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Cluster chemistry

LXXXVIII *. Reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and thiols. Formation and X-ray structures of Ru_5 clusters containing C_2H, C_2PPh_2 and $CCH(PPh_2)$ ligands

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Abstract

Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) with RSH (R = Me, Ph) gave, as the major product in each case, $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SR)(\mu\text{-}PPh_2)(CO)_{12}$ [R = Me (**2**; 58%), Ph (**3**; 64%)]. In the case of the reaction with thiophenol four other products were identified: $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (**4**) (5%), $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (**5**) (6%), $Ru_5\{\mu_4\text{-}C_2H(PPh_2)\}(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (**6**) (2%) and $Ru_5(\mu_5\text{-}C_2H)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**7**). Complexes **2**–**7** were identified by single crystal X-ray diffraction studies. Compounds **2** and **3** contain a 'scorpion' Ru_5 cluster with $\mu_5\text{-}C_2PPh_2$ and $\mu_3\text{-}SR$ groups; in **4**, **5** and **6** the edge-bridged square clusters have envelope conformations; in **7** the cluster has a spiked rhomboidal framework. In **4** and **5**, the square Ru_4 base is bridged by one C of the C_2PPh_2 (**4**) or C_2H (**5**) ligands, the other C atom holding the envelope flap open. In **6**, a $\mu_4\text{-}CCH(PPh_2)$ ligand is on the opposite side of the envelope, the flap being attached to a $\mu_3\text{-}SPh$ group. Complex **7** is an isomer of **5**, the SPh group in the former acting as a 5e donor to three Ru atoms, an Ru–Ru bond being broken as a consequence; however, the two complexes are not directly interconvertible.

1. Introduction

The core geometries of pentanuclear metal complexes show a variety of interesting structures ranging from open chains to *closo*-trigonal bipyramidal clusters. The particular geometry adopted depends on the accompanying ligands and there appears to be little tendency for the formation of particularly stable arrangements as found, for example, for M_4 (tetrahedron, butterfly) or M_6 systems (octahedron, trigonal prism). We have been studying the chemistry of the open Ru_5 cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; Scheme 1); some of these results have been summarised recently [2]. Addition of 4e or 6e ligand combinations resulted in cleavage of two Ru–Ru bonds to give scorpion clusters [3,4], while with Me_2S_2, open-chain complexes were formed [5]. It was thus of interest to examine the reactions between **1** and thiols as sources of the (H + SR) ligand group.

2. Experimental section

2.1. General conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

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2.2. Materials

Complex **1** was prepared by the published method [6]. Methanethiol (Matheson) was used as received. Thiophenol (Aldrich) was distilled before use.

2.3. Spectra

Infrared spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrophotometer. NMR spectra were recorded on a Bruker ACP300 spectrometer (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). Fast atom bombardment (FAB) mass spectra were recorded on a VG ZAB 2HF mass spectrometer, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7.

2.4. Reaction of 1 with methanethiol

Methanethiol was bubbled through a solution of **1** (105 mg, 0.083 mmol) in benzene (20 ml) for 20 min. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3, v/v). The product from the major red band (R_f 0.5) was recrystallised from CH_2Cl_2/MeOH to yield **2** (62 mg, 58%), m.p. 205–211°C (dec.). Found: C, 36.08; H, 1.77; M, 1285 (mass spectrometry). $C_{39}H_{24}O_{12}P_2Ru_5S$ requires C, 36.48; H, 1.88%; M, 1285. IR: ν(CO) (cyclohexane) 2078m, 2056s, 2016(sh), 2012vs, 1999vs, 1988m, 1979m, 1970m, 1964w, 1946w cm^{-1}. ^1H NMR: δ ($CDCl_3$) −24.12 (1H, s, Ru–H), 1.18 (3H, s, SMe), 7.42–8.16 (20H, m, Ph). FAB MS: 1285, $[M]^+$; 1257–1033, $[M-nCO]^+$ ($n = 1$–9).

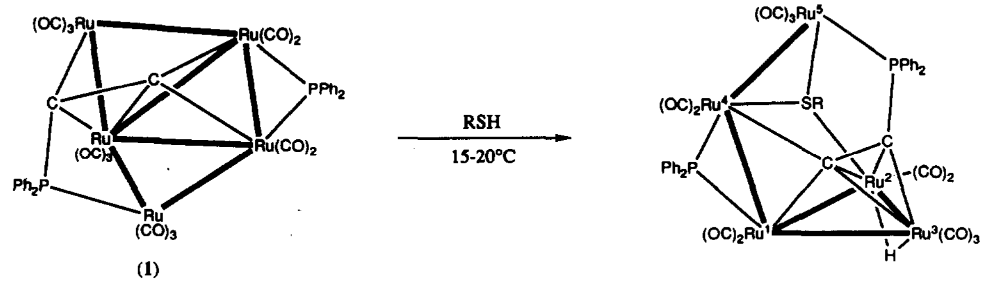
2.5. Reaction of 1 with thiophenol

2.5.1. At 18°C

A solution of **1** (100 mg, 0.079 mmol) and thiophenol (50 mg, 0.47 mmol) in toluene (30 ml) was stirred at RT (18°C) for 120 min. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3 v/v) to yield four bands. The product from the major band (R_f 0.65) was recrystallised (CH_2Cl_2/MeOH) to yield black crystals of **3** (68 mg, 64%), m.p. 194–197°C (dec.). Found: C, 38.67; H, 2.06; M, 1347 (mass spectrometry). $C_{44}H_{26}O_{12}P_2Ru_5S$ requires C, 39.22; H, 1.95%; M, 1347. IR: ν(CO) (cyclohexane) 2078m, 2060s, 2013vs, 1988m, 1981m, 1971m, 1949w cm^{-1}. ^1H NMR: δ ($CDCl_3$) −22.30 (1H, s, Ru–H), 6.39–8.20 (25H, m, Ph). ^{13}C NMR: δ ($CDCl_3$) 105.96 (d, J(CP) 33.9 Hz, $CCPPh_2$), 127.96–137.23 (m, Ph), 142.16 (d, J(CP) 24.9 Hz), 144.71 (d, J(CP) 34.1 Hz) (*ipso* C(PPh)), 188.42 (br), 190.06 (s), 191.93 (br), 193.55 (d, J(CP) 7.2 Hz), 195.27 (br), 198.53 (d, J(CP) 5.4 Hz), 198.74 (d, J(CP) 3.2 Hz), 200.01 (d, J(CP) 5.2 Hz), 203.33 (br), 207.04 (s), 210.59 (d, J(CP) 3.2 Hz) (CO). FAB MS: 1347, $[M]^+$; 1319–1011, $[M-nCO]^+$ ($n = 1$–12). A yellow band (R_f 0.5; 19 mg) and two minor brown bands (R_f 0.40, 0.35; 8, 7 mg) were not identified.

2.5.2. At 40°C

A solution of **1** (200 mg, 0.16 mmol) and thiophenol (150 mg, 1.4 mmol) in benzene (30 ml) was stirred at 40°C for 45 min. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3 v/v) to yield four bands. The product from the major band (R_f 0.65) was recrystallised (CH_2Cl_2/MeOH) to yield black crystals of **3** (107 mg, 50%). That from an orange band (R_f 0.50) was recrystallised from CH_2Cl_2/MeOH to yield **4** (10 mg, 5%), m.p. 210–214°C (dec.). Found: C, 39.11; H, 2.04; M, 1347 (mass spectrometry). $C_{44}H_{26}O_{12}P_2Ru_5S$ requires C, 39.22; H, 1.95%; M, 1347. IR: ν(CO) (cyclohexane) 2083m, 2044m, 2029vs, 2018w, 2007m, 1993vw, 1981m, 1976(sh) cm^{-1}. ^1H NMR: δ ($CDCl_3$) −19.86 (1H, t, J(HP) 4.7 Hz, Ru–H), 7.23–7.79 (25H, m, Ph). FAB MS: 1347, $[M]^+$; 1319–1011, $[M-nCO]^+$ ($n = 1$–12). A yellow band (R_f 0.30) was recrystallised from



(1)

R = Me (2) (58%), Ph (3) (64%)

Scheme 1.

CH_2Cl_2/MeOH to yield **5** (13 mg, 6%), m.p. > 300°C (dec.). Found: C, 38.81; H, 2.06; $[M-CO]^+$, 1319 (mass spectrometry). $C_{44}H_{26}O_{12}P_2Ru_5S$ requires C, 39.22; H, 1.95%; M, 1347. IR: ν(CO) (cyclohexane) 2076s, 2046vs, 2032vs, 2025m, 2010s, 1992m, 1986m, 1978m, 1972m, 1962w; (CH_2Cl_2) 2078s, 2042vs, 2032vs, 2021s, 2008s, 1976m, 1955(sh), 1844m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.40 (2H, d, J(HH) 7.4 Hz, Ph), 6.91–7.81 (23H, m, Ph), 9.66 (1H, d, J(HP) 1.2 Hz, C_2H). FAB MS: 1319–1011, $[M-nCO]^+$ ($n = 1$–12). The product from a red band (R_f 0.20) was recrystallised from CH_2Cl_2/MeOH to yield **6** (5 mg, 2%), m.p. > 300°C (dec.). Found: C, 38.61; H, 2.07; M, 1347 (mass spectrometry). $C_{44}H_{26}O_{12}P_2Ru_5S$ requires C, 39.22; H, 1.95%; M, 1347. IR: ν(CO) (CH_2Cl_2) 2055m, 2027(sh), 2023s, 2008m, 1998m, 1982(sh), 1977m, 1969(sh), 1864w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.61 (1H, d, J(HP) 5.9 Hz, CCH), 6.48–6.56 (3H, m, Ph), 6.64 (2H, t, J(HH) 7.7 Hz, Ph), 6.83 (1H, t, J(HH) 7.3 Hz, Ph), 7.00 (2H, td, J(HH) 7.6, 1.8 Hz, Ph), 7.16–7.51 (16H, m, Ph), 7.88 (1H, dd, J(HH) 11.7, 7.0 Hz, Ph). FAB MS: 1347, $[M]^+$; 1319–1011, $[M-nCO]^+$ ($n = 1$–12).

2.5.3. At 80°C

A solution of **1** (100 mg, 0.079 mmol) and thiophenol (100 mg, 0.91 mmol) in benzene (30 ml) was heated at reflux for 20 min. The solvent was removed and the residue purified by preparative TLC (light petroleum/

TABLE 1. Crystal data and refinement details for complexes **2–7**

Compound	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{39}H_{24}O_{12}P_2Ru_5S$	$C_{44}H_{26}O_{12}P_2Ru_5S$	$C_{44}H_{26}O_{12}P_2Ru_5S$	$C_{44}H_{26}O_{12}P_2Ru_5S \cdot CHCl_3$	$C_{44}H_{26}O_{12}P_2Ru_5S$	$C_{44}H_{26}O_{12}P_2Ru_5S$
MW	1284.0	1346.0	1346.0	1465.4	1346.0	1346.0
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	12.113(2)	22.493(5)	19.02(1)	20.745(15)	21.449(2)	16.739(6)
b, Å	19.883(8)	11.365(4)	11.793(1)	13.832(11)	18.345(9)	14.701(4)
c, Å	20.052(13)	9.762(2)	11.106(6)	20.079(16)	25.566(10)	9.924(3)
α, deg.	–	104.55(2)	71.24(4)	–	–	74.07(2)
β, deg.	117.57(4)	97.09(2)	85.99(5)	119.00(6)	113.11(2)	81.37(3)
γ, deg.	–	101.50(2)	74.55(6)	–	–	84.23(3)
V, Å^3	4281	2327	2273	5039	9252	2317
Z	4	2	2	4	8	2
D_c g cm^{-3}	1.99	1.92	1.96	1.93	1.93	1.93
$F(000)$	2480	1304	1304	2840	5216	1304
Crystal size, mm	0.15 × 0.42 × 0.47	0.20 × 0.18 × 0.43	0.40 × 0.06 × 0.18	0.18 × 0.14 × 0.30	0.06 × 0.33 × 0.14	0.22 × 0.10 × 0.44
A^* (min, max)	1.19, 1.78	1.26, 1.35	1.10, 1.37	1.18, 1.26	1.11, 1.31	1.18, 1.47
μ, cm^{-1}	17.3	15.9	16.1	16.2	16.0	17.3
$2\theta_{max}$, deg.	50	50	60	50	50	55
N	7522	8197	12918	8853	16245	8574
N_0	6588	7330	8502	5790	4353	6850
R	0.034	0.023	0.065	0.046	0.101	0.028
R_w	0.045	0.026	0.073	0.046	0.100	0.031

Abnormal features / variations in procedure

2 and **3** For both compounds, H(23) was located in difference maps and refined in (x, y, z, U_{iso}).

4 In spite of measurement to $2\theta_{max} = 60°$, data were weak with a consequent high residual; in consequence, the location of the core hydrogen atom could not be postulated with any confidence.

5 Compensation for crystal decomposition of *ca.* 5% during data collection, as estimated by the behaviour of the standard reflections, was by appropriate scaling. Difference map residues indicated the presence of chloroform, site occupancy 1 from refinement, but with very high thermal motion. The core hydrogen was not located.

