ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 584 (1999) 254–264

Journal of Organometallic Chemistry

Reactions of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ with $C_2(SiMe_3)_2$: formation of butatrienylidene complexes and related chemistry. X-ray crystal structures of $Ru_5\{\mu_5\text{-}CC[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$, $Ru_5(\mu_5\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ and $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$

Chris J. Adams [a], Michael I. Bruce [a,*], Brian W. Skelton [b], Allan H. White [b]

[a] *Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia*

Received 18 January 1999; received in revised form 8 March 1999

Abstract

The reaction between the dicarbon-containing complex $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) and $C_2(SiMe_3)_2$ afforded two isomers of $Ru_5\{\mu_5\text{-}CCCCH(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**2a**,**b**). A minor product from this reaction was $Ru_5\{\mu_5\text{-}CC[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**3**) in which an SMe ligand is lost from **1**. The major products from reactions of **1** with $HC\equiv CBu^t$ were analogues of **2a**,**b**, namely $Ru_5(\mu_5\text{-}CCCCHBu^t)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**6a**,**b**). Treatment of **2** with KOH results in desilylation and formation of the first structurally characterised butatrienylidene complex $Ru_5(\mu_5\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**4**). Carbonylation (80°C, 1.5 h) afforded $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**5**). The molecular structures of **3**, **4** and **5** were determined by single-crystal X-ray studies. In **3** and **4**, the Ru_5 core has an open envelope conformation; in **5**, one Ru–Ru bond of the flap has been cleaved. Two molecules of alkyne have become attached to the same carbon atom of the C_2 unit in **3**, with concomitant loss of $(MeS + SiMe_3)$. In **4** and **5**, the organic ligand is butatrienylidene, formed by formal 'end-to-end' coupling of the C_2 moiety with the vinylidene $:C{=}CH(SiMe_3)$; the unsaturated carbene ligand is attached to the cluster by three of its four carbon atoms. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Carbonyls; Clusters; Dicarbon; Ruthenium

1. Introduction

We have been involved in a detailed study of the reactions of the dicarbon cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**1**) [1] with unsaturated hydrocarbons and the results obtained with mono- and disubstituted alkynes have been described in two recent papers [2,3]. These confirm the propensity of the cluster-bonded C_2 ligand to enter into new C–C bond-forming reactions, one or two molecules of alkyne combining with atom C(2) (Scheme 1). One of the latter products is formed by isomerisation of the 1-alkyne to the corresponding vinylidene before incorporation into the new organic ligand. This paper describes products obtained from reactions between **1** and $C_2(SiMe_3)_2$, which involve loss of one $SiMe_3$ group and include an example of a cluster bearing a butatrienylidene ligand. Structural identification of this product (which was not obtained from similar reactions of $HC\equiv CSiMe_3$) enabled resolution of the identity of a major product from the reaction between **1** and $HC\equiv CBu^t$, which had remained uncharacterised [3]. Some of these results have been communicated earlier [4].

---

* Corresponding author. Fax: + 61-8-83034358.

E-mail address: mbruce@chemistry.adelaide.edu.au (M.I. Bruce)

