Reactions of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ with dimethyl disulfide. Synthesis of an open Ru_5 cluster containing the dicarbon (C_2) ligand and related chemistry

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The reaction between $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ and Me_2S_2 yielded $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{13}]$ as the major product. When heated the latter yielded the dicarbon complexes $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}]$ and $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$. In large-scale preparations of the latter four minor products were isolated: two isomers of $[Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{12}]$, the tetranuclear complex $[Ru_4(\mu_4\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{10}]$ and $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_4(\mu\text{-}PPh_2)_2(CO)_{10}]$. The latter is also formed by direct reaction of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ with Me_2S_2. All new complexes have been fully characterised by single-crystal X-ray studies. In the three $Ru_5(C_2PPh_2)$ complexes the C_2PPh_2 ligand acts as a seven-electron donor, whereas in the Ru_4 complex it donates only five electrons to the cluster. In the C_2 complexes, the different C–C separations [between 1.26(2) and 1.305(5) Å] suggest a variable degree of interaction with the metal core (electron donation and back-bonding), the ligand formally donating either six or four electrons to the cluster. This is borne out by the Ru–Ru separations, average values of which range between 2.791 and 2.916 Å. The conversion of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ into $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ involves sequential formation of several of these complexes, which reactions are discussed.

The chemistry of new forms of carbon is currently exciting much interest.[1] Although much of the appeal lies in the area of fullerene chemistry,[2] all-carbon molecules with fewer carbon atoms have inherent interest. Small carbon molecules are too reactive to isolate[3] but some can be stabilised as their transition-metal complexes.[4] Single carbon atoms are present in metal carbide clusters,[5] while chains of carbon atoms C_n ($n = 2$, 3, 4, ...), terminated by an ML_x fragment at each end,[6] and complexes containing cyclo[n]carbons ($n = 3$, 18, 24, 30) are now known.[7] Part of the interest in studying these compounds lies in the possibility of using them, either directly or as precursors, for electronic or non-linear optical applications, or as catalysts, while there is an inherent interest in these novel types of molecules, both in themselves and as models for metal carbides or of molecules on metal surfaces.[8]
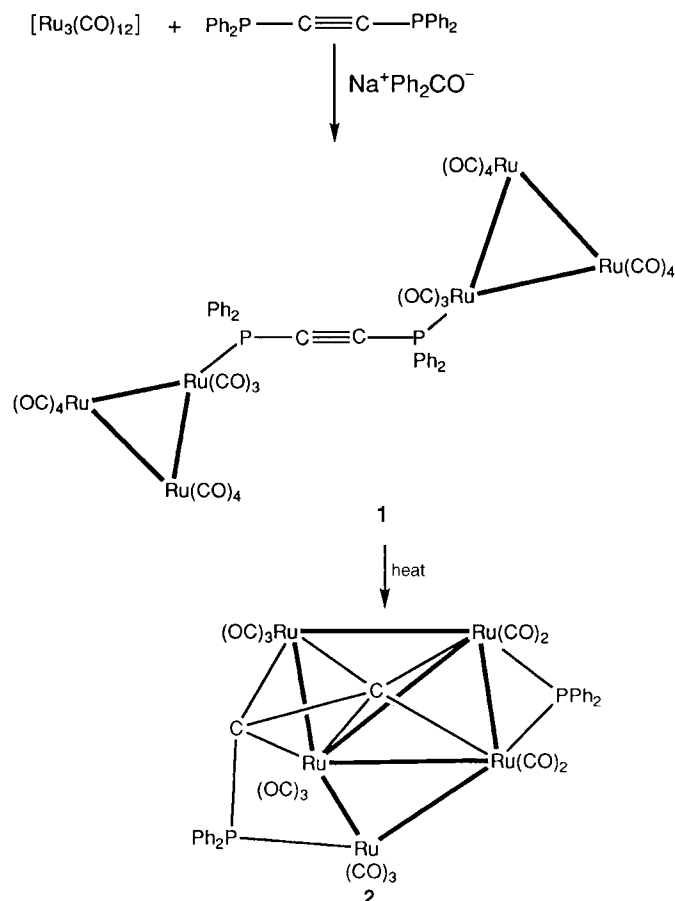
We have been interested in the simplest all-carbon molecule for several years. The electronic properties of complexes containing C_2 as a simple end-on bonded moiety depend on the metal–ligand combinations. Both structural and spectroscopic evidence suggest that in adducts with $ML_n = W(OBu^t)_3$,[9] Ta{Si(OBu^t)_3}_3$[10] and $PtCl(PR_3)_2$,[11] for example, the formal valence-bond representations as dicarbyne (**A**), dicarbene (**B**) and yndi-

$$M\text{–}C\equiv C\text{–}M \qquad M=C=C=M \qquad M\equiv C\text{–}C\equiv M$$
$$\textbf{A} \qquad\qquad\quad \textbf{B} \qquad\qquad\quad \textbf{C}$$
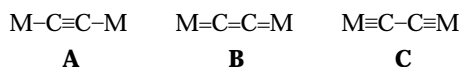
yl (**C**) complexes respectively are appropriate. Recent theoretical studies have thrown some light on the reasons for this behaviour.[12] The C_2 unit has been found attached to many metal clusters, including the fully encapsulated examples, as in **D**,[13] while we and others have reported several examples of complexes containing C_2 supported upon metal clusters (such as **E**, cp = $\eta^5\text{-}C_5H_5$; CO ligands omitted from both diagrams).[14–16] This interest has also prompted theoretical analyses of C_2 in various environments, including both a series of tetrametallic clusters[12] and higher-nuclearity systems.[17]

D

E
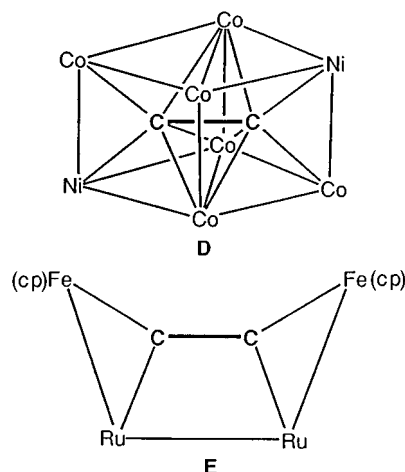
Our interest in the reactivities of small molecules attached to metal clusters, particularly those containing ruthenium, coupled with the discovery of a facile route to tertiary phosphine-substituted derivatives of $[Ru_3(CO)_{12}]$ and related systems,[18] prompted us to devise a route to a ruthenium cluster containing C_2 *via* cleavage of P–C (sp) bonds in the diphosphine $Ph_2PC\equiv C\text{-}PPh_2$ (dppa). Breaking of P–C bonds in tertiary phosphines co-ordinated to metal clusters is a well known reaction.[19–21] The bis(trinuclear cluster) complex $[\{Ru_3(CO)_{11}\}_2\{(PPh_2)_2C_2\}]$ **1** can be prepared in essentially quantitative yield[22] and can be converted into the pentanuclear complex $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)\text{-}(CO)_{13}]$ **2** by heating it in refluxing benzene or cyclohexane (Scheme 1) thereby cleaving of one of the P–C (sp) bonds in **1**. While several reactions of **2** gave products containing either C_2 of ligands formed by reactions involving cleavage of the second P–C bond,[23] the former complexes were either unreactive[24] or obtained in amounts too small for further study. However, these drawbacks were overcome by our finding that the major prod-

[Ru₃(CO)₁₂] + Ph₂P—C≡C—PPh₂

$Na^+Ph_2CO^-$

(OC)₄Ru
Ru(CO)₄
(OC)₃Ru

Ph₂
P—C≡C—P
Ph₂

(OC)₄Ru
Ru(CO)₃
Ru(CO)₄

1

heat

(OC)₃Ru ——— Ru(CO)₂
C
PPh₂
C
Ru ——— Ru(CO)₂
(OC)₃
Ph₂P ——— Ru
(CO)₃

2

Scheme 1

uct obtained by heating **2** with Me_2S_2 in benzene for about an hour was the remarkable open Ru_5 cluster containing an exposed C_2 ligand, $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$.[24] The stabilisation of C_2 on this complex certainly allows its isolation and further study, but the reactivity of this all-carbon ligand is by no means completely suppressed.[25]

This paper describes the results of a detailed study of the reaction between compound **2** and dimethyl disulfide, from which several other complexes which have been isolated and fully characterised by X-ray studies are shown to be intermediates in the formation of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$. Other related complexes were obtained in small amounts from larger scale syntheses of the latter. The synthesis of its PBu^n_2 analogue has been described elsewhere.[26]

Results

The reaction between compound **2** and Me_2S_2 was carried out in benzene or toluene at 70 °C for periods of 30 min to 3 h. Separation of the products by preparative tlc gave seven complexes, all of which have been fully characterised by X-ray crystallographic studies. These reactions are summarised in Schemes 2–4, which also indicate interconversions which have been established by independent experiments.
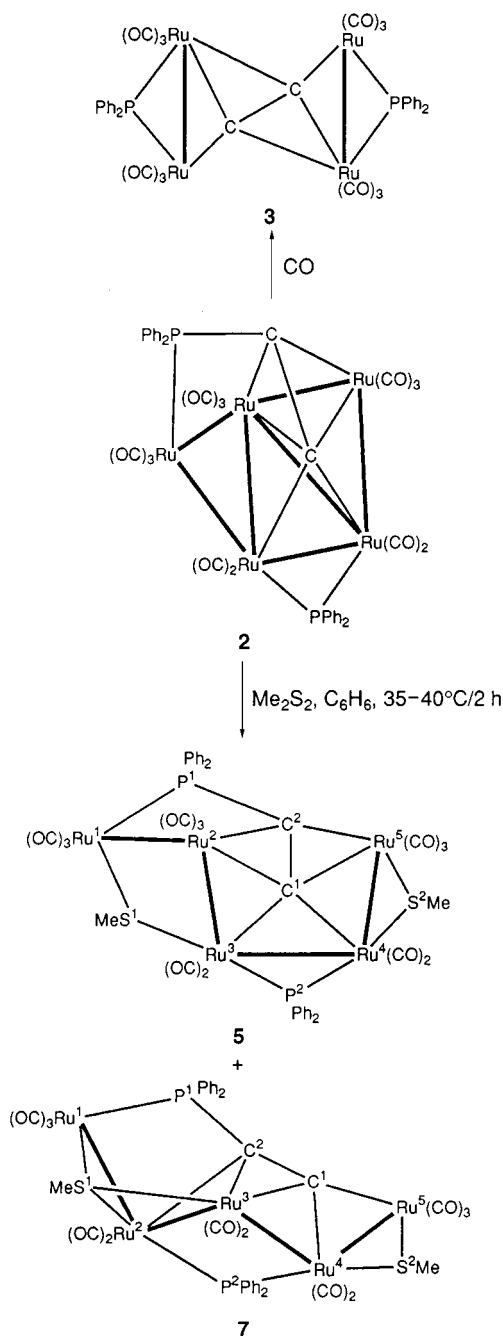
Under mild conditions (35–40 °C, 2 h), the isolated major product is $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{13}]$ **5**, which is formed by oxidative addition of the Me_2S_2 to the cluster with concomitant cleavage of three Ru–Ru bonds. Since no CO groups are lost in this reaction, the addition of two 3e SMe ligands is electronically equivalent to the cleavage of the three Ru–Ru bonds, so that the product is isoelectronic with **2**. The five ruthenium atoms form a bent chain, with P(1) of the C_2PPh_2 ligand attached to one of the end Ru atoms. The C_2 fragment is attached more-or-less symmetrically to the other four metal atoms [Ru(2)–Ru(5)]. The two SMe groups are

attached differently, one bridging a non-bonded pair of metal atoms, while the other bridges two bonded Ru atoms at the other end of the chain. A small amount of complex **7** (see below) is also obtained under these conditions.

