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Reactions of the cluster complex $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{11}]$ with terminal alkynes $HC{\equiv}CR$ (R = Ph, Bu^t or $SiMe_3$)

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Reaction of the dicarbon-containing complex $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** with monosubstituted alkynes $HC{\equiv}CR$ (R = Ph, Bu^t or $SiMe_3$) yielded $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ (R = Ph, Bu^t or $SiMe_3$) in which the Ru_5 pentagon in **1** is retained. Coupling of the C_2 and alkyne moieties forms a CCCHCR ligand which in combination with one Ru atom forms a metallacycle. The unsubstituted terminal carbon has a strong carbidic interaction with four of the Ru atoms. Carbonylation of the R = Ph and $SiMe_3$ complexes yields $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ (R = Ph or $SiMe_3$), in which one Ru atom has been extruded from the cluster, although retained by co-ordination to bridging PPh_2, SMe and hydrocarbon ligands. A minor product in each case was identified as $[Ru_5\{\mu_5\text{-}CC[C(O)SMe]CHCR\}(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (R = Ph or $SiMe_3$). Here, the organic ligand is formed by combination of the CCCHCR ligand with CO and one of the SMe groups and is attached to an Ru_5 core with an open-envelope conformation. Pyrolysis of $[Ru_5(\mu\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ afforded $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ and $[Ru_5(\mu_5\text{-}CCCHCR)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_9]$ (R = Ph or $SiMe_3$), in which one SMe group becomes triply bridging. The complex $[Ru_5\{\mu_5\text{-}CC(CHCSiMe_3)C({=}CHSiMe_3)CO\}\text{-}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8]$, in which the organic ligand, formed by combination of CO, HC_2SiMe_3 and $CCHSiMe_3$ molecules, is attached to the opposite side of the open-envelope cluster from that in $[Ru_5\{\mu_5\text{-}CC[C(O)SMe]CHCR\}\text{-}(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$, has also been isolated. The structures of five complexes were determined from single-crystal X-ray studies.

Introduction

Elsewhere we have described the reactions between $[Ru_5(\mu_5\text{-}C_2)\text{-}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** and disubstituted alkynes, C_2R_2 (R = Me or Ph), which proceed by addition of the alkyne to the C_2 ligand in **1** with formation of a metallacycle and concomitant loss of CO to give complexes **2** (R = Ph) or **3** (R = R′ = Me or Ph) (Scheme 1).[1] Subsequent reactions with CO were also described, which lead to expulsion of one Ru atom from the cluster, although this atom is retained in the product **4** (R = R′ = Ph) by virtue of bridging SMe, PPh_2 and organic ligands from the remaining Ru_4 core. This paper addresses similar chemistry with the 1-alkynes $HC{\equiv}CR$ (R = Ph, Bu^t or $SiMe_3$), which afford cluster complexes with subtly different geometries. Carbonylation reactions have afforded complexes with ligands which are formed by incorporation of CO and, in one case, also of one of the bridging SMe ligands. Part of this work has been presented in an earlier communication[2] and in recent reviews of the chemistry of **1**.[3,4]

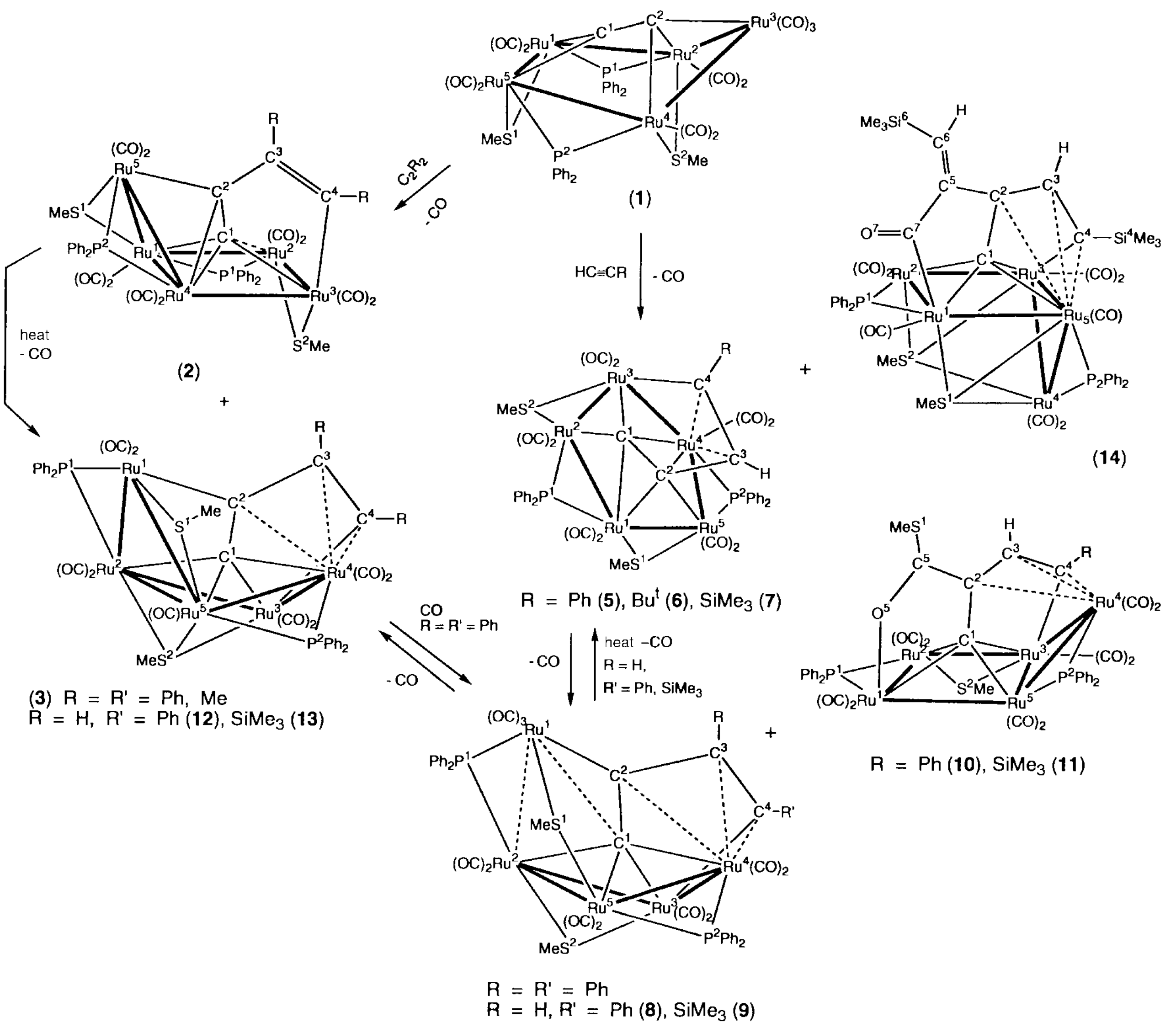
Results

Reactions of complex **1** with $HC{\equiv}CR$ (R = Ph, Bu^t or $SiMe_3$) occur readily in refluxing toluene over periods of hours. Work-up by conventional preparative tlc methods has afforded several complexes having a variety of structural types (Scheme 1). Thus, the product mixture from phenylethyne was separated into five bands, of which the major brown fraction was $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **5**.[2] This complex was obtained in 86% yield from the reaction of $HC{\equiv}CPh$ with the acetonitrile derivative of **1**, $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}(NCMe)]$.[5] The ν(CO) spectrum contained eight bands in the terminal region, but none due to μ-CO ligands. The resonance for the CH of the organic ligand appeared at δ 4.66, showing coupling to one ^{31}P nucleus; the analogous complexes $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ (R = Bu^t **6** or $SiMe_3$ **7**) were obtained from reactions of **1** with $HC{\equiv}CBu^t$ and $HC{\equiv}CSiMe_3$ at *ca.* 90 °C in 35 and 74% yields, respectively; higher temperatures result in the formation of other products. Their spectroscopic properties (Table 1) were similar to those of **5**, with the Bu^t and $SiMe_3$ resonances at δ 0.57 and −0.18, respectively, while the H atoms attached to the organic ligands are at δ 4.66 (**5**), 4.85 (**6**) and 5.07 (**7**), all showing coupling to only one phosphorus. Of interest are the resonances of the four carbons of the CCCHCPh chain in **5** at δ 243.84 and 186.95 (CC), 113.09 (CH) and 88.86 (CPh); the first showed coupling to two phosphorus nuclei (10.8 Hz).