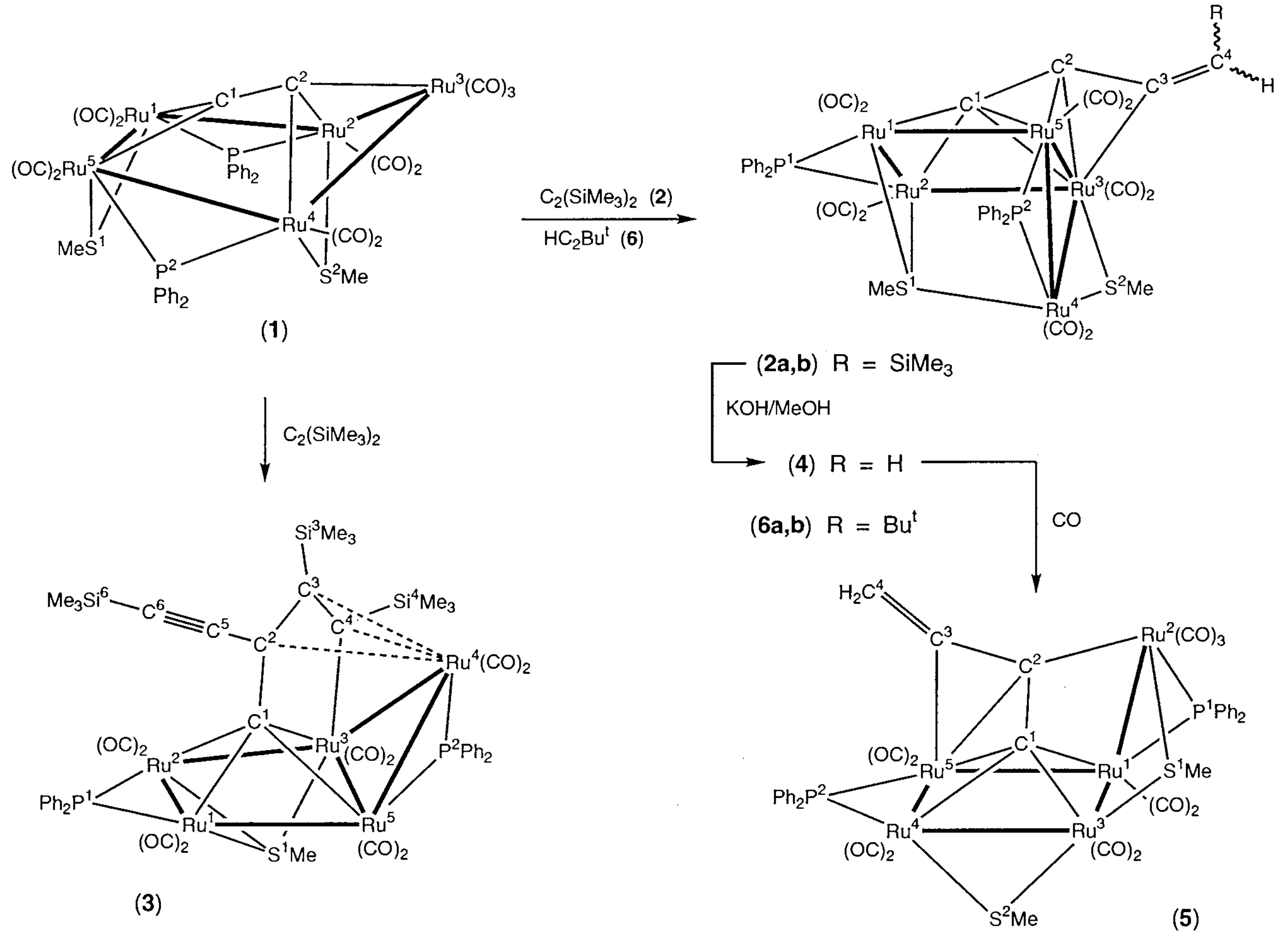
PII: S0022-328X(99)00150-3

2. Results and discussion

Two products were isolated from the reaction between **1** and $C_2(SiMe_3)_2$ after heating in toluene for 26 h. The major product was obtained in 94% yield and characterised as a mixture of the two isomers of $Ru_5\{\mu_5\text{-}CCCCH(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}$ (**2a**,**b**) where the H and $SiMe_3$ groups are exchanged. The FAB MS (Table 1) contained M^+ at *m*/*z* 1374. The presence of the two isomers is shown by two closely related sets of Me resonances with approximately 2/3 ratio in the ^1H- and ^{13}C-NMR spectra. For example, the $SiMe_3$ resonances are found at δ 0.18 and 0.20 (^1H) and at δ −1.27 and −1.23 (^{13}C); singlet and doublet proton resonance pairs are found for the SMe groups in the two isomers at δ 0.55 and 2.70, and at δ 0.57 and 2.79, respectively. The CH signals are doublets at δ 5.58 and 5.69. The IR ν(CO) spectrum was essentially identical with that of the structurally characterised desilylated complex (see below). In the ^{13}C-NMR spectrum, the four carbons of the $CCCCH(SiMe_3)$ chain were observed at δ 240.84/238.39, 174.20, 168.93 and 105.27/100.81; the former pair showed coupling to one ^{31}P nucleus.

The first and minor fraction formed brown crystals which were identified as $Ru_5\{\mu_5\text{-}CC[C_2(SiMe_3)]C\text{-}(SiMe_3)C(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**3**) by means of a single-crystal X-ray structural determination. The spectroscopic properties (Table 1) include an all-terminal ν(CO) spectrum between 2038 and 1947 cm^{-1} and a ^1H-NMR spectrum which contains four singlet resonances between δ −0.09 and 0.48, assigned to the SMe and three $SiMe_3$ groups. The highest mass ion in the FAB MS corresponds to $[M-CO]^+$.

Treatment of **2** with KOH in methanol afforded a red complex which contained no $SiMe_3$ groups: it was identified as the parent butatrienylidene complex $Ru_5(\mu_5\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**4**) by a single-crystal X-ray study. The IR ν(CO) spectrum differs little from that of **2** (the frequencies are ca. 2 cm^{-1} higher) and the ^1H-NMR spectrum is characterised by two broad CH resonances at δ 5.48 and 5.72, while the SMe groups give singlet and doublet resonances at δ 0.53 and 2.72, respectively, again comparable to those found for **2**. The M^+ ion in the FAB MS is at *m*/*z* 1300.



Scheme 1.

Table 1
Analytical and spectroscopic data

Complex and analyses	*ν*(CO) (cm^{-1})[a]	NMR[b] and FAB MS
2 Ru$_5${μ$_5$-CCCCH(SiMe$_3$)}(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{10}$. Found: C, 37.53; H, 2.66. Anal. Calc. C$_{43}$H$_{36}$O$_{10}$P$_2$Ru$_5$S$_2$Si: C, 37.64; H, 2.64; M, 1374	2069vw, 2046m, 2029s, 2021vs, 2010m, 1995m, 1993m, 1981s, 1976(sh), 1965w, 1960m, 1945m	^{1}H-NMR: δ 0.18 (6H, s, SiMe$_3$), 0.20 (9H, s, SiMe$_3$), 0.55 (2H, s, SMe), 0.57 (3H, s, SMe), 2.70 (3H, d, J_{HP} 1.8 Hz, Sme), 2.79 (2H, d, J_{HP} 2.3 Hz, SMe), 5.58 (0.67H, d, J_{HP} 1.7 Hz, CH), 5.69 (1H, d, J_{HP} 0.8 Hz, CH), 6.22 (3.3H, m, Ph), 7.02-8.10 (33.3H, m, Ph). ^{13}C-NMR: δ −1.27, −1.23 (2s, SiMe$_3$), 22.11, 22.18, 28.51, 29.06 (4s, SMe), 100.81, 105.27 (2s, CH), 127.87–133.41 (m, Ph), 139.99–146.88 (m, *ipso* C), 168.93 (s, $\underline{C}$CH(SiMe$_3$)), 174.20 (d, J_{CP} 15 Hz, C$\underline{C}$), 191.98–202.18 (m, CO), 238.39 (d, J_{CP} 14.3 Hz, $\underline{C}$C), 240.84 (d, J_{CP} 15.3 Hz, $\underline{C}$C). MS (*m*/*z*): 1374, M$^+$; 1346-1094, [M−*n*CO]$^+$ ($n+1-10$).
3 Ru$_5${μ$_5$-CC(C$_2$SiMe$_3$) C(SiMe$_3$)C(SiMe$_3$)}-(μ$_3$-SMe)(μ-PPh$_2$)$_2$(CO)$_{10}$. Found: C, 39.96; H, 3.33. Anal. Calc. C$_{50}$H$_{50}$O$_{10}$P$_2$Ru$_5$SSi$_3$: C, 40.18; H, 3.37; M, 1496	2038w, 2021s, 2010vs, 1994m, 1989m, 1969m, 1964m, 1947w	^{1}H-NMR: δ −0.09, 0.41, 0.43 (27H, 3s, SiMe$_3$), 0.48 (3H, s, SMe), 7.10-8.34 (20H, m, Ph). MS (*m*/*z*) 1468–1216, [M−*n*CO]$^+$ ($n+1-10$)
4 Ru$_5$(μ$_5$-CCCCH$_2$)(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{10}$. Found: C, 34.98; H, 2.22. Anal. Calc. C$_{40}$H$_{28}$O$_{10}$P$_2$Ru$_5$S$_2$·CH$_2$Cl$_2$: C, 35.56; H, 2.17; M, 1301	2048m, 2031s, 2024vs, 2012m, 1997m (br), 1982s, 1961m, 1946m	^{1}H-NMR: δ 0.53 (3H, s, SMe), 2.72 (3H, d, J_{HP} 1.5 Hz, SMe), 5.24 (2H, s, CH$_2$Cl$_2$), 5.48 [s (br), CH], 5.72 [s (br), CH], 6.24 (2H, dd, J_{HH} 13.6, 7.7 Hz, Ph), 7.07–8.05 (20H, m, Ph). MS (*m*/*z*): 1300, M$^+$; 1272–1020, [M−*n*CO]$^+$ ($n+1-10$)
5 Ru$_5$(μ$_5$-CCCCH$_2$)(μ-Sme)$_2$(μ-PPh$_2$)$_2$(CO)$_{11}$. Found: C, 36.83; H, 2.17. Anal. Calc. C$_{41}$H$_{28}$O$_{11}$P$_2$Ru$_5$S$_2$: C, 37.08; H, 2.13; M, 1329	2093m, 2048m, 2033m, 2022m, 2017vs, 2008m, 1995m, 1982m, 1976m, 1969s, 1961m, 1950w	^{1}H-NMR: δ 1.70 (3H, s, SMe), 2.27 (3H, s, SMe), 4.67 (1H, d, J_{HP} 2.2 Hz, CH), 5.18 (1H, d, J_{HP} 2.2 Hz, CH), 7.19–8.19 (20H, m, Ph). MS (*m*/*z*): 1329, M$^+$; 1301–1021, [*M*−*n*CO]$^+$ ($n+1-11$)
6 Ru$_5$(μ$_5$-CCCCHBu^t)(μ$_3$-SMe)(μ-SMe)(μ-PPh$_2$)$_2$ (CO)$_{10}$. Found: C, 39.81; H, 2.89. Anal. Calc. C$_{44}$H$_{36}$O$_{10}$P$_2$Ru$_5$S$_2$: C, 38.97; H, 2.89; M, 1357	2046m, 2029s, 2022vs, 2010m, 1996m, 1993m, 1981m, 1976(sh), 1966w, 1960m, 1944m	^{1}H-NMR: δ 0.51 (1.5H, s, SMe), 0.53 (3H, s, SMe), 1.10 (4.5H, s, CMe$_3$), 1.17 (s, 9H, CMe$_3$), 2.69 (3H, d, J_{HP} 2.2 Hz, SMe), 2.79 (0.5H, d, J_{HP} 2.6 Hz, SMe), 5.56 (H, d, H_{HP} 1 Hz, CH), 5.60 (1H, d, J_{HP} 1.2 Hz, CH), 6.16-6.25 (3H, m, Ph), 7.01-8.09 (30H, m, Ph). MS (*m*/*z*): 1357, M$^+$; 1329–1077, [M−*n*CO]$^+$ ($n+1-10$)

