(1)–C(2) separation is shorter [at 1.35(1) Å] than that found in **2**. Each



Scheme 1

Ru atom carries two terminal CO groups except Ru(5), which has only one.

The c.v.e. count for this complex is 80 [5Ru (40) + 9CO (18) + 2SMe (8; $\mu_2 = 3$; $\mu_3 = 5$) + 2PPh₂ (6) + the organic ligand (8)]. This is two more than found for **2**, in spite of the loss of a CO ligand, since one SMe group is now μ_3 and the organic ligand uses the C(3)–C(4) multiple bond in its attachment to the cluster. The extra electron density is accommodated in M–M anti-bonding orbitals, leading to lengthening of the two bonds between Ru(1) and Ru(4) or Ru(5) to over 3.0 Å in **3**. This feature is now becoming common for clusters containing bridging SR or PR₂ groups and has been fully considered elsewhere in a theoretical treatment of Ru₃{ μ_3 -PPh(C₅H₄N)}(μ -PPh₂)₃(CO)₆.⁸

Whereas heating **2** in toluene (4 h, 110 °C) with a CO purge resulted in no change being found, carbonylation of **3** gave the yellow complex formulated as Ru₅(CCCPhCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁ **5**. Brief heating of **5** in refluxing toluene gave a mixture of **2** and **3**. The new complex is assigned the structure shown in Scheme 1 on the basis of close resemblances of its ν (CO) and NMR spectra (Table 1) to those of the structurally characterised complex Ru₅{ μ_5 -CCCHC(SiMe₃)}(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁ **6** which was obtained from a similar reaction of Ru₅{ μ_5 -CCCHC(SiMe₃)}(μ -SMe)₂(μ -PPh₂)₂(CO)₁₀ **7** with

CO.⁹ Both complexes show eight medium to strong ν (CO) bands, of which the strong bands at 2039, 2022, 2005 and 1997 cm⁻¹ in **5** compare directly with those at 2038, 2020, 2008 and 1997 cm⁻¹ for **6**; both complexes also show a characteristic high energy absorption around 2085 cm⁻¹, not found in any other product. The SMe resonances are also characteristic: the proton resonances at δ 1.36s and 2.26d in **5** are comparable with signals at δ 1.07s and 2.25d in **6**. In the ¹³C NMR spectrum of **5**, a triplet splitting of the resonance at δ 21.74 suggests that it should be assigned to the SMe group bridging Ru(1)–Ru(5), both metal atoms being bonded to phosphorus. The four carbons of the CCCPhCPh chain are found at δ 343.75, 179.25, 151.44 and 133.35, the extreme shielding of the former being notable.

Discussion

The sterically exposed location of the C₂ ligand in **1** makes it unusually reactive for a cluster-bound carbon ligand. The present account confirms that this reactivity extends to alkynes, with ready formation of a new C–C bond with the electron-rich carbon of the C₂ ligand and incorporation into a metallacycle via a new bond to Ru(3) occurring during the reaction.

The overall structure of **2** is similar to that found for the product Ru₅(μ_5 -CCCHCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₀ obtained from **1** and HC≡CPh, but with the C(3)=C(4) double bond no longer coordinated to Ru(4) and a new Ru(1)–Ru(4) bond being present.⁹ The net electron count is the same, the systems providing a novel example of structural isomerism within this fairly large cluster system. Other detailed changes are found on close examination of the structural data, but appear to have little influence on the overall structure. In particular, changes in the asymmetry of the μ -PPh₂ ligands and in the relative positions of all bridging groups around the edges of the pentagons are evident and will be discussed elsewhere.

The organic ligand in **2** can be considered to be an alkenylated carbide and is related to similar systems studied by Carty and his group, who considered that they are closely related to μ_4 -alkynyl groups.¹⁰ The ¹³C NMR parameters of the two complexes can be related to differences in their molecular structures, with the resonance for C(1) being found at δ 325.81 in **2** and 207.80 in **3**, consistent with stronger bonding of this carbon to the Ru₄ rhombus in the former (av. Ru–C 2.15 Å) compared with that in **3** (2.24 Å). These Ru–C separations are longer than those found in Ru₅C(CO)₁₅, for example [av. 2.02(2) Å],¹¹ which shows a chemical shift of δ 480.¹²

Some similarity exists between the metallacycles in complexes **2**, **3** and **4** and the ligands formed from two molecules of alkyne on triruthenium clusters, for example.^{13,14} However, the terminal carbon which is strongly attached to the square base of the cluster [C(1)] also serves to hold the cluster atoms together so that subsequent reactions take a different path.