Further heating of compound **5** results in cleavage of the P–C (sp) bond to give $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}]$ **6** with loss of one CO ligand. This molecule also contains an open-chain arrangement of the five metal atoms, this time arranged approximately in a pentagon with one non-bonded edge. The four Ru–Ru bonds are bridged by the two SMe and two PPh₂ groups alternately. The P–C (sp) bond has broken, the C_2 ligand residing in the interior of the pentagon, unsymmetrically bridging the two outer pairs of Ru atoms in an $\eta^1:\eta^2$ mode while being strongly σ-bonded to the central metal atom.

Continued heating results in loss of a second molecule of CO and closure of the ring to give compound **4**. Here we draw attention to the exposed situation of the C_2 ligand, sitting atop the Ru_5 cluster, while the bridging groups (and more importantly, their substituents) lie below, which results in little if any steric hindrance to the approach of reactants. Separate experiments have shown that both compounds **6** and **4** are formed by heating **5** and that **4** can be obtained similarly from **6**. Overall, **4** is obtained in 64% isolated yield from **2**, which corresponds to about 60% from $[Ru_3(CO)_{12}]$. As described in the Experimental section, gram quantities can be obtained from this series of reactions, which takes about 3 d.

In the course of large-scale preparations of compound **4** we have isolated four further complexes, albeit all were obtained in small yield. These were characterised from single-crystal X-ray studies as two isomers of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{12}]$ **7** and **8** and the tetranuclear complex $[Ru_4(\mu_4\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{10}]$ **9**, all retaining the C_2PPh_2 ligand, and a further example of a C_2 complex containing four SMe groups, $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_4(\mu\text{-}PPh_2)_2(CO)_{10}]$ **10**. The latter can also be obtained by heating **4** in the presence of an excess of Me_2S_2.

Scheme 2 (structures of compounds **3**, **2**, **5**, **7**)

Structure **3**:
(OC)₃Ru, (CO)₃Ru, Ph₂P, C, C, PPh₂, (OC)₃Ru, Ru(CO)₃

— labeled **3**

CO

Structure **2**:
Ph₂P—C, (OC)₃Ru, Ru(CO)₃, (OC)₃Ru, C, (OC)₂Ru, Ru(CO)₂, PPh₂

— labeled **2**

Me₂S₂, C₆H₆, 35–40 °C/2 h

Structure **5**:
Ph₂P¹, (OC)₃Ru¹, (OC)₃Ru², C², C¹, Ru⁵(CO)₃, MeS¹, S²Me, (OC)₂Ru³, Ru⁴(CO)₂, P²Ph₂

— labeled **5**

+

Structure **7**:
P¹Ph₂, (OC)₃Ru¹, C², C¹, Ru⁵(CO)₃, MeS¹, Ru³, (OC)₂Ru², (CO)₂, S²Me, P²Ph₂, Ru⁴, (CO)₂

— labeled **7**

Scheme 2

Ru(1,2,5) and two on each of Ru(3,4). Each Ru atom thereby has an 18-electron count with the C_2PPh_2 group contributing seven electrons. Alternatively, the complex has a total cluster valence electron (c.v.e.) count of 82, as expected for a system with four M–M bonds.

(*b*) **[Ru₅(μ₅-C₂PPh₂)(μ₃-SMe)(μ-SMe)(μ-PPh₂)(CO)₁₂]·1.8-CH₂Cl₂ 7.** In compound **7** the ruthenium chain is W-shaped, with Ru–Ru distances along the chain of 2.822, 2.823, 2.769 and 2.751(1) Å, and internal angles at Ru(2,3,4) of 92.31, 88.25 and 93.54(4)°, respectively. Atom P(2) bridges the non-bonded Ru(2)–Ru(4) vector [Ru(2,4)–P(2) 2.383, 2.346(3) Å] and S(2) bridges Ru(4)–Ru(5) [Ru(4,5)–S(2) 2.416, 2.390(3) Å]. In contrast with **5**, S(1) is bonded to three Ru atoms [Ru(1,2,3)–S(1) 2.351, 2.378, 2.327(3) Å], thus displacing a CO group from the complex. As before, the C_2PPh_2 ligand is attached to Ru(1) by P(1) [2.381(3) Å] and by the C_2 unit to the other four Ru atoms [Ru(2,3)–C(2) 2.179(9), 2.144(9); Ru(3,4,5)–C(1), 2.27, 2.18(1), 2.025(9) Å]. The C(1,2)–Ru(2,3,4) portion resembles that found in μ₃-alkyne-trimetal clusters, *i.e.* with a 2σ,π interaction; the Ru(2)–P(2)–Ru(4) unit resembles that found in [Ru₃(μ₃-C₂Prⁱ)-(μ-PPh₂)(CO)₉].[27] The C(1)–C(2) distance is 1.38(1) Å.
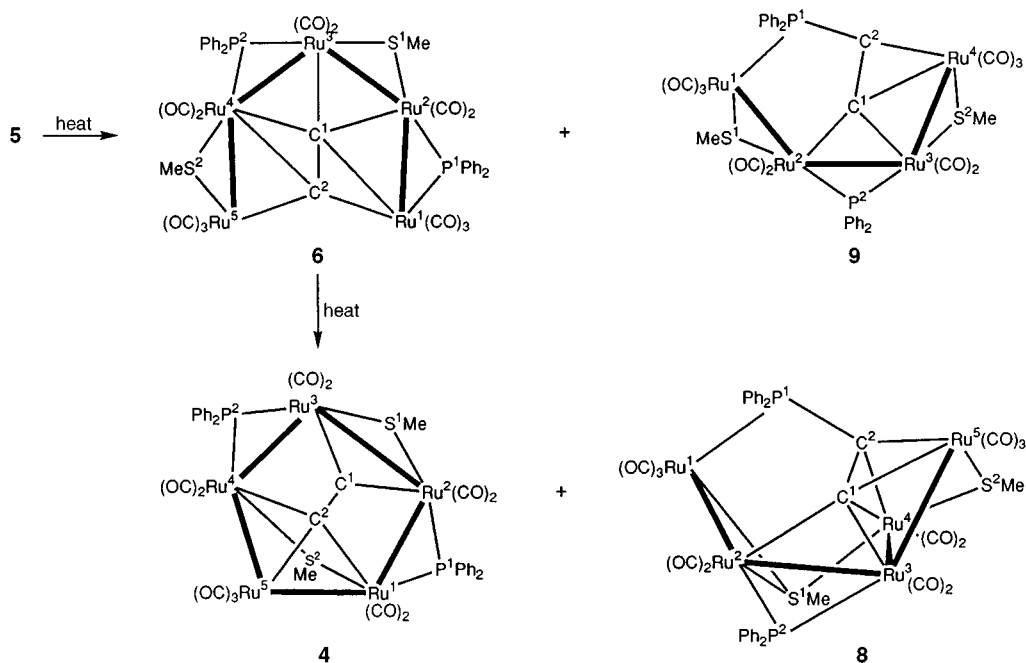
Each ruthenium achieves an 18-electron count with the aid of the 12 CO groups [three on each of Ru(1,5), two on each of Ru(2,3,4)]. Although the mode of attachment of the C_2PPh_2 ligand differs from that in compound **5** (see below for further discussion), it still donates seven electrons to the cluster, which also has a c.v.e. count of 82.

(*c*) **[Ru₅(μ₅-C₂PPh₂)(μ₃-SMe)(μ-SMe)(μ-PPh₂)(CO)₁₂] 8.** This complex is an isomer of **7**. The unprecedented metal skeleton found in **8** consists of a spiked Ru₄ chain of which an internal metal atom is bonded to the fifth Ru [Ru(3)–Ru(4) 2.934(1) Å]. Other Ru–Ru distances along the chain are Ru(3)–Ru(2,5) 2.850(1), 2.8865(9) and Ru(1)–Ru(2) 2.923(1) Å. Non-bonded separations are Ru(4)···Ru(1,2,5) 4.052, 3.623, 3,305(1) Å. The PPh₂ group bridges the Ru(2)–Ru(3) vector [Ru(2,3)–P(2) 2.326, 2.271 (2) Å]. Atom S(1) bridges three rutheniums [Ru(1,2,4)–S(1) 2.388, 2.343, 2.376(2) Å] and S(2) bridges Ru(4)···Ru(5) [Ru(4,5)–S(2) 2.369, 2.411(2) Å]. The C_2PPh_2 ligand is again attached to all five metal atoms, by P(1) to the end of the chain [Ru(1)–P(1) 2.412(2) Å] and *via* the C_2 unit, which asymmetrically spans three Ru atoms [Ru(3)–C(1) 1.937(8), Ru(4)–C(1,2) 2.254, 2.259(7), Ru(5)–C(1,2) 2.353(7), 2.223(8) Å] while C(1) also interacts with Ru(2) [2.297(7) Å]. The C(1)–C(2) distance is 1.361(9) Å. The twelve CO groups are distributed three each to Ru(1,5) and two each to Ru(2,3,4). The c.v.e. count is 82, as found for the other complexes discussed above.
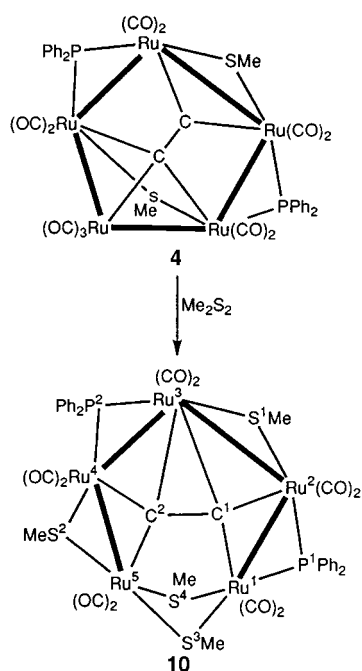
(*d*) **[Ru₄(μ₄-C₂PPh₂)(μ-SMe)₂(μ-PPh₂)(CO)₁₀]·0.25CH₂Cl₂ 9.** Complex **9** consists of a chain of four Ru atoms [Ru–Ru 2.8699(7), 2.8902(6), 2.8159(6) Å; internal angles at Ru(2,3) 125.51(2), 107.94(2)°] of which the outer segments are bridged by the two SMe groups [Ru(1,2)–S(1) 2.388, 2.397(1), Ru(3,4)–S(2) 2.443, 2.404(1) Å] and the central Ru(2)–Ru(3) bond by the PPh₂ group [Ru(2,3)–P(2) 2.337, 2.283(1) Å]. The C_2PPh_2 ligand bonds *via* P(1) to Ru(1) [2.420(1) Å] and C(2) to Ru(4) [2.146(5) Å] while C(1) bridges Ru(2,3) [2.162, 2.087(5) Å]. The C(1)–C(2) distance is 1.284(7) Å, consistent with the C_2 portion being a two-electron donor. Three CO groups are attached to each of Ru(1,4) and two to each of Ru(2,3). The cluster is electron-precise (66 c.v.e.) with the C_2PPh_2 group giving only five electrons in this complex.