[a] Cyclohexane.

[b] CDCl$_3$

Carbonylation of **5** (toluene at 80°C, 1.5 h, CO purge) gave the new complex $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**5**), isolated in 62% yield, which exhibited ν(CO) and ^{1}H-NMR spectra which were different from those of **2**. In particular, both SMe signals are now singlets at δ 1.70 and 2.27 and the CH signals have sharpened to well-resolved doublets at δ 4.67 and 5.18. The molecular structure of **6** was determined from a single-crystal X-ray diffraction study.

Comparison of the ν(CO) spectra of **2** with that of a red–brown complex isolated from the reaction products of **1** with $HC{\equiv}CBu^t$ showed an essentially identical pattern with no frequency differing by more than 1 cm^{-1}. In the ^{1}H-NMR spectrum, the SMe singlets and doublets had almost identical chemical shifts, this time appearing with relative intensities 2/1, while the CH doublets were at δ 5.56 and 5.60. The CMe_3 singlets were found at δ 1.10 and 1.17. The FAB MS contained M^+ at m/z 1357. On the basis of this spectroscopic evidence and the analytical results which confirm the stoichiometry, we can now say that this compound is a 2/1 isomeric mixture of the t-butylbutatrienylidene cluster $Ru_5(\mu_5\text{-}CCCCHBu^t)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}$ (**6a**,**b**), in which the H and Bu^t groups are exchanged.

2.1. Molecular structures of 3, 4 and 5

Plots of molecules of these three complexes are given in Figs. 1–3 and significant structural parameters are collected in Table 1.

2.1.1. $Ru_5\{\mu_5\text{-}CC[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}\text{-}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (3)

The Ru_5 core has the now-familiar open-envelope conformation, with the dihedral between the Ru_3 and Ru_4 polygons being 46.74(4)° [2,3]. Atoms Ru(3,4,5) form the flap of the envelope, the body of which is bent along the Ru(1)···Ru(3) vector (dihedral 23.28(5)°). The Ru–Ru distances range between 2.762(1) and 2.899(1) Å and are not exceptional, with an average separation of 2.819 Å. While the two PPh_2 groups bridge the Ru(1)–Ru(2) and Ru(4)–Ru(5) vectors (Ru–P 2.283–2.325(2) Å), in contrast to previously described complexes obtained from the reactions of **1**, only one SMe group is present, spanning three atoms Ru(1,2,3) of the Ru_4 rhombus [Ru–S 2.379-2.508(2) Å]. The organic ligand contains two alkyne moieties attached to C(2), one of which has lost one $SiMe_3$ group and is attached as a trimethylsilylethynyl group. The $C_2(SiMe_3)_2$ group links C(2) with Ru(3) [Ru(3)–C(4) 2.130(7) Å]. Atoms C(2,3) are asymmetrically attached to Ru(4); in addition, there is a weak interaction between Ru(4) and C(3) [2.439(5) Å]. The original C_2 ligand is recognisable in the C(1)–C(2) fragment, of which C(1) is strongly attached to the Ru_4 rhombus [Ru–C(1) 2.082-2.217(7) Å].

There are ten CO ligands, two on each ruthenium. The cluster valence electron count is 78 (40 (5Ru) + 20 (10CO) + 5 (SMe) + 6 ($2PPh_2$) + 7 (the organic ligand)), as expected for an M_5 cluster with seven M–M bonds.

2.1.2. $Ru_5(\mu_5\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}$ (4)

The Ru_5 cluster in **4** has the open envelope conformation, with the dihedral angle between the flap and the body of the envelope 86.26(3)°. Atoms Ru(1,2,3,5) are coplanar [$\chi^2 = 99$; δ(Ru) $\pm 0.006(1)$ Å]. The Ru–Ru separations range between 2.745(1) [Ru(1)–Ru(2)] and 3.0903(9) Å [Ru(4)–Ru(5)], both extremes being bridged by the μ-PPh_2 groups [Ru–P 2.302–2.324(2) Å]; the average Ru–Ru distance is 2.96_3 Å. One SMe group bridges the Ru(3)–Ru(4) vector [Ru(3,4)–S(2) 2.394, 2.387(3) Å], while the second μ_3-SMe group holds the flap open, with (longer) Ru–S(1) distances of between 2.405 and 2.437(2) Å.

The organic ligand consists of the C(1)–C(2)–C(3)–C(4) chain, of which C(1) is on the opposite side to the μ_3-SMe group. Atoms C(1)–C(2) bridge the Ru(3)–Ru(5) bond [Ru–C 2.094–2.228(7) Å], atom C(1) also being tightly bonded to Ru(1) and Ru(2) [2.126, 2.117(7) Å, respectively]. Atom C(3) is also attached to Ru(3) [2.196(8) Å] and forms a double bond with C(4) [1.32(1) Å]. Other C–C separations are 1.35 and 1.37(1) Å, consistent with π-complexed C=C double bonds. The C_4 ligand thus can be formulated as a cluster-bonded butatrienylidene, $:C{=}C{=}C{=}CH_2$, a member of the unsaturated carbene series $:C({=}C{=})_nCH_2$ [5]. The two hydrogens on C(4) were located and refined. While the interaction of C(1)–C(2) with the cluster is approximately symmetrical, atom C(3) is bent towards Ru(4) [angle C(1)–C(2)–C(3) 131.0(8)°], while atom C(4) is similarly bent back [angle C(2)–C(3)–C(4) 148.6(8)°].