Carbonylation of **5** and **7** afforded the complexes $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ (R = Ph **8** or $SiMe_3$ **9**, respectively), as shown by a crystal structure determination of the latter. Complex **8** was obtained in 84% yield as dark red crystals. The IR ν(CO) spectrum contained eleven terminal bands, while the ^1H NMR spectrum contained resonances at δ 1.07 and 2.25 (the SMe groups), and at δ 5.91 for the single CH proton on the organic ligand. The FAB MS contained M^+ at *m*/*z* 1405. The $SiMe_3$ complex **9** has similar spectroscopic properties to the phenyl analogue, with the $SiMe_3$ resonances found at δ 0.42 (^1H) and −0.01 (^{13}C).

Minor products from both reactions were the brown thiocarboxylato derivatives $[Ru_5\{CC[C(O)SMe]CHCR\}(\mu\text{-}SMe)\text{-}(\mu\text{-}PPh_2)_2(CO)_{10}]$ (R = Ph **10** or $SiMe_3$ **11**) which had M^+ at *m*/*z* 1405 and 1402, respectively, and identified by a crystal structural determination of **10**. The ^1H NMR spectra contained singlet resonances for the SMe groups at δ 1.79, 2.40 (for **10**) and 2.03, 2.29 (for **11**), while the CHPh proton was found at δ 5.81 and 5.82, respectively. The $SiMe_3$ singlet of **11** was at δ 0.38.

We sought to determine whether complex **8** was an inter-



Scheme 1

mediate in the formation of **5**. On heating a solution of **8** in toluene at 95–100 °C for 14 h two major fractions were separated by TLC. The first contained brown $[Ru_5(\mu_5\text{-CCCHCPh})(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(CO)_9]$ **12** while the second contained **5** as expected, but only in low yield (12%). The IR spectrum of **12** contained nine terminal ν(CO) bands, while the ^{1}H NMR spectrum contained doublet resonances at δ 1.43 and 2.45 (SMe) together with a singlet for the CH proton at δ 5.54. In the ^{13}C NMR spectrum the SMe groups gave signals at δ 17.71 and 27.70, while resonances for the four carbons of the CCCHCPh chain were found at δ 209.54, 186.86, 156.87 and 87.97. Similarly, pyrolysis of **9** (toluene, 100–105 °C, 15 h) gave brown $[Ru_5(\mu_5\text{-CCCHCSiMe}_3)(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(CO)_9]$ **13** in 82% yield, accompanied by **7** (16%). The spectroscopic properties of this complex are similar to those of **12**: in particular the ^{1}H NMR spectrum contains singlet resonances for the SiMe$_3$ and CH protons at δ −0.07 and 5.39, respectively, and doublets for the two SMe groups at δ 1.49 and 2.37. In the ^{13}C NMR spectrum the SiMe$_3$ and two SMe carbons are at δ 1.60, 17.73 and 27.70, respectively, while the CCCHC(SiMe$_3$) chain carbons resonated at δ 216.68, 174.49, 159.10 and 90.02.

If the reaction between complex **1** and HC≡CSiMe$_3$ was carried out at 110 °C for 6 h three fractions were obtained. The fastest moving on the TLC plate remains unidentified, although the analytical and spectroscopic properties suggest that it incorporates two molecules of the alkyne; the yield is only about 5%. The second fraction contained **7** (36%). A yellow fraction contained $[Ru_5\{\mu_5\text{-CC(CHCSiMe}_3)\text{C(=CHSiMe}_3)\text{CO}\}(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_8]$ **14**, as shown by a crystal structural determination. This complex shows ten terminal ν(CO) bands in its IR spectrum and has M$^+$ at *m*/*z* 1444. The ^{1}H NMR spectrum contains SiMe$_3$ resonances at δ −0.37 and 0.02 with two SMe singlets at δ 1.40 and 2.92. The corresponding signals in the ^{13}C NMR spectrum are found at δ 0.02 and 1.28 (SiMe$_3$), and at δ 25.00 and 30.84 (SMe). The organic ligand gives two CH signals at δ 5.61 and 6.38 (^{1}H); the carbons are found at δ 96.84, 126.22 (2 × CH), 151.73, 182.13 (2 × CSiMe$_3$), 231.56 and 237.19.

Molecular structures of complexes 5, 7, 9, 10 and 14

Molecules of each of the four complexes **7**, **9**, **10** and **14** are shown in Figs. 1–4, respectively, and selected bond parameters for these complexes, together with those of **5** for comparison, are collected in Table 2. Note that the numbering scheme for **5** differs from that previously presented,[2] being reset for compatibility with the other compounds. There are three different geometries for the Ru$_5$ cores: in **5** and **7**, the distorted pentagonal framework closely resembles that in **1**, while for **10** and **14** the metal core has an open envelope conformation. In **9** one of the metal atoms is no longer bonded directly to any of the remaining four, which form a rhombus.