Complexes containing C_2 ligands

Although the molecular structures of compounds **6** and **4** were illustrated in our preliminary communication,[24] no detailed discussion of them has yet been given, and hence plots of each

Molecular structures of complexes retaining the C_2PPh_2 ligand

Figs. 1–4 contain plots of molecules of complexes **5**, **7**, **8** and **9**, respectively, and relevant bond parameters are collected in Table 1. The structures will be discussed individually.

(*a*) **[Ru₅(μ₅-C₂PPh₂)(μ-SMe)₂(μ-PPh₂)(CO)₁₃]·0.5CH₂Cl₂ 5.** The five ruthenium atoms in compound **5** form a bent chain, in profile resembling a dipper, with Ru–Ru distances along the chain of 2.903(1), 2.826(2), 2.912(1) and 2.748(1) Å. Internal angles at the Ru atoms are 83.61(4), 95.97(6) and 107.46(6)° for Ru(2,3,4), respectively. Atom S(1) bridges the non-bonded Ru(1)···Ru(3) vector, while S(2) bridges Ru(4)–Ru(5) [Ru–S 2.408–2.432(2) Å]. Atom P(2) symmetrically bridges Ru(3)–Ru(4) [Ru–P 2.308(2) Å (×2)]. The C_2PPh_2 ligand is attached to all five Ru atoms, by P(1) to Ru(1) [2.351(2) Å] and by the C_2 unit within the bowl of the dipper [Ru(2,5)–C(2) 2.369, 2.196(3) Å; Ru(2,3,4,5)–C(1) 2.241, 2.203, 2.183, 2.469(4) Å]. The C(1)–C(2) distance is 1.338(7) Å. Co-ordination about each ruthenium is completed by CO groups, three on each of

Scheme 3

Scheme 4

of these molecules are given in Figs. 5 and 6, respectively; the molecular structure of **10** is shown in Fig. 7. Selected bond parameters of all three complexes are collected in Table 2.

(*a*) **[Ru$_5$(μ_5-C$_2$)(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{12}$] 6.** The C$_2$ ligand in compound **6** is partially encircled by a chain of five Ru atoms. The four Ru–Ru bonds are bridged alternately, two by PPh$_2$ groups [molecule 1: Ru(1)–Ru(2) 2.752(2), Ru(3)–Ru(4) 2.964(2); Ru(1,2)–P(1) 2.350, 2.300(5); Ru(3,4)–P(2) 2.267, 2.309(4) Å] and two by SMe groups [Ru(2)–Ru(3) 2.792(2), Ru(4)–Ru(5) 2.704(2); Ru(2,3)–S(1) 2.418, 2.373(4); Ru(4,5)–S(2) 2.458, 2.372(4) Å]. The pentagon is much more distorted than those found in **10** and **11**, for example, probably because there is no group bridging the Ru(1)···Ru(5) vector [3.956(2) Å]. For a least-squares plane through Ru(1)–Ru(5), χ^2 is 4×10^5, δ[Ru(1)–Ru(5)] being $-0.498(2)$, 0.383(2), 0.074(2), $-0.550(2)$ and 0.659(2) Å. [The two molecules of the asym-
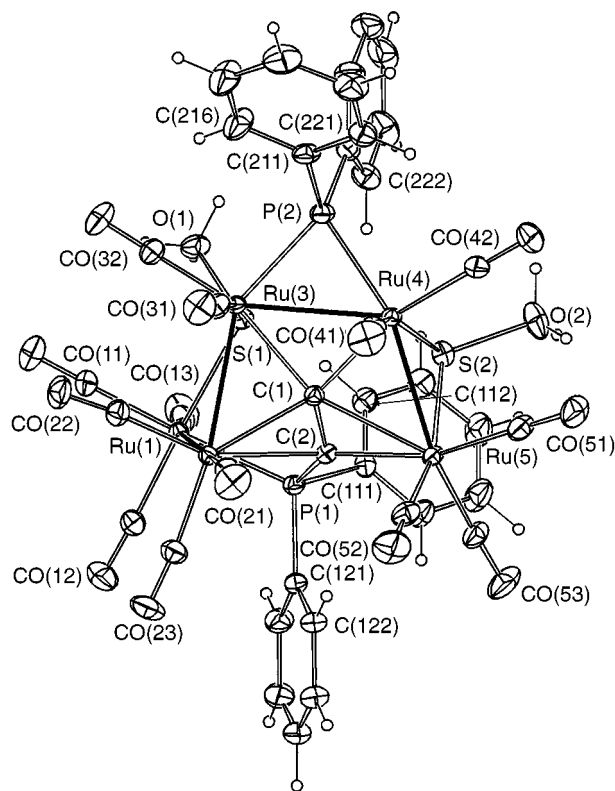
metric unit are similar, showing minor but significant differences exemplified for the second plane, for which χ^2 is 4×10^5, δ[Ru(1)–Ru(5)] being $-0.495(2)$, 0.290(2), 0.075(2), $-0.549(2)$ and 0.790(2) Å].

Both the PPh$_2$ and SMe groups are found approximately above and below the 'plane' of the five Ru atoms. However, there is no alternating effect, as S(1) and P(2), bridging adjacent edges, are both on the same side of the pentagon, but P(1) and S(2) are on the opposite side.

Fig. 1 Plot of a molecule of [Ru$_5$(μ_5-C$_2$PPh$_2$)(μ-SMe)$_2$(μ-PPh$_2$)-(CO)$_{13}$]·0.5CH$_2$Cl$_2$ **5**, showing the atom numbering scheme. For this and other figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å
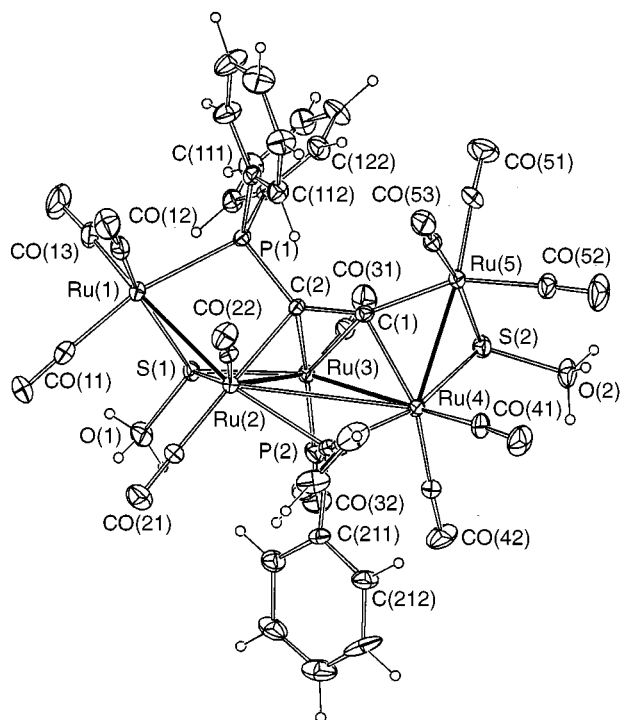
Fig. 2 Plot of a molecule of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)(CO)_{12}]$ **7**, showing the atom numbering scheme

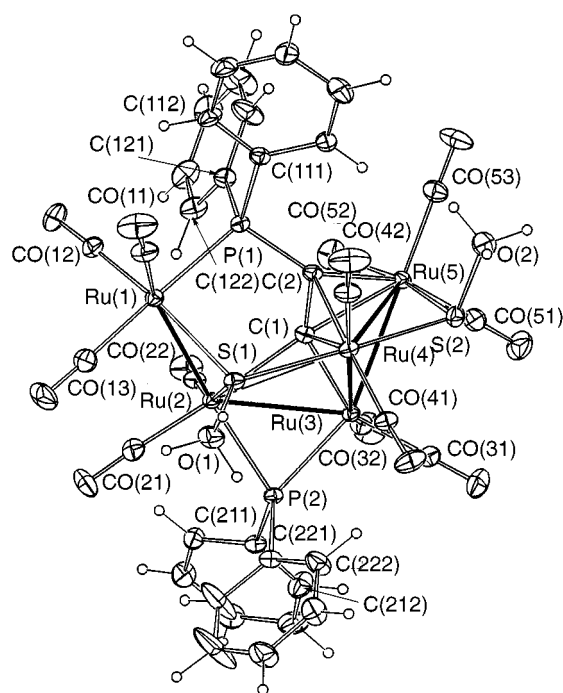**Fig. 3** Plot of a molecule of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)(CO)_{12}]\cdot1.8CH_2Cl_2$ **8**, showing the atom numbering scheme

The C_2 ligand is bonded to all five of the Ru atoms, having asymmetric η^2 interactions with Ru(1) and Ru(4) [Ru(1)–C(1,2) 2.36, 2.30(1); Ru(4)–C(1,2) 2.45, 2.27(1) Å], while C(1) asymmetrically bridges the Ru(2)–Ru(3) vector [Ru(2,3)–C(1) 2.10, 2.41(1) Å] and C(2) is attached to Ru(5) [2.06(1) Å]. The C(1)–C(2) separation is 1.26(2) Å. Consequently, we are inclined to view this ligand as an acetylide only slightly lengthened by the weak π-type interaction with Ru(1) and Ru(4).

Co-ordination to the five metal atoms is completed by twelve terminal CO groups. The cluster has a total of 82 c.v.e. (if the C_2 ligand gives six electrons) as expected for a five-atom cluster with four M–M bonds.

Table 1 Structural parameters (bond lengths in Å, angles in °) for C_2PPh_2 complexes, **5**, **7**, **8** and **9**[*]

	5	7	8	9
Ru(1)–Ru(2)	2.9030(8)	2.822(1)	2.923(1)	2.8699(7)
Ru(2)–Ru(3)	2.826(2)	2.823(2)	2.850(1)	2.8902(6)
Ru(2)–Ru(4)			*3.623(2)*	
Ru(3)–Ru(4)	2.912(1)	2.769(1)	2.934(1)	2.8159(6)
Ru(3)–Ru(5)			2.8865(9)	
Ru(4)–Ru(5)	2.748(1)	2.751(1)	*3.305(1)*	
Ru(1)–S(1)	2.432(2)	2.351(3)	2.388(2)	2.388(1)
Ru(2)–S(1)		2.378(3)	2.343(2)	2.397(1)
Ru(3)–S(1)	2.422(1)	2.327(3)		
Ru(4)–S(1)			2.376(2)	
Ru(3)–S(2)				2.443(1)
Ru(4)–S(2)	2.416(1)	2.416(3)	2.369(3)	2.404(1)
Ru(5)–S(2)	2.408(1)	2.390(3)	2.411(2)	
Ru(1)–P(1)	2.351(2)	2.381(3)	2.412(2)	2.420(1)
Ru(2)–P(2)		2.383(3)	2.326(2)	2.337(1)
Ru(3)–P(2)	2.308(2)		2.271(2)	2.283(1)
Ru(4)–P(2)	2.308(2)	2.346(3)		
Ru(2)–C(1)	2.241(3)		2.297(7)	2.162(5)
Ru(3)–C(1)	2.203(4)	2.27(1)	1.937(8)	2.087(5)
Ru(4)–C(1)	2.183(4)	2.18(1)	2.254(7)	2.552(5)
Ru(5)–C(1)	2.469(4)	2.025(9)	2.353(7)	
Ru(2)–C(2)	2.369(3)	2.179(9)		
Ru(3)–C(2)		2.144(9)		
Ru(4)–C(2)			2.259(7)	2.146(5)
Ru(5)–C(2)	2.196(3)		2.223(8)	
P(1)–C(2)	1.777(4)	1.81(1)	1.770(8)	1.764(5)
C(1)–C(2)	1.338(7)	1.38(1)	1.361(9)	1.284(7)
Ru(1)–Ru(2)–Ru(3)	83.61(4)	92.31(4)	123.82(3)	125.51(2)
Ru(2)–Ru(3)–Ru(4)	95.97(6)	88.25(4)	77.55(4)	107.94(2)
Ru(2)–Ru(3)–Ru(5)			105.64(3)	
Ru(2)–Ru(4)–Ru(5)			82.42(3)	
Ru(3)–Ru(4)–Ru(5)	107.46(6)	93.54(4)		
Ru(1)–S(1)–Ru(2)		73.28(9)	76.30(6)	73.71(4)
Ru(1)–S(1)–Ru(3)	103.79(5)	121.0(1)		
Ru(1)–S(1)–Ru(4)			116.54(8)	
Ru(2)–S(1)–Ru(3)		73.75(9)		
Ru(2)–S(1)–Ru(4)			100.31(8)	
Ru(3)–S(2)–Ru(4)				71.03(4)
Ru(4)–S(2)–Ru(5)	69.44(4)	69.84(9)	87.49(8)	
Ru(1)–P(1)–C(2)	105.6(1)	100.8(3)	107.5(2)	108.6(2)
Ru(2)–C(1)–Ru(3)	79.0(1)		84.2(2)	85.7(2)
Ru(3)–C(1)–Ru(4)	83.2(2)	77.0(3)	88.5(3)	74.0(1)
Ru(4)–C(1)–Ru(5)	72.13(8)	81.6(4)	91.7(3)	
Ru(2)–C(2)–Ru(3)		81.6(3)		
Ru(4)–C(2)–Ru(5)			95.0(3)	
Ru(2)–C(1)–C(2)	78.5(2)		129.0(6)	138.6(4)
Ru(3)–C(1)–C(2)	139.9(2)		144.7(6)	130.3(4)
P(1)–C(2)–C(1)	135.8(3)	131.7(8)	118.5(6)	118.5(4)