The cluster is an 80 c.v.e. system (40 (5Ru) + 20 (10CO) + 5 (μ_3-SMe) + 9 (μ-SMe + $2PPh_2$) + 6 (the organic ligand)), which is in excess of the 78 c.v.e. expected for an M_5 cluster with six M–M bonds. This can be rationalised by the extra electron density being accommodated in Ru–Ru anti-bonding orbitals, leading to lengthening of the three edges of the Ru_3 flap, which are all > 3.0 Å. Such lengthening has been often observed in Ru_3 clusters containing μ-SMe, μ-PPh_2 or related ligands [6].

2.1.3. $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (5)

In **5**, the Ru_5 cluster is a spiked rhombus, slightly buckled about the Ru(3)···Ru(5) diagonal (dihedral 11.20(5)°). The Ru–Ru separations range between 2.8385(8) and 2.9506(9) Å, with an average value of 2.877 Å. The two SMe groups bridge the Ru(3)–Ru(4) bond and the non-bonded Ru(2)···Ru(3) vector, while the PPh_2 groups bridge the Ru(1)–Ru(2) and Ru(4)–

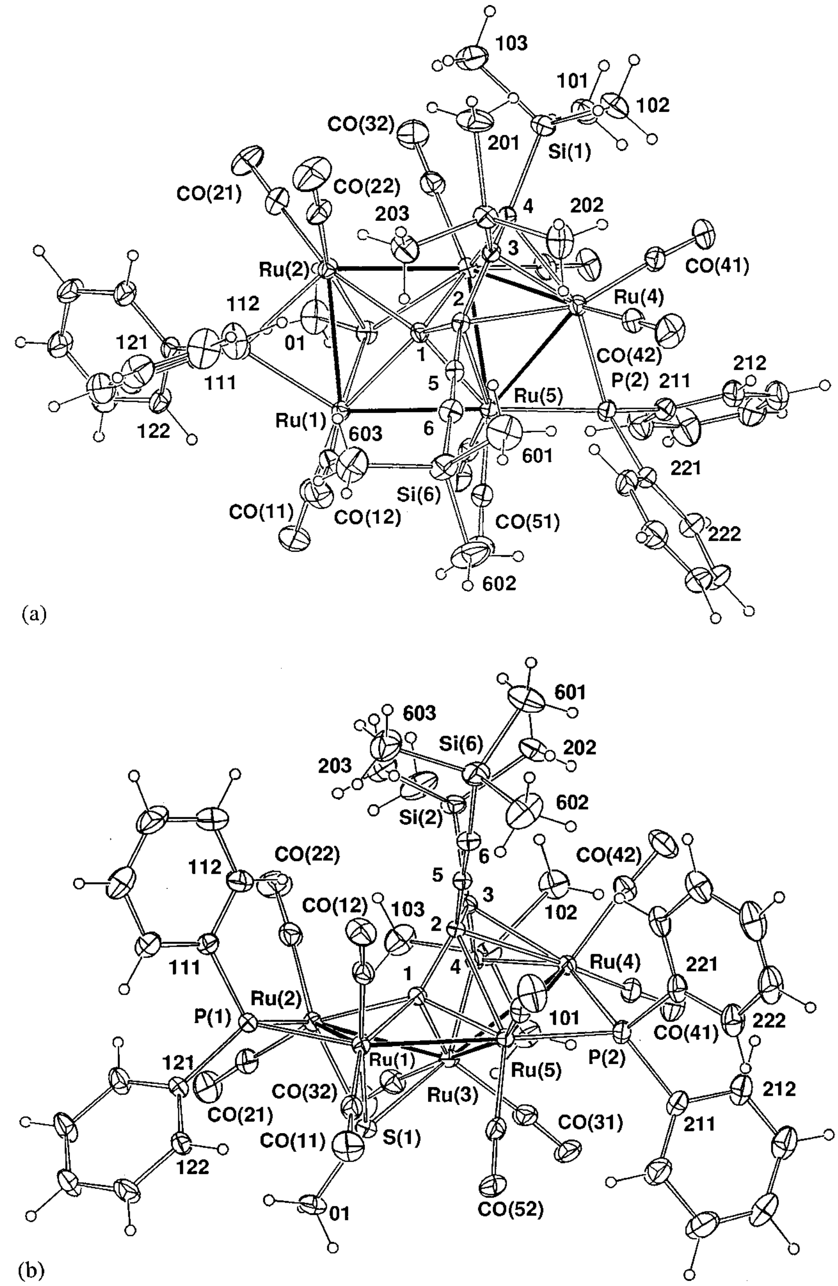


Fig. 1. Plots of a molecule of $Ru5\{\mu_5\text{-}CC[C_2(SiMe_3)]C(SiMe_3)C(SiMe_3)\}(\mu_3\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**3**) (a) normal to, and (b) oblique to the Ru_4 'plane', showing the atom numbering scheme. In this and subsequent figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1

Ru(5) bonds. As expected, the Ru(2)-S(1)–Ru(3) angle (106.25(8)°) is considerably larger than Ru(3)–S(2)–Ru(4) (72.73(6)°).

The attachment of the organic ligand, which is on the same side of the Ru_4 rhombus as the spike Ru(2) atom, is similar to that found in **4**, in that C(1)–C(2) bond bridges the Ru(1)–Ru(5) bond and atom C(3) also interacts with Ru(5). In this case, however, atom C(2) has a further interaction with Ru(2). The cluster has 80 c.v.e. (40 (5Ru) + 22 (11CO) + 6 (2SMe) + 6 ($2PPh_2$) + 6 (the organic ligand)), consistent with the observed structure with five Ru–Ru bonds.

The formation of **3** involves double addition to C(2) of precursor complex **1**, with concomitant elimination of one SMe and one $SiMe_3$ group, presumably in combination as $MeSSiMe_3$. Double addition of an alkyne to C(2) was also found in one of the products from the reaction between **1** and $HC{\equiv}CSiMe_3$; in this case, isomerisation to vinylidene was accompanied by attack on a cluster-bound CO ligand to give a dimetallabicycle [3]. In **3**, the organic ligand is anchored to the Ru_4 rhombus by strong interactions with C(1), the C(3)=C(4) double bond resulting from addition of one of the $C_2(SiMe_3)_2$ molecules to C(2) and Ru(3) interacting further with Ru(4), as found in related complexes obtained from **1** and disubstituted alkynes [2]. It is not possible to determine the mechanism of addition of the second $C_2(SiMe_3)_2$ molecule or how the adduct eliminates (MeS + $SiMe_3$): the result is the $Me_3SiC{\equiv}C$ substituent on C(3).