6 Two pseudo-symmetrically related molecules comprise the asymmetric unit of a structure whose data contains a weak superlattice. In consequence, only a small proportion of data were observed and much of those were weak, resulting in a high residual and supporting meaningful anisotropic thermal parameter refinement for Ru, P, S only; the other non-hydrogen atoms were refined using the isotropic form. Hydride atoms were not located.

7 H(1) was located in a difference map and refined in (x, y, z, U_{iso}).

acetone 10/3) to yield four major bands containing **3** (R_f 0.65; 22 mg, 21%), **4** (R_f 0.50; 28 mg, 26%), **6** (R_f 0.20; 8 mg, 8%) and an unidentified orange compound (R_f 0.40; 5 mg).

2.6. *Pyrolysis of 3*

A solution of **3** (40 mg, 0.030 mmol) in benzene (25 ml) was heated at reflux point for 3 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield **6** (13 mg, 32% yield, 71% conversion). A large amount of **3** was also recovered (18 mg, 45%). Further heating resulted in the formation of a number of minor products a significant decomposition, without giving a higher yield of **6**. Neither **4** nor **7** were observed among the products.

2.7. *Pyrolysis of 4*

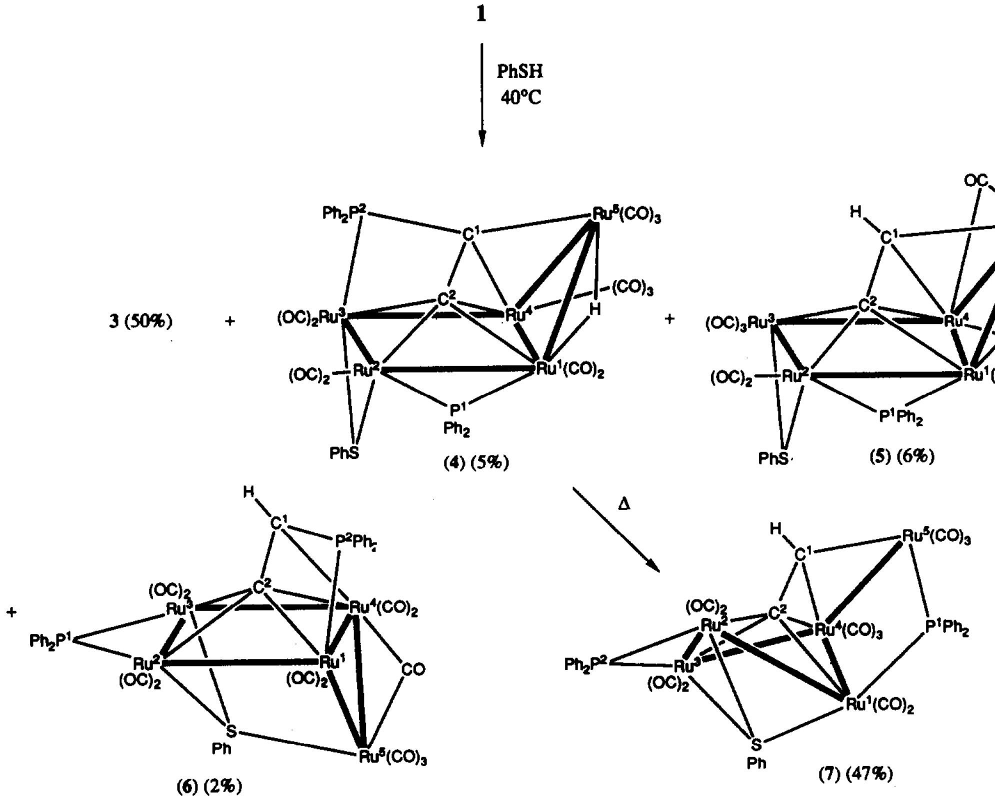
A solution of **4** (40 mg, 0.030 mmol) in benzene (25 ml) was heated at the reflux point for 2 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield four bands. The product from a brown band (R_f 0.65) was recrystallised from CH_2Cl_2/MeOH to yield **3** (3 mg, 7%). That from a yellow band (R_f 0.60) was recrystallised from CH_2Cl_2/MeOH to yield yellow crystals of **7** (19 mg, 47%). Found: C, 39.07; H, 1.99; $[M - CO]^+$, 1319 (mass spectrometry). $C_{44}H_{26}O_{12}P_2Ru_5S$ requires C, 39.26; H, 1.95%; M, 1347. IR: ν(CO) (cyclohexane) 2082s, 2040m, 2025vs, 2018vs, 2009(sh), 2000m, 1986m, 1976m, 1963m, 1958w, 1913vw(br) cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.24–7.68 (25H, m, Ph), 8.95 (1H, dd, J(HP) 3.6, 1.3 Hz, CCH). FAB MS: 1319–1011 $[M - nCO]^+$ ($n = 1$–12). The product from a red band (R_f 0.20) was recrystallised from CH_2Cl_2/MeOH to yield **6** (8 mg, 20%). That in a brown band (R_f 0.30; 2 mg) was not identified.

2.8. *Pyrolysis of 6*

A solution of **6** (13 mg, 0.010 mmol) in toluene (20 ml) was heated at 90°C for 4 h. Only decomposition to an intractable baseline (TLC) was observed.

3. Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limit using an Enraf-Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); *N* independent reflections



Scheme 2.

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. Data collection and refinement details are in Table 1. 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 $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [7] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in

TABLE 2. Selected bond lengths (Å) and angles (deg.) for $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}X)(\mu\text{-}PPh_2)(CO)_{12}$ (X = SMe (**2**), SPh (**3**) and I (**8**) [4])

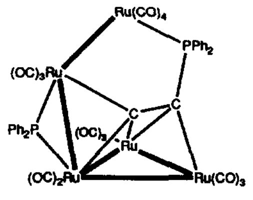
Bond lengths	2	3	8
Ru(1)-Ru(2)	2.851(2)	2.8715(7)	2.858(1)
Ru(1)-Ru(3)	2.856(1)	2.8821(6)	2.848(1)
Ru(1)-Ru(4)	2.883(1)	2.8989(8)	2.881(1)
Ru(2)-Ru(3)	2.794(1)	2.7686(7)	2.775(1)
Ru(4)-Ru(5)	2.888(1)	2.889(1)	2.936(1)
Ru(1)-P(2)	2.281(2)	2.2776(9)	2.264(2)
Ru(4)-P(2)	2.335(1)	2.328(1)	2.332(3)
Ru(5)-P(1)	2.406(2)	2.3987(9)	2.400(2)
Ru(2)-S	2.386(2)	2.403(1)	2.727(1) (I)
Ru(4)-S	2.374(2)	2.4013(9)	2.740(1) (I)
Ru(5)-S	2.415(1)	2.4574(9)	2.751(1) (I)
Ru(1)-C(2)	1.947(4)	1.940(3)	1.962(9)
Ru(2)-C(1)	2.187(6)	2.215(3)	2.176(9)
Ru(2)-C(2)	2.190(6)	2.177(3)	2.183(7)
Ru(3)-C(1)	2.132(5)	2.136(3)	2.129(8)
Ru(3)-C(2)	2.370(5)	2.368(3)	2.355(8)
Ru(4)-C(2)	2.337(5)	2.373(3)	2.277(8)
S-C(R)	1.791(9)	1.798(3)	
P(1)-C(1)	1.768(4)	1.757(3)	1.774(9)
C(1)-C(2)	1.351(7)	1.347(3)	1.33(1)
Ru(2)-H(23)	1.59(6)	1.70(3)	
Ru(3)-H(23)	1.92(8)	1.87(3)	
Ru-CO	1.875-1.955(9) av. 1.905	1.875-1.931(4) av. 1.900	
C-O	1.103-1.157(9) av. 1.134	1.126-1.143(5) av. 1.135	
P-C(Ph)	1.814-1.827(6) av. 1.821	1.812-1.831(3) av. 1.822	

Angles	2	3	8
Ru(1)-Ru(4)-Ru(5)	123.66(4)	123.59(2)	125.2(1)
Ru(4)-Ru(1)-Ru(2)	75.79(5)	75.37(2)	78.2(1)
Ru(4)-Ru(1)-Ru(3)	109.01(3)	109.12(2)	106.8(1)
Ru(1)-Ru(2)-S	93.25(6)	94.06(3)	96.2(1) (I)
Ru(3)-Ru(2)-S	129.95(5)	131.60(2)	134.6(1) (I)
Ru(1)-Ru(4)-S	92.71(5)	93.40(3)	95.3(1) (I)
Ru(5)-Ru(4)-S	53.57(4)	54.41(3)	57.8(1) (I)
Ru(4)-Ru(5)-S	52.25(4)	52.62(3)	57.5(1) (I)
Ru(4)-Ru(5)-P(1)	92.65(5)	92.65(3)	90.2(1)
Ru(4)-S-Ru(5)	74.18(6)	72.96(3)	64.7(1) (I)
Ru(2)-S-Ru(4)	95.45(7)	94.50(4)	83.0(1) (I)
Ru(2)-S-Ru(5)	117.71(7)	116.58(3)	103.1(1) (I)
Ru(5)-P(1)-C(1)	106.5(2)	107.5(1)	106.8(3)
Ru(2)-C(1)-Ru(3)	80.6(2)	79.0(1)	80.2(3)
Ru(2)-C(2)-Ru(3)	75.5(2)	74.9(1)	75.3(2)
Ru(1)-C(2)-C(1)	142.6(4)	145.1(3)	143.1(6)
Ru(4)-C(2)-C(1)	129.6(4)	128.4(1)	129.7(6)
P(1)-Ru(5)-S	87.71(5)	87.80(3)	92.5(1) (I)

the Figures and Tables; material deposited with the Cambridge Crystallographic Data Centre comprises thermal and hydrogen atom parameters and full non-hydrogen geometries.

4. Results

When methanethiol was bubbled through a solution of **1** in benzene for a short time at ambient temperature, a red complex was formed in good yield as the only isolated product (by preparative TLC). This material was identified by single-crystal X-ray crystallography as $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SR)(\mu\text{-}PPh_2)(CO)_{12}$ (Scheme 1: **2**; R = Me). A similar reaction carried out using thiophenol gave several products, including **3**, the phenyl analogue of **2**, which was also formed in good yield. When this reaction was carried out at 40°C three other products were isolated: $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (**4**), the μ_5-ethynyl cluster $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (**5**) and $Ru_5\{\mu_4\text{-}C_2H(PPh_2)\}(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (**6**) (Scheme 2). When the reaction was carried out in refluxing benzene the yields of **4** and **6** were increased while that of **3** was decreased. Complexes **3** and **4** were



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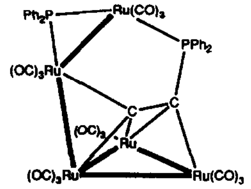

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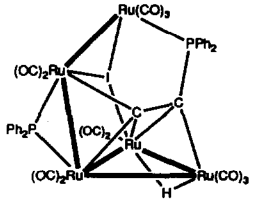
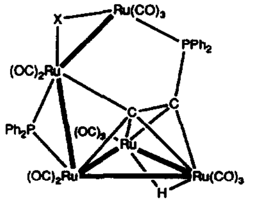
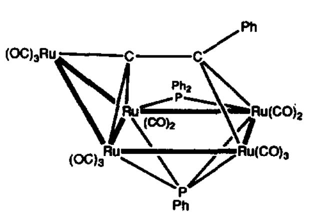


(8)



(10; X = Cl, Br)



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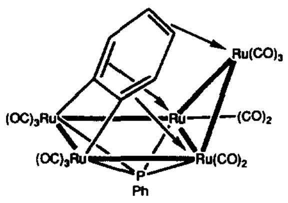

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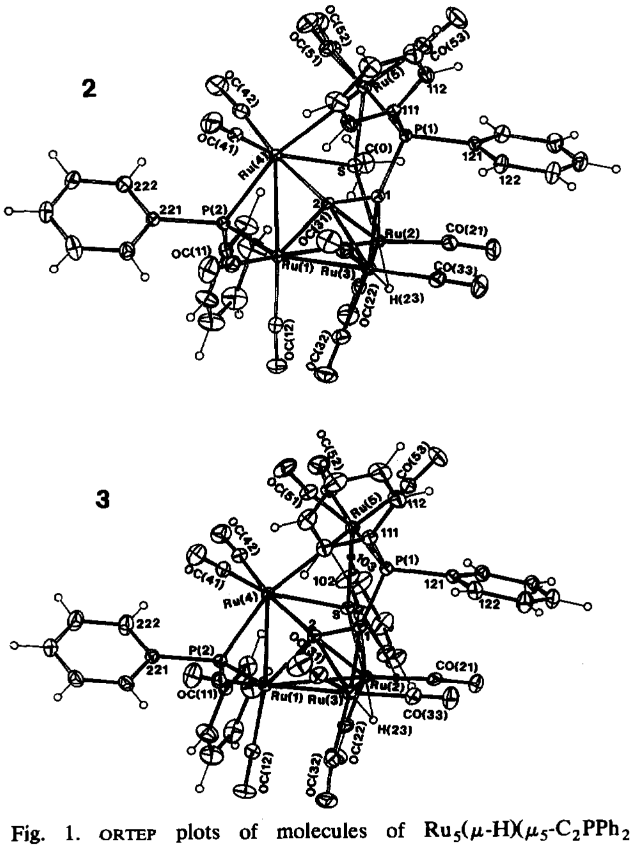