[*] Non-bonded Ru–Ru separations in italics.

(*b*) **$[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ 4.** The pentagon of Ru atoms in compound **4** is not planar, but the bridging groups lie all on one side of the plane of four of the metal atoms, while the C_2 ligand is mounted on the opposite side. The fifth Ru atom is brought up out of the plane as a result of the very short interaction with C(2) [1.936(4) Å]. In detail, the Ru–Ru separations around the ring are 2.898, 2.882(1) (PPh$_2$-bridged), 2.855(2) (SMe-bridged) and 2.890, 2.898(1) Å [bonds to Ru(5)], with the Ru–P [Ru(1,2)–P(1) 2.341(1), 2.290; Ru(3,4)–P(2) 2.294, 2.341(1) Å] and Ru–S distances [Ru-(2,3)–S(1) 2.386, 2.391(1) Å] normal. The second SMe group bridges the non-bonded Ru(1) $\cdots$ Ru(4) vector, with considerably longer Ru–S distances [Ru(1,4)–S(2) 2.454, 2.449(1) Å] than found for S(1).

The C_2 ligand is strongly bonded *via* C(2) to Ru(5), while lying between the other four atoms [Ru(2,3)–C(1) 2.133, 2.135(4); Ru(1,4)–C(2) 2.232, 2.260(4) Å]. The C(1)–C(2) bond length is 1.307(5) Å.

There are eleven terminal CO groups; with the other ligands, a total of 40 electrons is supplied to the cluster to give 80 c.v.e., as expected for an Ru$_5$ cluster with five Ru–Ru bonds.
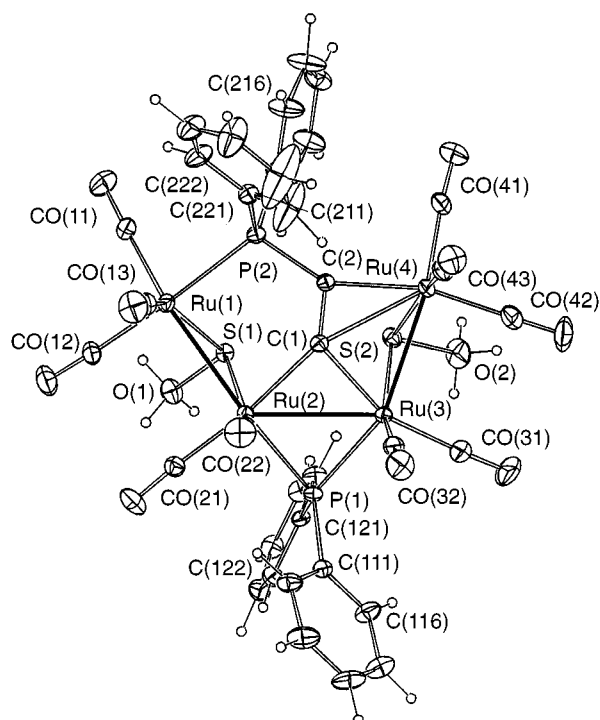
Fig. 4 Plot of a molecule of [Ru$_4$(μ_4-C$_2$PPh$_2$)(μ-SMe)$_2$(μ-PPh$_2$)-(CO)$_{10}$]·0.25CH$_2$Cl$_2$ **9**, showing the atom numbering scheme
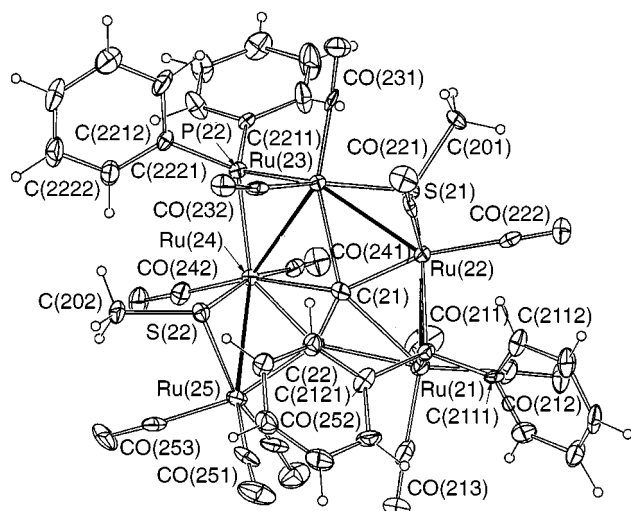
Fig. 5 Plot of [Ru$_5$(μ_5-C$_2$)(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{12}$] **6** (molecule 2), showing the atom numbering scheme

The molecular structure is similar to that found for [Ru$_5$-(μ_5-C$_2$)(μ-Cl)$_2$(μ-PPh$_2$)$_2$(CO)$_{11}$] **11**, a product from the reaction between **2** and the photodimer of methallyl chloride.[28]

(*c*) **[Ru$_5$(μ_5-C$_2$)(μ-SMe)$_4$(μ-PPh$_2$)$_2$(CO)$_{10}$] 10.** The structure of compound **10** is similar to that of **4**, but in this case a Ru–Ru vector, non-bridged in **4**, is now bridged by two SMe groups. As both are 3e donors, this has the effect of reducing the order of the Ru(1) · · · Ru(5) 'bond' to zero. The long Ru(1) · · · Ru(5) separation [3.540(2) Å] is consistent with this feature. Nevertheless, the five Ru atoms form a pentagon, four sides of which are bonded. Two are bridged by PPh$_2$ groups [Ru(1)–Ru(2) 3.071(2), Ru(3)–Ru(4) 3.003(2), Ru(1,2)–P(1) 2.328, 2.277(4), Ru(3,4)–P(2) 2.299, 2.297(3) Å], associated dimensions being similar to those found in **4**. The other two Ru–Ru vectors are bridged by SMe groups [Ru(2)–Ru(3) 2.741(2), Ru(4)–Ru(5) 2.848(3); Ru(2,3)–S(1) 2.434, 2.438(5); Ru(4,5)–S(2) 2.398, 2.392(3) Å] and again the associated geometries are similar to those found for **4**. The Ru$_5$ chain is more nearly planar than
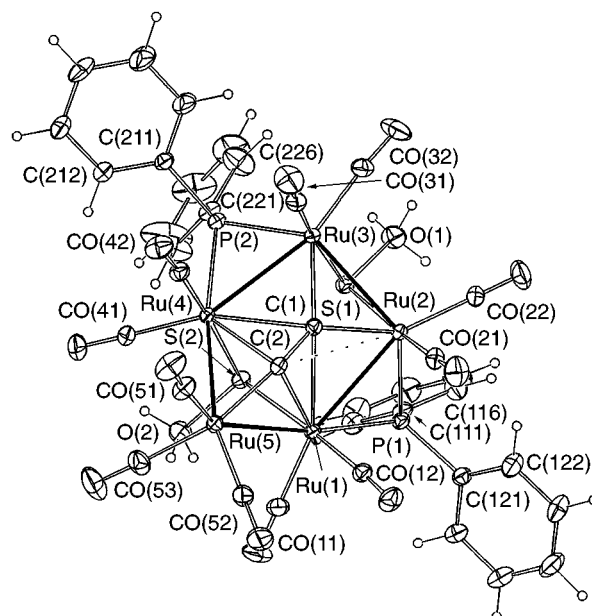

Fig. 6 Plot of a molecule of [Ru$_5$(μ_5-C$_2$)(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{11}$] **4**, showing the atom numbering scheme
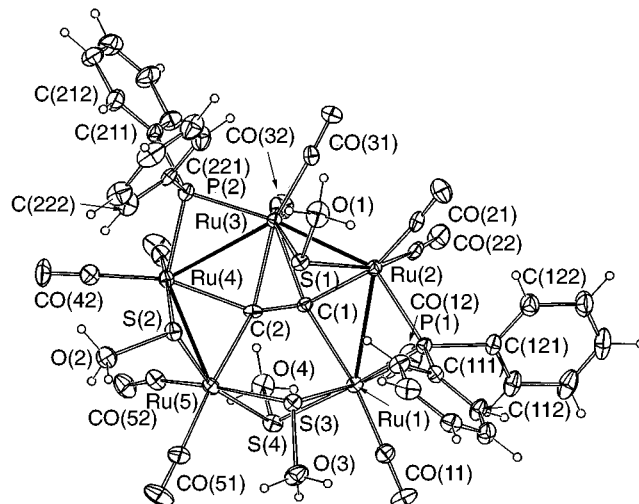
Fig. 7 Plot of a molecule of [Ru$_5$(μ_5-C$_2$)(μ-SMe)$_4$(μ-PPh$_2$)$_2$(CO)$_{10}$] **10**, showing the atom numbering scheme
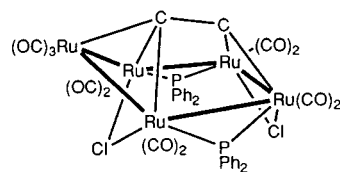
11

12
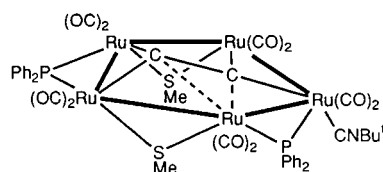
that found for **4** {χ^2(Ru$_5$) 2 × 10^5; δ[Ru(1)–Ru(5)] −0.364(1), 0.330(1), −0.146(1), −0.147(1) and 0.324(1) Å}. The SMe groups are bent up or down from the plane, with dihedrals (SRu$_2$/Ru$_4$ plane) of 85.90(8) and 78.64(8)° for S(1) and S(2); both Me groups are pointing away from the centre of the cluster. For SMe(3,4), the dihedrals are 84.73(9) and 48.62(10)°, respectively. In this case, Me(3) points away from the centre, Me(4) points in to the centre.