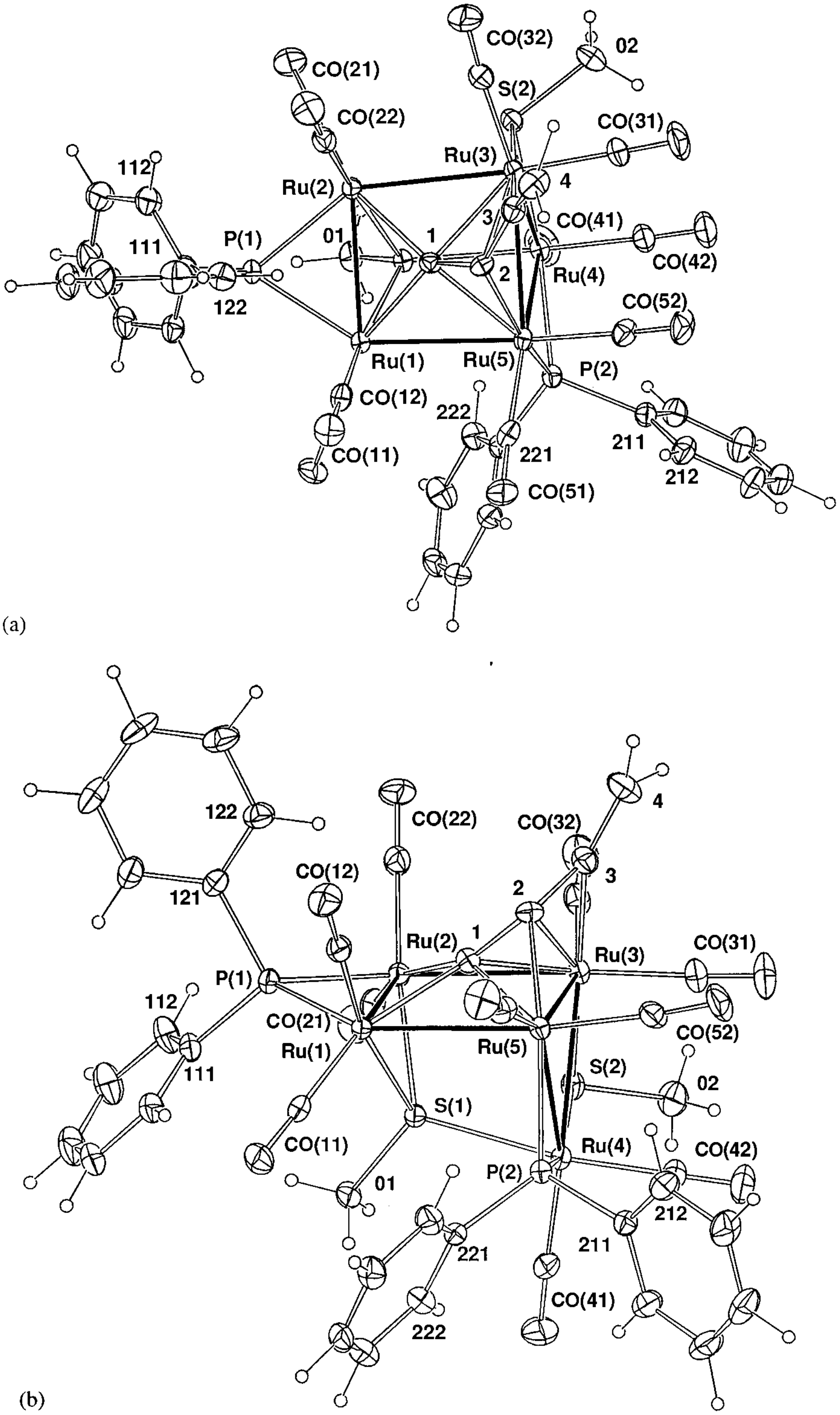


Fig. 2. Plot of a molecule of $Ru_5(\mu_5\text{-}CCCCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{10}$ (**4**) (a) normal to, and (b) oblique to the Ru_4 'plane', showing the atom numbering scheme.

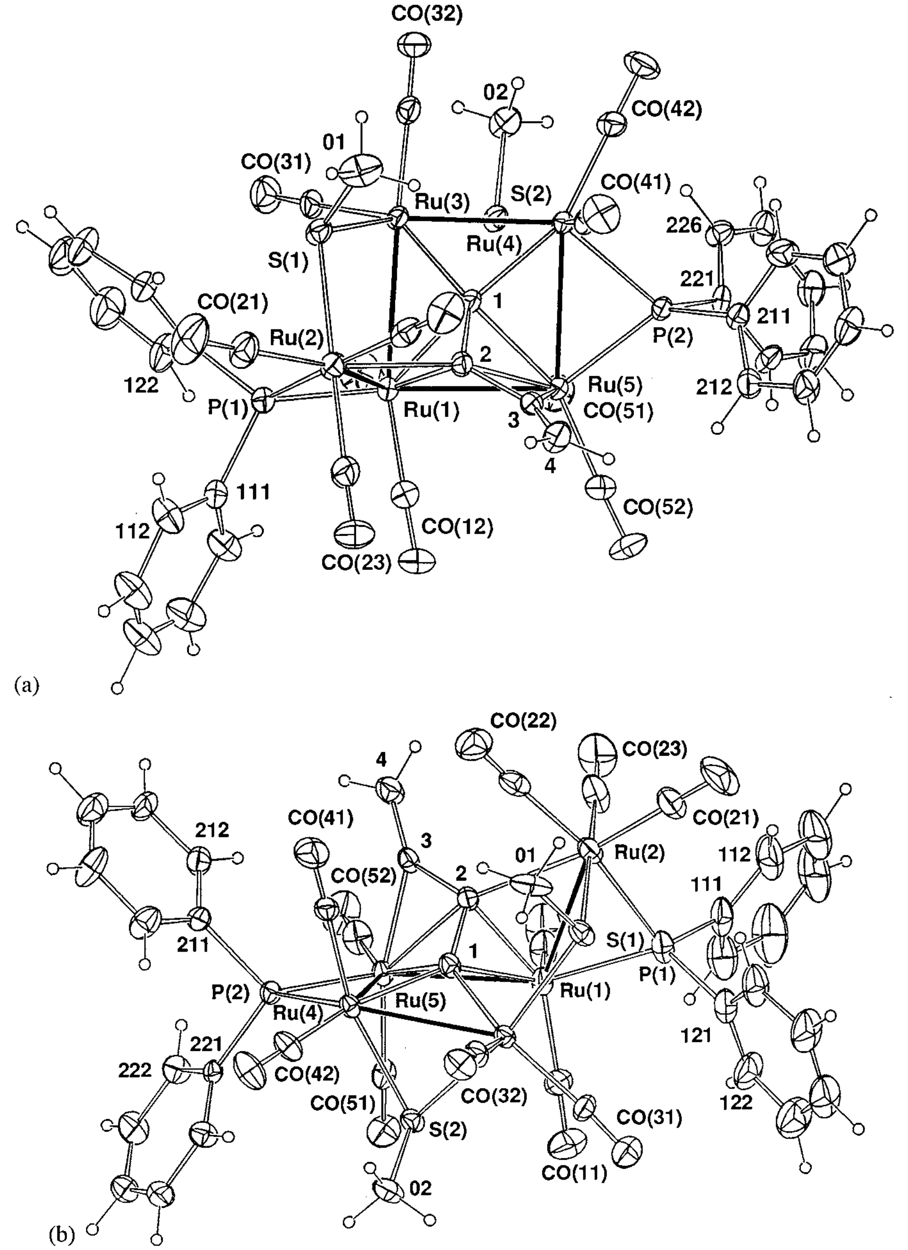
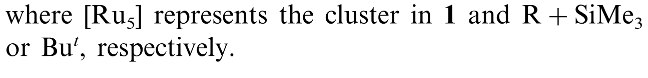


Fig. 3. Plot of a molecule of $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**5**) (a) normal to, and (b) oblique to the Ru_4 'plane', showing the atom numbering scheme.