Fig. 1. ORTEP plots of molecules of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)(CO)_{12}$ (2) and $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (3), showing atom numbering scheme. Non-hydrogen atoms shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

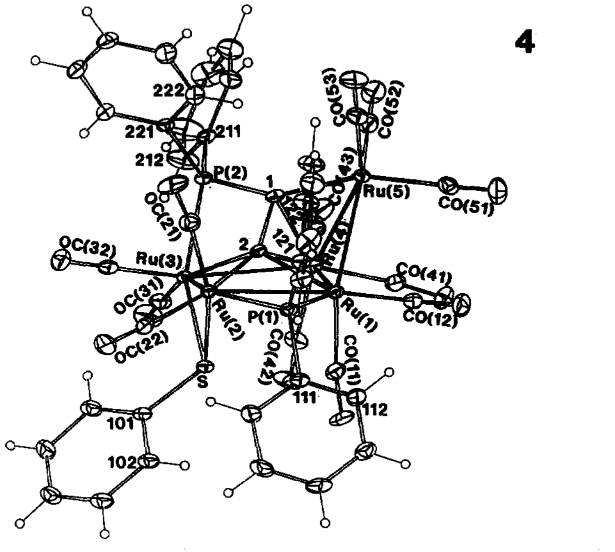

Fig. 2. ORTEP plot of a molecule of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (4).

formed in similar amounts, while no **5** was observed. Complexes **4–6** were also fully characterised by single crystal X-ray studies. Heating a solution of **3** in refluxing benzene gave a low yield of **6** but no **4** or **5** was formed. When a solution of **4** in toluene was heated the major product formed was the spiked rhomboidal

TABLE 3. Selected bond lengths (Å) and angles (deg.) for Ru$_5$(μ-H)(μ$_5$-C$_2$PPh$_2$)(μ-SPh)(μ-PPh$_2$)(CO)$_{12}$ (**4**) and Ru$_5${μ$_4$-C$_2$H(PPh$_2$)}(μ$_3$-SPh)(μ-PPh$_2$)(μ-CO)(CO)$_{11}$ (**6**) (values for the two pseudosymmetrically related molecules of **6** are given)

Bond lengths	**4**	**6**
Ru(1)–Ru(2)	2.900(1)	2.937(8), 2.935(7)
Ru(1)–Ru(4)	2.806(2)	2.883(6), 2.867(5)
Ru(1)–Ru(5)	2.992(2)	2.795(5), 2.804(5)
Ru(2)–Ru(3)	2.821(2)	2.734(5), 2.747(5)
Ru(3)–Ru(4)	2.940(1)	2.859(8), 2.887(7)
Ru(4)–Ru(5)	2.807(1)	2.866(6), 2.855(6)
Ru(1)–P(1)	2.296(3)	
Ru(2)–P(1)	2.293(3)	2.30(2), 2.31(1)
Ru(3)–P(1)		2.30(2), 2.30(2)
Ru(1)–P(2)		2.32(1), 2.31(1)
Ru(3)–P(2)	2.337(3)	
Ru(2)–S	2.447(3)	2.40(1), 2.43(1)
Ru(3)–S	2.402(3)	2.35(1), 2.35(1)
Ru(5)–S		2.41(2), 2.42(2)
Ru(1)–C(2)	2.209(9)	2.27(4), 2.17(4)
Ru(2)–C(2)	2.129(9)	2.24(4), 2.16(4)
Ru(3)–C(2)	2.103(9)	2.09(4), 2.24(4)
Ru(4)–C(2)	2.155(9)	1.94(4), 2.03(4)
Ru(4)–C(1)	2.207(9)	2.26(5), 2.11(4)
Ru(5)–C(1)	2.032(8)	
Ru(4)–C(42)		1.91(4), 1.93(4)
Ru(5)–C(42)		2.49(5), 2.40(4)
Ru(1)–C(52)		2.39(5), 2.25(5)
S–C(Ph)	1.792(8)	1.82(6), 1.68(5)
P(2)–C(1)	1.83(1)	1.67(6), 1.69(4)
C(1)–C(2)	1.44(1)	1.45(7), 1.55(6)

Ru–CO **4**: range 1.851–1.971(9), av. 1.91; **6** range 1.70–2.00(5), av. 1.93 Å
C–O **4**: range 1.11–1.15(1), av. 1.13; **6** range 1.11–1.38(7), av. 1.21 Å
P–C(Ph) **4**: range 1.82–1.85(1), av. 1.84; **6** range 1.78–1.93(5), av. 1.83 Å

Angles	**4**	**6**
Ru(1)–Ru(2)–Ru(3)	89.22(4)	92.1(2), 92.8(2)
Ru(2)–Ru(3)–Ru(4)	90.22(4)	90.7(2), 89.3(2)
Ru(3)–Ru(4)–Ru(1)	88.70(4)	90.7(2), 91.3(2)
Ru(2)–Ru(1)–Ru(4)	91.34(4)	86.3(2), 86.2(2)
Ru(4)–Ru(1)–Ru(5)	57.80(4)	60.6(1), 60.4(1)
Ru(1)–Ru(4)–Ru(5)	64.43(5)	58.2(1), 58.7(1)
Ru(1)–Ru(5)–Ru(4)	57.77(4)	61.2(1), 60.9(1)
Ru(4)–C(42)–Ru(5)		80(2), 82(1)
Ru(4)–C(42)–O(42)		160(4), 149(4)
Ru(5)–C(42)–O(42)		117(4), 129(4)
Ru(1)–C(52)–Ru(5)		79(2), 83(2)
Ru(1)–C(52)–O(52)		132(4), 136(4)
Ru(5)–C(52)–O(52)		149(4), 141(4)

Dihedrals **4** Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5) 110.09(3)°
6 Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(4)–Ru(1)–Ru(5) 87.6(2), 87.4(2)°
Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(2)–Ru(3)–P(1) 175.3(4), 173.4(4)°
Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(2)–Ru(3)–S 103.0(4), 102.8(4)°

cluster $Ru_4(\mu_5\text{-}C_2H)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**7**), together with complexes **3** and **6** in low yield. Pyrolysis of a solution of **6** resulted in decomposition.

4.1. Molecular structures of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SR)(\mu\text{-}PPh_2)(CO)_{12}$ (R = Me (2), Ph (3))

The molecular structure of **2** is shown in Fig. 1 together with that of **3** which is essentially the same, with the *S*-methyl group replaced by phenyl. Bond distances and angles are collected in Table 2. As can be seen, two of the metal–metal bonds in **1** have been cleaved to give a central core which has been described either as a dimetallated triangle, or as a 'scorpion' cluster [3,4]. The C_2PPh_2 ligand interacts with all five ruthenium atoms, the phosphorus atom being attached to the tail of the scorpion [Ru(5)–P(1) 2.406(2) Å for **2**, 2.399(1) Å for **3**]. The acetylide ligand is bonded in the usual $\mu_3\text{-}\eta^2\text{-}\perp$ fashion, but C(2) also interacts with Ru(4) [2.337(5), 2.373(3) Å, respectively]. The $\mu\text{-}PPh_2$ group bridges Ru(1)–Ru(4), while the thiolato group is

TABLE 4. Selected bond lengths (Å) and angles (deg.) for $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (**5**) and $Ru_5(\mu_5\text{-}C_2H)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**7**).

Bond lengths	5	Bond lengths	7
Ru(3)–Ru(4)	2.848(2)	Ru(1)–Ru(2)	2.8292(8)
Ru(1)–Ru(4)	2.989(2)	Ru(1)–Ru(4)	2.8693(8)
Ru(4)–Ru(5)	2.657(2)	Ru(2)–Ru(3)	2.7464(7)
Ru(2)–Ru(3)	2.796(2)	Ru(3)–Ru(4)	2.8881(8)
Ru(1)–Ru(2)	2.843(2)	Ru(4)–Ru(5)	2.8526(8)
Ru(1)–Ru(5)	2.826(2)	Ru(1)–P(1)	2.322(1)
Ru(2)–P(1)	2.290(3)	Ru(5)–P(1)	2.418(1)
Ru(1)–P(1)	2.323(3)	Ru(2)–P(2)	2.285(1)
Ru(1)–P(2)	2.457(3)	Ru(3)–P(2)	2.318(2)
Ru(5)–P(2)	2.275(3)	Ru(1)–S	2.410(1)
Ru(2)–S	2.423(3)	Ru(2)–S	2.397(1)
Ru(3)–S	2.393(3)	Ru(3)–S	2.434(1)
Ru(4)–C(1)	2.178(9)	Ru(4)–C(1)	2.169(4)
Ru(5)–C(1)	2.079(7)	Ru(5)–C(1)	2.097(5)
Ru(1)–C(2)	2.260(9)	Ru(1)–C(2)	2.127(4)
Ru(2)–C(2)	2.13(1)	Ru(2)–C(2)	2.091(5)
Ru(3)–C(2)	2.233(7)	Ru(3)–C(2)	2.367(4)
Ru(4)–C(2)	2.155(8)	Ru(4)–C(2)	2.161(4)
Ru(5)–C(53)	2.15(1)	Ru(4)–C(42)	1.907(5)
Ru(4)–C(53)	2.069(8)	Ru(5)–C(42)	2.706(4)
S–C(Ph)	1.788(9)	S–C(Ph)	1.782(5)
C(1)–C(2)	1.41(1)	C(1)–C(2)	1.400(6)
		C(1)–H(1)	0.93(3)

Ru–CO 5 range 1.859–1.967(10), av. 1.899; 7 range 1.857(5)–1.945(6), av. 1.901 Å
C–O 5 range 1.11–1.16(1), av. 1.133; 7 range 1.115(5)–1.150(6), av. 1.133 Å
P–C(Ph) 5 range 1.820–1.823(8), av. 1.821; 7 range 1.819(5)–1.846(4), av. 1.831 Å

Angle	5	Angle	7
Ru(1)–Ru(2)–Ru(3)	93.25(6)	Ru(1)–Ru(2)–Ru(3)	82.45(3)
Ru(2)–Ru(1)–Ru(4)	86.61(6)	Ru(1)–Ru(4)–Ru(3)	79.33(2)
Ru(1)–Ru(4)–Ru(3)	89.18(6)	Ru(2)–Ru(3)–Ru(4)	92.58(3)
Ru(2)–Ru(3)–Ru(4)	90.30(6)	Ru(2)–Ru(1)–Ru(4)	91.28(2)
Ru(4)–C(53)–Ru(5)	78.0(3)	Ru(1)–Ru(4)–Ru(5)	82.29(3)
Ru(5)–C(53)–O(53)	140.5(7)	Ru(3)–Ru(4)–Ru(5)	122.76(3)
Ru(4)–C(53)–O(53)	141.3(8)	Ru(4)–C(42)–Ru(5)	74.1(1)
		Ru(4)–C(42)–O(42)	162.8(4)
		Ru(5)–C(42)–O(42)	122.9(4)

Dihedrals 5 Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5) 53.72(4)°
Ru_4 plane/P(1)–Ru(2)–Ru(1) 21.47(8)°
Ru_3 plane/P(2)–Ru(1)–Ru(5) 96.83(8)°
Ru_4 plane/S–Ru(2)–Ru(3) 31.46(8)°
7 Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(4)–Ru(3) 38.30(5)°

attached to Ru(2) and also bridges Ru(4)–Ru(5). The hydrogen atom bridges Ru(2)–Ru(3) [2.794(1), 2.7686(7) Å], as found in the μ_3-iodo complex **8** (see below) [4], and possibly lies somewhat nearer to Ru(3). Although this Ru–Ru separation is the shortest, nevertheless it is comparable with the Ru–Ru separations bridged by acetylide and H in $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2R)(\mu\text{-}dppm)(CO)_7$ (2.787(5) Å (R = Ph) [8]; 2.798(1) Å (R = C_6F_5) [9]), for example. Significant differences between the core geometries of **2** and **3** are found in the Ru–Ru and Ru–S separations.

This metal geometry has been found previously in the carbonylation products of **1**, namely **9k** and **9t** [3], and also in the products of addition of HX (X = Cl, Br or I) [4] or of $AuX(PPh_3)$ (X = Cl [4], C_2Ph) [10]) to **1**. In the latter, the X atom can be μ_2 (as in **10**) or μ_3 (as in **8**); the skeletal geometries of **2**, **3** and **8** are virtually identical (Table 2).

The spectroscopic properties of **2** and **3** are consistent with the solid state structures. The ^1H NMR spectra contain Ru-H resonances at δ −24.12 and −22.30, respectively, while the *S*–Me resonance in **2** is found at δ 1.18. In the FAB mass spectra, molecular ions at m/z 1285 and 1347, respectively, decompose by loss of the CO groups.