Table 2 Structural parameters (bond lengths in Å, angles in °) for C_2 complexes, **4**, **6** and **10**[*]

	4	6	10
Ru(1)–Ru(2)	2.898(1)	2.752(2), 2.770(2)	3.071(2)
Ru(1)–Ru(4)	*3.449(2)*		
Ru(1)–Ru(5)	2.898(1)		*3.540(2)*
Ru(2)–Ru(3)	2.855(2)	2.792(2), 2.794(2)	2.741(2)
Ru(3)–Ru(4)	2.882(1)	2.964(2), 2.947(2)	3.003(2)
Ru(4)–Ru(5)	2.890(1)	2.704(2), 2.716(2)	2.848(3)
Ru(2)–S(1)	2.386(1)	2.418(5), 2.421(5)	2.434(3)
Ru(3)–S(1)	2.391(1)	2.373(4), 2.370(3)	2.438(5)
Ru(1)–S(2)	2.454(1)		
Ru(4)–S(2)	2.449(1)	2.458(5), 2.457(4)	2.398(5)
Ru(5)–S(2)		2.372(4), 2.372(4)	2.392(3)
Ru(1)–S(3)			2.452(3)
Ru(5)–S(3)			2.466(3)
Ru(1)–S(4)			2.481(3)
Ru(5)–S(4)			2.412(3)
Ru(1)–P(1)	2.341(1)	2.350(4), 2.354(5)	2.328(3)
Ru(2)–P(1)	2.290(1)	2.300(5), 2.302(5)	2.277(4)
Ru(3)–P(2)	2.294(1)	2.267(4), 2.249(5)	2.299(3)
Ru(4)–P(2)	2.341(1)	2.309(4), 2.315(4)	2.297(3)
Ru(1)–C(1)	2.470(3)	2.36(1), 2.41(1)	2.303(9)
Ru(2)–C(1)	2.133(3)	2.10(1), 2.08(1)	2.148(9)
Ru(3)–C(1)	2.135(4)	2.41(1), 2.37(1)	2.253(9)
Ru(4)–C(1)	2.409(4)	2.45(1), 2.44(2)	
Ru(1)–C(2)	2.232(3)	2.30(1), 2.29(1)	
Ru(3)–C(2)			2.335(9)
Ru(4)–C(2)	2.260(4)	2.27(1), 2.27(1)	2.249(9)
Ru(5)–C(2)	1.936(4)	2.06(1), 2.06(1)	2.138(9)
C(1)–C(2)	1.307(5)	1.26(2), 1.31(2)	1.28(1)
Ru(2)–Ru(1)–Ru(5)	117.51(2)		96.68(5)
Ru(1)–Ru(2)–Ru(3)	96.39(2)	109.14(6), 109.98(7)	101.59(6)
Ru(2)–Ru(3)–Ru(4)	95.37(2)	99.17(5), 98.20(5)	125.93(6)
Ru(3)–Ru(4)–Ru(5)	119.30(2)	124.14(7), 123.10(7)	95.98(4)
Ru(1)–Ru(5)–Ru(4)	73.14(4)		110.50(5)
Ru(2)–S(1)–Ru(3)	73.40(4)	71.3(1), 71.3(1)	68.47(9)
Ru(1)–S(2)–Ru(4)	89.39(5)		
Ru(4)–S(2)–Ru(5)		68.1(1), 68.4(1)	72.97(9)
Ru(1)–S(3)–Ru(5)			92.1(1)
Ru(1)–S(4)–Ru(5)			92.65(9)
Ru(1)–C(1)–Ru(2)	77.7(1)	75.9(4), 75.8(4)	87.2(3)
Ru(1)–C(1)–Ru(3)	137.1(2)	143.0(7), 144.4(6)	163.3(4)
Ru(2)–C(1)–Ru(3)	84.0(1)	76.2(4), 77.4(5)	77.0(3)
Ru(2)–C(1)–Ru(4)	138.1(2)	148.7(7), 148.2(7)	
Ru(1)–C(2)–Ru(4)	100.3(1)	134.2(8), 133.6(7)	
Ru(1)–C(2)–Ru(5)	87.8(1)	130.1(6), 131.5(7)	
Ru(3)–C(2)–Ru(5)			152.9(4)
Ru(4)–C(2)–Ru(5)	86.7(1)	77.1(5), 77.7(5)	80.9(3)
Ru(2)–C(1)–C(2)	134.8(2)	143(1), 142(1)	144.4(7)
Ru(3)–C(1)–C(2)		140(1), 141(1)	77.4(6)
Ru(4)–C(2)–C(1)	80.1(2)	82(1), 81(1)	151.9(7)
Ru(5)–C(2)–C(1)	163.1(3)	153(1), 149(1)	126.4(7)

[*] Non-bonded Ru–Ru separations in italics.

The major point of interest lies in the C_2 ligand. The expansion of the Ru_5 pentagon has the result of pulling the C_2 ligand almost into the plane of the five metal atoms. We have recently reported a similar effect when adding $CNBu^t$ to compound **4** to give **12** and indeed, the geometry of **10** is also similar to that complex.[29] This is not surprising, as the formal addition of two SMe groups to **4** to give **10** has resulted in loss of only two CO groups, so that this complex has two electrons more than **4**.

The C_2 unit is attached to all five Ru atoms, and may be considered to be a tetrametallated ethene of which the central C=C bond has a π-type interaction with Ru(3) [Ru(3)-C(1,2) 2.253, 2.335(9) Å]. The other Ru–C contacts are between 2.148–2.303(9) Å for Ru(1,2)–C(1) and 2.138–2.249(9) Å for Ru(4,5)–C(2). The geometry about C(2), as found for the corresponding atom in **12**, is almost planar [sum of angles around C(2) 359.4°], so that this atom could be considered to be another example of planar four-co-ordinate carbon. However, the C(1)–C(2) separation is 1.28(1) Å, which argues against this interpretation, and an alternative rationale is of an electron-

rich cluster in which the C_2 ligand donates only four electrons. The electron-rich nature of **10** is also reflected in the long Ru–Ru bonding distances which result from extra electron density being accommodated in a metal cluster antibonding orbital.

Co-ordination about individual Ru atoms is completed by a total of ten terminal CO groups, resulting in the complex having a total of 84 c.v.e. if the C_2 ligand is a six-electron donor. With four Ru–Ru bonds, an 82e system would be expected, again suggesting that the C_2 ligand donates only four electrons. This is consistent with the relatively long interactions found between it and the various metal atoms and with the short C–C bond length.

Comparison of structures of C_2 co-ordinated to Ru_5 clusters

The complexes described above and in other publications[14] are an unusual set of systems containing a simple diatomic ligand more-or-less strongly attached to five Ru atoms. Theoretical calculations of the electron distributions in C_2 complexes have been carried out by Halet and co-workers,[12,17] who have considered that C_2 is best described as the ethynyl dianion (C_2^{2-}), which may donate either six or eight electrons to whatever metal framework it is associated with.

An interesting finding from the present work is the readiness with which this ligand can adopt different electronic configurations. This feature is also apparent in the electronic structure of the parent C_2 ligand, for which many electronic states are relatively easily accessible.[30] A variety of C_2 complexes is readily accessible from **4**, while the reactivity of the C_2 ligand itself has also generated a rich and varied chemistry.[25]

Spectroscopic properties

Of considerable interest are the NMR spectroscopic properties of these complexes. We have only limited information concerning the ^{13}C NMR chemical shifts of the two carbons in the C_2PPh_2 ligand. For **2**, the P-bonded carbon is found at δ 64.96, while the other carbon resonates at δ 215.64; both signals are doublets by coupling to ^{31}P. For **8** these two resonances are found at δ 55.02 and as an unidentified signal in the range δ 189.1–209.7, where it occurs amid several CO resonances.

The clusters containing C_2 ligands exhibit a range of chemical shifts for the two carbon atoms. Thus, for **4**, broad signals at δ 184.89 and 206.66 are assigned to C(1) and C(2), respectively. For **3** the two resonances are found at δ 183.41 and 163.01; the latter is a double doublet from the two ^{31}P nuclei, whereas the second is a simple doublet. For **10** two singlets are found at δ 146.26 and 154.21. There is no correlation between the chemical shifts and any obvious structural or electronic property.

The SMe resonances are generally found between δ 1.07 and 1.93 (^1H) and between δ 18.4 and 26.0 (^{13}C), although for **3** the low-field signal is at δ 2.75. There is no correlation between chemical shift and bridging mode.

Discussion

The experiments reported above have demonstrated the formation of several cluster complexes containing C_2 ligands from the precursor **2** by reaction with Me_2S_2. The conversions have been shown to proceed through several intermediates and the reaction sequence is summarised in the Schemes. Some of these react further to give related complexes. Nevertheless, with appropriate control of reaction conditions, **4** can be isolated in good yield. The first isolated product, **5**, is formed from **2** by addition of two SMe groups and concomitant breaking of three Ru–Ru bonds to give a chain of five Ru atoms. Electronically, there is equivalence between three Ru–Ru bonds and two SMe groups (both totalling six electrons), so that this is a facile transformation which does not involve the loss of any CO groups.

A second product from this reaction was characterised as the dodecacarbonyl complex **7**, an isomer of **8**. Here, the W-shaped Ru_5 chain supports the C_2PPh_2 ligand along its length, the C_2 fragment being attached to the central Ru(2)–Ru(3)–Ru(4) portion in the familiar $2\sigma,\pi$ bonding mode found in $Ru_3(\mu_3\text{-alkyne})$ clusters. Loss of CO results from one of the SMe groups triply bridging atoms Ru(1)–Ru(3), while the PPh_2 ligand spans a non-bonded Ru $\cdots$ Ru vector. This cluster is electron precise, with 80 c.v.e.

On further reaction (heating at 70 °C for 5 h), one of the SMe groups interacts with a third Ru atom (thus donating five electrons to the core atoms), with concomitant loss of a CO ligand, resulting in conversion of compound **5** into **8**. This is accompanied by rearrangement of the cluster core to the rather unusual configuration shown, namely a branched chain. Complex **8** was only isolated from large-scale reactions.

However, the major product from further heating of compound **5** is the first of the C_2-containing clusters, **6**. This complex is an isomer of **8** and it is presently not clear whether the latter is an intermediate or just the product of a competing transformation. In **6** the desired cleavage of the second P–C (sp) bond has occurred to give a second PPh_2 group and the C_2 ligand. The four edges of the Ru_5 chain are alternately bridged by PPh_2 and SMe groups, each acting as three-electron donors. As described above, the C_2 ligand is somewhat asymmetrically bonded to the five metal atoms.

The final product **4** is formed by ring closure to give a rare example of a ring of five transition-metal atoms. Other examples now known include $M_5(C_6H_2Me_3\text{-}2,4,6)_5$ (M = Au or Cu[31]) and $[Mn_5(\mu_5\text{-In})(CO)_{20}]^{2-}$.[32] The ring closure is accompanied by loss of a CO ligand and migration of one SMe group to bridging a non-bonded Ru $\cdots$ Ru vector. The molecule has an approximate C_s symmetry, with the C_2 ligand sitting on the opposite side of the ring from the edge-bridging groups. This has the happy result that this part of the molecule is open to attack by incoming reagents, there being no steric hindrance from either the P-phenyl or the S-methyl groups. In addition, the ring is non-planar, Ru(5) being bent out of the plane of the other four metal atoms by virtue of a short interaction with C(1).