Table 1 Analytical and spectroscopic data

Compound [a]	IR ν(CO) [b]	NMR [c]
5 [Ru$_5$(μ$_5$-CCCHCPh)(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_{10}$] C$_{46}$H$_{32}$O$_{10}$P$_2$Ru$_5$S$_2$: C, 39.81 (40.15); H, 2.46 (2.34) FAB MS: *m/z* 1377, M$^+$; 1349–1069 M − *n*CO]$^+$ (*n* = 1–10)	2046m, 2034s, 2018vs, 2001s, 1984m, 1970s, 1960m, 1942m	^{1}H: 2.83 (3 H, d, J_{HP} 1.9, SMe), 2.86 (3 H, d, J_{HP} 3.5, SMe), 4.66 (1 H, d, J_{HP} 3.3, CCH), 6.78 (2 H, dd, J_{HP} 7.9, 2.1, Ph), 6.99–7.76 (23 H, m, Ph) ^{13}C: 26.88 (s, 2 × SMe), 88.86 (s, CCH*C*Ph), 113.09 (s, C*C*HCPh), 127.02–134.76 (m, Ph), 136.05 (d, J_{CP} 30.7, *ipso* C (PPh)), 140.39 (d, J_{CP} 36.0, *ipso* C (PPh)), 141.21 (d, J_{CP} 34.3, *ipso* C (PPh)), 142.15 (d, J_{CP} 28.8, *ipso* C (PPh)), 147.58 (s, *ipso* C (CPh)), 186.95 (s(br), C*C*CHCPh), 192.46 (d, J_{CP} 6.9, CO), 194.96 (d, J_{CP} 7.4, CO), 195.98 (d, J_{CP} 9.1, CO), 196.27 (d, J_{CP} 6.9, CO), 197.60 (s, CO), 199.62–199.81 (m, 2CO), 200.49 (d, J_{CP} 5.1, CO), 200.57 (s, CO), 200.73 (d, J_{CP} 8.6 Hz, CO), 243.84 (t, J_{CP} 10.8, *C*CCHCPh)
6 [Ru$_5$(μ$_5$-CCCHCBu^t)(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_{10}$] C$_{44}$H$_{36}$O$_{10}$P$_2$Ru$_5$S$_2$·0.5CH$_2$Cl$_2$: C, 38.18 (38.22); H, 2.74 (2.67) FAB MS: *m/z* 1357, M$^+$: 1329–1077 [M − *n*CO]$^+$ (*n* = 1–10)	2045m, 2033s, 2017vs, 1999s, 1978m, 1970m, 1962 (sh), 1959m, 1935m	^{1}H: 0.57 (9 H, s, C(CH$_3$)$_3$), 2.72 (3 H, d, J_{HP} 1.7, SMe), 2.76 (3 H, d, J_{HP} 3.5, SMe), 4.85 (1 H, d, J_{HP} 2.9, CH), 5.24 (1 H, s, 0.5CH$_2$Cl$_2$), 7.06–7.65 (m, Ph)
7 [Ru$_5$(μ$_5$-CCCHCSiMe$_3$)(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_{10}$] C$_{43}$H$_{36}$O$_{10}$P$_2$Ru$_5$S$_2$Si: C, 37.58 (37.64); H, 2.59 (2.64) FAB MS: *m/z* 1374, M$^+$; 1346–1094 [M − *n*CO]$^+$ (*n* = 1–10)	2047m, 2034vs, 2019vs, 2015s, 2001s, 1983m, 1970s, 1964m, 1959m, 1935m	^{1}H: −0.18 (9 H, s, SiMe$_3$), 2.748, 2.757, 2.759, 2.762 (6 H, 2 × d (overlapping), SMe), 5.07 (1 H, d, J_{HP} 3.5, CH), 7.06–7.63 (20 H, m, Ph)
8 [Ru$_5$(μ$_5$-CCCHCPh)(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_{11}$] C$_{47}$H$_{32}$O$_{11}$P$_2$Ru$_5$S$_2$: C, 39.75 (40.20); H, 2.29 (2.30) FAB MS: *m/z* 1405, M$^+$; 1377–1097 [M − *n*CO]$^+$ (*n* = 1–11)	2085m, 2038s, 2026m, 2020vs, 2008vs, 2003 (sh), 1997m, 1972m, 1967m, 1953w, 1942w	^{1}H: 1.07 (3 H, s, SMe), 2.25 (3 H, d, J_{HP} 3.3, SMe), 5.91 (1 H, s, CH), 7.15–7.82 (25 H, m, Ph)
9 [Ru$_5$(μ$_5$-CCCHCSiMe$_3$)(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_{11}$] C$_{44}$H$_{36}$O$_{11}$P$_2$Ru$_5$S$_2$Si: C, 37.20 (37.74); H, 2.58 (2.59) FAB MS: *m/z* 1402, M$^+$; 1374–1094 [M − *n*CO]$^+$ (*n* = 1–11)	2085m, 2037s, 2026m, 2017vs, 2008vs, 2000m, 1995s, 1975m, 1968m, 1961 (sh), 1947m, 1936m, 1931m	^{1}H: 0.42 (9 H, s, SiMe$_3$), 1.07 (3 H, s, SMe), 2.25 (3 H, d, J_{HP} 3.3, SMe), 6.01 (1 H, s, CH), 7.11–7.81 (20 H, m, Ph) ^{13}C: −0.01 (s, SiMe$_3$), 21.06 (t, J_{CP} 3.6, SMe), 27.04 (s, SMe), 110.36 (s, CCCH*C*SiMe$_3$), 126.22–134.53 (m, Ph), 139.18 (d, J_{CP} 19.9, *ipso* C), 141.44, 141.51, 141.81, 141.86 (2 × d (overlapping), *ipso* C), 146.59 (d, J_{CP} 17.5, *ipso* C), 151.90 (s, CC*C*HCSiMe$_3$), 174.70 (d, J_{CP} 12.1, C*C*CHCSiMe$_3$), 178.78 (d, J_{CP} 5.4, CO), 188.80 (s, CO), 189.85 (s, CO), 190.47–190.88 (m, CO), 195.83 (s, CO), 197.37 (m, CO), 199.22 (s, CO), 199.64 (d, J_{CP} 5.7,CO), 200.58 (d, J_{CP} 7.6, CO), 202.77 (s, CO), 204.67 (t, J_{CP} 5.1, CO), 344.15 (d, J_{CP} 9.2, *C*CCHCSiMe$_3$)
10 [Ru$_5${CC[C(O)SMe]CHCPh}-(μ-SMe)(μ-PPh$_2$)$_2$(CO)$_{10}$] C$_{47}$H$_{32}$O$_{11}$P$_2$Ru$_5$S$_2$: C, 40.10 (40.20); H, 2.32 (2.30) FAB MS: *m/z* 1405, M$^+$; 1377–1097 [M − *n*CO]$^+$ (*n* = 1–11)	2044m, 2025vs, 2020s, 2008w, 2000m, 1994m, 1986m, 1979m, 1969 (sh), 1964m, 1955m, 1942w, 1922w, 1918w	^{1}H: 1.79 (3 H, s, SMe), 2.40 (3 H, s, SMe), 5.81 (1 H, s, CH), 7.09–7.91 (25 H, m, Ph)
11 [Ru$_5${CC[C(O)SMe]CHCSiMe$_3$}(μ-SMe)(μ-PPh$_2$)$_2$(CO)$_{10}$] C$_{44}$H$_{36}$O$_{11}$P$_2$Ru$_5$S$_2$Si: C, 37.20 (37.74); H, 2.58 (2.59) FAB MS: *m/z* 1402, M$^+$; 1374–1094 [M − *n*CO]$^+$ (*n* = 1–11)	2041m, 2027vs, 2015s, 1997s, 1988m, 1979m, 1973m, 1969m, 1965m, 1955m, 1944w	^{1}H: 0.38 (9 H, s, SiMe$_3$), 2.03 (3 H, s, SMe), 2.29 (3 H, s, SMe), 5.82 (1 H, s, CH), 6.67 (2 H, dd, J_{HH} 13.6, 7.2, Ph), 7.23–8.35 (18 H, m, Ph)
12 [Ru$_5$(μ$_5$-CCCHCPh)(μ$_3$-SMe)-(μ-SMe)(μ-PPh$_2$)$_2$(CO)$_9$] C$_{45}$H$_{32}$O$_9$P$_2$Ru$_5$S$_2$: C, 39.93 (40.09); H, 2.41 (2.39) FAB MS: *m/z* 1349, M$^+$; 1321–1097 [M − *n*CO]$^+$ (*n* = 1–9)	2041m, 2027s, 2016vs, 2003s, 1980m, 1975m, 1966m, 1960w, 1938m	^{1}H: 1.43 (3 H, d, J_{HP} 2.9, SMe), 2.45 (3 H, d, J_{HP} 2.3, SMe), 5.54 (1 H, s, CH), 6.89–7.75 (25 H, m, Ph) ^{13}C: 17.71 (s, SMe), 27.70 (s, SMe), 87.97 (d, J_{CP} 4.7, CH*C*Ph), 127.34–135.05 (m, Ph), 134.68 (s, *ipso* C (CPh)), 140.01 (d, J_{CP} 35.18, *ipso* C (PPh)), 142.01 (d, J_{CP} 34.73, *ipso* C (CPPh)), 145.06 (d, J_{CP} 33.90, *ipso* C (PPh)), 148.43 (s, *ipso* C (CPh)), 156.87 (s, C*C*HCPh), 186.86 (d, J_{CP} 4.8, C*C*CHCPh), 192.52 (d, J_{CP} 6.7, CO), 193.50 (d, J_{CP} 8.2, CO), 195.33 (d, J_{CP} 7.5, CO), 196.12 (s, CO), 196.89 (d, J_{CP} 8.5, CO), 201.08 (s, CO), 201.71 (s, CO), 202.03 (d, J_{CP} 4.6, CO), 204.32 (d, J_{CP} 10.6, CO), 209.54 (m, *C*CCHCPh)
13 [Ru$_5$(μ$_5$-CCCHCSiMe$_3$)-(μ$_3$-SMe)(μ-SMe)(μ-PPh$_2$)$_2$(CO)$_9$] C$_{42}$H$_{36}$O$_9$P$_2$Ru$_5$S$_2$Si: C, 37.13 (37.53); H, 2.69 (2.70) FAB MS: *m/z* 1346, M$^+$; 1318–1094, [M − *n*CO]$^+$ (*n* = 1–9)	2041m, 2026s, 2016vs, 1996s, 1978m, 1972m, 1963m, 1938m	^{1}H: −0.07 (9 H, s, SiMe$_3$), 1.49 (3 H, d, J_{HP} 2.5, SMe), 2.37 (3 H, d, J_{HP} 2.3, SMe), 5.39 (1 H, s, CH), 7.11–7.78 (20 H, m, Ph) ^{13}C: 1.60 (s, SiMe$_3$), 17.73 (s, SMe), 27.70 (s, SMe), 90.02 (d, J_{CP} 5.1, CCH*C*SiMe$_3$), (127.51–134.68 (m, Ph), 135.43 (d, J_{CP} 28.2, *ipso* C), 140.70 (d, J_{CP} 36.5, *ipso* C), 142.03 (d, J_{CP} 34.7, *ipso* C), 145.00 (d, J_{CP} 32.6, *ipso* C), 159.10 (s, C*C*HCSiMe$_3$), 174.49 (d, J_{CP} 3.5, C*C*CHCSiMe$_3$), 192.97 (d, J_{CP} 6.9, CO), 193.60 (d, J_{CP} 8.8, CO), 195.15 (s, CO), 195.32 (d, J_{CP} 7.3, CO), 196.75 (d, J_{CP} 7.6, CO), 200.87 (s, CO), 202.14 (d, J_{CP} 5.0, CO), 203.60 (s, CO), 205.08 (d, J_{CP} 11.1, CO), 216.68 (d, J_{CP} 3.7, *C*CCHCSiMe$_3$)
14 [Ru$_5${μ$_5$-CC(CHCSiMe$_3$)-C(=CHSiMe$_3$)CO}(μ-SMe)$_2$-(μ-PPh$_2$)$_2$(CO)$_8$] C$_{47}$H$_{46}$O$_9$P$_2$Ru$_5$S$_2$Si$_2$: C, 39.44 (39.14); H, 3.30 (3.21) FAB MS: *m/z* 1444, M$^+$; 1416–1220 [M − *n*CO]$^+$ (*n* = 1–8)	2084vw, 2043m, 2019s, 2008w, 1992s, 1978m, 1972vs, 1962m, 1960m, 1945m	^{1}H: −0.37 (9 H, s, SiMe$_3$), 0.02 (9 H, s, SiMe$_3$), 1.40 (3 H, s, SMe), 2.92 (3 H, s, SMe), 5.61 (1 H, s, CH), 6.38 (1 H, s, CH), 6.80–7.97 (20 H, m, Ph) ^{13}C: 0.02 (s, SiMe$_3$), 1.28 (s, SiMe$_3$), 25.00 (s, SMe), 30.84 (s, SMe), 96.84 (s, CH), 126.22 (d, J_{CP} 2.4, CH), 127.56–133.57 (m, Ph), 137.49 (d, J_{CP} 40.3, *ipso* C), 144.01 (d, J_{CP} 33.5, *ipso* C), 144.79 (d, J_{CP} 27.3, *ipso* C), 145.41 (d, J_{CP} 26.1, *ipso* C), 151.73 (s, CSiMe$_3$), 182.13 (s, CSiMe$_3$), 191.43 (dd, J_{CP} 10.2, 3.1, CO), 194.64 (s, CO), 194.91 (d, J_{CP} 2.9, CO), 198.88 (s, CO), 198.99 (s, CO), 200.02 (s, CO), 200.63 (s, CO), 200.90 (s, CO), 201.00 (s, CO), 231.56 (d, J_{CP} 3.1, *C*C), 237.19 (d, J_{CP} 5.3, C*C*)

[a] Analysis [Found (Calc.)] in %. [b] In cm^{-1}. [c] Chemical shifts and coupling constants (Hz) in CDCl$_3$.