Each of the remaining products that we have obtained (**4**–**7**) contains a different arrangement of ligands derived from the C_2PPh_2 unit in **1**. Single crystal X-ray studies were carried out for each complex. The FAB mass spectra were not always reliable indicators of the molecular composition, the ions of highest mass being M^+ for **4** and **6**, but only $[M - CO]^+$ for **5** and **7**.

4.2. Molecular structure of $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (4)

A molecule of **4** is depicted in Fig. 2 and selected bond lengths and angles are given in Table 3. The Ru_5 core has an edge-bridged rhomboidal structure with an open-envelope conformation [dihedral angle 110.09(3)°]. The envelope is kept open by the μ_5-C_2PPh_2 ligand which is retained from **1**. The μ-SPh ligand bridges Ru(2)–Ru(3) [Ru(2)–S 2.447(3), Ru(3)–S 2.402(3) Å] at the bottom of the envelope. Another edge of the rhombus is bridged by a μ-PPh_2 group [Ru(1)–P(1) 2.296(3), Ru(2)–P(1) 2.293(3) Å]. The Ru–Ru bonds range from 2.806(2)–2.992(2) Å, the shortest being the hinge bond and the longest being Ru(1)–Ru(5), which is probably bridged by the hydride atom. The ^1H NMR spectrum contained a resonance at δ −19.86, indicating the presence of a metal hydride although this was not located in the X-ray study. Its postulated location is based on electron counts at individual Ru atoms and the length of the Ru-Ru bond. There are twelve terminal CO groups, three each on Ru(4) and Ru(5) with two on each of the remaining Ru atoms. With 78 cluster valence electrons (c.v.e.) coming from 5Ru (40), 12CO (24), μ-SPh (3), μ-PPh_2 (3), μ-H (1) and μ_5-C_2PPh_2 (7), the electron count is in accord with the PSEP rules which predict 78 c.v.e. for an edge-bridged square.

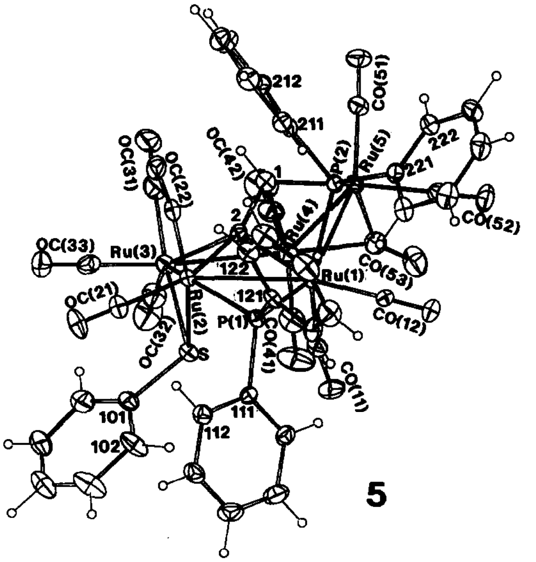

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Fig. 3. ORTEP plot of a molecule of $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (5).

4.3. Molecular structure of $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (5)

A molecule of **5** is depicted in Fig. 3 and selected bond lengths and angles are given in Table 4. The pentanuclear core has an open-envelope conformation [dihedral angle 126.28(4)°] similar to that found in **4**. Two of the edges of the rhombus are bridged by SPh [Ru(2)–S 2.423(3), Ru(3)–S 2.393(3) Å] and PPh_2 groups [Ru(1)–P(1) 2.323(3), Ru(2)–P(1) 2.290(3) Å], while the second PPh_2 group bridges one edge of the flap [Ru(1)–P(2) 2.457(3), Ru(5)–P(2) 2.275(3) Å]. The other edge of the flap is bridged by CO [Ru(5)–C(53) 2.15(1), Ru(4)–C(53) 2.069(8) Å]. The Ru–Ru distances range from 2.657(2)–2.989(2) Å, the shortest being that bridged by the CO ligand and the longest being the hinge of the envelope. Keeping the envelope open is a μ_5-ethynyl (C_2H) ligand, which essentially caps the triangular flap in the μ_3-η^2-$\|$ mode often found for alkynes [Ru(1)–C(2) 2.260(9), Ru(5)–C(1) 2.079(7), Ru(4)–C(1,2) 2.178(9), 2.155(8) Å], while C(2) also interacts with the other two Ru atoms [2.13(1), 2.233(7) Å]; this carbon caps the Ru_4 square and has certain features in common with μ_4-alkylidyne car-

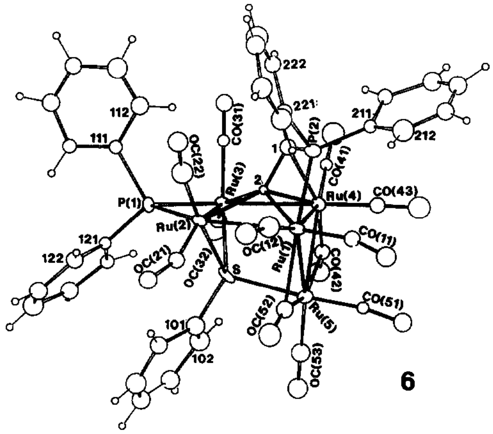


Fig. 4. ORTEP plot of molecule 1 of $Ru_5\{\mu_4$-$C_2H(PPh_2)\}(\mu_3$-$SPh)(\mu$-$PPh_2)(\mu$-$CO)(CO)_{11}$ (6).

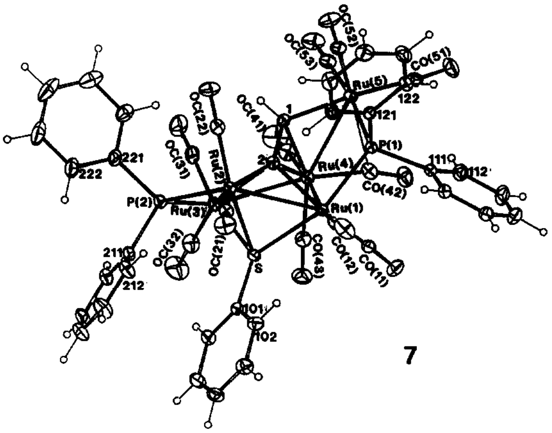


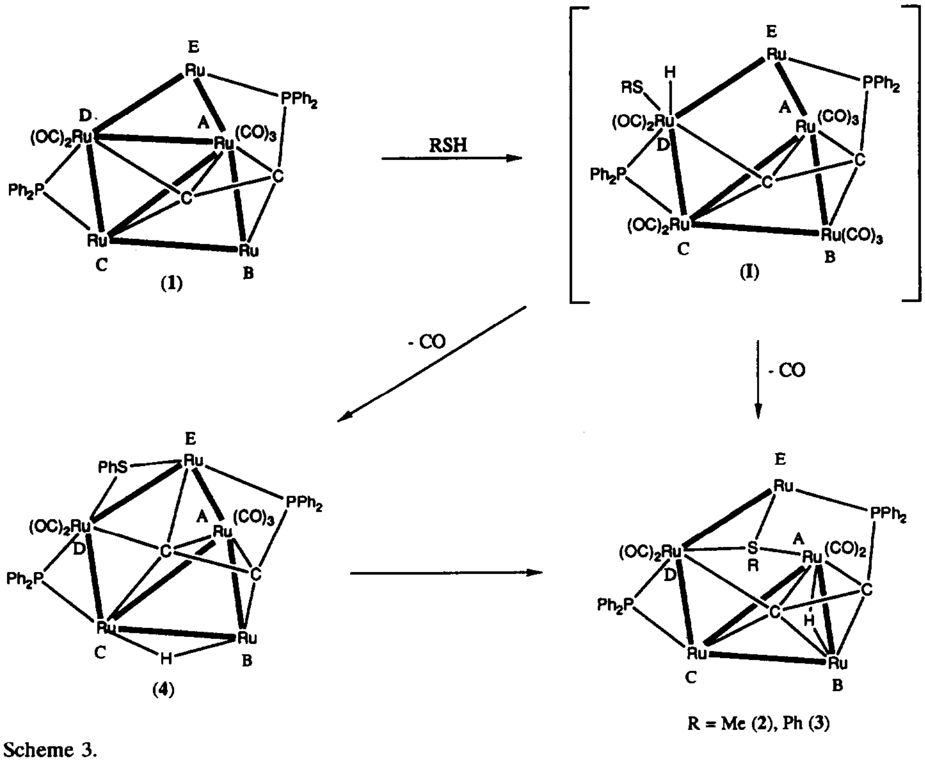
Fig. 5. ORTEP plot of a molecule of $Ru_5(\mu_5$-$C_2H)(\mu_3$-$SPh)(\mu$-$PPh_2)_2(CO)_{12}$ (7).

bons. Overall, the attachment of C(1)–C(2) to the Ru_4 base is similar to that found in **4**.

The identification of the capping group as C_2H is based on the expected electron count: after the other ligands are taken into consideration, this group is required to donate five electrons for the cluster to have the expected 78-electron configuration. The ^1H NMR spectrum is consistent with this, a resonance at δ 9.66 being assigned to the C_2H proton. No Ru–H resonance was observed. The ion of highest mass in the FAB mass spectrum is at m/z 1319, assigned to $[M - CO]^+$.

4.4. Molecular structure of $Ru_5\{\mu_5$-$C_2H(PPh_2)\}(\mu_3$-$SPh)(\mu$-$PPh_2)(\mu$-$CO)(CO)_{11}$ (6)

A molecule of **6** is depicted in Fig. 4 and selected bond lengths and angles are given in Table 3. The Ru_5



Scheme 3.

TABLE 5. Non-hydrogen coordinates and equivalent isotropic displacement parameters for **2**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.64554(4)	0.21144(2)	0.80462(2)	0.0267(2)
Ru(2)	0.63902(4)	0.27945(2)	0.92793(2)	0.0272(2)
Ru(3)	0.71036(4)	0.35031(2)	0.83376(2)	0.0299(2)
Ru(4)	0.80868(4)	0.13359(2)	0.93438(2)	0.0278(2)
Ru(5)	0.96653(4)	0.19163(2)	1.07996(2)	0.0305(2)
C(11)	0.6922(6)	0.2052(3)	0.7278(3)	0.044(3)
O(11)	0.7233(6)	0.2080(3)	0.6818(3)	0.082(3)
C(12)	0.4732(6)	0.2289(3)	0.7419(3)	0.043(3)
O(12)	0.3711(4)	0.2418(3)	0.7059(3)	0.069(3)
C(21)	0.6285(5)	0.3445(3)	0.9938(3)	0.043(3)
O(21)	0.6118(5)	0.3874(3)	1.0271(3)	0.073(3)
C(22)	0.4731(5)	0.2477(3)	0.8909(3)	0.042(3)
O(22)	0.3734(4)	0.2302(3)	0.8696(3)	0.072(3)
C(31)	0.8291(6)	0.3596(3)	0.7974(3)	0.046(3)
O(31)	0.8953(5)	0.3654(3)	0.7723(3)	0.077(3)
C(32)	0.5793(6)	0.3646(3)	0.7309(3)	0.048(3)
O(32)	0.5101(5)	0.3735(3)	0.6720(3)	0.074(3)
C(33)	0.7247(6)	0.4406(3)	0.8690(3)	0.049(3)
O(33)	0.7299(5)	0.4940(2)	0.8906(3)	0.081(3)
C(41)	0.9157(5)	0.1182(3)	0.8917(3)	0.041(3)
O(41)	0.9816(5)	0.1108(3)	0.8661(3)	0.076(3)
C(42)	0.8391(6)	0.0473(3)	0.9765(4)	0.054(3)
O(42)	0.8535(5)	−0.0066(2)	0.9983(3)	0.091(3)
C(51)	1.1050(6)	0.1700(3)	1.0623(3)	0.044(3)
O(51)	1.1912(4)	0.1564(2)	1.0563(3)	0.068(3)
C(52)	0.9729(6)	0.1050(3)	1.1253(3)	0.045(3)
O(52)	0.9809(5)	0.0564(2)	1.1562(3)	0.075(3)
C(53)	1.0479(6)	0.2270(3)	1.1798(3)	0.051(3)
O(53)	1.1035(6)	0.2441(3)	1.2399(3)	0.091(3)
C(1)	0.8232(4)	0.3025(2)	0.9389(3)	0.028(2)
C(2)	0.7815(4)	0.2462(2)	0.8969(3)	0.025(2)
P(1)	0.9574(1)	0.30157(7)	1.02753(7)	0.0270(6)
C(111)	1.0885(5)	0.3187(3)	1.0089(3)	0.029(2)
C(112)	1.1946(5)	0.3503(3)	1.0621(3)	0.043(3)
C(113)	1.2954(6)	0.3573(4)	1.0475(4)	0.061(4)
C(114)	1.2932(6)	0.3349(4)	0.9839(4)	0.067(4)
C(115)	1.1878(6)	0.3026(4)	0.9313(4)	0.070(4)
C(116)	1.0860(5)	0.2949(3)	0.9443(3)	0.047(3)
C(121)	0.9460(5)	0.3747(3)	1.0782(3)	0.031(2)
C(122)	0.9613(6)	0.4390(3)	1.0558(3)	0.044(3)
C(123)	0.9453(7)	0.4948(3)	1.0910(4)	0.057(4)
C(124)	0.9165(6)	0.4880(3)	1.1502(4)	0.054(4)
C(125)	0.9009(6)	0.4263(3)	1.1716(4)	0.054(4)
C(126)	0.9148(6)	0.3685(3)	1.1362(3)	0.043(3)
P(2)	0.6289(1)	0.10051(7)	0.82746(8)	0.0301(6)
C(211)	0.4915(5)	0.0742(3)	0.8353(3)	0.034(3)
C(212)	0.4958(6)	0.0569(4)	0.9028(4)	0.060(4)
C(213)	0.3858(8)	0.0428(5)	0.9071(4)	0.087(5)
C(214)	0.2717(7)	0.0448(4)	0.8430(5)	0.078(5)
C(215)	0.2690(6)	0.0594(4)	0.7766(4)	0.073(4)
C(216)	0.3769(6)	0.0747(4)	0.7718(4)	0.058(4)
C(221)	0.6402(5)	0.0341(3)	0.7680(3)	0.034(2)
C(222)	0.6772(6)	−0.0300(3)	0.7973(3)	0.050(3)
C(223)	0.6849(6)	−0.0816(3)	0.7546(4)	0.058(4)
C(224)	0.6541(6)	−0.0711(3)	0.6798(4)	0.053(3)
C(225)	0.6163(7)	−0.0084(4)	0.6494(4)	0.064(4)
C(226)	0.6116(6)	0.0441(3)	0.6943(3)	0.050(3)
S	0.7417(1)	0.18991(7)	1.01368(7)	0.0311(6)
C(0)	0.6633(6)	0.1553(3)	1.0628(4)	0.053(4)
H(23)	0.586(6)	0.337(3)	0.867(3)	0.07(2)