Of interest is the formation of the butatrienylidene complexes **2** and **4**–**6**. When first prepared, these were the only cluster complexes containing this unsaturated carbene, and **4** and **5** are still the only structurally characterised examples of the unsubstituted ligand. Several mononuclear derivatives have since been reported as intermediates [7–10]. The formation of **2** must involve loss of one of the $SiMe_3$ groups during the reaction: in this case, accompanying loss of an SMe group does not occur, but addition of a proton results. As mentioned above, similar reactions with $HC{\equiv}CBu^t$ have given complexes with similar IR ν(CO) and NMR spectra, leading us to assign the structure shown for **6**. The NMR spectra of both complexes **2** and **6** show that mixtures of isomers are present, in 2/3 ratio for **2** and 1/2 for **6**. These are assigned to the two possible geometrical isomers shown. An attractive route to these complexes involves end-to-end coupling of two C_2 moieties, the one present in precursor **1** [C(1)–C(2)] with a vinylidene formed by cluster-induced isomerisation of the corresponding 1-alkyne. For **2**, this is $HC{\equiv}CSiMe_3$, formed by the desilylation mentioned above. The net reaction is thus:

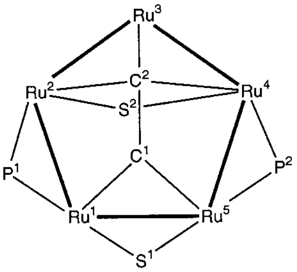


where $[Ru_5]$ represents the cluster in **1** and R + $SiMe_3$ or Bu^t, respectively.

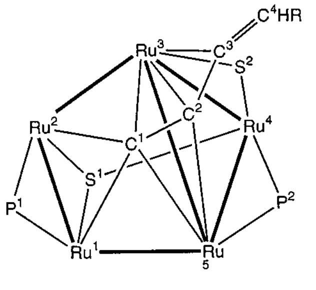
In our recent theoretical study of higher nuclearity clusters containing C_2 ligands [11], we showed that the C_2 ligand is electron-rich and is expected to react as a nucleophile. In **1**, the C_2 ligand can be considered as a metallated vinylidene. This reaction is thus a rare instance of the coupling of two vinylidenes to give the cumulenic C_4 chain. One example of a related reaction occurring on a mononuclear centre has been reported in the reaction of $HC{\equiv}CBu^t$ with $RuH_2(CO)(PPh_3)_3$ [12].

The subsequent chemistry of **3** is conventional, replacement of the $SiMe_3$ group by H occurring readily on treatment with KOH in methanol to give **4** in excellent yield. Addition of CO to **4** results in rearrangement to give **5**, in which the butatrienylidene ligand interacts with all five ruthenium atoms. It is not obvious how this rearrangement proceeds. For the purposes of discussion, it is relevant to note that while the Ru_5 core still has the open envelope conformation, the relative positions of the flap, SMe and organic groups have changed so that in **4**, the organic ligand is on the 'lower' face of the Ru_4 rhombus and the flap is now held open by the μ_3-SMe group. In contrast, in complex **5** one edge of the flap has been cleaved by addition of the CO ligand to Ru(2), this atom now bending to interact with C(2) of the C_4 ligand.

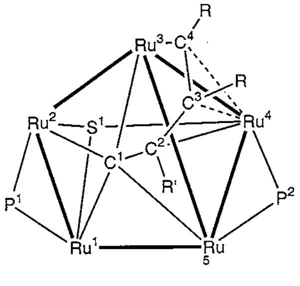
As in previous papers [2,3], we have attempted to relate the various structures encountered in these studies by a common numbering system, presented below (Chart 1), which shows the present complexes from a common viewpoint.



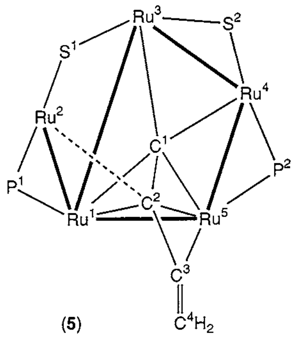
(1)



R = $SiMe_3$ (**2a,b**); H (**4**); Bu^t (**6a,b**)



(**3**) R = $SiMe_3$, R' = C_2SiMe_3



(**5**)

Reference to these diagrams shows that a plausible route from **4** to **5** is addition of CO to Ru(2), which results in cleavage of the Ru(2)–Ru(3) bond together with conversion of the μ_3-SMe group in **4** to μ_2, bridging the non-bonding Ru(2)···Ru(3) vector. This process is encouraged by the long Ru–Ru bonds present in the flap of **4**, as a result of the extra electrons occupying Ru–Ru anti-bonding orbitals.

3. Conclusions

These further reactions of **1** with alkynes have resulted in the discovery of complexes containing ligands formed by addition of two molecules of the alkyne to one carbon of the C_2 ligand in **1**, or by 'end-to-end' coupling of the C_2 ligand with a vinylidene formed by formal isomerisation of the 1-alkyne. For **4**, this has been generated during the reaction by an unspecified conversion of the precursor $C_2(SiMe_3)_2$ to $HC{\equiv}CSiMe_3$. The analogous complex **6** was isolated from reactions between **1** and $HC{\equiv}CBu^t$, although we did not observe the formation of either **4** or **5** in reactions between **1** and $HC{\equiv}CSiMe_3$. Desilylation of **3** gave the parent butatrienylidene complex **4**, which adds CO to give **5** by cleavage of an Ru–Ru bond and migration of the cluster-bonded ligands between Ru atoms.

4. Experimental

4.1. General conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

4.1.1. Reagents

Complex **1** was prepared by the literature method [13]. $HC{\equiv}CBu^t$, $C_2(SiMe_3)_2$ (Fluka) and CO (BOC Gases) were used as received.