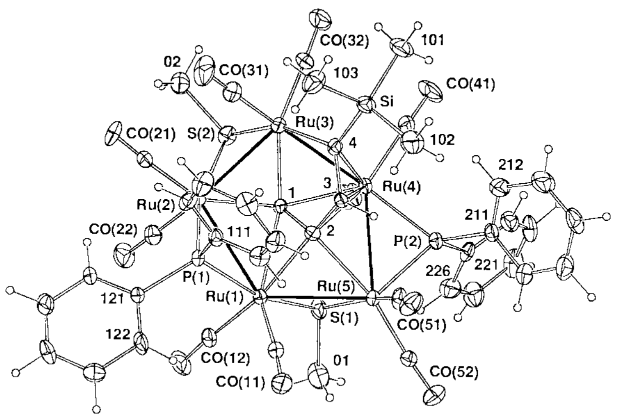


Fig. 1 Plot of a molecule of $[Ru_5\{\mu_5\text{-}CCCHC(SiMe_3)\}(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}]$ **7** normal to the Ru_4 "plane". In this and following figures, non-hydrogen atoms are shown as 20% thermal ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å. Numbering schemes are also shown, orientations in the figures corresponding to those of Chart 1 and Scheme 1.

(a) $[Ru_5(\mu_5\text{-}CCCHCR)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ [R = Ph 5 or $SiMe_3$ 7]. These two complexes have the same structure except for the presence of Ph and $SiMe_3$ groups, respectively, on C(4). The non-planar Ru_5 pentagon is flattened compared with **1**, the dihedrals Ru(1)–Ru(2)–Ru(3)–Ru(4)/Ru(1)–Ru(4)–Ru(5) being 171.16(3) and 168.81(4)°, respectively [*cf.* 132.21(1)° in **1**[6]]. The Ru–Ru separations fall within the range 2.781–3.028(2) Å [*cf.* 2.855–2.898 Å in **1**, although the average Ru–Ru separation in each is similar: 2.882, 2.894 *vs.* 2.885 Å] and alternate Ru–Ru vectors are bridged by SMe [Ru(1)–Ru(5), Ru(2)–Ru(3); Ru–S, 2.370–2.453(2) Å] and PPh_2 groups [Ru(1)–Ru(2), Ru(4)–Ru(5); Ru–P, 2.263–2.339(2) Å]. In contrast with **1**, however, both SMe groups bridge adjacent pairs of Ru atoms. While the PPh_2 groups are close to coplanar with and "above" (on the same side as the organic ligand) the Ru_3 or Ru_4 portions of the Ru_5 pentagon, the SMe groups are both significantly out of and "below" these planes.

The organic ligand is formed by addition of the 1-alkyne across the Ru(3) ··· C(3) vector *via* new C(2)–C(3) [1.462(8) for **5**, 1.48(2) Å for **7**] and Ru(3)–C(4) bonds [2.071(7), 2.10(1) Å], and forms a five-membered metallacycle incorporating Ru(3). The C(3)=C(4) double bond is η^2 bonded to Ru(4) [*ca.* 2.29, 2.42 Å], the latter interactions being very long. The bonds from the original C(1)–C(2) unit to the five Ru atoms are preserved but weakened. The reaction is similar to the well known dimerisation of alkynes on Ru_3 clusters, for example, where the two molecules of the alkyne combine with one Ru to form a metallacycle which is η^4 bonded to a second Ru atom.[7,8] The C(1)–C(2) separations are considerably lengthened compared with those in **1**, to 1.394(9), 1.34(2) Å; atom C(1) is also bonded to Ru(2) [2.064(5), 2.10(1) Å], while atom C(2) strongly interacts with Ru(1) [2.173(6), 2.20(1) Å] and weakly with Ru(5) [2.340(5), 2.38(1) Å].

Other features of the organic ligand are of interest. Atom C(4) is attached to three Ru atoms [although Ru(4)–C(4) is long at 2.415(5), 2.40(1) Å, indicating a very weak interaction] in a manner similar to that found in several related complexes. It donates 3e to the cluster and corresponds to a μ_4-alkylidyne-carbide. The sequence of C–C separations is consistent with a degree of multiple bond character in the C(1)–C(2) and C(3)–C(4) bonds, which show the usual lengthening resulting from their interaction with the Ru atoms.

Co-ordination about the metal atoms is completed by two terminal CO ligands on each atom. With five M–M bonds, the cluster valence electron (c.v.e.) count of 80 [5Ru (40) + 10CO (20) + 2SMe (6) + 2 PPh_2 (6) + the organic ligand (8)] is that expected by conventional cluster electron counting rules.

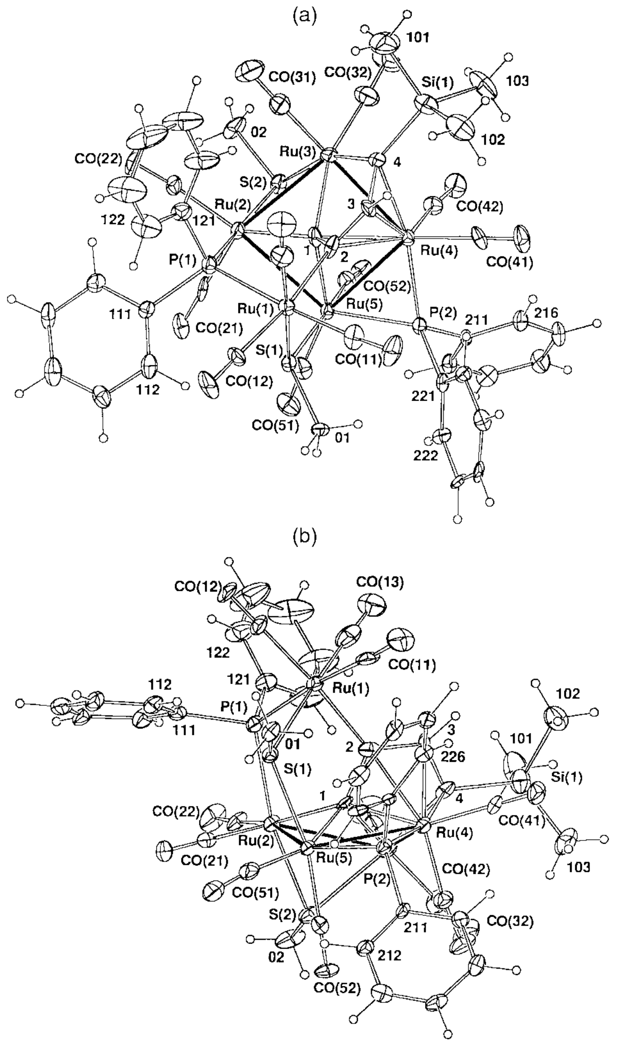


Fig. 2 Plots of a molecule of $[Ru_5\{CCCHC(SiMe_3)\}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **9** (a) normal to and (b) oblique to the Ru_4 "plane".

(b) $[Ru_5\{\mu_5\text{-}CCCHC(SiMe_3)\}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ 9. From Fig. 2, it can be seen that carbonylation of complex **6** has resulted in extrusion of one Ru atom from the cluster to give a novel rhomboidal Ru_4 cluster Ru(1)–Ru(2)–Ru(3)–Ru(4) [2.816–2.971(2) Å] which is bent across the Ru(3) ··· Ru(5) vector [dihedral 149.09(8)°]. Two opposite edges are bridged by SMe [Ru(2,3)–S(2) 2.405, 2.443(5) Å] and PPh_2 groups [Ru(4,5)–P(2) 2.329, 2.280(5) Å]. Each ruthenium atom in the cluster contains two terminal CO groups. The fifth Ru atom, which carries three terminal CO groups, is chelated by the SMe and PPh_2 groups also attached to Ru(1) and Ru(4), respectively [Ru(1)–S(1) 2.402(5); Ru(1)–P(1), 2.437(5) Å] and also by atom C(2) of the organic ligand [Ru(1)–C(2) 2.13(2) Å], resulting in overall approximate octahedral geometry for this atom.