TABLE 6. Non-hydrogen positional and equivalent isotropic displacement parameters for **3**

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Ru(1)	0.25710(1)	1.20032(2)	0.73836(3)	0.03076(9)
Ru(2)	0.26519(1)	0.98891(2)	0.51353(3)	0.02821(9)
Ru(3)	0.16239(1)	1.08637(2)	0.48544(3)	0.03339(9)
Ru(4)	0.27437(1)	1.01277(2)	0.88325(3)	0.02834(9)
Ru(5)	0.21985(1)	0.74812(2)	0.75963(3)	0.03050(9)
C(11)	0.2096(2)	1.2948(3)	0.8437(4)	0.049(1)
O(11)	0.1768(1)	1.3463(3)	0.9012(3)	0.083(1)
C(12)	0.2991(2)	1.3362(3)	0.6793(4)	0.053(1)
O(12)	0.3229(2)	1.4195(3)	0.6461(4)	0.090(2)
C(21)	0.2593(1)	0.8645(3)	0.3374(4)	0.040(1)
O(21)	0.2551(1)	0.7956(2)	0.2278(3)	0.073(1)
C(22)	0.3408(1)	1.0962(3)	0.5095(4)	0.042(1)
O(22)	0.3855(1)	1.1588(2)	0.5007(3)	0.070(1)
C(31)	0.0954(2)	1.1334(3)	0.5665(4)	0.053(2)
O(31)	0.0551(1)	1.1623(3)	0.6136(4)	0.087(2)
C(32)	0.1845(2)	1.2382(3)	0.4296(4)	0.051(1)
O(32)	0.1989(1)	1.3215(2)	0.3864(3)	0.075(1)
C(33)	0.1114(2)	0.9878(3)	0.3050(4)	0.046(1)
O(33)	0.0804(1)	0.9308(3)	0.1999(3)	0.069(1)
C(41)	0.2233(2)	1.0711(3)	1.0111(4)	0.044(1)
O(41)	0.1922(1)	1.1058(3)	1.0867(3)	0.077(1)
C(42)	0.3249(1)	0.9804(3)	1.0300(4)	0.041(1)
O(42)	0.3565(1)	0.9658(3)	1.1211(3)	0.066(1)
C(51)	0.1699(2)	0.7828(3)	0.9002(4)	0.047(1)
O(51)	0.1392(1)	0.7918(3)	0.9844(3)	0.075(1)
C(52)	0.2755(2)	0.7028(3)	0.8930(4)	0.046(1)
O(52)	0.3040(1)	0.6667(3)	0.9692(3)	0.072(1)
C(53)	0.1854(2)	0.5740(3)	0.6734(4)	0.051(1)
O(53)	0.1589(2)	0.4716(2)	0.6366(4)	0.087(1)
C(1)	0.1732(1)	0.9343(3)	0.5700(3)	0.030(1)
C(2)	0.2098(1)	1.0277(3)	0.6799(3)	0.030(1)
P(1)	0.14531(3)	0.78349(7)	0.58605(9)	0.0301(3)
C(111)	0.0723(1)	0.7829(3)	0.6475(4)	0.038(1)
C(112)	0.0277(2)	0.6730(3)	0.6212(5)	0.059(2)
C(113)	−0.0241(2)	0.6725(4)	0.6851(6)	0.077(2)
C(114)	−0.0311(2)	0.7794(5)	0.7759(5)	0.073(2)
C(115)	0.0133(2)	0.8894(4)	0.8042(4)	0.059(2)
C(116)	0.0646(1)	0.8920(3)	0.7392(4)	0.046(1)
C(121)	0.1259(1)	0.6783(3)	0.4049(4)	0.035(1)
C(122)	0.0749(2)	0.6793(3)	0.3102(4)	0.050(1)
C(123)	0.0634(2)	0.6094(4)	0.1673(5)	0.065(2)
C(124)	0.1028(2)	0.5366(4)	0.1177(4)	0.063(2)
C(125)	0.1530(2)	0.5331(3)	0.2110(4)	0.052(1)
C(126)	0.1650(1)	0.6037(3)	0.3531(4)	0.042(1)
P(2)	0.33514(3)	1.21300(7)	0.91792(9)	0.0337(3)
C(211)	0.4150(1)	1.2293(3)	0.8895(4)	0.041(1)
C(212)	0.4438(1)	1.1328(3)	0.8822(5)	0.058(2)
C(213)	0.5046(2)	1.1475(4)	0.8599(5)	0.074(2)
C(214)	0.5359(2)	1.2561(5)	0.8456(5)	0.077(2)
C(215)	0.5075(2)	1.3530(5)	0.8498(6)	0.087(2)
C(216)	0.4474(2)	1.3401(4)	0.8732(5)	0.072(2)
C(221)	0.3449(1)	1.3286(3)	1.0925(4)	0.036(1)
C(222)	0.3725(2)	1.3093(3)	1.2148(4)	0.063(2)
C(223)	0.3797(2)	1.3957(4)	1.3474(4)	0.075(2)
C(224)	0.3591(2)	1.5025(3)	1.3584(4)	0.057(2)
C(225)	0.3321(2)	1.5227(3)	1.2372(5)	0.054(2)
C(226)	0.3250(2)	1.4374(3)	1.1045(4)	0.049(1)
S	0.30011(3)	0.88005(7)	0.67723(9)	0.0305(3)
C(101)	0.3729(1)	0.8399(3)	0.6625(4)	0.036(1)
C(102)	0.4003(2)	0.7917(4)	0.7606(5)	0.067(2)
C(103)	0.4564(2)	0.7591(5)	0.7464(5)	0.080(2)

TABLE 6 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(104)	0.4844(2)	0.7805(5)	0.6359(5)	0.070(2)
C(105)	0.4583(2)	0.8310(4)	0.5393(5)	0.061(2)
C(106)	0.4016(2)	0.8594(3)	0.5507(4)	0.049(1)
H(23)	0.233(1)	1.068(3)	0.410(3)	0.047(9)

framework again has an edge-bridged rhomboidal structure. However, in contrast with **4** and **5**, the envelope is kept open by a μ_3-SPh group, the dihedral angles being 87.6(2), 87.4(2)° (values for the two pseudosymmetrically related molecules which comprise the asymmetric unit are given). On the other side of the Ru_4 square is a μ_4-CCH(PPh_2) group. In the present case it is formed by addition of an H atom from thiophenol to C_β of the C_2PPh_2 group in **1**. Although this hydrogen was not located in the X-ray study, the ^{1}H NMR spectrum contains a resonance at δ 5.61, in the region where vinylidene H resonances are usually found [11], which is consistent with the above formulation. No Ru hydride resonances were observed. The Ru_4 base is also bridged by a μ-PPh_2 ligand [Ru(2)–P(1) 2.30(2), 2.31(1); Ru(3)–P(1) 2.30(2) (×2) Å], while the flap is semi-bridged by a μ-CO ligand [Ru(4)–C(42) 1.91(4), 1.93(4); Ru(5)–C(42) 2.49(5), 2.40(4) Å; Ru(4)–C(42)–O(42) 160(4), 149(4)°]. Of the remaining CO groups, three are located on Ru(5) and each of the remaining Ru atoms bears two. Atom C(2) caps the Ru_4 face, with C(1)–C(2) interacting with Ru(1) in an η^2-fashion; P(2) is also bonded to Ru(1), resulting in the formation of a C_2PRu ring. The c.v.e. count of 78 is obtained from 5Ru (40), 12CO (24), μ-PPh_2 (3), μ_3-SPh (5) and μ_4-CCH(PPh_2) (6).

4.5. Molecular structure of $Ru_5(\mu_5\text{-}C_2H)(\mu_3\text{-}SPh)(\mu\text{-}PPh_2)_2(CO)_{12}$ (7)

A molecule of **7** is depicted in Fig. 5 and selected bond lengths and angles are given in Table 4. The core consists of a folded Ru_4 rhomboid [dihedral across Ru(1) ··· Ru(3) 38.30(5)°] which is metallated at one corner by the fifth Ru atom [Ru(4)–Ru(5) 2.8526(8) Å]. The Ru–Ru separations range between 2.8292(8)–2.8881(8) Å, except for Ru(2)–Ru(3) [2.7464(7) Å], which is bridged by both a PPh_2 and the SPh groups, and the non-bonded cross-ring vector. The second PPh_2 group bridges the non-bonded Ru(1) ··· Ru(5) vector [Ru–P 2.322–2.418(1) Å], while the SPh group caps the Ru(1)–Ru(2)–Ru(3) portion of the core [Ru–S 2.397–2.434(1) Å].

Significant differences between the Ru–P bond lengths associated with the two PPh_2 groups are found: that bridging the bonded Ru(2)–Ru(3) vector is closer to the metal atoms [Ru(2,3)–P(2) 2.285, 2.318(2) Å] than the other which bridges a non-bonded Ru ··· Ru vector [Ru(1,5)–P(1) 2.322, 2.418(2) Å]. The angles subtended by the two bridged metal atoms at P(1) and P(2) are 105.18(4) and 73.26(5)°, respectively. Long Ru–PR_2 distances and obtuse Ru–P–Ru angles have previously been found when PPh_2 groups bridge non-bonded Ru ··· Ru vectors, *e.g.* 2.398 Å and 92.8° in the open 50 c.v.e. cluster $Ru_3(\mu_3\text{-}C_2{}^iPr)(\mu\text{-}PPh_2)(CO)_9$ compared with 2.341 Å and 74.4° in the closed 48 c.v.e. complex $Ru_3(\mu_3\text{-}C_2{}^tBu)(\mu\text{-}PPh_2)(CO)_8$ [12].

The three Ru–S distances are unequal, that to Ru(2) being the shortest. Formally the SPh group donates only one electron to Ru(2) as does P(2) (the Ru(2)–S and –P separations are the shortest in the complex), although Ru(2) is formally electron-deficient, while Ru(4) is electron-rich.

The organic ligand is a μ_5-C_2H group, C(2) being closely attached to Ru(1,2,4) [Ru–C 2.091–2.161(4) Å] but more distant from Ru(3) [2.367(4) Å] and C(1) is within bonding distance of Ru(4) and Ru(5) [Ru(4,5)–C(2) 2.169, 2.097(5) Å]. The 12 CO groups are all terminal and distributed three to each of Ru(4) and Ru(5) and two to each of the other Ru atoms. The presence of the C_2H group in **7** was confirmed from the ^{1}H NMR spectrum which contained the CH resonance at δ 8.95, but no high-field resonance. Complex **7** has the 80-c.v.e. count expected for a species with one fewer Ru–Ru bond than **5**.