Two other products have been isolated from large-scale preparations of compound **4**. One is closely related to **4** and is formed from it by addition of a second molecule of Me_2S_2 (or two SMe groups). Loss of a further CO group has also occurred. In **10** the mode of attachment of the C_2 ligand strongly resembles that found in the $CNBu^t$ adduct of **4**,[29] even to the point of having an apparent planar four-co-ordinate carbon atom.

The other product is the tetranuclear complex **9**, in which the C_2PPh_2 ligand is still present, but donating only five electrons. This is because excision of a ruthenium atom has removed a co-ordination site for the bridging C_2 part of the ligand and further bonding along the Ru_4 chain is not sterically possible. Other features of the structure resemble those found in the larger clusters containing two bridging SMe groups and one bridging PPh_2 ligand. In principle, further co-ordination of metal–ligand groups to **9** might be possible, but we have not yet explored these possibilities.

The conversion of compound **2** into **4** can be understood in terms of the skeletal rearrangements shown in Scheme 5. Addition of two SMe groups to **2** occurs across Ru(1)–Ru(3), which bond is cleaved, and across Ru(4)–Ru(5), with resulting cleavage of bonds between these atoms and Ru(2). A total of three 2e Ru–Ru bonds is broken by the two 3e SMe donor ligands. Subsequent loss of CO from Ru(2) occurs when the MeS(1) group becomes triply bridging by attachment to this atom, thus generating **7**. A similar sequence, but with cleavage of Ru(4)–Ru(5) and formation of Ru(3)–Ru(5) bonds, can account for the formation of **8**. Conversion of **5** into **6** results from cleavage of the P–C_2 bond, the resulting PPh_2 group bridging

Ru(1)–Ru(2), with loss of CO from the latter atom. Concomitant migration of MeS(1) from Ru(1) to Ru(2) completes the formation of **6**. Ring closure by formation of a new Ru(1)–Ru(5) bond, with loss of CO, and concomitant migration of S(1) from Ru(5) to Ru(1), results in formation of **4**. In all of these transformations subtle rearrangement of the mode of attachment of the C_2 fragment, whether bonded to P(1) or free, also occurs.

Bonding of the C_2 ligand

Complexes **4**, **6** and **10** are novel examples of clusters containing C_2 ligands. As mentioned in the Introduction, several clusters containing fully encapsulated C_2 groups are known, and since our communication appeared,[24] several other examples of more open clusters containing C_2 ligands have been described.[12,15,33] We have also reported further examples of complexes containing essentially the same structures as that found for **4**, namely the PBu^n_2 analogue of **4**[26] and $[Ru_5(\mu_5\text{-}C_2)\text{-}(\mu\text{-Cl})_2(\mu\text{-PPh}_2)_2(CO)_{13}]$ **12**.[28] These have been summarised in a recent paper by Frapper and Halet,[12,17] who have examined the attachment of this novel carbon species in some detail. Their preference is to consider the ligand as the ethynediyl dianion (C_2^{2-}, an eight-electron donor), which serves to simplify the understanding of their calculations. Their calculations suggest that in **4** electron density is concentrated on the exposed C(2) atom, a result which is consistent with the experimentally observed electrophilic attack on this atom. Relatively large separations of C(1) from Ru(3,4) are apparently responsible for there being less electron density on this carbon, since back bonding from the metal is inhibited.

The case of compound **10**, in which the C_2 unit is more closely associated with the Ru_5 cluster, but which also has relatively long C(1,2)–Ru(2) separations, deserves further comment. Here we find that the C_2 ligand donates only four electrons (or six, if considered as C_2^{2-}). The C_2 ligand is electron-rich, and reduced back bonding results in a short C–C bond length. We have previously described the Bu^tNC adduct of **4**, which contains a similarly flattened C_2Ru_5 arrangement, and for which calculations show much weaker π donation and π^* back bonding than found for **4**.[29] Consequently, addition of a ligand to **4** results in weakening of the C_2–Ru_5 framework interaction and suggests that the C_2 ligand is highly flexible in its interaction with polymetallic systems. That this should be so is no surprise, since C_2^{2-} is isoelectronic with CO, whose variable electron-acceptor powers are well known.

Conclusion

This paper describes the successful designed synthesis of an Ru_5 cluster complex containing the dicarbon ligand, achieved by successive P–C bond cleavage reactions in complexes of the linear bis(tertiary phosphine) $C_2(PPh_2)_2$ (dppa) mediated by ruthenium cluster complexes. Several complexes have been identified as intermediates in the conversion of **2** {the pyrolysis product of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$} into **4** in high yield by reaction with S_2Me_2. From the point of view of further work, it is perhaps unfortunate that **4** has so many bridging groups, although at this stage we have not observed any reactions of either the PPh_2 or the SMe groups with other reagents (save the $\mu \longrightarrow \mu_3$ conversions of the latter mentioned above), probably because the C_2 ligand is such a reactive centre.

Experimental

General conditions

All reactions were carried out under dry, high-purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. Prep-
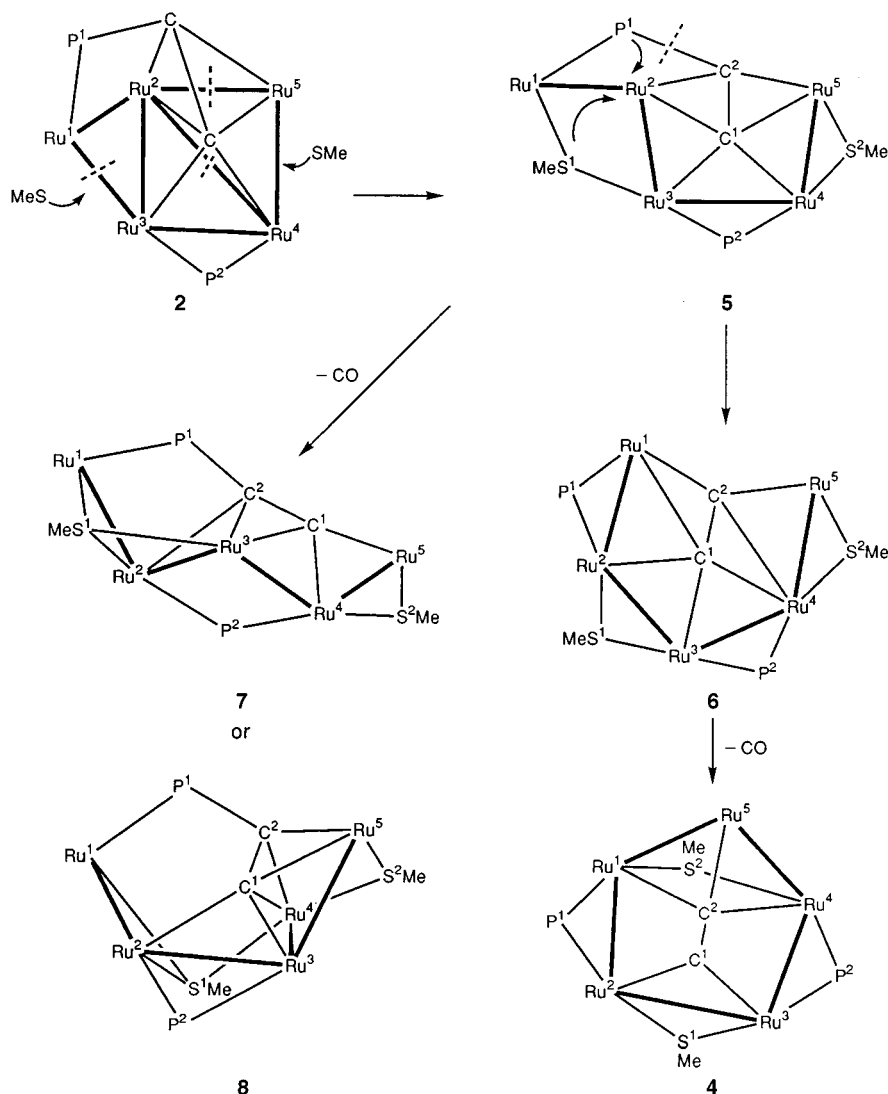
Scheme 5

arative tlc was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick). Light petroleum had b.p. 60–80 °C.

Reagents

Complex **2** was prepared by the literature method;[22] Me_2S_2 (Ralph Emanuel) was used as received.

Instrumentation

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

Reactions of [$Ru_5(\mu_5$-$C_2PPh_2)(\mu$-$PPh_2)(CO)_{13}$] 2 with dimethyl disulfide. *At* 70 °C. A solution of compound **2** (100 mg, 0.079 mmol) and dimethyl disulfide (25 mg, 0.26 mmol) in benzene was heated at 70 °C (oil-bath) for 30 min. The solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10:3) to yield three major bands. A red band (R_f 0.55) was recrystallised from CH_2Cl_2–MeOH to yield [$Ru_5(\mu_5$-$C_2PPh_2)(\mu$-$SMe)_2(\mu$-$PPh_2)(CO)_{12}$] **6** (2 mg, 2%), m.p. 232–234 °C (decomp.) [Found: C, 35.93; H, 1.93%; M − CO, 1303 (mass spectrometry). $C_{40}H_{26}O_{12}P_2Ru_5S_2$ requires C, 36.21; H, 1.97%; M − CO, 1303]. IR (cyclohexane): ν(CO) 2081m, 2057m, 2025m, 2006s, 1994m, 1981m, 1962m and 1949m cm^{-1}.

^{1}H NMR: δ(CDCl$_3$) 1.30 (s, 3 H, SMe), 2.75 (d, J_{HP} = 2.3 Hz, 3 H, SMe) and 6.91–8.02 (extended m, 20 H, Ph). ^{13}C NMR: δ(CDCl$_3$) 22.64 (s, SMe), 26.00 (s, SMe), 127.26–134.35 (m, Ph), 140.14 [d, J_{CP} = 37.5, 2(?) × *ipso*-C], 141.99 (d, J_{CP} = 32.2, *ipso*-C), 142.96 (d, J_{CP} = 25.1, *ipso*-C), 163.01 [dd, J_{CP} = 14.4, 3.6, C(2)], 183.41 [d, J_{CP} = 8.8, C(1)], 191.83 (d, J_{CP} = 8.8, CO), 193.21 (d, J_{CP} = 9.0, CO), 193.98 (s, CO), 194.79 (s, CO), 195.87 (d, J_{CP} = 13.4, CO), 198.34 (d, J_{CP} = 7.1, CO), 198.67 (t, J_{CP} = 5.3, CO), 202.41 (d, J_{CP} = 8.0, CO), 203.58 (d, J_{CP} = 4.8 Hz, CO) and 205.19 (s, CO). FAB mass spectrum: m/z 1303–995, [M − nCO]$^+$ (n = 1–12).