The organic ligand is similar to those found in complexes **5** and **7**, with the $SiMe_3$ group found on C(4). Atom C(1) forms a distorted trigonal bipyramid with the Ru_4 rhombus [Ru-(2,3,4,5)-C(1) 2.05(2), 2.14(1), 2.23(1), 2.27(2) Å], some 0.79 Å above the mean plane. Atoms C(1)–C(4) form an η^4-C_4 ligand bonded to Ru(4) [2.23–2.36(2) Å] and form a five-membered metallocycle with Ru(3) [Ru(3)–C(4) 2.03(2) Å]. The Ru_4 cluster is a 64 c.v.e. system [4Ru (32) + 8CO (16) + μ-SMe (3) + μ-PPh_2 (3) + (SMe + PPh_2) (3) + the organic ligand (7)], as expected with only four Ru–Ru bonds.

(c) $[Ru_5\{CC[C(O)SMe]CHCPh\}(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ 10. As can be seen from Fig. 3, the Ru_5 cluster in this complex adopts the open envelope conformation [Ru–Ru 2.8204–2.9571(5) Å; dihedral 125.34(4)°], with Ru(2)–Ru(3) bridged by

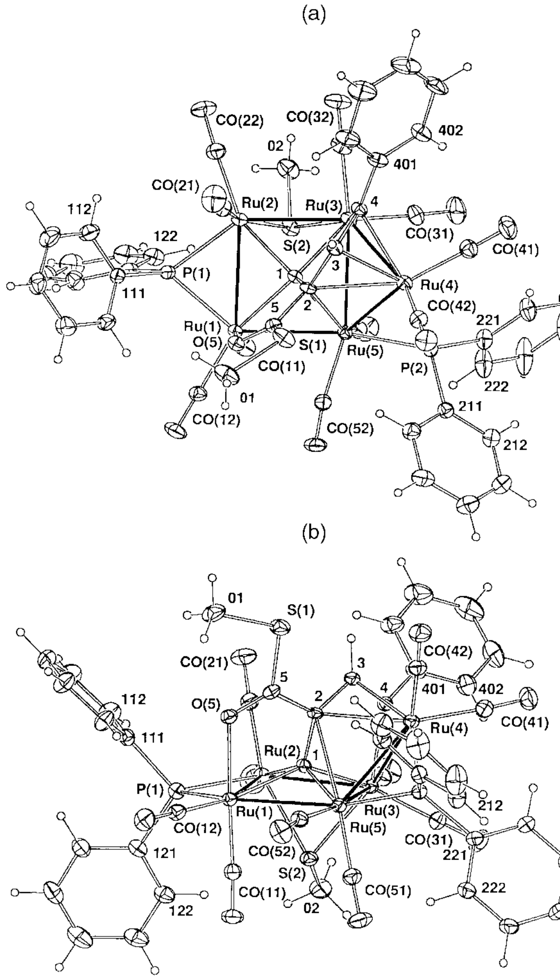


Fig. 3 Plots of a molecule of $[Ru_5\{\mu_5\text{-}CC[C(O)SMe]CHCPh\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ **10**, (a) normal to and (b) oblique to the Ru_4 "plane".

S(2) [Ru(2,3)–S(2) 2.427, 2.432(1) Å] and Ru(1)–Ru(2) and Ru(4)–Ru(5) bridged by the two PPh_2 groups [Ru–P 2.294–2.336(1) Å]. Each Ru atom carries two terminal CO groups.

The organic ligand is formed by combination of the C_4 ligand found in precursor **5** with the second SMe group and a CO molecule to form a thiocarboxylate group attached to Ru(1) *via* O(5) [Ru(1)–O(5) 2.177(3) Å]. The attachment of the C_4 chain involves C(1) bonding to all atoms of the Ru_4 rhombus [Ru–C(1) 2.065–2.197(4) Å] and being 0.670(4) Å above the mean plane; the C(3)=C(4) fragment acts as an η^2 ligand to Ru(4) [Ru(4)–C(3,4) 2.191, 2.226(4) Å], the Ru(3)–C(4) bond [2.106(5) Å] completing the metallacycle. Within the organic ligand, C–C separations indicate a double bond between C(3)–C(4) [1.391(7) Å], while some degree of multiple bonding probably exists between C(1)–C(2), C(2)–C(3) and C(2)–C(5); the Ru(4)–C(2) separation [2.486(4) Å] is long, but may also be involved in a weak π-type interaction. The dihedral angle between the two five-membered rings is 169.5(1)°. The total c.v.e. count is 78 [5Ru (40) + 10CO (20) + SMe (3) + $2PPh_2$ (6) + the organic ligand (9)], as expected for an M_5 cluster with six M–M bonds.

(d) $[Ru_5\{\mu_5\text{-}CC(CHCSiMe_3)C(=CHSiMe_3)CO\}(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8]$ 14. In complex **14** (Fig. 4) the open envelope conformation is again found [Ru–Ru 2.858–3.053(1) Å; dihedral 92.99(3)°], with the two PPh_2 groups bridging the Ru(1)–Ru(2) and Ru(4)–Ru(5) vectors. Eight CO ligands are distributed so that Ru(2,3,4) have two each, while only one is attached to each of Ru(1,5). The two SMe groups are now in the μ_3 mode, symmetrically arranged to span Ru(1)–Ru(4)–Ru(5) and Ru(2)–Ru(3)–Ru(4) [Ru–S 2.375–2.433(2) Å]. In contrast to other complexes described herein, these groups are the ones which hold the envelope flap open, rather than the organic ligands. Consequently, atom Ru(2) is on the opposite side of the Ru_4 rhombus to the organic ligand.

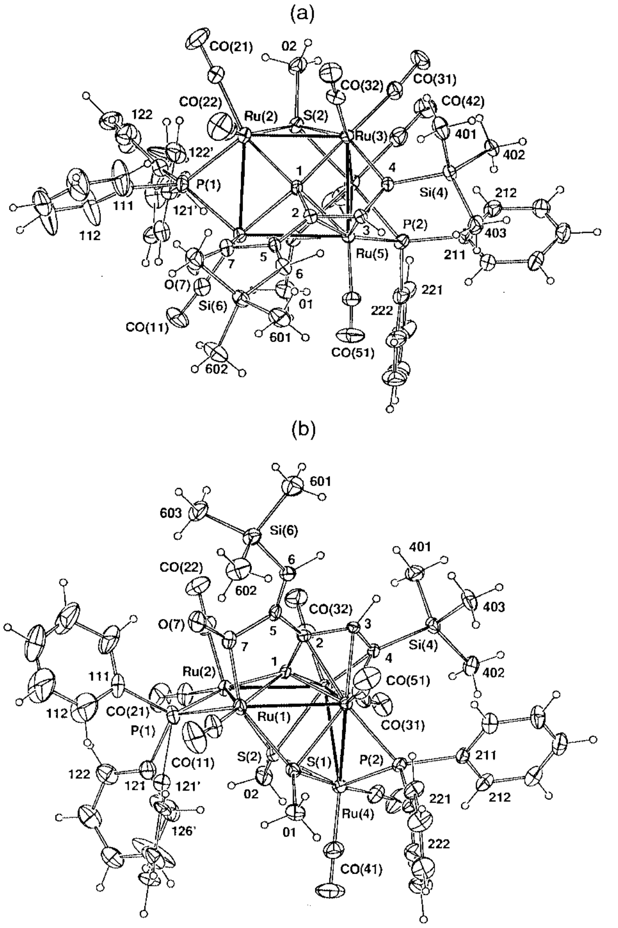


Fig. 4 Plots of a molecule of $[Ru_5\{\mu_5\text{-}CC(CHCSiMe_3)C(=CHSiMe_3)\text{-}CO(\mu_3\text{-}SMe)_3(\mu\text{-}PPh_2)_2(CO)_8]$ **14**, (a) normal to and (b) oblique to the Ru_4 "plane".