Carbonylation of **3** resulted in degradation of the cluster by extrusion of one of the ruthenium atoms. The fifth Ru remains within the complex, however, by virtue of bridging ligands extending from the cluster to this atom (SMe, PPh₂, the organic ligand). Consequently, the degradation is reversible and we find that heating **5** briefly in refluxing toluene regenerates a mixture of **2** and **3**. The high energy band at 2088 cm⁻¹ is characteristic of the isolated Ru(CO)₃ group. The only other complex containing a *fac*-Ru(CO)₃(S)(P)(C) system appears to be the butatrienyldiene cluster Ru₅(μ_5 -CCCCH₂)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁, where a similar arrangement to **5** is found, albeit with a bond to the adjacent Ru atom. In this complex also, there is a ν (CO) band at 2093 cm⁻¹.¹⁵ Since we have independently shown that **2** can be decarbonylated to **3** under similar conditions, the three complexes are related by the reaction sequence summarised in Scheme 1.

The structural relationships between **1** and the products of its reactions with alkynes described herein can be further appreci-

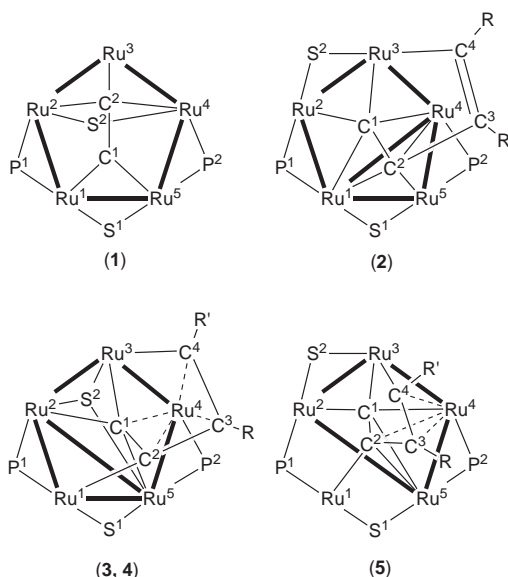


Chart 1

ated from Chart 1, which compares the four structural types mentioned above. It can be seen that by preserving the μ -SMe and μ -PPh₂ coordination positions as closely as possible, the formation of the η^2 -C₄ ligand in **2** and its subsequent conversion into η^4 -C₄ ligands in **3–5** by coordination to the closest Ru atom can be followed. The η^4 bonding to Ru(4) is preserved in **3–5**. In this manner, we have generated a common numbering scheme, although the actual metal core, and in particular, the atoms which form the flap of the envelope, for example, differ in the various complexes. We take this as indicating again the relative softness of the metal core, allowing great flexibility in the manner in which it adapts to the ligands present. Notwithstanding this feature, the SMe groups are mobile also. Thus the SMe group which bridges the non-bonded Ru(2)···Ru(4) vector in **1** migrates to bridge Ru(2)–Ru(3) in **2** and becomes μ_3 -bridging Ru(2,3,5) in **5**.

Conclusions

This work has demonstrated the propensity for the C₂ ligand in **1** to enter into combination with disubstituted alkynes to form new substituted C₄ ligands, one end of the carbon chain remaining strongly attached to four of the five Ru atoms which take up an “open envelope” conformation. Further reactivity is shown towards CO, which results in partial cluster degradation. However, as a result of the five rutheniums remaining within the product molecule **5**, reversal of this reaction is possible, on heating, to regenerate complexes of types **2** and **3**.

Experimental

General conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were carried out by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF₂₅₄, 0.5 mm thick).

Reagents

Complex **1** was prepared by the literature method;² C₂Me₂ (Fluka), C₂Ph₂ (Aldrich) and CO (CIG Ltd) were used as received.

Instrumentation

IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics;

NMR: Bruker CXP300 or ACP300 (¹H NMR at 300.13 MHz, ¹³C NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Reaction of **1 with diphenylacetylene.** A solution of **1** (40 mg, 0.31 mmol) and diphenylacetylene (20 mg, 0.11 mmol) in toluene (15 ml) were heated at 100 °C for 7 h. After cooling to room temperature the solvent was removed and the residue purified by preparative TLC (hexane–acetone, 10:3). A brown band (*R*_f 0.6) was recrystallised from CH₂Cl₂/MeOH to yield black crystals of Ru₅(μ_5 -CCPhCPh)(μ_3 -SMe)(μ -SMe)(μ -PPh₂)₂(CO)₉, **3** (9 mg, 20%). A dark brown band (*R*_f 0.4) was recrystallised from CH₂Cl₂–MeOH to yield black crystals of Ru₅(μ_5 -CCCPhCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₀, **2** (22 mg, 49%).

Reaction of **1 with but-2-yne.** A solution of **1** (80 mg, 0.061 mmol) and but-2-yne (0.5 g, 9.2 mmol) in toluene (10 cm³) were heated in a Carius tube for 5 h at 95 °C (tube oven). After cooling to room temperature the solvent was removed and the residue purified by preparative TLC (hexane–acetone 4:1) to yield six bands. A brown band (*R*_f 0.60) was recrystallised from CH₂Cl₂–MeOH to yield Ru₅(μ_5 -CCPhCPh)(μ_3 -SMe)(μ -SMe)(μ -PPh₂)₂(CO)₉, **4** (32 mg, 41%). A number of minor products were not identified.