An orange band (R_f 0.50) was recrystallised from CH_2Cl_2–MeOH to yield [$Ru_5(\mu_5$-$C_2PPh_2)(\mu$-$SMe)_2(\mu$-$PPh_2)(CO)_{13}$] **5** (23 mg, 21%), m.p. 158–160 °C (decomp.) [Found: C, 35.29; H, 1.72%; M − 2CO, 1303 (mass spectrometry). $C_{41}H_{26}O_{13}P_2Ru_5S_2 \cdot CH_2Cl_2$ requires C, 34.96; H, 1.96%; M − 2CO, 1303]. IR (cyclohexane): ν(CO) 2074m, 2058vs, 2037s, 2021s, 2014m, 2003m, 1991m, 1975 (sh), 1970m and 1962m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.07 (3 H, s, SMe), 1.57 (3 H, s, SMe), 5.28 (2 H, s, CH_2Cl_2), 7.03–7.67 (18 H, m, Ph) and 8.31 (2 H, dd, J_{HH} = 11.6, 7.2 Hz, Ph). ^{13}C NMR: δ(CDCl$_3$) 19.71 (d, J_{CP} = 6.0, SMe), 20.03 (s, SMe), 64.96 (d, J_{CP} = 38.2 Hz, PCC), 126.91–134.47 (m, Ph), 141.34 (d, J_{CP} = 36.0, *ipso*-C), 138.87, 138.94, 139.04, 139.13 [2 × d (overlapping), *ipso*-C], 138.38 (d, J_{CP} = 27.3, *ipso*-C), 187.15 (d, J_{CP} = 6.3, CO), 189.69 [s, (br), CO], 191.78 (dd, J_{CP} = 8.6, 3.4, CO), 194.71 (dd, J_{CP} = 8.3, 2.0, CO), 195.12 (s, CO), 197.24 (dd, J_{CP} = 10.9, 3.6, CO), 198.15 (dd, J_{CP} = 6.2, 3.3, CO), 198.81 (s, CO), 200.19 (s, CO), 200.51

(d, J_{CP} = 5.0, CO), 201.48 (s, CO), 203.11 (d, J_{CP} = 3.1, CO), 206.76 (s, CO) and 215.64 (dd, J_{CP} = 11.9, 4.5 Hz, CCP). FAB mass spectrum: m/z 1303–995, $[M - nCO]^+$ (n = 2–13).

A purple band (R_f 0.45) was recrystallised from toluene–hexane to yield black crystals of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{11}]$ **4** (38 mg, 37%), m.p. 240–243 °C (decomp.) [Found: C, 36.59; H, 2.05%; M, 1303 (mass spectrometry). $C_{39}H_{26}O_{11}P_2Ru_5S_2$ requires C, 35.97; H, 2.01%; M, 1303]. IR (cyclohexane): ν(CO) 2070s, 2034vs, 2016m, 1996m, 1987w, 1971m and 1966m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.072 (3 H, s, SMe), 1.933 (3 H, s, SMe) and 7.08–7.78 (20 H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 21.02 (s, SMe), 22.65 (s, SMe), 127.53–131.48 (m, Ph), 141.79–142.04 (m, *ipso*-C), 143.75–144.16 (m, *ipso*-C), 184.89 [s (br), C(1)], 186.42 (s, CO), 192.48 (s, CO), 195.50 (s, CO), 204.43 (s, CO), 206.31 (s, CO) and 206.66 [s, (br), C(2)]. FAB mass spectrum; m/z 1303, M^+; 1275–995, $[M - nCO]^+$ (n = 1–11).

At 35 °C. A solution of compound **2** (200 mg, 0.016 mmol) and dimethyl disulfide (25 mg, 0.26 mmol) in benzene (40 cm^3) was heated at 35 °C (oil-bath) for 5 h. The solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10:3) to yield three bands. The major orange band (R_f 0.45) was recrystallised from CH$_2$Cl$_2$–MeOH to yield red crystals of **5** (135 mg, 62%). A purple band (R_f 0.40) was recrystallised from toluene–hexane to yield black crystals of **4** (25 mg, 12%). A minor orange band (R_f 0.35) was recrystallised from CH$_2$Cl$_2$–MeOH to yield red crystals of $[Ru_5(C_2PPh_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)(CO)_{12}]$ **7** (10 mg, 5%) [Found: C, 34.02; H, 2.04%; M, 1331 (mass spectrometry). $C_{40}H_{26}O_{12}P_2Ru_5S_2 \cdot 1.8CH_2Cl_2$ requires C, 33.86; H, 2.01%; M, 1331]. IR (cyclohexane): ν(CO) 2074 (sh), 2072m, 2054 (sh), 2041m, 2037m, 2025vs, 2016s, 2011s, 2004s, 1996m, 1986m, 1978m, 1964m, 1957m and 1947m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.07 (3 H, s, SMe), 1.57 (3 H, s, SMe), 5.29 (3.6 H, s, 1.8 CH$_2$Cl$_2$) and 7.03–8.31 (20 H, m, Ph). FAB mass spectrum: m/z 1331, M^+; 1303–995, $[M - nCO]^+$ (n = 1–12).

Pyrolyses

$[Ru_5(C_2PPh_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)(CO)_{13}]$ 5. A solution of compound **5** (30 mg, 0.022 mmol) in benzene (25 cm^3) was heated at 70 °C with a nitrogen purge for 2 h (after 0.75 h spot tlc showed the presence of **6** as well as starting material). The solvent was removed and the residue recrystallised from CH$_2$Cl$_2$–MeOH to yield **4** (26 mg, 91%).

$[Ru_5(C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{12}]$ 6. A solution of compound **6** (20 mg, 0.015 mmol) in benzene (25 cm^3) was heated at reflux with a nitrogen purge for 2.5 h. The solvent was removed and the residue recrystallised from CH$_2$Cl$_2$–MeOH to yield **4** (18 mg, 92%).

Reaction of $[Ru_5(C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{11}]$ 4 with CO (purge)

A solution of compound **4** (100 mg, 0.077 mmol) in toluene (30 cm^3) was heated at 80 °C with a CO purge for 3 h. The solvent was removed and the residue purified by preparative tlc (light petroleum–acetone 10:3) to yield three major bands. A red band (R_f 0.65) was recrystallised from CH$_2$Cl$_2$–MeOH to yield **6** (16 mg, 16%). A yellow band (R_f 0.70) contained 40 mg of a complex which has not been identified. Some starting material (R_f 0.55, 33 mg) was also recovered. During the reaction a black complex (R_f 0.55) was observed. However, both on removal of the solvent and running up the tlc plate this complex converted back into the starting material. Formation of this black complex was suppressed at higher reaction temperatures.

Large-scale synthesis of $[Ru_5(C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{11}]$ 4

A dry, nitrogen-flushed Schlenk tube (250 cm^3) was charged with compound **2** (1.00 g, 0.79 mmol), Me$_2$S$_2$ (100 mg, 1.1

mmol) and distilled toluene (100 cm^3). A magnetic stirring bar was added and the solution heated at 30 °C for 3 h. After the solvent was removed the residue was adsorbed onto Florisil and eluted from a short column with light petroleum–dichloromethane (6:1). After removal of the solvent the residue was dissolved in toluene (100 cm^3) and the solution heated at 80–100 °C for 1.5 h. The solvent was removed and the residue dissolved in CH$_2$Cl$_2$ (15 cm^3). A layer of MeOH (35 cm^3) was carefully added and the mixture placed in a freezer. After 3 d black crystalline **4** (0.62 g) was recovered by filtration. The remaining solution was evaporated to dryness and the residue further purified by preparative tlc (light petroleum–acetone 4:1) to yield further **4** (R_f 0.45, 0.04 g). Total yield: 0.66 g (64%). A red band (R_f 0.70) was recrystallised from CH$_2$Cl$_2$–MeOH to yield red crystals of $[Ru_4(\mu_4\text{-}C_2PPh_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)(CO)_{10}]$ **9** (15 mg, 2%) [Found: C, 38.22; H, 2.26%; M, 1174 (mass spectrometry). $C_{38}H_{26}O_{10}P_2Ru_4S_2 \cdot 0.25CH_2Cl_2$ requires C, 38.47; H, 2.24%; M, 1174]. IR (cyclohexane): ν(CO) 2068m, 2053vs, 2022s, 2004m, 1990m, 1978m, 1969m and 1962m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.66 (3 H, s, SMe), 2.05 (3 H, s, SMe), 5.29 (0.5 H, s, 0.25 CH$_2$Cl$_2$) and 7.34–8.02 (20 H, m, Ph). FAB mass spectrum: m/z 1174, M^+, 1146–894, $[M - nCO]^+$ (n = 1–10).

A red band (R_f 0.60) was further purified by preparative tlc (light petroleum–CH$_2$Cl$_2$ 100:35) to yield three bands. A brown band (R_f 0.60) was recrystallised from CH$_2$Cl$_2$–MeOH to yield compound **2** (7 mg). A red band (R_f 0.55) was recrystallised from CH$_2$Cl$_2$–MeOH to yield **6** (23 mg, 3%). An orange band (R_f 0.45) was recrystallised from CH$_2$Cl$_2$–MeOH to yield red crystals of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)(CO)_{12}]$ **8** (2 mg, 0.2%) [Found: C, 35.97; H, 2.06%; M, 1331 (mass spectrometry). $C_{40}H_{26}O_{12}P_2Ru_5S_2$ requires C, 36.12; H, 1.97%; M, 1331]. IR (cyclohexane): ν(CO) 2073 (sh), 2071m, 2058s, 2054s, 2014 (sh), 2010 (sh), 2008vs, 1995m, 1984m, 1978m, 1965m, 1959 (sh) and 1947m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.04 (3 H, s, SMe), 1.53 (3 H, s, SMe) and 7.33–8.39 (20 H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 28.07 (s, SMe), 28.97 (s, SMe), 55.02 (d, J_{CP} = 17.7, PCC), 128.31–134.02 (m, Ph), 136.92 (d, J_{CP} = 45.0, *ipso*-C), 143.06 (d, J_{CP} = 24.7, *ipso*-C), 144.82 (d, J_{CP} = 30.8, *ipso*-C), 189.14 (s, CO), 192.61 (t, J_{CP} = 4.0, CO), 194.34 (d, J_{CP} = 9.6, CO), 198.00 (s, CO), 198.97 (s, CO), 199.21 (s, CO), 199.31 (d, J_{CP} = 6.4, CO), 199.48 (t, J_{CP} = 4.3, CO), 201.11 (d, J_{CP} = 4.2 Hz, CO), 204.95 (s, CO), 207.17 (s, CO) and 209.71 (s, CO) (PCC resonance probably amongst the listed CO resonances). FAB mass spectrum: m/z 1331, M^+, 1303–995, $[M - nCO]^+$ (n = 1–12).

A light brown band (R_f 0.50, from light petroleum–acetone separation) was further purified by preparative tlc (light petroleum–CH$_2$Cl$_2$ 100:35) to yield two bands. A brown band (R_f 0.60) was recrystallised from CH$_2$Cl$_2$–MeOH to yield black crystals of compound **2** (15 mg, total yield 22 mg, 2%). An orange band (R_f 0.45) was recrystallised from CH$_2$Cl$_2$–MeOH to yield **8** (18 mg, total yield 20 mg, 2%). An orange band (R_f 0.45, from light petroleum–acetone separation) was recrystallised from CH$_2$Cl$_2$–MeOH to yield red crystals of **7** (25 mg, 2%).