The organic ligand differs from those described above in that two $HC\equiv CSiMe_3$ molecules have combined with the C_2 ligand and a CO molecule to give a bicyclic diruthenocycle having a substituted *exo* methylene group. Thus, C(1) is attached to the four atoms of the Ru_4 rhombus [2.100–2.245(7) Å], some 1.220(7) Å above the mean plane. With C(2), this formed the original C_2 ligand; the separation [1.420(9) Å] indicates some degree of multiple bonding between them is retained. Atom C(2) forms a new bond to C(3) from one molecule of the alkyne, C(4) with the $SiMe_3$ group bridging the Ru(1)–Ru(3) vector. With Ru(4), these four carbons form one five-membered metallacycle, which is fused to that formed by C(1) and C(2) (as a common edge) in combination with C(7) and C(5). The latter is the unsubstituted carbon of a vinylidene formed by isomerisation of the 1-alkyne; atom C(6), carrying H and $SiMe_3$ substituents, is joined to C(5) by a double bond [1.33(1) Å]. Atoms C(7)–O(7), originally a CO group attached to Ru(1), now form a conventional keto group. The dihedral angle between the two five-membered rings is 134.4(2)°. Again, the cluster has 78 c.v.e. [5Ru (40) + 8CO (16) + 2SMe(10) + $2PPh_2$ (6) + the organic ligand (6)].

Discussion

As has been described on other occasions, the sterically exposed location of the C_2 ligand in **1** makes it unusually reactive for a cluster-bound carbon ligand. Recent calculations suggest that electron density is concentrated on C(2), making it particularly prone to attack by electrophiles.[8] The present account confirms that this reactivity extends to alkynes, with ready formation of

Table 2 Selected bond distances (Å) and angles (°) for complexes **5**, **7**, **9**, **10** and **14**

	5	**7**	**9**	**10**	**14**
Ru(1)–Ru(2)	2.981(1)	3.028(2)		2.8729(5)	2.871(2)
Ru(1)–Ru(5)	2.8206(8)	2.877(2)		2.8299(5)	3.022(1)
Ru(2)–Ru(3)	2.821(1)	2.801(2)	2.868(2)	2.8204(5)	2.858(1)
Ru(3)–Ru(4)	2.781(1)	2.774(2)	2.816(2)	2.9571(5)	3.053(1)
Ru(3)–Ru(5)				2.9137(5)	2.877(2)
Ru(4)–Ru(5)	3.008(1)	2.991(2)	2.894(2)	2.8249(5)	2.936(1)
Ru(1)–S(1)	2.453(2)	2.427(4)	2.402(5)		2.375(2)
Ru(2)–S(2)	2.407(3)	2.412(5)	2.405(5)	2.427(2)	2.433(2)
Ru(3)–S(2)	2.429(2)	2.428(5)	2.443(5)	2.432(1)	2.395(2)
Ru(5)–S(1)	2.371(2)	2.370(5)	2.459(5)		2.401(2)
Ru(1)–P(1)	2.299(1)	2.296(3)	2.437(5)	2.315(1)	2.215(3)
Ru(2)–P(1)	2.339(2)	2.327(5)	2.417(5)	2.294(1)	2.303(2)
Ru(4)–P(2)	2.310(2)	2.320(4)	2.329(5)	2.336(1)	2.321(2)
Ru(5)–P(2)	2.263(2)	2.270(4)	2.280(5)	2.300(1)	2.341(2)
Ru(1)–C(1)	2.432(7)	2.42(1)	3.09(2)	2.197(4)	2.245(7)
Ru(1)–C(2)	2.173(6)	2.20(1)	2.13(2)	3.023(4)	2.795(6)
Ru(2)–C(1)	2.064(5)	2.10(1)	2.05(2)	2.133(3)	2.154(7)
Ru(3)–C(1)	2.067(7)	2.09(1)	2.14(1)	2.125(5)	2.104(7)
Ru(3)–C(4)	2.071(7)	2.10(1)	2.03(2)	2.106(5)	2.100(6)
Ru(4)–C(1)	2.301(5)	2.27(1)	2.23(1)	3.109(3)	
Ru(4)–C(2)	2.232(6)	2.21(1)	2.36(2)	2.486(4)	
Ru(4)–C(3)	2.294(6)	2.30(1)	2.29(2)	2.191(5)	
Ru(4)–C(4)	2.415(5)	2.40(1)	2.30(2)	2.226(4)	
Ru(5)–C(1)			2.27(2)	2.065(4)	2.192(7)
Ru(5)–C(2)	2.340(5)	2.38(1)	3.14(2)	2.574(5)	2.270(6)
C(1)–C(2)	1.394(9)	1.34(2)	1.44(3)	1.466(6)	1.420(9)
C(2)–C(3)	1.462(8)	1.48(2)	1.38(2)	1.454(6)	1.426(9)
C(3)–C(4)	1.42(1)	1.39(2)	1.50(2)	1.391(7)	1.420(9)
C(4)–Si(4)		1.87(1)	1.90(2)		1.891(7)
C(2)–C(5)				1.473(7)	1.48(1)

Other distances: For **9**, Ru(2)–Ru(5) 2.971(3); for **10**, C(5)–O(5), 1.226(5), S(1)–C(5), 1.754(5), Ru(1)–O(5) 2.177(3); for **14**, Ru(4)–S(1) 2.376(2), Ru(4)–S(2) 2.421(2), Ru(3)–C(4) 2.100(7), Ru(1)–C(7) 2.019(7), Ru(5)–C(3) 2.216(6), Ru(5)–C(4) 2.309(6), C(5)–C(6) 1.33(1), C(5)–C(7) 1.53(1), C(7)–O(7), 1.21(1), C(6)–Si(6) 1.878(8)

	5	**7**	**9**	**10**	**14**
Ru(2)–Ru(1)–Ru(5)	122.33(4)	122.06(5)		89.07(2)	88.59(3)
Ru(1)–Ru(2)–Ru(3)	100.33(3)	99.80(6)		91.70(1)	91.52(3)
Ru(3)–Ru(2)–Ru(5)			82.10(6)		
Ru(2)–Ru(3)–Ru(4)	99.21(3)	99.57(6)	94.07(7)	117.19(2)	
Ru(2)–Ru(3)–Ru(5)				88.44(2)	91.75(3)
Ru(3)–Ru(4)–Ru(5)	122.71(3)	123.97(5)	84.37(7)	60.47(1)	
Ru(1)–Ru(5)–Ru(3)				90.67(1)	88.13(3)
Ru(1)–Ru(5)–Ru(4)	86.65(3)	85.24(4)		122.25(2)	
C(1)–Ru(3)–C(4)	77.1(2)	77.2(5)	76.7(6)	81.1(2)	76.9(3)
Ru(1)–C(1)–Ru(3)	164.0(2)	164.3(5)		141.9(2)	141.4(3)
Ru(2)–C(1)–Ru(4)	155.6(4)	153.7(8)			
Ru(2)–C(1)–Ru(5)				83.2(1)	142.7(3)
Ru(1)–C(1)–C(2)	62.4(4)	64.4(6)		109.6(3)	96.8(4)
Ru(2)–C(1)–C(2)	135.0(5)	136(1)	130(1)	123.3(3)	141.7(5)
Ru(3)–C(1)–C(2)	120.5(4)	119.8(8)	115(1)	107.7(3)	116.0(5)
Ru(4)–C(1)–C(2)	69.4(3)	69.8(6)	77(1)		
Ru(5)–C(1)–C(2)			114(1)	92.0(2)	74.5(4)
Ru(5)–C(2)–C(1)	127.4(4)	129(1)		53.3(2)	68.5(3)
Ru(3)–C(4)–C(3)	115.6(4)	114.1(9)		113.5(3)	114.0(5)
C(1)–C(2)–C(3)	110.1(6)	112(1)	114(1)	116.6(4)	111.7(6)
C(2)–C(3)–C(4)	116.6(6)	117(1)	115(1)	115.6(4)	117.5(6)

Other angles: for **9**, Ru(3)–Ru(2)–Ru(5) 82.10(6), Ru(2)–Ru(5)–Ru(4) 90.32(7), Ru(2)–C(1)–Ru(4) 152.6(9), Ru(3)–C(1)–Ru(5) 120.8(8), Ru(1)–C(2)–C(1) 118(1), Ru(1)–C(2)–C(3) 127(1); for **10**, Ru(2)–Ru(3)–Ru(5) 88.44(2), Ru(1)–Ru(5)–Ru(3) 90.67(1), Ru(2)–S(2)–Ru(3) 70.69(4), Ru(4)–P(2)–Ru(5) 75.08(4), C(1)–Ru(3)–C(4) 81.1(2), C(1)–C(2)–C(5) 115.0(3), C(2)–C(5)–S(1) 117.8(3), C(2)–C(5)–O(5) 119.7(4), C(1)–Ru(1)–O(5) 76.7(2); for **14**, Ru(1)–C(7)–C(5) 106.7(5), C(2)–C(5)–C(6) 124.8(7), C(2)–C(5)–C(7) 111.9(6)

Dihedral angles (°)

