DALTON

# Reaction of a dicarbon $Ru_5$ cluster with CO: crystal structures of $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}]$ and $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$*

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The reaction between $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** and CO (30 atm) yielded $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}]$ **2** and $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**, both characterised by single-crystal X-ray crystallography. In **2**, addition of 2 CO results in the net cleavage of two Ru–Ru bonds and expansion of the resulting $Ru_3$ cluster. The $C_2$ ligand bridges one edge of the $Ru_3$ core and the isolated Ru–Ru bonded fragment in a $\mu,\mu\text{-}\eta^1,\eta^2$ mode, albeit with asymmetric Ru–$C_2$ $\pi$ interactions. In **3**, one Ru atom has been excised from the cluster present in **1**. One Ru–Ru bond is bridged by two SMe groups as a result of migration of one of these. Although the $C_2$ ligand bridges all four metal atoms, only two Ru–Ru bonds are present, with the non-bonded Ru $\cdots$ Ru vector being bridged by $PPh_2$. Extended-Hückel molecular orbital calculations have been used to rationalise the observed structures.

There is much interest in metal complexes containing all-carbon ligands which arises both from their intrinsic interest and from possible applications as new materials (in the electronics and optical industries) and as catalysts.[1] In addition, relationships between the carbon ligands in these molecular compounds and analogous ligands on metal surfaces[2] or in metal carbides[3] have prompted continuing searches for new syntheses and new understanding of their properties.

Many examples of co-ordinated dicarbon ($C_2$) have been described[4] and a recent detailed theoretical study of tetranuclear systems containing this ligand casts considerable light on the variety of different bonding modes found.[5] The synthesis of the pentanuclear cluster $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ **1** (Scheme 1),[4c] containing an unusually exposed $C_2$ ligand, has prompted a detailed study of its chemistry. We have already described its reactions with hydrogen[6] and with olefins,[7,8] in which insertion of one carbon of the $C_2$ ligand into H–H, C–H or C–C bonds has occurred. With $Bu^tNC$, addition to the $Ru_5$ cluster occurs, resulting in a cluster expansion which pulls the $C_2$ ligand into the plane; one of the carbons thereby acquires a planar four-co-ordinate geometry.[9] It was therefore of interest to examine the reactions of **1** with CO. While there was no reaction at ambient temperature and pressure, conversion into several products occurred on heating under pressure. In the present paper we report on two complexes obtained from reactions carried out at 120 °C and 30 atm.

## Results

Toluene solutions of complex **1** were treated with CO (30 atm, 120 °C, 2 h) and worked up by thin-layer chromatography to give three complexes. Two of these were isolated, each in about 20% yield, and characterised by analysis and mass spectrometry as $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}]$ **2** and $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**. In their IR spectra only terminal ν(CO) bands were present (ten for **2**, nine for **3**, all of medium to very strong intensity). The $^1H$ NMR spectrum of **3** contained two SMe resonances at δ 2.31 and 2.33 (the latter showing a 2.7 Hz coupling to phosphorus), together with a multiplet for the aromatic protons of the $PPh_2$ groups. Further characterisation was sought from single-crystal X-ray diffraction analysis, the results of which are reported below.