5. Discussion

The course of the reaction between **1** and PhSH is summarised in Scheme 1; with MeSH, which reaction was not as thoroughly investigated, complex **2**, analogous to **3**, was obtained as the only isolable product. These clusters belong to an interesting family of relatively open pentanuclear clusters, formed from **1** by cleavage of two Ru–Ru bonds. The precise course of the transformations has not been determined by this study. However, the formation of **2** and **3** as major products by oxidative addition of the thiols to **1** has parallels in the previously described reactions between

TABLE 7. Non-hydrogen positional and equivalent isotropic displacement parameters for 4

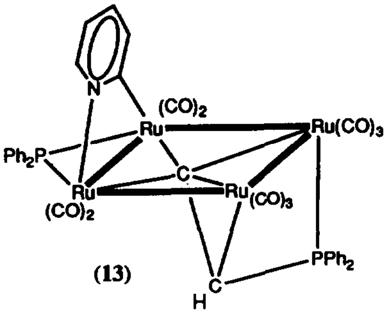
Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.75191(4)	0.55791(7)	0.68274(7)	0.0294(3)
Ru(2)	0.84288(4)	0.34203(7)	0.86534(7)	0.0295(3)
Ru(3)	0.79013(4)	0.18908(7)	0.76393(7)	0.0310(3)
Ru(4)	0.68766(4)	0.40844(8)	0.59764(7)	0.0319(3)
Ru(5)	0.59854(4)	0.54192(7)	0.74508(7)	0.0323(3)
C(11)	0.8227(6)	0.555(1)	0.552(1)	0.047(4)
O(11)	0.8603(4)	0.5665(8)	0.4684(7)	0.067(4)
C(12)	0.7218(5)	0.728(1)	0.609(1)	0.043(4)
O(12)	0.7020(5)	0.8340(7)	0.5669(9)	0.072(4)
C(21)	0.8045(6)	0.328(1)	1.030(1)	0.047(5)
O(21)	0.7898(5)	0.3116(9)	1.1337(7)	0.080(5)
C(22)	0.9356(6)	0.262(1)	0.9447(9)	0.044(4)
O(22)	0.9904(4)	0.2135(8)	0.9969(8)	0.073(4)
C(31)	0.7966(6)	0.082(1)	0.666(1)	0.049(5)
O(31)	0.7988(5)	0.0204(9)	0.6043(9)	0.081(5)
C(32)	0.8425(5)	0.069(1)	0.904(1)	0.047(4)
O(32)	0.8721(4)	−0.0080(8)	0.9899(8)	0.072(4)
C(41)	0.6542(6)	0.572(1)	0.484(1)	0.050(5)
O(41)	0.6360(5)	0.6619(7)	0.4011(7)	0.065(4)
C(42)	0.7568(6)	0.358(1)	0.475(1)	0.054(5)
O(42)	0.7905(5)	0.333(1)	0.3973(8)	0.090(5)
C(43)	0.6191(6)	0.335(1)	0.552(1)	0.053(5)
O(43)	0.5774(5)	0.300(1)	0.5161(8)	0.088(5)
C(51)	0.5558(5)	0.714(1)	0.639(1)	0.045(4)
O(51)	0.5317(4)	0.8117(7)	0.5780(9)	0.073(4)
C(52)	0.5142(6)	0.489(1)	0.724(1)	0.047(5)
O(52)	0.4644(4)	0.4596(8)	0.7114(8)	0.071(4)
C(53)	0.5697(5)	0.573(1)	0.901(1)	0.045(5)
O(53)	0.5523(5)	0.5902(8)	0.9935(8)	0.071(4)
P(1)	0.8380(1)	0.5475(2)	0.8236(2)	0.0321(9)
C(111)	0.9164(5)	0.6105(9)	0.7550(9)	0.038(4)
C(112)	0.9029(5)	0.732(1)	0.681(1)	0.051(5)
C(113)	0.9609(6)	0.781(1)	0.631(1)	0.056(5)
C(114)	1.0307(6)	0.711(1)	0.657(1)	0.061(6)
C(115)	1.0440(6)	0.591(1)	0.732(1)	0.074(6)
C(116)	0.9861(6)	0.538(1)	0.783(1)	0.067(6)
C(121)	0.8104(5)	0.6161(9)	0.9499(9)	0.037(4)
C(122)	0.7432(6)	0.605(1)	1.010(1)	0.058(6)
C(123)	0.7226(6)	0.649(1)	1.113(1)	0.066(6)
C(124)	0.7657(7)	0.702(1)	1.155(1)	0.064(6)
C(125)	0.8301(8)	0.716(1)	1.097(1)	0.068(6)
C(126)	0.8524(6)	0.671(1)	0.997(1)	0.055(5)
C(1)	0.6664(5)	0.3685(9)	0.8031(8)	0.033(4)
C(2)	0.7417(5)	0.3672(8)	0.7767(8)	0.029(3)
P(2)	0.6783(1)	0.2003(2)	0.8671(2)	0.0327(9)
C(211)	0.6059(5)	0.1386(9)	0.8328(9)	0.040(4)
C(212)	0.6210(7)	0.056(1)	0.769(1)	0.076(7)
C(213)	0.5675(8)	0.007(2)	0.742(2)	0.11(1)
C(214)	0.4993(7)	0.042(2)	0.784(2)	0.099(9)
C(215)	0.4840(6)	0.123(1)	0.852(1)	0.076(7)
C(216)	0.5359(6)	0.174(1)	0.875(1)	0.059(5)
C(221)	0.6726(5)	0.1611(9)	1.0410(9)	0.039(4)
C(222)	0.6447(6)	0.250(1)	1.099(1)	0.059(5)
C(223)	0.6384(7)	0.216(1)	1.229(1)	0.069(6)
C(224)	0.6585(6)	0.096(1)	1.301(1)	0.059(5)
C(225)	0.6860(6)	0.006(1)	1.246(1)	0.059(5)
C(226)	0.6933(6)	0.037(1)	1.114(1)	0.048(4)
S	0.8874(1)	0.2837(2)	0.6758(2)	0.0349(9)
C(101)	0.9773(5)	0.1814(9)	0.6951(9)	0.034(4)
C(102)	1.0363(5)	0.234(1)	0.673(1)	0.044(4)
C(103)	1.1059(5)	0.157(1)	0.677(1)	0.051(5)

TABLE 7 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(104)	1.1176(5)	0.031(1)	0.702(1)	0.054(5)
C(105)	1.0596(6)	−0.021(1)	0.723(1)	0.059(5)
C(106)	0.9892(5)	0.056(1)	0.721(1)	0.050(5)

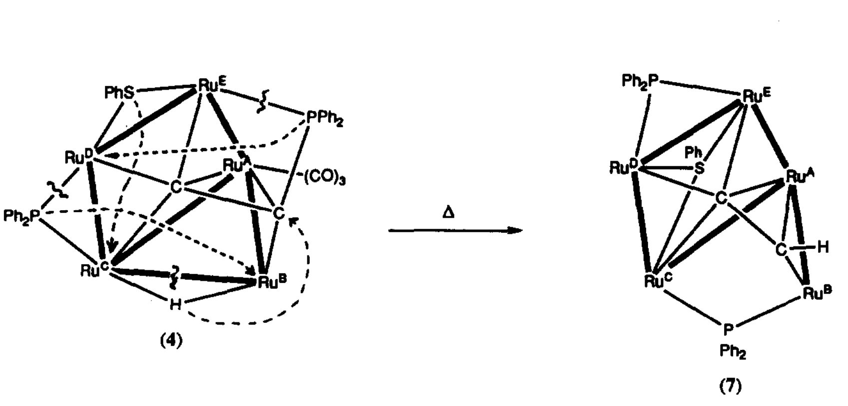
1 and other 4e donor sets (2CO [3]; H + X, X = Cl, Br, I [4]; Au(PR$_3$) + X, X = Cl [4], C$_2$Ph [10]). The presence of extra lone pairs on the sulphur or halogen atom can result in further reaction by loss of a molecule of CO from Ru(2) to form **2**, **3** or **8**, for example, in which the X ligand connects three metal atoms. In the thiolate reactions, we have not observed any intermediates that might have structures analogous to **10**. In all of these cases, it is likely that the *closo*-trigonal bipyramidal C_2Ru_3 nucleus is stable enough to resist further bond breaking, so that CO ligands are lost after its formation if there is a need to coordinate more electron pairs. In these complexes the C_2PPh_2 ligand remains unchanged; the H atom from the thiol is found bridging Ru(2)–Ru(3) in a position which allows each Ru atom to achieve an 18e configuration.

As revealed by their molecular structures, the minor product, **6**, from the low temperature reaction between **1** and PhSH, and the other complexes formed in the high temperature reaction (**4** and **5**) or on pyrolysis of **3** and **4** (**5** and **7**, respectively) contain ligands formed by major alterations of the C_2PPh_2 group. Complex **4** is isomeric with **3**, but contains one more Ru–Ru bond. This geometry is achieved by the formation of a bond between Ru(2)–Ru(5), with the SPh group bridging only two metal atoms. In **6**, addition of H to C_2PPh_2, presumably *via* the cluster, has given the diphenylphosphinovinylidene ligand, which has also been characterised in $Ru_4\{\mu_4\text{-}CCH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (**13**) [13]. Cleavage of the P–C bond and addition of the H atom to a carbon of the resulting C_2 ligand (or *vice versa*) has given cluster-bonded CCH ligands in **5** and **7**, with formation of a second PPh_2 group. In **7**, the SPh group adopts a μ_3-bridging mode. Indeed, complexes **5** and **7** are isomers (although apparently not directly interconvertible) by virtue of $\mu_2 \rightarrow \mu_3$ bonding of the SPh group with cleavage of an Ru–Ru bond. The H atom of the HSPh molecule is found in different locations in each of **4–7**. Bridging the long Ru(1)–Ru(5) bond is the likely position in **4**, whereas in **5–7**, it is bonded to a carbon of the ethynyl or vinylidene group.



(**13**)

As we have commented previously, the metal cores in pentanuclear clusters are quite flexible, adopting a conformation that is likely to be the minimum energy arrangement consistent with bonding of the organic groups to the metal atoms. This is best seen by comparing the skeletons of **4** and **6**, where the flap of the



Scheme 4.

TABLE 8. Non-hydrogen positional and equivalent isotropic displacement parameters for 5

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.80710(4)	0.44737(5)	0.44236(4)	0.0348(3)
Ru(2)	0.68625(4)	0.39255(5)	0.29998(4)	0.0361(3)
Ru(3)	0.58591(4)	0.50569(6)	0.32107(4)	0.0460(4)
Ru(4)	0.69684(4)	0.54974(5)	0.47230(4)	0.0458(4)
Ru(5)	0.78444(4)	0.41593(5)	0.56854(4)	0.0407(3)
C(11)	0.8101(5)	0.5812(6)	0.4241(5)	0.049(5)
O(11)	0.8266(4)	0.6616(4)	0.4238(4)	0.072(4)
C(12)	0.9080(5)	0.4629(7)	0.5086(5)	0.051(4)
O(12)	0.9681(3)	0.4789(6)	0.5503(4)	0.084(4)
C(21)	0.6435(5)	0.3697(7)	0.1927(5)	0.055(5)
O(21)	0.6169(4)	0.3567(5)	0.1302(3)	0.082(4)
C(22)	0.6707(5)	0.2623(7)	0.3102(5)	0.049(4)
O(22)	0.6525(4)	0.1826(5)	0.3090(3)	0.070(4)
C(31)	0.5319(5)	0.4405(9)	0.3618(6)	0.077(6)
O(31)	0.5001(4)	0.4017(7)	0.3865(4)	0.104(5)
C(32)	0.5381(6)	0.6265(8)	0.3125(6)	0.074(6)
O(32)	0.5108(4)	0.6977(6)	0.3096(5)	0.111(5)
C(33)	0.5209(5)	0.4522(7)	0.2243(6)	0.059(5)
O(33)	0.4798(3)	0.4219(5)	0.1668(4)	0.077(4)
C(41)	0.6978(6)	0.6834(7)	0.4509(6)	0.070(6)
O(41)	0.6988(5)	0.7641(5)	0.4415(5)	0.115(7)
C(42)	0.6235(6)	0.5740(7)	0.4991(6)	0.069(6)
O(42)	0.5795(5)	0.5864(6)	0.5158(5)	0.108(6)
C(51)	0.7474(5)	0.3537(7)	0.6260(5)	0.054(5)
O(51)	0.7237(4)	0.3124(5)	0.6578(4)	0.078(4)
C(52)	0.8831(5)	0.4370(7)	0.6559(5)	0.055(5)
O(52)	0.9392(4)	0.4503(6)	0.7037(4)	0.086(4)
C(53)	0.7848(6)	0.5706(7)	0.5803(6)	0.066(6)
O(53)	0.8188(5)	0.6315(5)	0.6222(4)	0.115(5)
C(1)	0.6851(4)	0.3931(6)	0.4697(5)	0.042(4)
C(2)	0.6862(4)	0.4247(6)	0.4037(4)	0.038(4)
P(1)	0.8087(1)	0.3931(2)	0.3337(1)	0.037(1)
C(111)	0.8337(4)	0.4710(6)	0.2766(5)	0.040(4)
C(112)	0.8132(5)	0.4406(7)	0.2029(5)	0.048(4)
C(113)	0.8305(5)	0.4957(7)	0.1562(5)	0.056(5)
C(114)	0.8670(6)	0.5811(8)	0.1815(6)	0.069(6)
C(115)	0.8876(6)	0.6115(7)	0.2538(6)	0.076(6)
C(116)	0.8713(5)	0.5553(7)	0.3016(5)	0.056(5)
C(121)	0.8643(5)	0.2883(6)	0.3399(4)	0.041(4)
C(122)	0.8394(5)	0.1948(7)	0.3320(5)	0.053(5)
C(123)	0.8852(6)	0.1171(7)	0.3422(6)	0.068(6)
C(124)	0.9569(6)	0.1332(8)	0.3613(6)	0.079(6)
C(125)	0.9823(5)	0.2247(8)	0.3690(6)	0.075(6)
C(126)	0.9368(5)	0.3021(7)	0.3579(5)	0.056(5)
P(2)	0.8217(1)	0.2986(2)	0.5153(1)	0.038(1)
C(211)	0.7722(5)	0.1841(6)	0.4859(4)	0.043(4)
C(212)	0.7080(5)	0.1669(6)	0.4903(5)	0.048(4)
C(213)	0.6711(5)	0.0806(7)	0.4683(6)	0.063(5)
C(214)	0.6987(5)	0.0082(7)	0.4433(5)	0.065(5)
C(215)	0.7635(5)	0.0219(6)	0.4406(5)	0.059(5)
C(216)	0.7993(5)	0.1092(6)	0.4620(5)	0.048(4)
C(221)	0.9131(5)	0.2480(6)	0.5750(5)	0.046(4)
C(222)	0.9299(5)	0.2079(7)	0.6445(5)	0.054(5)
C(223)	0.9945(5)	0.1595(7)	0.6883(5)	0.066(5)
C(224)	1.0443(5)	0.1492(7)	0.6616(6)	0.074(6)
C(225)	1.0298(5)	0.1891(7)	0.5928(6)	0.067(6)
C(226)	0.9636(5)	0.2389(7)	0.5487(5)	0.058(5)
S	0.6690(1)	0.5655(2)	0.2799(1)	0.044(1)
C(101)	0.6258(5)	0.6002(6)	0.1818(5)	0.050(5)
C(102)	0.6700(6)	0.6074(8)	0.1496(6)	0.078(6)
C(103)	0.6404(8)	0.6363(9)	0.0738(7)	0.104(8)