When the reaction is carried out at reflux temperature a significant amount (*ca.* 20%) of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-SMe})_4(\mu\text{-PPh}_2)_2(CO)_{10}]$ **10** was obtained from a red band which has the same R_f as that of **4** (preparative tlc, light petroleum–acetone 10:3). The two complexes separate when light petroleum–CH$_2$Cl$_2$ (5:2) is used. Complex **10** [Found: C, 35.98; H, 2.71%; M, 1370 (mass spectrometry). $C_{40}H_{32}O_{10}P_2Ru_5S_4$ requires C, 35.11; H, 2.36%; M, 1370]. IR (cyclohexane) ν(CO) 2051m, 2033m, 2021vs, 2015 (sh), 2010 (sh), 2002vw, 1992w, 1983m, 1972m, 1965m, 1948w and 1924vw cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.59 (3 H, s, SMe), 2.04–2.06 [6 H, s + d (overlapping), 2 × SMe], 2.14 (3 H, s, SMe) and 7.20–8.26 (20 H, m, Ph). ^{13}C NMR: δ(CDCl$_3$) 18.44 (s, SMe), 19.55 (s, SMe), 20.74 (s, SMe), 24.48 (s, SMe), 127.70–133.31 (m, Ph), 140.98 (d, J_{CP} = 26.9, *ipso*-C), 142.42 (d, J_{CP} = 38.8, *ipso*-C), 142.89 (d, J_{CP} = 33.4, *ipso*-C), 143.95 (d, J_{CP} = 18.5, *ipso*-C), 146.26 (s, CC), 154.21 (s, CC), 190.26 (d,

Table 3 Crystal data and refinement details for C_2PPh_2 complexes **5**, **7**, **8** and **9** and C_2 complexes **4**, **6** and **10**

	5	7	8	9	4	6	10
Formula	$C_{41}H_{26}O_{13}P_2Ru_5S_2 \cdot 0.5CH_2Cl_2$	$C_{40}H_{26}O_{12}P_2Ru_5S_2 \cdot 1.8CH_2Cl_2$	$C_{40}H_{26}O_{12}P_2Ru_5S_2$	$C_{38}H_{26}O_{10}P_2Ru_4S_2 \cdot 0.25CH_2Cl_2$	$C_{39}H_{26}O_{11}P_2Ru_5S_2$	$C_{40}H_{26}O_{12}P_2Ru_5S_2$	$C_{40}H_{32}O_{10}P_2Ru_5S_4$
M	1400.6	1482.5	1330.1	1194.2	1302.1	1330.1	1368.2
Crystal system	Monoclinic	Triclinic	Triclinic	Tetragonal	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{4}2_1c$ (no. 114)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/ Å	14.10(1)	16.195(7)	18.478(7)	21.930(2)	14.691(9)	19.099(7)	10.84(2)
b/ Å	19.135(5)	13.842(5)	12.062(1)		15.784(9)	17.927(5)	21.44(1)
c/ Å	22.58(1)	11.946(3)	10.411(5)	17.752(5)	19.112(8)	14.193(6)	20.37(1)
α/°		90.77(2)	77.81(3)			72.34(2)	
β/°	125.90(5)	103.17(3)	81.15(4)		91.38(4)	89.44(3)	99.2(1)
γ/°		94.75(2)	82.65(2)			76.37(3)	
U/Å³	4935	2597	2230	8538	4430	4490	4673
Z	4	2	2	8	4	4	4
D_c/g cm⁻³	1.88	1.89	1.98	1.86	1.95	1.97	1.94
$F(000)$	2716	1439.2	1288	4660	2520	2576	2664
Crystal size/mm	$0.26 \times 0.45 \times 0.34$	$0.33 \times 0.08 \times 0.20$	$0.38 \times 0.13 \times 0.13$	$0.26 \times 0.26 \times 0.15$	$0.20 \times 0.40 \times 0.18$	$0.17 \times 0.18 \times 0.09$	$0.66 \times 0.26 \times 0.15$
μ/cm⁻¹	15.7	15.7	17.0	14.9	17.1	16.9	18.8
A^* (minimum, maximum)	1.40, 1.46	1.13, 1.40	1.10, 1.18	1.24, 1.41	1.44, 1.63	1.13, 1.24	1.22, 1.45
$2\theta_{max}$/°	60	50	50	55	65	50	60
N	11 677	9126	7848	5307	15 981	15 151	13 330
N_o	8930	6838	6535	5220	12 756	7539	7445
R	0.029	0.052	0.042	0.031	0.038	0.054	0.058
R'	0.032	0.068	0.054	0.027	0.048	0.052	0.063

$J_{CP} = 7.3$, CO), 191.71 (d, $J_{CP} = 2.2$, CO), 191.85 (d, $J_{CP} = 6.9$, CO), 193.40 (m, CO), 194.52 (d, $J_{CP} = 4.5$, CO), 195.02 (d, $J_{CP} = 5.8$, CO), 195.87 [s(br), CO], 199.63 (d, $J_{CP} = 2.0$, CO), 203.70 (d, $J_{CP} = 6.0$, CO) and 204.76 (d, $J_{CP} = 2.0$ Hz, CO). FAB mass spectrum: m/z 1370, M^+, 1342–1090, $[M - nCO]^+$ ($n = 1$–10).

Reaction of $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{11}]$ 4 with Me_2S_2

A solution of compound **4** (80 mg, 0.061 mmol) and Me_2S_2 (20 mg, 0.21 mmol) in toluene (20 cm³) were heated at reflux for 6 h. The solvent was removed and the residue purified by preparative tlc (light petroleum–CH_2Cl_2 10:3) to yield three bands. The major red band (R_f 0.40) was recrystallised from CH_2Cl_2–MeOH to yield **10** (51 mg, 61%). Some starting material (R_f 0.45, 6 mg) was also recovered.

Crystallography

Unique room-temperature diffractometer data sets were measured (Enraf-Nonius CAD-4 four-circle diffractometer; $2\theta_{max}$ limits as specified, 2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107₃ Å; $T \approx 295$ K) yielding N independent reflections, N_o of which, with $I > 3\sigma(I)$ were considered 'observed' and used in the full-matrix (large-block) least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted at convergence, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were used, the XTAL 3.0 program system[34] implemented by S. R. Hall being employed. Pertinent results are given in Tables 1–3 and the figures (showing 20% thermal envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å).

Individual variations in procedure. *Compound* **5**. Difference-map residues were modelled as a CH_2Cl_2 molecule of solvation, disordered about an inversion centre, with a rigid body approximation.

Compound **7**. Difference-map residues were modelled as three CH_2Cl_2 molecules with constrained geometry, site occupancy set at 0.5, 0.5, 0.76(1) after trial refinement, and with C atom thermal parameters isotropic.

Compound **8**. Residuals are quoted for the preferred chirality. Difference-map residues were modelled as CH_2Cl_2 solvent disordered about the $\bar{4}$ axis.

Compound **9**. Difference-map residues were modelled as a molecule of CH_2Cl_2 of solvation disordered about the $\bar{4}$ axis, site occupancy of the C1 atoms set at 0.25 after trial refinement.

Note that atom numberings as presented in the preliminary report[24] of compounds **4** and **6** are not necessarily retained in the present record where, for the sake of extensive comparison, consistency across a number of compounds is the desideratum.

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References

1 F. Diederich and Y. Rubin, *Angew. Chem.*, 1992, **104**, 1123; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101.
2 G. S. Hammond and V. J. Kuck, *ACS Symp. Ser.*, 1992, **481**.
3 W. Weltner, jun. and R. J. van Zee, *Chem. Rev.*, 1989, **89**, 1713.
4 W. Weng, J. A. Ramsden, A. M. Arif and J. A. Gladysz, *J. Am.*

Chem. Soc., 1993, **115**, 3824; H. Lang, *Angew. Chem.*, 1994, **106**, 569; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547.
5 J. S. Bradley, *Adv. Organomet. Chem.*, 1983, **22**, 1; F. Calderoni, F. Demartin, M. C. Iapalucci and G. Longoni, *Angew. Chem.*, 1996, **108**, 2393; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2225; C.-J. Su, P.-C. Su, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Am. Chem. Soc.*, 1996, **118**, 3289 and refs. therein.
6 W. Beck, B. Niemer and M. Wieser, *Angew. Chem.*, 1993, **105**, 969; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923; H. Lang, *Angew. Chem.*, 1994, **106**, 569; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547; U. Bunz, *Angew. Chem.*, 1996, **108**, 1047; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; see also refs. 2–7 in B. E. Woodworth and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 7418.
7 M. S. Morton and J. P. Selegue, *J. Am. Chem. Soc.*, 1995, **117**, 7005; F. Diederich, Y. Rubin, O. L. Chapman and N. S. Goroff, *Helv. Chim. Acta*, 1994, **77**, 1441.
8 C. Zheng, Y. Apeloig and R. Hoffmann, *J. Am. Chem. Soc.*, 1988, **110**, 749; J. Silvestre and R. Hoffmann, *Langmuir*, 1985, **1**, 621.
9 M. L. Listeman and R. R. Schrock, *Organometallics*, 1985, **4**, 74.
10 D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. van Duyne and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1989, **111**, 9056.
11 H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto and H. Yamazaki, *Organometallics*, 1988, **7**, 2257.
12 G. Frapper and J.-F. Halet, *Organometallics*, 1995, **14**, 5044.
13 A. Arrigoni, A. Ceriotti, R. Della Pergola, M. Manassero, N. Masciocchi and M. Sansoni, *Angew. Chem.*, 1984, **102**, 290; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 322.
14 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1992, **423**, 97.
15 M. Akita and Y. Moro-oka, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 420; M. Akita, S. Sugimoto, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1992, **114**, 7581.
16 W. Beck, B. Niemer and M. Wieser, *Angew. Chem.*, 1993, **105**, 969; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923.
17 G. Frapper, J.-F. Halet and M. I. Bruce, *Organometallics*, 1997, **16**, 2590.
18 M. I. Bruce, J. G. Matisons and B. K. Nicholson, *J. Organomet. Chem.*, 1983, **247**, 321.
19 W. R. Cullen, D. A. Harbourne, B. Liengme and J. R. Sams, *Inorg. Chem.*, 1970, **9**, 702; W. R. Cullen, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 323.
20 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland and R. Mason, *Chem. Commun.*, 1972, 87; G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford and R. S Nyholm, *J. Organomet. Chem.*, 1972, **40**, C70; C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 1973, 529.
21 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.
22 M. I. Bruce, M. L. Williams, J. M. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1229.
23 M. I. Bruce, *J. Organomet. Chem.*, 1990, **394**, 365.
24 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1992, 26.
25 M. I. Bruce, *Coord. Chem. Rev.*, 1997, in the press; *J. Cluster Sci.*, 1997, **8**, 293.
26 C. J. Adams and M. I. Bruce, *Aust. J. Chem.*, 1996, **49**, 517.
27 D. Nucciarone, S. A. MacLaughlin, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 106.
28 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, **506**, 191.
29 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 975.
30 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, vol. 4, Constants of Diatomic Molecules*, Van Nostrand and Reinhold, Princeton, 1979.
31 E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, **8**, 1067.
32 M. Schollenberger, B. Nuber and M. L. Ziegler, *Angew. Chem.*, 1992, **104**, 329; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 350.
33 G. A. Kotsantonis, J. P. Selegue and J.-G. Wang, *Organometallics*, 1992, **11**, 2704; M. P. Jensen, D. A. Phillips, M. Sabat and D. F. Shriver, *Organometallics*, 1992, **11**, 1859; M. P. Jensen, M. Sabat and D. R. Shriver, *J. Cluster Sci.*, 1990, **1**, 75; T. Weidmann, V. Weinrich, B. Wager, C. Robl and W. Beck, *Chem. Ber.*, 1991, **124**, 1363.
34 S. R. Hall and J. M. Stewart (Editors), *XTAL Users' Manual*, Version 3.0, Universities of Western Australia and Maryland, 1990.
35 C. J. Adams, M. I. Bruce, M. J. Liddell, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1992, 1314.