### Molecular structure of $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}]$ 2

A molecule of complex **2** is depicted in Fig. 1 and selected bond parameters are given in Table 1. The five ruthenium atoms present in **1** now appear as an enlarged $Ru_3$ cluster linked by the $C_2$ ligand to an $Ru_2(\mu\text{-}SMe)(CO)_6$ fragment. The three Ru–Ru edges in the former are bridged by a $PPh_2$ group [Ru(1)–Ru(2) 3.087(4), Ru(1,2)–P(1) 2.342(7), 2.401(7) Å], by SMe and $PPh_2$ groups [Ru(1)–Ru(3) 2.956(4); Ru(1,3)–P(2) 2.331(8), 2.310(8); Ru(1,3)–S(1) 2.445(8), 2.409(7) Å], and by the $C_2$ ligand [Ru(2)–Ru(3) 3.170(4) Å]. These distances are longer than those normally found for Ru–Ru single bonds; in $[Ru_3(CO)_{12}]$, for example, the average Ru–Ru separation is 2.854(1) Å.[10] Although no complex containing an Ru–Ru bond bridged by both SR and $PR_2$ groups has been structurally characterised, the value for Ru(1)–Ru(3) found here is longer than simple Ru–Ru bonds bridged by SEt and H in $[Ru_3(\mu\text{-}H)(\mu\text{-}SEt)(CO)_{10}]$ [2.843(1) Å][11] and by $PPh_2$ and H in $[Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$ [2.8700(3) Å].[12] The $Ru_2$ fragment is symmetrically bridged by the second SMe group [Ru(4,5)–S(2) 2.405(9), 2.407(7) Å] and a short Ru(4)–Ru(5) separation [2.694(6) Å] is found here. In precursor complex **1** the two P-bridged Ru–Ru bonds are 2.898, 2.882(1) Å and the S-bridged Ru–Ru bond is 2.855(2) Å.[4c]

The $C_2$ ligand is found bridging four of the Ru atoms in an approximate $\eta^1,\eta^2$ mode reminiscent of that found in $[\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu,\mu\text{-}C_2)]$ **4**.[4b] However, whereas Ru(2) and Ru(4) are within σ-bonding distance of C(1) and C(2), respectively [Ru(2)–C(1) 2.06(3), Ru(4)–C(2) 2.13(3) Å], the $\eta^2$ interactions are less well defined. Thus, Ru(3)–C(1,2) distances are 2.27(2)

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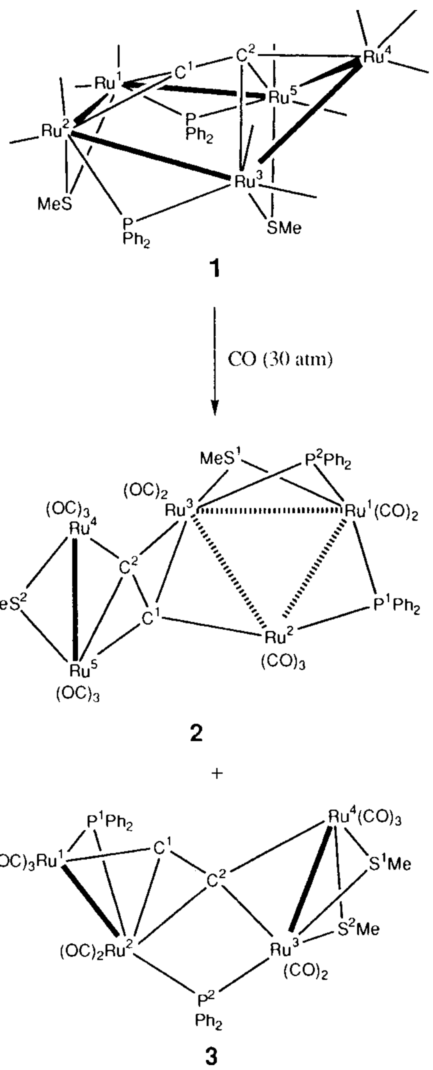
* *Non-SI units employed:* atm = 101 325 Pa, eV ≈ 1.60 × $10^{-19}$ J.



**Scheme 1**

and 2.47(2) Å, while Ru(5)–C(1,2) distances are 2.65(2) and 2.34(3) Å, respectively. The short C(1)–C(2) separation [1.20(4) Å] and the Ru(2)–C(1)–C(2) and Ru(4)–C(2)–C(1) angles [172(2), 155(2)°] are also consistent with there being little π interaction of C(1)–C(2) with Ru(2) and Ru(4).