4.1.2. Instrumentation

IR: Perkin–Elmer 1700X FT IR; 683 double beam, NaCl optics. NMR: Bruker CXP300 or ACP300 (^{1}H-NMR at 300.13 MHz; ^{13}C-NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Table 2
Selected bond parameters for **3**, **4** and **5**

	3	**4**	**5**[a]
Bond lengths (Å)[b]			
Ru(1)–Ru(2)	2.762(1)	2.745(1)	2.861(2)/2.867(1)
Ru(1)–Ru(3)			2.943(2)/2.9506(9)
Ru(1)–Ru(5)	2.802(1)	2.9345(9)	2.877(1)/2.8819(8)
Ru(2)–Ru(3)	2.772(1)	2.9242(9)	-
Ru(3)–Ru(4)	2.899(1)	3.073(1)	2.830(1)/2.8385(8)
Ru(3)–Ru(5)	2.861(1)	3.009(1)	-
Ru(4)–Ru(5)	2.820(1)	3.0903(9)	2.874(2)/2.8863(9)
Ru(1)–S(1)	2.480(2)	2.405(2)	
Ru(2)–S(1)	2.379(2)	2.432(3)	2.428(4)/2.430(2)
Ru(3)–S(1)	2.508(2)		2.396(3)/2.391(2)
Ru(3)–S(2)		2.394(2)	2.386(3)/2.390(2)
Ru(4)–S(1)		2.437(2)	
Ru(4)–S(2)		2.387(3)	2.399(4)/2.397(2)
Ru(1)–P(1)	2.292(2)	2.302(2)	2.267(3)/2.269(2)
Ru(2)–P(1)	2.283(2)	2.306(2)	2.382(4)/2.387(3)
Ru(4)–P(2)	2.325(2)	2.324(2)	2.281(3)/2.293(2)
Ru(5)–P(2)	2.291(2)	2.317(3)	2.257(3)/2.269(2)
Ru(1)–C(1)	2.212(7)	2.126(8)	2.19(1)/2.191(7)
Ru(1)–C(2)			2.10(1)/2.126(8)
Ru(2)–C(1)	2.217(5)	2.117(7)	
Ru(2)–C(2)			2.430(9)/2.421(6)
Ru(3)–C(1)	2.125(5)	2.219(6)	2.08(1)/2.051(6)
Ru(3)–C(2)		2.228(7)	
Ru(3)–C(3)		2.196(8)	
Ru(3)–C(4)	2.130(7)		
Ru(4)–C(1)			2.10(1)/2.107(6)
Ru(4)–C(2)	2.439(5)		
Ru(4)–C(3)	2.246(5)		
Ru(4)–C(4)	2.194(6)		
Ru(5)–C(1)	2.082(6)	2.187(8)	2.21(1)/2.245(6)
Ru(5)–C(2)	2.558(6)	2.094(9)	2.337(9)/2.364(6)
Ru(5)–C(3)			2.11(1)/2.136(8)
C(1)–C(2)	1.475(7)	1.37(1)	1.37(2)/1.40(1)
C(2)–C(3)	1.49(1)	1.35(1)	1.44(2)/1.43(1)
C(2)–C(5)	1.448(7)		
C(3)–C(4)	1.417(6)	1.32(1)	1.28(2)/1.31(1)
C(5)–C(6)	1.194(7)		
C(4)–Si(1)	1.892(8)		
C(3)–Si(2)	1.944(6)		
C(6)–Si(6)	1.839(5)		
Bond angles (°)[c]			
Ru(2)–Ru(1)–Ru(5)	94.33(3)	91.97(3)	109.14(6)/109.15(3)
Ru(3)–Ru(1)–Ru(5)			86.77(5)/86.88(2)
Ru(1)–Ru(2)–Ru(3)	85.01(2)	93.20(3)	
Ru(1)–Ru(3)–Ru(4)			91.30(5)/91.30(2)
Ru(2)–Ru(3)–Ru(5)	92.83(2)	87.05(3)	
Ru(3)–Ru(4)–Ru(5)	60.00(3)	58.44(2)	89.00(5)/88.94(2)
Ru(1)–Ru(5)–Ru(3)	82.64(2)	87.78(3)	
Ru(1)–Ru(5)–Ru(4)	128.30(3)		91.76(5)/91.75(2)
Ru(1)–C(1)–Ru(4)			148.9(7)/148.8(4)
Ru(3)–C(1)–Ru(5)			137.6(7)/137.9(4)
Ru(1)–C(1)–Ru(3)	119.1(2)	143.0(4)	
Ru(2)–C(1)–Ru(5)	143.3(3)	143.4(4)	
Ru(1)–C(1)–C(2)	133.1(4)	135.6(6)	
Ru(2)–C(1)–C(2)	126.0(4)	140.8(7)	
Ru(3)–C(1)–C(2)	106.0(4)		134.3(7)/135.5(4)
Ru(4)–C(1)–C(2)			135.0(9)/132.8(5)
Ru(5)–C(1)–C(2)	90.3(3)		
Ru(1)–C(2)–C(3)			129.2(9)/128.3(5)
Ru(2)–C(2)–C(3)			128.7(9)/128.7(6)
Ru(3)–C(4)–C(3)	112.7(5)		
C(1)–Ru(3)–C(4)	82.0(2)		
C(1)–C(2)–C(3)	116.5(4)	131.0(8)	115.9(9)/117.6(5)
C(2)–C(3)–C(4)	113.3(5)	148.6(8)	135(1)/136.7(7)
C(5)–C(6)–Si(6)	175.4(7)		
Ru(2)–S(1)–Ru(3)			106.0(5)/106.25(8)
Ru(3)–S(2)–Ru(4)			72.5(1)/72.73(6)

[a] Values for determinations carried out with CAD4/Bruker AXS instruments.

[b] Other distances for **3**: C(5)–C(6) 1.194(7); C(3)–Si(2) 1.944(6); C(4)–Si(3) 1.892(8); C(6)–Si(6) 1.839(5) Å.

[c] Other angles for **3**: C(2)–C(5)–C(6) 178.7(6)°; C(5)–C(6)–Si(6) 175.4(7)°. Interplanar angles: for **3** Ru(1,2,3)/Ru(1,3,5) 23.28(5), Ru(1,3,5)/Ru(3,4,5) 38.51(4); for **4** Ru(1,2,3,5)/Ru(3,4,5) 86.26(3); for **5** Ru(1,3,5)/Ru(3,4,5) 11.35(5)/11.20(5), Ru(1)–Ru(2)/Ru(1,3,4,5) 19.17(2)/19.26(2), Ru(1)–Ru(2)/Ru(1,3,5) 20.84(3)/20.89(2)°.

4.2. Reaction of *1* with bis(trimethylsilyl)acetylene

A solution of **1** (310 mg, 0.24 mmol) and bis(trimethylsilyl)acetylene (80 mg, 0.46 mmol) in toluene (10 ml) was heated for 26 h at 110°C in a Carius tube. 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 light brown band (R_f 0.60) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}CC \equiv C_2SiMe_3)C(SiMe_3)CSiMe_3)(\mu\text{-}PPh_2)_2(\mu_3\text{-}SMe)(CO)_{10}$ (**3**) (18 mg, 5%). A red band (R_f 0.50) was recrystallised from CH_2Cl_2/MeOH to yield two isomers of $Ru_5\{\mu_5\text{-}CCCCH(SiMe_3)\}(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**2**) (309 mg, 94%).