TABLE 8 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(104)	0.5703(7)	0.6629(9)	0.0331(6)	0.093(7)
C(105)	0.5270(6)	0.6615(9)	0.0672(6)	0.097(7)
C(106)	0.5541(6)	0.6297(8)	0.1410(6)	0.081(6)
Cl(1)	0.6811(3)	0.9860(3)	0.2114(3)	0.185(4)
Cl(2)	0.6421(3)	0.8371(3)	0.2777(2)	0.139(3)
Cl(3)	0.7647(3)	0.8176(5)	0.2629(5)	0.280(6)
C	0.6802(6)	0.8661(9)	0.2205(6)	0.083(7)

envelope is found on different sides of the Ru_4 rhombus relative to the organic ligand, and in **5** and particularly **7**, where the envelopes (or edge-bridged rhombi) distort more markedly on breaking of one of the 'flap' Ru–Ru bonds as a result of the interaction of the SPh group with a third Ru atom. In **4**, **5** and **6**, for the central 'plane', Ru deviations are *ca.* ±0.07, ±0.07–0.09 and ±0.05, 0.06 Å, respectively, with C(2) 0.71(1), 0.84(1) and 0.69(4), 0.72(4) Å above the plane. In **7**, deviations are much larger (±0.34–0.36 Å) and C(2) is 0.94 Å above the plane.

Once again we find a key feature of these structures is coordination of a C_2 fragment to the M_5 cluster by formation of a tightly, if asymmetrically, bonded $CCRu_4$ core. The metal-bonded carbon atom (C_α) is bonded to all four metal atoms, if somewhat asymmetrically, in these complexes and is apparently relatively inert, the chemistry of the system occuring at the second carbon (C_β). At this stage, the function of the fifth metal atom is not clear: does it play a fundamental role in stabilising the cluster, or is it just a convenient anchor point for the extended ligand systems?

The $Ru_5(\mu_5\text{-}C_2R)$ system has been found before in complex **11**, which has been isolated from several reactions of **1** [14]. Complex **11** is an isomer of **1** and is formed by migration of Ph from P to C (probably *via* the cluster) with formal extrusion of PPh to cap the Ru_4 face; the resulting phenylethynyl ligand interacts with all five metal atoms in a similar fashion to the parent ethynyl ligand in **5**. The Ru_5 complex **12**, obtained by pyrolysis of $Ru_3(CO)_{11}(PPh_3)$, contains a μ_5-benzyne ligand on a similar cluster [15]. As might be expected for an alkyne ligand, however, a different geometry is found for the $\mu_4\text{-}C_2$ unit in **12**.

This particular five-atom cluster geometry has been compared to the step-site in a metal (111) surface [14,15] and it has been suggested [16] that small molecules (particularly benzene) can undergo facile C–H bond activation as a result of the close approaches of the H atoms to metal atoms in a layer below that containing the metal atoms to which the molecules are initially bound. Consequently, it will be interesting to determine the reactivity of molecules supported on five metal atom-clusters of this type. Although **5** was isolated only a very small amount, other reactions of **1**, to be described elsewhere, have given related molecules in amounts large enough to study their chemistry.

A plausible route to **3** (and **2**) and **4** is shown in Scheme 3. We have shown previously that the preferred site of substitution of CO in **1** by tertiary phosphites is Ru(D) [17]. Oxidative addition of RSH to Ru(D) with loss of CO affords the intermediate **I** (not isolated); the RS group then bridges Ru(D)–Ru(E) with concomitant cleavage of Ru(A)–Ru(D), to give the edge-bridged core found in **4**. Conversion of **4** to **3** by the SR group acting as a triply-bridging group, with cleavage of Ru(A)–Ru(E), gives the scorpion cluster found in **3** (and **2**).

The formation of **5** involves cleavage of the C_β–P bond, the resulting PPh_2 ligand bridging an Ru–Ru bond, and migration of H from the cluster to the C_2 unit to give an ethynyl ligand. Its attachment to the Ru_3 portion of the cluster differs from the usual $\sigma,2\pi$ system and resembles more the $2\sigma,\pi$ bonding of an alkyne. The latter interpretation is given substance if the Ru(1)–Ru(5) moiety is considered to be the second alkyne substituent and is also consistent with the C–C bond length [1.44(1) Å]. The net reaction is:

$$H[Ru_5]CCPPh_2 \longrightarrow HCC[Ru_5]PPh_2$$

where $[Ru_5]$ represents the cluster framework.

It is noteworthy that all complexes **3**–**7** are isomers, the structural changes described above occurring without loss of CO, with **5** and **7** being strictly isomeric, containing the same ligands. However, the reaction is more complicated than implied by the simple approach described above, because while **3** is formed from **1** and RSH at low temperatures (18°C), **4** is also formed under more vigorous conditions. Heating **4** gives **3** and **6**, while heating **3** gives **6** but no **4**.

On heating **3**, conversion to **6** by migration of the cluster-bound H atom to C_β [C(1)] and formation of a vinylidene ligand occurs. In essence, the transformation of the organic ligand can be represented as:

$$H[Ru_5]C_2PPh_2 \longrightarrow [Ru_5]CCH(PPh_2)$$

TABLE 9. Non-hydrogen positional and equivalent isotropic displacement parameters for **6**

Atom	x	y	z	U_{eq} (Å^2)
Molecule 1				
Ru(11)	0.1966(2)	0.7134(2)	0.5247(2)	0.043(2)
Ru(12)	0.2781(2)	0.6959(2)	0.4562(2)	0.036(2)
Ru(13)	0.1873(2)	0.5994(2)	0.3846(2)	0.037(2)
Ru(14)	0.1084(2)	0.6036(2)	0.4524(2)	0.041(2)
Ru(15)	0.0889(2)	0.7557(3)	0.4250(2)	0.047(2)
C(111)	0.153(2)	0.736(3)	0.567(2)	0.05(2)
O(111)	0.126(2)	0.772(2)	0.594(2)	0.08(1)
C(112)	0.277(3)	0.760(4)	0.572(3)	0.09(2)
O(112)	0.327(2)	0.799(2)	0.592(2)	0.10(1)
C(121)	0.309(3)	0.783(3)	0.462(2)	0.05(2)
O(121)	0.354(2)	0.840(2)	0.472(2)	0.07(1)
C(122)	0.359(3)	0.663(4)	0.514(3)	0.09(2)
O(122)	0.403(2)	0.640(2)	0.552(2)	0.08(1)
C(131)	0.206(2)	0.497(2)	0.396(2)	0.03(1)
O(131)	0.217(2)	0.437(2)	0.403(1)	0.06(1)
C(132)	0.131(3)	0.578(3)	0.313(2)	0.06(2)
O(132)	0.095(2)	0.563(2)	0.268(2)	0.10(1)
C(141)	0.080(2)	0.510(2)	0.425(2)	0.03(1)
O(141)	0.066(2)	0.443(2)	0.414(2)	0.10(2)
C(142)	0.037(2)	0.636(3)	0.384(2)	0.05(1)
O(142)	−0.004(2)	0.636(2)	0.336(2)	0.08(1)
C(143)	0.059(2)	0.606(3)	0.492(2)	0.05(2)
O(143)	0.024(2)	0.612(2)	0.522(2)	0.10(2)
C(151)	0.033(2)	0.770(2)	0.456(2)	0.03(1)
O(151)	−0.010(2)	0.790(2)	0.475(1)	0.07(1)
C(152)	0.158(3)	0.825(3)	0.475(2)	0.06(2)
O(152)	0.182(2)	0.882(2)	0.481(2)	0.10(2)
C(153)	0.032(3)	0.807(3)	0.361(2)	0.07(2)
O(153)	−0.001(2)	0.844(2)	0.324(2)	0.08(1)
C(11)	0.211(3)	0.563(3)	0.512(2)	0.05(2)
C(12)	0.204(2)	0.620(2)	0.470(2)	0.02(1)
P(11)	0.2881(7)	0.6359(8)	0.3809(5)	0.037(6)
C(1111)	0.357(2)	0.563(3)	0.396(2)	0.04(1)
C(1112)	0.370(3)	0.515(3)	0.444(2)	0.07(2)
C(1113)	0.414(3)	0.466(4)	0.451(3)	0.08(2)
C(1114)	0.449(3)	0.459(3)	0.417(2)	0.06(2)
C(1115)	0.439(3)	0.503(3)	0.375(2)	0.06(2)
C(1116)	0.393(2)	0.557(3)	0.360(2)	0.04(1)
C(1121)	0.293(2)	0.682(2)	0.321(2)	0.03(1)
C(1122)	0.240(2)	0.672(3)	0.266(2)	0.04(1)
C(1123)	0.250(3)	0.708(3)	0.220(2)	0.06(2)
C(1124)	0.303(3)	0.757(4)	0.226(3)	0.08(2)
C(1125)	0.346(3)	0.771(3)	0.282(2)	0.06(2)
C(1126)	0.342(3)	0.734(3)	0.330(2)	0.06(2)
P(12)	0.2287(7)	0.6043(8)	0.5742(6)	0.049(7)
C(1211)	0.184(2)	0.562(2)	0.612(2)	0.03(1)
C(1212)	0.179(3)	0.590(4)	0.662(3)	0.10(2)
C(1213)	0.146(3)	0.558(3)	0.691(2)	0.06(2)
C(1214)	0.120(3)	0.495(3)	0.676(2)	0.07(2)
C(1215)	0.118(3)	0.467(3)	0.631(2)	0.07(2)
C(1216)	0.155(2)	0.492(3)	0.598(2)	0.05(1)
C(1221)	0.316(2)	0.588(3)	0.622(2)	0.05(2)
C(1222)	0.344(3)	0.513(3)	0.625(2)	0.06(2)
C(1223)	0.401(3)	0.502(4)	0.662(3)	0.10(2)
C(1224)	0.434(3)	0.543(3)	0.699(3)	0.08(2)
C(1225)	0.422(3)	0.618(4)	0.703(3)	0.09(2)
C(1226)	0.351(3)	0.629(4)	0.659(3)	0.09(2)
S(1)	0.1697(6)	0.7261(7)	0.3839(5)	0.041(6)
C(101)	0.152(3)	0.783(3)	0.321(2)	0.07(2)
C(102)	0.101(3)	0.769(3)	0.271(3)	0.08(2)