## Molecular structure of [$Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$] 3

A molecule of complex **3** is depicted in Fig. 2 and selected bond parameters are given in Table 2. Scission of one metal atom from the cluster present in **1** and migration of an SMe group has occurred, with the $C_2$ ligand bridging all four metal atoms. The two carbons in the $C_2$ ligand are separated by 1.239(9) Å. This ligand is σ bonded to Ru(1) [Ru(1)–C(1) 2.027(7) Å], π bonded to Ru(2) [Ru(2)–C(1,2) 2.280(5), 2.499(6) Å] and unsymmetrically bridges Ru(3)–Ru(4) [Ru(3,4)–C(2) 2.325(6), 2.135(6) Å]. The Ru(1)–Ru(2) and Ru(2)···Ru(3) vectors [2.7964(9), 3.571(1) Å, respectively] are bridged by P(1) [Ru(1,2)–P(1) 2.357(2), 2.338(2) Å] and P(2) [Ru(2,3)–P(2) 2.384(2), 2.362(2) Å], while the rather long Ru(3)–Ru(4) bond [3.130(1) Å] is doubly bridged by the two SMe groups [Ru(3,4)–S(1,2) range between 2.420(2) and 2.468(2) Å].

## Theoretical considerations

(*a*) **Compound 2.** Is the $C_2$ ligand acting as a four- or a six-electron donor to the metallic framework in compound **2**? The answer may not be straightforward. Consideration of the electron counts may highlight the structural findings. Application of the effective atomic number formalism leads us to propose two tautomeric forms (**2a** and **2b**). In **2a** the $C_2$ ligand provides only four electrons for the metallic core. Consequently, the $Ru_2$ fragment has only 32 cluster valence electrons and is electron-poor, leading to a formal Ru(4)=Ru(5) double bond, somewhat in agreement with the rather short separation measured in **2**. The $C_2$ ligand acts as a six-electron donor *vis-à-vis* the metallic cluster in **2b**. An Ru(4)–Ru(5) single bond is then formally present in the $Ru_2$ fragment. In both tautomers the $Ru_3$ moiety has a total of 50 cluster valence electrons instead of 48 as generally expected for triangular complexes.

**Table 1** Selected bond lengths (Å) and angles (°) for [$Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}$] **2**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 3.087(4) | Ru(2)–P(1) | 2.401(7) |
| Ru(1)–Ru(3) | 2.956(4) | Ru(3)–P(2) | 2.310(8) |
| Ru(2)–Ru(3) | 3.170(4) | Ru(2)–C(1) | 2.06(3) |
| Ru(4)–Ru(5) | 2.694(6) | Ru(3)–C(1) | 2.27(2) |
| Ru(1)–S(1) | 2.445(8) | Ru(3)–C(2) | 2.47(2) |
| Ru(3)–S(1) | 2.409(7) | Ru(4)–C(2) | 2.13(3) |
| Ru(4)–S(2) | 2.405(9) | Ru(5)–C(1) | 2.65(2) |
| Ru(5)–S(2) | 2.407(7) | Ru(5)–C(2) | 2.34(3) |
| Ru(1)–P(1) | 2.342(7) | C(1)–C(2) | 1.20(4) |
| Ru(1)–P(2) | 2.331(8) | | |
| Ru–CO | range 1.78(3)–1.94(3), average 1.87 | | |
| C–O | range 1.12(4)–1.22(3), average 1.17 | | |
| P–C (Ph) | range 1.70(3)–1.87(3), average 1.84 | | |
| Ru(2)–C(1)–C(2) | 172(2) | Ru(4)–C(2)–C(1) | 155(2) |

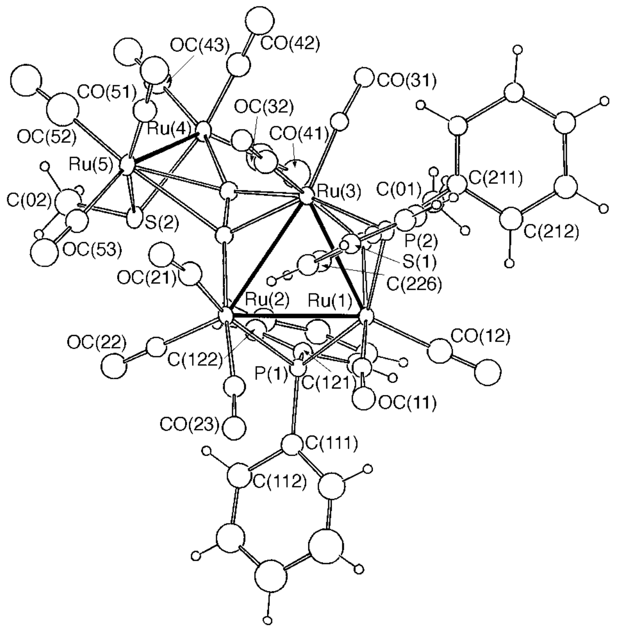
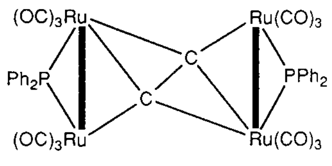