Pyrolysis of Ru₅(μ_5 -CCCPhCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₀, **2. A solution of **2** (40 mg, 0.028 mmol) in toluene (20 ml) was refluxed for 16 h. After cooling to room temperature the solvent was removed and the residue purified by preparative TLC (hexane–acetone 10:3) to yield one major band which was recrystallised from CH₂Cl₂–MeOH to yield black crystals of Ru₅(μ_5 -CCCPhCPh)(μ_3 -SMe)(μ -SMe)(μ -PPh₂)₂(CO)₉, **3** (32 mg, 80%).**

Reaction of Ru₅(μ_5 -CCCPhCPh)(μ_3 -SMe)(μ -SMe)(μ -PPh₂)₂(CO)₉, **3 with CO.** A solution of **3** (20 mg, 0.014 mmol) in toluene (20 ml) was heated at 110 °C for 2 h with a CO purge. After cooling to room temperature and removing the solvent the residue was recrystallised from CH₂Cl₂–MeOH to yield Ru₅(μ_5 -CCCPhCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁, **5** (18 mg, 87%).

Pyrolysis of Ru₅(μ_5 -CCCPhCPh)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁, **5. A solution of **5** (15 mg, 0.010 mmol) in toluene (15 ml) was refluxed until no starting material remained (0.5 h). After cooling to room temperature the solvent was removed and the residue purified by preparative TLC (hexane–acetone 10:3) to yield two bands. A light brown band (*R*_f 0.6) was recrystallised from CH₂Cl₂–MeOH to yield black crystals of **3** (6 mg, 42%). A dark brown band (*R*_f 0.4) was recrystallised from CH₂Cl₂–MeOH to yield black crystals of **2** (8 mg, 55%).**

Crystallography

Unique data sets were measured at *ca.* 295 K within the limit $2\theta_{\max} = 50^\circ$ using a single counter/four-circle diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K α radiation, λ 0.71073 Å); *N* independent reflections were obtained, *N*_o with $I > 3\sigma(I)$ being considered ‘observed’ and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*_{iso})_H were included constrained at estimated values. Conventional residuals *R*, *R*' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Computation used the XTAL 2.6 program system¹⁶ implemented by S. R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the Figures and Tables.

CCDC reference number 186/1363. See <http://www.rsc.org/suppdata/dt/1999/1283/> for crystallographic files in .cif format.

Crystal and refinement data. Complex **2**: $\text{Ru}_5(\mu_5\text{-C}_2\text{C}_2\text{Ph}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}\cdot\text{PhMe} \equiv \text{C}_{52}\text{H}_{36}\text{O}_{10}\text{P}_2\text{Ru}_5\text{S}_2\cdot\text{C}_7\text{H}_8$, $M = 1544.4$. Monoclinic, space group $P2_1/c$, $a = 12.705(7)$, $b = 24.031(10)$, $c = 20.159(9)$ Å, $\beta = 108.50(4)^\circ$, $V = 5837$ Å³, $Z = 4$, $\rho_c = 1.76$ g cm⁻³, $F(000) = 3040$. Crystal dimensions: $0.08 \times 0.19 \times 0.27$ mm, $\mu(\text{Mo-K}\alpha) = 14.5$ cm⁻¹, A^* (min, max) = 1.12, 1.27. $N = 10326$, $N_o = 5634$, $R = 0.042$, $R_w = 0.039$. Complex **3**: $\text{Ru}_5(\mu_5\text{-C}_2\text{C}_2\text{Ph}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_9\cdot 0.5\text{CHCl}_3 \equiv \text{C}_{51}\text{H}_{36}\text{O}_9\text{P}_2\text{Ru}_5\text{S}_2\cdot 0.5\text{CHCl}_3$, $M = 1484.0$. Monoclinic, space group $C2/c$, $a = 27.063(9)$, $b = 10.314(5)$, $c = 39.137(14)$ Å, $\beta = 102.97(3)^\circ$, $V = 10646$ Å³, $Z = 8$, $\rho_c = 1.85$ g cm⁻³, $F(000) = 5800$. Crystal dimensions: $0.15 \times 0.26 \times 0.25$ mm, $\mu(\text{Mo-K}\alpha) = 16.2$ cm⁻¹, A^* (min, max) = 1.22, 1.44. $N = 6404$, $N_o = 4176$, $R = 0.046$, $R_w = 0.050$.

Further comments. After trial refinement, the solvent toluene in **2** was refined as a rigid group, unit site occupancy (with thermal parameters isotropic); the chloroform in **3** was modelled similarly, disordered about a crystallographic two-fold axis.

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