TABLE 9 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(103)	0.094(3)	0.816(3)	0.223(2)	0.07(2)
C(104)	0.138(3)	0.870(3)	0.229(2)	0.07(2)
C(105)	0.187(3)	0.879(4)	0.275(3)	0.08(2)
C(106)	0.203(3)	0.837(3)	0.325(2)	0.06(2)
Molecule 2				
Ru(21)	0.7197(2)	0.5873(2)	1.0303(2)	0.030(2)
Ru(22)	0.7934(2)	0.5663(2)	0.9560(2)	0.028(2)
Ru(23)	0.6988(2)	0.4698(2)	0.8872(2)	0.030(2)
Ru(24)	0.6288(2)	0.4769(2)	0.9632(2)	0.028(2)
Ru(25)	0.6066(2)	0.6274(2)	0.9331(2)	0.035(2)
C(211)	0.679(2)	0.619(2)	1.076(2)	0.03(1)
O(211)	0.653(2)	0.650(2)	1.105(2)	0.07(1)
C(212)	0.796(3)	0.637(3)	1.066(2)	0.06(2)
O(212)	0.849(2)	0.668(2)	1.087(1)	0.06(1)
C(221)	0.834(2)	0.653(3)	0.958(2)	0.04(1)
O(221)	0.869(2)	0.704(2)	0.961(2)	0.07(1)
C(222)	0.872(3)	0.533(3)	1.006(3)	0.08(2)
O(222)	0.923(2)	0.504(2)	1.044(2)	0.07(1)
C(231)	0.711(2)	0.372(2)	0.896(2)	0.02(1)
O(231)	0.728(2)	0.311(2)	0.901(1)	0.05(1)
C(232)	0.635(3)	0.451(3)	0.814(2)	0.06(2)
O(232)	0.598(2)	0.436(2)	0.768(2)	0.09(1)
C(241)	0.604(2)	0.379(3)	0.943(2)	0.044(8)
O(241)	0.574(2)	0.330(2)	0.921(1)	0.048(9)
C(242)	0.554(2)	0.513(2)	0.897(2)	0.029(6)
O(242)	0.503(1)	0.500(2)	0.856(1)	0.032(7)
C(243)	0.590(2)	0.483(2)	1.013(2)	0.02(1)
O(243)	0.564(1)	0.498(2)	1.045(1)	0.031(8)
C(251)	0.554(2)	0.645(2)	0.968(2)	0.02(1)
O(251)	0.513(2)	0.662(2)	0.990(1)	0.05(1)
C(252)	0.680(3)	0.691(3)	0.981(2)	0.06(2)
O(252)	0.701(1)	0.754(2)	0.984(1)	0.042(9)
C(253)	0.550(2)	0.681(3)	0.870(2)	0.04(1)
O(253)	0.512(2)	0.715(2)	0.831(2)	0.08(1)
C(21)	0.723(2)	0.434(2)	1.018(2)	0.02(1)
C(22)	0.728(2)	0.496(2)	0.979(2)	0.02(1)
P(21)	0.7984(6)	0.5028(7)	0.8799(5)	0.028(5)
C(2111)	0.867(2)	0.435(2)	0.889(2)	0.02(1)
C(2112)	0.876(2)	0.389(3)	0.938(2)	0.05(2)
C(2113)	0.927(3)	0.337(3)	0.944(3)	0.08(2)
C(2114)	0.964(3)	0.330(3)	0.914(2)	0.05(2)
C(2115)	0.959(3)	0.376(4)	0.874(3)	0.09(2)
C(2116)	0.903(3)	0.431(3)	0.863(2)	0.06(2)
C(2121)	0.804(2)	0.558(3)	0.819(2)	0.03(1)
C(2122)	0.756(3)	0.539(3)	0.766(2)	0.06(2)
C(2123)	0.755(3)	0.577(4)	0.723(3)	0.08(2)
C(2124)	0.800(3)	0.629(4)	0.729(3)	0.09(2)
C(2125)	0.851(3)	0.645(3)	0.783(3)	0.08(2)
C(2126)	0.850(3)	0.604(3)	0.831(3)	0.08(2)
P(22)	0.7523(6)	0.4795(6)	1.0807(6)	0.030(6)
C(2211)	0.710(2)	0.441(2)	1.123(2)	0.02(1)
C(2212)	0.707(2)	0.471(2)	1.166(2)	0.03(1)
C(2213)	0.678(2)	0.439(2)	1.201(2)	0.03(1)
C(2214)	0.642(3)	0.375(3)	1.184(2)	0.06(2)
C(2215)	0.646(2)	0.341(3)	1.136(2)	0.04(1)
C(2216)	0.681(2)	0.368(3)	1.106(2)	0.03(1)
C(2221)	0.842(2)	0.470(3)	1.129(2)	0.05(1)
C(2222)	0.878(3)	0.406(3)	1.120(3)	0.08(2)
C(2223)	0.945(3)	0.390(4)	1.155(3)	0.11(3)
C(2224)	0.974(3)	0.444(3)	1.204(2)	0.07(2)

TABLE 9 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(2225)	0.941(3)	0.498(3)	1.204(2)	0.07(2)
C(2226)	0.878(2)	0.509(3)	1.167(2)	0.04(1)
S(2)	0.6813(6)	0.5961(7)	0.8859(5)	0.034(5)
C(201)	0.671(2)	0.646(3)	0.828(2)	0.04(1)
C(202)	0.617(3)	0.633(3)	0.774(2)	0.07(2)
C(203)	0.602(4)	0.672(4)	0.729(3)	0.11(3)
C(204)	0.634(3)	0.740(3)	0.733(2)	0.07(2)
C(205)	0.683(4)	0.766(4)	0.786(3)	0.12(3)
C(206)	0.693(3)	0.716(3)	0.835(2)	0.07(2)

However, the reaction is not so simple, as inspection of the two complexes shows that isomerisation by Ru–Ru bond breaking/reformation and/or similar processes involving the PPh_2 and SPh ligands must also occur. It is also interesting to note that the sense of opening of the envelope in **6** is the opposite to that in **4** and **5**, in

TABLE 10. Non-hydrogen positional and equivalent isotropic displacement parameters for **7**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.17877(2)	0.42493(2)	0.24151(4)	0.0297(1)
Ru(2)	0.24953(2)	0.32010(2)	0.04886(3)	0.0301(1)
Ru(3)	0.29897(2)	0.19762(2)	0.28899(4)	0.0356(1)
Ru(4)	0.30100(2)	0.34845(2)	0.42319(4)	0.0332(1)
Ru(5)	0.37022(2)	0.52434(2)	0.28027(4)	0.0327(1)
C(11)	0.1133(3)	0.4431(3)	0.4071(5)	0.043(2)
O(11)	0.0766(2)	0.4503(3)	0.5097(4)	0.068(2)
C(12)	0.1063(3)	0.4880(3)	0.1123(5)	0.049(2)
O(12)	0.0666(2)	0.5327(3)	0.0323(5)	0.079(2)
C(21)	0.1734(3)	0.3477(3)	−0.0862(5)	0.043(2)
O(21)	0.1275(2)	0.3648(3)	−0.1628(4)	0.071(2)
C(22)	0.3349(3)	0.3709(3)	−0.0871(5)	0.042(2)
O(22)	0.3890(2)	0.3999(3)	−0.1663(4)	0.068(2)
C(31)	0.4099(3)	0.1760(3)	0.2933(5)	0.052(2)
O(31)	0.4775(2)	0.1603(3)	0.3003(5)	0.080(2)
C(32)	0.2835(3)	0.0836(4)	0.4273(5)	0.061(2)
O(32)	0.2736(3)	0.0144(3)	0.5111(5)	0.103(2)
C(41)	0.3910(3)	0.2878(4)	0.5199(5)	0.053(2)
O(41)	0.4446(3)	0.2530(3)	0.5743(4)	0.093(2)
C(42)	0.2845(3)	0.4403(3)	0.5296(5)	0.046(2)
O(42)	0.2666(2)	0.4767(3)	0.6189(3)	0.066(2)
C(43)	0.2236(3)	0.2669(3)	0.5466(5)	0.049(2)
O(43)	0.1774(2)	0.2196(3)	0.6256(4)	0.069(2)
C(51)	0.3648(3)	0.6322(3)	0.3599(5)	0.045(2)
O(51)	0.3648(2)	0.6971(3)	0.3995(4)	0.071(2)
C(52)	0.4211(3)	0.5859(3)	0.0995(5)	0.044(2)
O(52)	0.4520(2)	0.6191(3)	−0.0079(4)	0.069(2)
C(53)	0.4732(3)	0.4728(3)	0.3457(5)	0.048(2)
O(53)	0.5332(2)	0.4412(3)	0.3815(4)	0.073(2)
P(1)	0.23803(6)	0.56755(7)	0.2032(1)	0.0293(4)
C(111)	0.1657(2)	0.6453(3)	0.2871(4)	0.034(2)
C(112)	0.1705(3)	0.6575(3)	0.4186(5)	0.049(2)
C(113)	0.1087(4)	0.7078(4)	0.4828(6)	0.068(3)
C(114)	0.0417(3)	0.7443(4)	0.4196(6)	0.069(2)
C(115)	0.0359(3)	0.7333(3)	0.2887(6)	0.055(2)
C(116)	0.0974(3)	0.6849(3)	0.2224(5)	0.041(2)
C(121)	0.2522(2)	0.6433(3)	0.0212(4)	0.032(1)
C(122)	0.2665(3)	0.7379(3)	−0.0029(5)	0.045(2)
C(123)	0.2866(3)	0.7945(3)	−0.1378(5)	0.059(2)

TABLE 10 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(124)	0.2932(3)	0.7576(4)	−0.2512(5)	0.063(2)
C(125)	0.2784(3)	0.6647(4)	−0.2296(5)	0.059(2)
C(126)	0.2582(3)	0.6078(3)	−0.0951(5)	0.043(2)
C(1)	0.3696(2)	0.3997(3)	0.2167(4)	0.032(1)
C(2)	0.2979(2)	0.3645(3)	0.2009(4)	0.030(1)
P(2)	0.29436(7)	0.16500(8)	0.0747(1)	0.0374(4)
C(211)	0.2240(3)	0.0792(3)	0.0719(5)	0.040(2)
C(212)	0.1694(3)	0.1007(3)	−0.0255(5)	0.057(2)
C(213)	0.1185(4)	0.0344(4)	−0.0296(6)	0.071(3)
C(214)	0.1201(4)	−0.0528(4)	0.0620(6)	0.069(3)
C(215)	0.1728(3)	−0.0757(3)	0.1610(6)	0.060(2)
C(216)	0.2262(3)	−0.0104(3)	0.1653(5)	0.050(2)
C(221)	0.3854(3)	0.1328(3)	−0.0323(5)	0.048(2)
C(222)	0.3854(4)	0.0681(4)	−0.1083(6)	0.066(2)
C(223)	0.4563(4)	0.0464(4)	−0.1912(7)	0.092(3)
C(224)	0.5253(4)	0.0880(5)	−0.1921(7)	0.098(3)
C(225)	0.5259(3)	0.1520(5)	−0.1174(6)	0.082(3)
C(226)	0.4563(3)	0.1758(4)	−0.0380(5)	0.060(2)
S	0.16054(7)	0.26093(7)	0.2618(1)	0.0345(4)
C(101)	0.0731(3)	0.2050(3)	0.2505(4)	0.034(2)
C(102)	0.0110(3)	0.2580(3)	0.1817(5)	0.045(2)
C(103)	−0.0582(3)	0.2161(4)	0.1801(5)	0.054(2)
C(104)	−0.0658(3)	0.1217(4)	0.2464(6)	0.058(2)
C(105)	−0.0050(3)	0.0688(4)	0.3147(6)	0.060(2)
C(106)	0.0654(3)	0.1103(3)	0.3186(5)	0.046(2)
H(1)	0.421(2)	0.372(2)	0.197(4)	0.03(1)

that the μ_4-C atom spans the Ru_4 face on the side opposite to that of the flap atom.

In the conversion of 4 to 7 (Scheme 4), the processes which occur include migration of the cluster-bound H atom to C_β with concomitant cleavage of the C–P bond. The resulting PPh_2 group then bridges the base of the envelope, while the SPh group becomes attached to a third Ru atom, with cleavage of one of the flap Ru–Ru bonds, and migration of the second PPh_2 group to bridge the resulting non-bonded Ru ⋯ Ru vector. These changes can be represented as

$$H[Ru_5]CC(PPh_2) \longrightarrow HC_2[Ru_5]PPh_2$$

6. Conclusions

The major products from the reaction of thiols and the open Ru_5 cluster **1** were the scorpion cluster complexes **2** and **3**. Addition of the 4e ligand combinations (H + SR) has resulted in cleavage of two Ru–Ru bonds in precursor **1**. The H is incorporated into the cluster as a metal hydride, the C_2PPh_2 ligand remaining intact. In the case of the reaction with thiophenol, when carried out at higher temperature, three other complexes (**4**–**6**) were isolated. All three have metal frameworks with envelope conformations. In **5**, a μ_5-ethynyl (C_2H) ligand is produced from the C_2PPh_2 ligand in **1** by cleavage of the P–C bond and addition of H from thiophenol. In **4** and **6** the C–P bond is retained, but in **6** an H has added to C_α to form a μ_4-vinylidene $[C_2H(PPh_2)]$. A fourth complex, **7**, which is also isomeric with **3**–**6**, was obtained by heating **4**. This compound again contains a μ_5-C_2H ligand, but differs from the others in having a spiked rhomboidal core rather than the envelope configuration; the SPh group bridges three of the four Ru atoms of the base.

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