**Fig. 1** Plot of a molecule of [$Ru_5(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{13}$] **2** showing the atom numbering scheme. In both figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å



**4**

Rather than cleaving an Ru–Ru bond, the extra electrons somewhat expand the metallic triangle. This is a characteristic of trinuclear $Ru_3$ clusters containing bridging $PR_2$ ligands, as found, for example, in [$Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)_3(CO)_6$], where the Ru–Ru separations are between 3.084(1) and 3.112(1) Å.[13] Extended-Hückel (EH) calculations have suggested that the extra electrons are accommodated in a metal–metal anti-

**Table 2** Selected bond lengths (Å) and angles (°) for $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.7964(9) | Ru(2)–P(2) | 2.384(2) |
| Ru(2)···Ru(3) | 3.571(1) | Ru(3)–P(2) | 2.362(2) |
| Ru(3)–Ru(4) | 3.130(1) | Ru(1)–C(1) | 2.027(7) |
| Ru(3)–S(1) | 2.468(2) | Ru(2)–C(1) | 2.280(5) |
| Ru(4)–S(1) | 2.420(2) | Ru(2)–C(2) | 2.499(6) |
| Ru(3)–S(2) | 2.445(2) | Ru(3)–C(2) | 2.325(6) |
| Ru(4)–S(2) | 2.425(2) | Ru(4)–C(2) | 2.135(6) |
| Ru(1)–P(1) | 2.357(2) | C(1)–C(2) | 1.239(9) |
| Ru(2)–P(1) | 2.338(2) | | |
| Ru–CO | range 1.837(7)–1.953(9), average 1.906 | | |
| C–O | range 1.10(1)–1.152(8), average 1.124 | | |
| S–Me | 1.815(9), 1.825(7) | | |
| P–C (Ph) | range 1.820–1.838(6), average 1.830 | | |
| Ru(1)–Ru(2)–Ru(3) | 95.06(3) | Ru(2)–Ru(3)–Ru(4) | 77.98(3) |

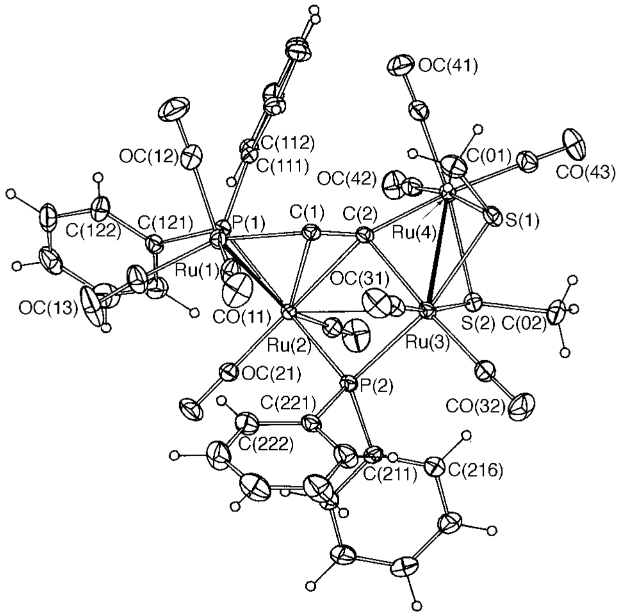
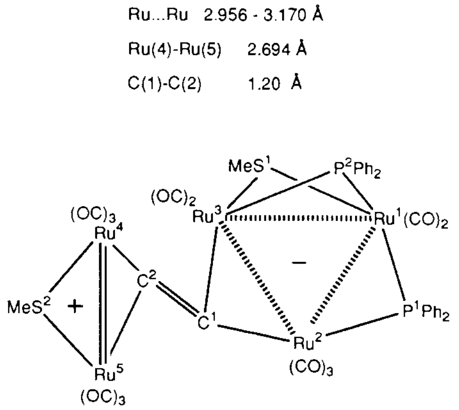