4.3. Reaction of *2a,b* with CO

A solution of **2** (30 mg, 0.022 mmol) in toluene (15 ml) was heated at 110°C for 6 h with a CO purge. No reaction was observed.

4.4. Preparation of $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (4)

A solution of KOH (100 mg) in H_2O (10 ml) and MeOH (40 ml) was added to **2** (309 mg, 0.23 mmol) in CH_2Cl_2 (40 ml). After stirring for 1 h further water (30 ml) was added and the layers separated. The aqueous layer was washed with CH_2Cl_2 (1 × 20 ml). The combined CH_2Cl_2 extracts were washed with H_2O (1 × 20 ml), dried ($MgSO_4$), filtered and the solvent removed to yield a red solid which was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ (**4**) (246 mg, 84%).

4.5. Reaction of **4** with CO

A solution of **4** (60 mg, 0.046 mmol) in toluene (20 ml) was heated at 80°C for 1.5 h with a CO purge. After cooling to room temperature and removing the solvent the residue was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_5\text{-}CCCCH_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{11}$ (**5**) (37 mg, 62%).

4.6. Pyrolysis of **4**

A solution of **4** (20 mg, 0.015 mmol) in toluene (20 ml) was refluxed for 16 h with a nitrogen purge. A large number of products and a large intractable baseline were obtained.

4.7. Reaction of **1** with t-butylacetylene

A solution of **1** (100 mg, 0.077 mmol) and $HC{\equiv}CBu^t$ (40 mg, 0.49 mmol) in toluene (10 ml) 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 $Ru_5(\mu_5\text{-}CCCHCBu^t)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(CO)_{10}$ (36 mg, 35%), as discussed elsewhere [3]. A red–brown band (R_f 0.45) was recrystallised from CH_2Cl_2/MeOH to give two isomers of $Ru_5(\mu_5\text{-}CCCCHBu^t)$ $(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2$ $(CO)_{10}$ (**6**) (36 mg, 35%).

5. Crystallography

Unique data sets were measured at ca. 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo–K_α radiation, $\lambda = 0.71073$ Å) as previously described [13]. Computation used the XTAL 3.4 program system [14] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the Figs. 1 and 2 and Tables 1–3.

5.1. Abnormal features/variations in procedure

(**4**) Hydrogen atoms on C(4) were located in a difference map. Solvent population (CH_2Cl_2) was set at unity after trial refinement.

(**5**) The original determination, recorded briefly previously [4], was of rather less than desirable precision, the data although extensive, being rather weak, diffuse and streaked. In the present context, with material still available, a redetermination was undertaken using a Bruker AXS CCD instrument at ca. 300 K. A full sphere of data was measured and processed using proprietary software SAINT with empirical absorption correction applied (SADABS). A total of 26924 reflections were measured merging to 11923 unique data ($R_{int} = 0.028$). Despite the more impressive data statistics, final residuals were again rather disappointing, the improvement in the precision of the geometries being achieved by the brute force of the increased body of data. Entries for both experiments are given in the Tables 1–3, the

Table 3
Crystal data and refinement details for complexes **3**, **4** and **5**

	3	**4**	**5**[a]
Formula	$C_{50}H_{50}O_{10}P_2Ru_5SSi_3$	$C_{40}H_{28}O_{10}P_2Ru_5S_2{\cdot}CH_2Cl_2$	$C_{41}H_{28}O_{11}P_2Ru_5S_2$
MW	1494.6	1385.0	1328.1
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.442(6)	15.807(2)	10.060(4)/10.074(1)
b (Å)	17.539(6)	14.549(5)	11.957(4)/11.998(1)
c (Å)	25.483(9)	11.302(2)	22.087(11)/22.214(3)
α (°)		67.33(2)	95.59(3)/95.471(3)
β (°)	128.07(3)	84.17(1)	95.65(3)/95.777(3)
γ (°)		76.29(2)	111.99(3)/112.048(2)
V (Å^3)	5785	2330	2425/2450
Z	4	2	2
Crystal size (mm)	0.20 × 0.43 × 0.40	0.20 × 0.10 × 0.20	0.15 × 0.15 × 0.42/0.30 × 0.23 × 0.13
A^* (min, max)	1.23, 1.47	1.23, 1.45	1.23, 1.30/1.09, 1.41
μ (cm^{-1})	14.5	18.7	16.9
$2\theta_{max}$ (°)	60	50	50/58
N	15960	8204	8526/11923
N_o	9570	5966	5490/8056
R	0.041	0.040	0.062/0/058
R_w	0.040	0.044	0.064/0.065

[a] Values for determinations with CAD4/Bruker AXS instruments.

discussion in the text being based on the results of the CCD experiment which form the basis of the present deposition.

Compounds **4** and **5** have been renumbered in this presentation to conform with Chart 1 and Scheme 1.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 114426–114428 for compounds **3**, **4** and **5**, respectively. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of $RuCl_3 \cdot nH_2O$.

References

[1] (a) M.I. Bruce, J. Cluster Sci. 1997, 8, 293. (b) M.I. Bruce, Coord. Chem. Rev. 166 (1997) 91.

[2] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1999), in press.

[3] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans., submitted for publication.

[4] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, Chem. Commun. (1996) 2663.

[5] M.I. Bruce, Chem. Rev. 98 (1998) 2797.

[6] N. Lugan, P.-L. Fabre, D. de Montauzon, G. Lavigne, J.-J. Bonnet, J.-Y. Saillard, J.-F. Halet, Inorg. Chem. 32 (1993) 1363.

[7] J.R. Lomprey, J.P. Selegue, Organometallics 12 (1993) 616.

[8] (a) M.I. Bruce, P. Hinterding, P.J. Low, B.W. Skelton, A.H. White, Chem. Commun. (1996) 1009. (b) M.I. Bruce, P. Hinterding, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1998) 467.

[9] M.I. Bruce, P. Hinterding, M. Ke, P.J. Low, B.W. Skelton, A.H. White, Chem. Commun. (1997) 715.

[10] R.F. Winter, F.M. Hornung, Organometallics 16 (1997) 4248.

[11] G. Frapper, J.-F. Halet, M.I. Bruce, Organometallics 16 (1997) 2590.

[12] (a) H. Yamazaki, J. Chem. Soc. Chem. Commun. (1976) 841. (b) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J.Y. Satoh, J. Am. Chem. Soc. 113 (1991) 9604.

[13] C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1997) 2937.

[14] S.R. Hall, G.S.D. King, J.M. Stewart (Eds.), The XTAL 3.4 Users' Manual, University of Western Australia, Lamb, Perth, 1994.