For **5**:	Ru(1,2,3,4)/Ru(1,4,5)	171.16(3)
For **7**:	Ru(1,2,3,4)/Ru(1,4,5)	168.81(4)
For **9**:	Ru(2,3,5)/Ru(3,4,5)	149.09(8)
For **10**:	Ru(1,2,3,5)/Ru(3,4,5)	125.34(4)
For **14**:	Ru(1,3,4,5)/Ru(1,2,3)	92.99(3)

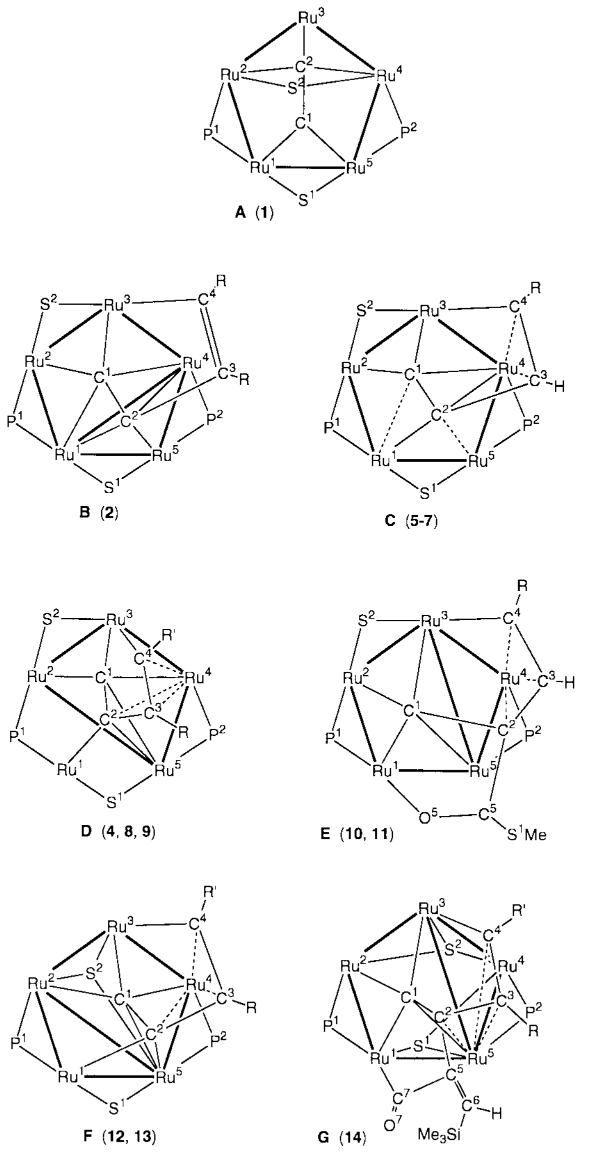
a new C–C bond and incorporation of the alkyne into a metallacycle occurring during the reaction. The reactions described above are summarised in Scheme 1. The high degree of unsaturation in the C_2 ligand is manifested by preservation of much of its interaction with the metal atoms, some of which may be considered to be “substituents” on the metallacycle. Following this interpretation of the structures of products **2**, some similarity exists between them and the metallacycles formed from two molecules of alkyne on triruthenium clusters, for example.[1,7,8]

However, the terminal carbon [C(1)] is strongly attached to three or four metal atoms of the square base of the cluster and serves to hold the cluster atoms together so that subsequent reactions take a different path. Thus carbonylation afforded two novel structural types, in which either the cluster extrudes one of the Ru atoms which still remains in the complex *via* the various bridging groups, or the organic ligand takes up CO and one of the SMe groups to form a novel thiocarboxylate system. There seem to be no structurally characterised examples of complexes containing either the Ru–OC(SMe) (as here) or Ru–SMeC(O) systems. The closest system that we have been able to find is that resulting from the reaction between $[Co_2(\mu\text{-}C_2H_2)(CO)_6]$ and $PPh_2(SPh)$, from which the complex $[Co_2\{\mu\text{-}\eta^2\text{-}S\text{-}CH{=}CHC(O)SPh\}(\mu\text{-}PPh_2)(CO)_4]$ was isolated; interestingly, treatment with $P(OMe)_3$ results in exchange of SPh and PPh_2 groups to give $[Co_2\{\mu\text{-}\eta^2{:}\eta^1\text{-}P\text{-}PPh_2CH{=}CHC(O)\}(\mu\text{-}SPh)(CO)_2\{P(OMe)_3\}_2]$.[10]

In another product (**14**) two molecules of alkyne have combined with the C_2 ligand and a CO molecule to give a novel bicyclic system. It is notable that the second addition occurs at the same C(2) atom as the first, the cluster-bound atom C(1) attaining even more carbidic character (as shown by its ^{13}C chemical shift) as a result. The observed structure suggests that the second molecule of alkyne is isomerised to the corresponding vinylidene before being incorporated, so the the substituted carbon appears as an *exo*-trimethylsilylmethylene group. Similar chemistry may be operative in the formation of cluster complexes containing butatrienylidene ligands.[11]

Other products from the reactions between complex **1** and the alkynes include complexes which have similar structures to those obtained with disubstituted alkynes, described elsewhere.[1] Although not structurally characterised in the present work, the close similarities of the *ν*(CO) and NMR spectra (particularly of the SMe groups) of **12** and **13** to those of **3** (R = R′ = Me or Ph) give us confidence in assigning the structures illustrated in Scheme 1 to these compounds.

There is an interesting difference in the (apparently) first-formed products from the reactions of complex **1** with 1-alkynes on the one hand (as described here) and the disubstituted alkynes on the other. The latter (complexes **2**) differ by having one CO group less and one Ru–Ru bond more than found in **5**–**7**, transforming the open pentagon into the open envelope configuration also found in **10** and **14**. There are also detail differences in the co-ordination of the SMe and PPh_2 ligands, and a major change in the interaction of the organic ligand with the cluster. In particular, the C(3)=C(4) double bond is free in complexes **2**, whereas it is η^2 bonded to Ru(4) in **5**–**7**. At this time it is not clear whether this feature is solely a response of the cluster framework to increasing steric pressures, or whether there is an electronic reason.


A (1)

B (2)

C (5-7)

D (4, 8, 9)

E (10, 11)

F (12, 13)

G (14)

Chart 1

Chart 1 depicts the seven core structures **A**–**G** found in the complexes described above, using a common numbering scheme. This emphasises the persistence of certain features, such as the alternate Ru–Ru vectors bridged by the PPh_2 groups and the common attachment of the new C_4 ligand to Ru(3,4,5). In some cases, however, it is evident that further migration of ligands has occurred. This is particularly the case for the SMe groups: in **A** one of these bridges a non-bonded Ru(2) · · · Ru(4) vector, but migrates to bridge Ru(2)–Ru(3) in structures **B**, **C**, **D** and **E**. It becomes triply bridging in **F** and **G**. We note that atom Ru(1) in **F** and atom Ru(2) in **G** are each attached to both SMe groups. Similarly, the RuC_4 metallacycle includes only Ru(3) in **B**, but then interacts further with Ru(4) in **C**, **D** and **E**. We have also commented earlier[3,4] on the flexibility of the Ru_5 cluster core geometries and our findings here emphasise the earlier conclusion that the final stereochemistry is driven by the nature of the organic ligands present, their electronic and steric requirements being the determining factors in the structures we have found. Consequently, although formally similar Ru_5 cores are present in these complexes, facile Ru–Ru bond-breaking and -making reactions result in different Ru atoms forming the flaps of the envelopes in **E**, **F** and **G**. Indeed, the formation of **G** involves considerable alteration of the original ligand arrangements, the C_4 ligand being η^2 and η^4 bonded to Ru atoms across the ring, rather than to two adjacent metal atoms. The most obvious feature of this complex, however, is that the flap of the envelope is on the opposite side of the Ru_4 rhombus from the organic ligand, which in this case is being held in place by the SMe groups.

Conclusions

This work has found further examples of complexes which have been formed by combination of the reactive C_2 ligand in **1** with unsaturated hydrocarbons, in this case 1-alkynes. Combination with one molecule of the alkyne has given a C_4 ligand, strongly held to the cluster by a terminal carbon in a μ_3- or μ_4-bridging mode. The other end of the chain forms a metallacycle with one of the Ru atoms. Further reactions have resulted in elaboration of the C_4 ligand by the incorporation of CO and a bridging SMe group to form a thiocarboxylate, or of CO and a second molecule of the alkyne (apparently isomerised to the corresponding vinylidene) to afford a bicyclic dimetallacycle.