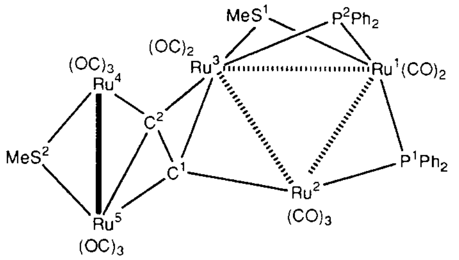
**Fig. 2** Plot of a molecule of $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$ **3** showing the atom numbering scheme

bonding orbital equally delocalised over the three metal atoms and that only two bonding electrons are responsible for the metal–metal bonding, resulting in a formal Ru–Ru bond order of $\frac{1}{3}$ in 50 cluster valence electron clusters of this type.[13] The EH calculations performed on compound **2** agree with this statement (the Ru–Ru overlap populations of *ca.* 0.06 are weak). A large gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO − LUMO) of 1.70 eV is computed in accord with the stability and diamagnetism of the complex, with two additional electrons housed in an Ru–Ru antibonding orbital localised mainly on the $Ru_3$ triangle. In **2** the Ru–Ru separations of the $Ru_3$ fragment differ slightly as a result of the different nature of the bridging ligands. The Ru(1)–Ru(3) vector is bridged by both $PPh_2$ and SMe groups, resulting in a bond about 0.12–0.22 Å shorter than the other two.

According to our EH calculations, the two π and two π* orbitals of the $C_2$ ligand participate in forward and back donation, respectively, towards the metal framework, thus favouring tautomer **2b** for the description of the bonding in **2**. However, their occupation after interaction with the metallic part indicates that the $C_2$ ligand is less involved in the M–C bonding than in other $M_4C_2$ complexes in which the $C_2$ ligand behaves as a six-electron donor.[5] This is reflected in the very strong C(1)–C(2) overlap population (1.77) and rather weak (but bonding) Ru(5)–C(1) (0.06) and Ru(3)–C(2) (0.10). Moreover,



**2a**

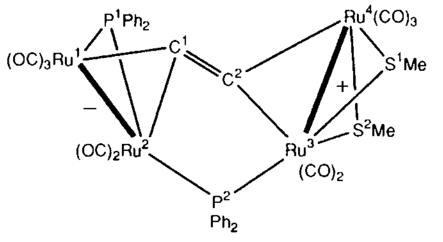


**2b**

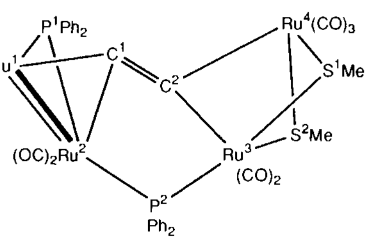
the Ru(4)–Ru(5) overlap population of 0.20 is strong [several Ru–Ru bonding orbitals participate in the Ru(4)–Ru(5) bond], suggesting some multiple-bonding character. These results suggest that tautomer **2a** also contributes to the description of the bonding in **2**. The net charges on the carbon atoms of the $C_2$ unit are slightly negative [−0.24 and −0.27 at C(1) and C(2), respectively], suggesting some nucleophilic character.

**(*b*) Compound 3.** Using the effective atomic number formalism, tautomers **3a**–**3c** can be proposed to account for the bonding in **3** in the light of the atomic separations. In **3a** and **3b** the $C_2$ moiety participates formally as a four-electron donor ligand to the metal core, leading to a 68-cluster valence electron count for **3**, with the other ligands contributing 32 electrons to the metal atoms [20 (10 CO) + 6 (2 $PR_2$) + 6 (2 SR)]. Only two Ru–Ru single bonds in **3a** or one Ru=Ru double bond in **3b** are required for each atom to be electron-precise. In accord with this, the Ru(2)–Ru(3) vector is too long for any significant bonding interaction. Structure **3a** is closely related to that of the complex $[Fe_2Ru_2(\mu_4\text{-}C_2)(CO)_{10}(\eta\text{-}C_5Me_5)_2]$ **5**,[14] of which a theoretical study has also been reported.[5] However, the cluster valence electron count for **3** is 68, compared with 66 for **5**, which has an additional Ru–Ru bond. Note also that the M–C and C–C bonding in tautomer **3a** is closely related to that in the tautomer **2a** proposed for compound **2** above. In tautomer **3c** the $C_2$ ligand acts as a six-electron donor, leading to a formal 70 cluster valence electron count. Only one Ru–Ru bond is then required for each metal atom to be electron-precise.

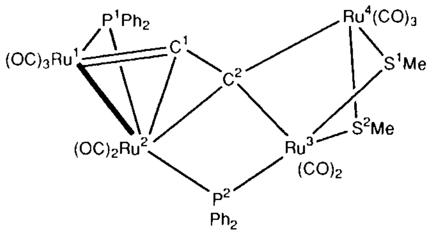
The EH calculations carried out on compound **3** show that, as for **2**, M–C bonding involves the σ orbitals and two π and two π* orbitals of the $C_2$ ligand. A close examination of the M–C overlap populations indicates that C(1) and C(2) are strongly σ bonded to Ru(1) and Ru(4), respectively (the corresponding M–C overlap populations are 0.56 and 0.43). We notice π bonding between Ru(2) and C(1) and between Ru(3) and C(2) (corresponding overlap populations: 0.15 and 0.21), and also a weaker bonding interaction between Ru(2) and C(2) (0.09). The Ru(3)–Ru(4) overlap population is very slightly negative (−0.02), indicating that formally there is no M–M bond between these two metal atoms. Therefore, these results



**3a**



**3b**



**3c**

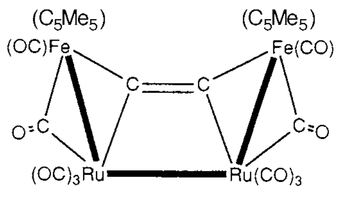
| | |
|---|---|
| Ru(1)-Ru(2) | 2.796 Å |
| Ru(3)-Ru(4) | 3.130 Å |
| C(1)-C(2) | 1.24 Å |

seem to give a strong preference for tautomer **3c**, accounting for the long but bonding Ru(2)–C(2) contact and the long non-bonding Ru(3)···Ru(4) separation. Nevertheless, the magnitude of the forward and back electron donation of $C_2$ with the metallic core, the strong C–C bond (overlap population 1.66) and the strong Ru(1)–Ru(2) overlap population (0.15) which suggests some M–M multiple bond character, all indicate that tautomer **3b** also contributes, to a lesser extent, to the description of the bonding in **3**.

A large energy gap of 1.80 eV separates the metallic HOMO from the Ru(1,2)–C(1) antibonding LUMO. Assuming that the MOs from the HOMO/LUMO regions will control the reactivity of the molecule, we would expect that the carbon atoms of the $C_2$ ligand, particularly C(1), would behave as electrophiles. On the other hand, if the reactions are charge controlled, electrophilic attack on C(1) is likely, as this atom carries more electronic charge than does C(2) (−0.38 *vs.* −0.18). Note that, due to the additional Ru(2)–C(2) bonding contact, electron density is reduced at C(2) compared to that at C(1).

## Discussion

In reactions of cluster **1** there is no interaction between the entering CO and the $C_2$ ligand. Instead, addition to the metal atoms has resulted in the cleavage of Ru–Ru bonds and, in the case of **3**, excision of one of the Ru atoms, presumably as $Ru(CO)_5$. Both molecules have formally electron-rich and electron-poor 'clusters' joined by the $C_2$ ligand. In the case of **2**, two CO ligands have added to give a molecule in which there are one short and three long Ru–Ru bonds, *i.e.* only one Ru–Ru bond in **1** has been formally cleaved. However, the presence of several bridging ligands, notably the polydentate $C_2$ molecule, has resulted in all five metal atoms remaining in the complex, albeit with considerably weakened interactions.