Experimental

General reaction conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed before use. Light petroleum refers to a fraction of bp 60–80 °C. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation

IR: Perkin-Elmer 1700X FT-IR; 683 double beam, NaCl optics. NMR: Gemini 200 (^1H at 199.975 MHz, ^{13}C at 50.289 MHz); Bruker ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz). FAB MS: VG ZAB 2HF (3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Reagents

The alkynes HC≡CPh (Aldrich), $HC{\equiv}CBu^t$ (Fluka) and CO (CIG Ltd) were used as received; complex **1**[6] and $HC{\equiv}CSiMe_3$[12] were prepared by literature methods.

Reactions of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ with 1-alkynes

(a) Phenylethyne. A solution of complex **1** (88 mg, 0.068 mmol) and phenylacetylene (100 mg, 0.98 mmol) in toluene (10 cm^3) were heated in a Carius tube for 5 h at 110 °C. After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10 : 3) to yield at least five bands. The major brown band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield black crystals of $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **5** (38 mg, 41%), mp 231–235 °C (decomp.).

(b) 3,3-Dimethylbut-1-yne. A solution of complex **1** (100 mg, 0.077 mmol) and $HC{\equiv}CBu^t$ (40 mg, 0.49 mmol) in toluene (10 cm^3) in a Carius tube was heated for 18 h at 90 °C. After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10 : 3) to yield two bands. A brown band (R_f 0.60) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5(\mu_5\text{-}CCCHCBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **6** as the hemi-CH_2Cl_2 solvate (36 mg, 35%). A red-brown band (R_f 0.45) was recrystallised from CH_2Cl_2–MeOH to yield an isomeric mixture, also formulated as $Ru_5(CCCHCBu^t)(SMe)_2(PPh_2)_2(CO)_{10}$ (36 mg, 35%), but presently structurally unidentified. Found: C, 39.81; H, 2.89. Calc. for $C_{44}H_{36}O_{10}P_2Ru_5S_2$: C, 38.97; H, 2.68%. IR: ν(CO) (cyclohexane) 2046m, 2029s, 2022vs, 2010m, 1996m, 1993m, 1981m, 1976(sh), 1966w, 1960m and 1944m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 0.51 (1.5 H, s, SMe), 0.53 (3 H, s, SMe), 1.10 (4.5 H, s, CMe_3), 1.17 (9 H, s, CMe_3), 2.69 (3 H, d, J_{HP} 2.2, SMe), 2.79 (0.5H, d, J_{HP} 2.6, SMe), 5.56 (H, d, J_{HP} 1, CH), 5.60 (1 H, d, J_{HP} 1.2 Hz, CH), 6.16–6.25 (3 H, m, Ph) and 7.01–8.09 (30 H, m, Ph). FAB MS (*m*/*z*): 1357, M^+; 1329–1077, $[M - nCO]^+$ (n = 1–10).

(c) Ethynyltrimethylsilane (at 95–100 °C). A solution of complex **1** (100 mg, 0.077 mmol) and $HC{\equiv}CSiMe_3$ (60 µl, 43 mg, 0.43 mmol) in toluene (10 cm^3) was heated in a Carius tube for 9 h at 95 °C. This temperature is somewhat critical. At higher temperatures a number of other products are formed. After cooling to room temperature the solvent was removed and the residue recrystallised from CH_2Cl_2–MeOH to yield black crystals of $[Ru_5(\mu_5\text{-}CCCHCSiMe_3)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **7** (78 mg, 74%).

(d) Ethynyltrimethylsilane (at 110 °C). A solution of complex **1** (100 mg, 0.077 mmol) and $HC{\equiv}CSiMe_3$ (100 µl, 71 mg, 0.72 mmol) in toluene (10 cm^3) was heated in a Carius tube for 6 h at 110 °C. After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10 : 3) to yield two major bands. A black band (R_f 0.7) contained 6 mg of an unidentified complex. A purple band (R_f 0.6) was recrystallised from CH_2Cl_2–MeOH to yield black crystals of **7** (32 mg, 36%). A yellow band (R_f 0.4) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5\{\mu_5\text{-}CC(CHCSiMe_3)C({=}CHSiMe_3)CO\}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_8]$ **14** (21 mg, 19%).

Reaction of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}(NCMe)]$ with phenylethyne

A mixture of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{10}(NCMe)]$ (100 mg, 0.076 mmol) and HC≡CPh (80 mg, 0.78 mmol) in toluene (10 cm^3) was heated in a Carius tube at 100 °C for 5 min. After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10 : 3). The major brown band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield black crystals of complex **5** (90 mg, 86%).

Reaction of $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ 5 with CO

A solution of complex **5** (100 mg, 0.073 mmol) in toluene (20 cm^3) was heated at 90 °C for 6 h with a CO purge. After cooling to room temperature and removing the solvent the residue was purified by preparative tlc (light petroleum–acetone 10 : 3) to yield two products. The major red band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **8** (86 mg, 84%). A minor dark brown band (R_f 0.45) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5\{\mu_5\text{-}CC[C(O)SMe]CHCPh\}(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ **10** (11 mg, 11%).

Reaction of $[Ru_5(\mu_5\text{-}CCCHCSiMe_3)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ 7 with CO

A solution of complex **7** (100 mg, 0.073 mmol) in toluene (20 cm^3) was heated at 90 °C for 2.5 h with a CO purge. After cooling to room temperature and removing the solvent the residue was purified by preparative tlc (light petroleum–acetone 10 : 3) to yield two major bands. A major red band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield **9** (84 mg, 82%). A minor light brown band (R_f 0.4) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5\{CC[C(O)SMe]CHC(SiMe_3)\}(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}]$ **11** (7 mg, 7%).

Pyrolysis of $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ 8

A solution of complex **8** (100 mg, 0.071 mmol) in toluene (25 cm^3) was heated at 95–100 °C until no starting material remained (14 h). After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10 : 3) to yield two major bands. A light brown band (R_f 0.60) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_5(\mu_5\text{-}CCCHCPh)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_9]$ **12** (55 mg, 57%). A dark brown band (R_f 0.55) was recrystallised from CH_2Cl_2–MeOH to yield **5** (12 mg, 12%). One of three minor bands contained **10** (R_f 0.55; 1 mg, 1%) by comparison of its IR ν(CO) spectrum with an authentic sample. This complex was observed in higher amounts earlier in the reaction (*ca.* 5–10% after 6 h).

Pyrolysis of $[Ru_5(\mu_5\text{-}CCCHCSiMe_3)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ 9

A solution of complex **9** (59 mg, 0.042 mmol) in toluene (25 cm^3) was heated at 100–105 °C until no starting material remained (15 h). After cooling to room temperature the solvent was removed and the residue purified by preparative tlc (light

Table 3 Crystal data and refinement details for complexes **7**, **9**, **10** and **14**

	7	**9**	**10**	**14**
Formula	$C_{43}H_{36}O_{10}P_2Ru_5S_2Si$	$C_{44}H_{36}O_{11}P_2Ru_5S_2Si$	$C_{47}H_{32}O_{11}P_2Ru_5S_2$	$C_{47}H_{46}O_9P_2Ru_5S_2Si_2$
M	1372.3	1400.3	1404.2	1442.5
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	18.461(4)	42.87(3)	13.579(1)	14.762(8)
b/Å	14.009(15)	11.861(7)	13.842(1)	16.682(8)
c/Å	20.78(2)	21.23(1)	15.787(1)	22.425(6)
α/°			94.447(1)	
β/°	116.07(3)	106.61(5)	114.924(1)	100.20(4)
γ/°			97.952(1)	
V/Å^3	4827	10345	2634.4	5435
Z	4	8	2	4
μ/cm^{-1}	15.9	16.5	15.9	15.5
N	8089	8685	12829	9551
N_o	4481	4009	9344	6384
R	0.051	0.058	0.040	0.040
R'	0.049	0.054	0.045	0.041

petroleum–acetone 10:3) to yield two major bands. A light brown band (R_f 0.60) was recrystallised from CH_2Cl_2–MeOH to yield **13** (46 mg, 82%). A dark brown band (R_f 0.55) was recrystallised from CH_2Cl_2–MeOH to yield **7** (9 mg, 16%).

Crystallography

Unique data sets were measured at *ca.* 295 K using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ 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, core hydrogens being observed in difference maps. Conventional residuals R, R' on $|F|$ are quoted (Table 3), 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[13] implemented by S. R. Hall; neutral atom complex scattering factors were employed.

Abnormal features/variations in procedure. A sphere of data was measured for complex **10** using a Bruker AXS CCD area detector instrument, a total of 29324 reflections merging to 12829 ($R_{int} = 0.030$); data were processed with proprietary software SAINT, SADABS ('empirical' absorption correction) and XPREP. For **14** ring C(12n) was modelled as disordered over two sets of positions, refined with constrained geometry and site occupancies set at 0.7/0.3 after trial refinement.

CCDC reference number 186/1482.

See http://www.rsc.org/suppdata/dt/1999/2451/ for crystallographic files in .cif format.

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