**5**

The role of the $C_2$ ligand in holding together the $Ru_2$ and $Ru_3$ fragments in compound **2** has resulted in quite unusual bonding to the four metal atoms with which it interacts. In $[\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}_2(\mu,\mu\text{-}C_2)]$ **4**, also a 68-electron complex, the Ru–Ru separations are 2.748(1) Å. Recent calculations[5] have suggested that the $C_2$ group in this molecule would contribute only four electrons in a planar $Ru_4C_2$ array. Experimentally a twist in the orientation of the $C_2$ ligand allows a greater π overlap, although the extent of this is limited by steric interactions between the other ligands present. These appear to be responsible for the stability (lack of reactivity) of this complex.[5] The short C–C bond [1.275(0) Å] also reflects this lack of π back bonding. Weak π back bonding is also observed in **2** and **3**, this also being consistent with the short C(1)–C(2) bonds found in these complexes. The situation resembles that found in **4**, for which it has been suggested[5] that these structural data are consistent with contributions from tautomers with C=C and Ru=Ru double bonds (or multiple-bond character in the C–C and Ru–Ru bonds). In contrast, the $Ru_3$ cluster found in **2** is formally electron rich, the 'extra' electrons being in an M–M antibonding orbital, leading to lengthening of all of the Ru–Ru bonds, the doubly bridged Ru(1)–Ru(3) bond being over 2.95 Å, and the other two over 3.0 Å in length.

The present study has shown further the versatility of the $C_2$ ligand in its bonding to metal atoms. It can probably act as a better electron sink than the CO ligand. While addition of CO to the $Bu^tNC$ derivative of **1** resulted in reversible cluster expansion, here we did not observe a similar addition of only one CO molecule: the complexes described above have added two or more CO groups. Calculations on the $C_2$ molecule (or ethynediyl dianion, $C_2^{2-}$) as a ligand have shown that the precise nature of the interactions are better described by MO calculations than by formal valence-bond representations.[5] Studies are continuing to define further the reactivities of the $C_2$ ligand in its various forms.

## Experimental

### Instrumentation

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

### General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up.

### Starting materials

Complex **1** was prepared by the literature method.[4c]

### Reaction of complex 1 with CO

A solution of complex **1** (100 mg, 0.077 mmol) in toluene (15 $cm^3$) was pressurised to 30 atm with CO and heated at 120 °C for 2 h. The solvent was removed and the residue purified by preparative TLC [light petroleum (b.p. 60–80 °C)–acetone, 10 : 3]

**Table 3** Crystal data and refinement details for compounds **2** and **3***

|  | **2** | **3** |
|---|---|---|
| Formula | $C_{41}H_{26}O_{13}P_2Ru_5S_2$ | $C_{38}H_{26}O_{10}P_2Ru_4S_2\cdot 0.5CH_2Cl_2$ |
| $M$ | 1358.1 | 1246.4 |
| $a$/Å | 15.795(8) | 18.948(8) |
| $b$/Å | 15.697(12) | 12.099(3) |
| $c$/Å | 9.914(18) | 10.825(4) |
| α/° | 103.41(11) | 72.27(3) |
| β/° | 94.78(11) | 77.86(3) |
| γ/° | 91.41(5) | 74.28(3) |
| $U$/Å$^3$ | 2380 | 2253 |
| $D_c$/g cm$^{-3}$ | 1.89 | 1.84 |
| $F$(000) | 1316 | 1186 |
| Crystal size mm | 0.12 × 0.03 × 0.33 | 0.20 × 0.50 × 0.38 |
| Minimum, maximum $A$* | 1.12, 1.44 | 1.32, 1.70 |
| μ/cm$^{-1}$ | 17.6 | 14.7 |
| $2\theta_{max}$/° | 40 | 50 |
| $N$ | 4401 | 7490 |
| $N_0$ | 2331 | 6520 |
| $R$ | 0.061 | 0.039 |
| $R'$ | 0.061 | 0.053 |

* Details in common: triclinic, space group $P\bar{1}$ (no. 2); $Z = 2$.

to yield three major bands. A yellow band ($R_f$ 0.60) was recrystallised ($CH_2Cl_2$–MeOH) to yield $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{13}]$ **2** (21 mg, 20%) [Found: C, 37.25; H, 2.2%; $M$, 1359 (mass spectrometry). $C_{41}H_{26}O_{13}P_2Ru_5S_2$ requires C, 36.25; H, 1.9%; $M$, 1359]. IR: ν(CO) (cyclohexane) 2085m, 2072s, 2054s, 2027vs, 2022m, 2010m, 2003s, 2000s, 1992 (sh), 1985w, 1965m and 1959m cm$^{-1}$. $^1$H NMR: δ($CDCl_3$) 1.15 (3 H, s, 3 SMe), 2.27 (3 H, s, SMe) and 6.84–8.03 (20 H, m, Ph). FAB mass spectrum: $m/z$ 1359, $M^+$; 1331–995, $[M - n\text{CO}]^+$ ($n$ = 1–13). A second yellow band ($R_f$ 0.45) was recrystallised ($CH_2Cl_2$–MeOH) to yield $[Ru_4(\mu_4\text{-}C_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(CO)_{10}]$ **3** (17 mg, 19%), m.p. 296–297 °C (decomp.) [Found: C, 38.1; H, 2.4%; $M$, 1174 (mass spectrometry). $C_{38}H_{26}O_{10}P_2Ru_4S_2$ requires C, 38.9; H, 2.25%; $M$, 1174]. IR: ν(CO) (cyclohexane) 2107m, 2063vs, 2049s, 2036s, 2008s, 1998m, 1986m, 1973s, 1950m and 1941 (sh) cm$^{-1}$. $^1$H NMR: δ($CDCl_3$) 2.31 (3 H, s, SMe), 2.33 (3 H, d, $J_{CP}$ = 2.7 Hz, SMe) and 7.05–7.77 (20 H, m, Ph). FAB mass spectrum: $m/z$ 1174, $M^+$; 1146–894, $[M - n\text{CO}]^+$ ($n$ = 1–10). A third red band [$R_f$ 0.55; 8 mg; IR ν(CO) (cyclohexane) 2068m, 2053vs, 2022m, 2004m, 1999m, 1978m, 1969m and 1962w cm$^{-1}$] was not identified.

### Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); $N$ independent reflections were obtained, $N_o$ with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals $R,R'$ on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system[15] implemented by S. R. Hall; neutral atom complex scattering factors were employed. Details are given in Table 3.

**Abnormal features/variations in procedure.** Crystals of compound **2** were small and data limited in scope, supportive of meaningful anisotropic thermal parameter refinement for Ru, S and P only. Difference map residues of **3** were modelled as a $CH_2Cl_2$, refined as a rigid body, site occupancy 0.5 after trial refinement, with C, Cl thermal parameter forms isotropic.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/298.

### EH calculations

All calculations were carried out within the extended-Hückel[16] formalism (using the weighted $H_{ij}$ formula) with the CACAO program.[17] The exponents (ζ) and the valence-shell ionisation potentials ($H_{ii}$ in eV) were respectively: 1.3, −13.6 for H 1s; 1.625, −21.4 for C 2s; 1.625, −11.4 for C 2p; 2.275, −32.3 for O 2s; 2.275, −14.8 for O 2p; 1.6, −18.6 for P 3s; 1.6, −14.0 for P 3p; 1.817, −20.0 for S 3s; 1.817, −13.3 for S 3p; 2.078, −8.6 for Ru 5s; 2.043, −5.1 for Ru 5p. The $H_{ii}$ value for Ru 4d was set equal to −12.2. A linear combination of two Slater-type orbitals of exponents $\zeta_1 = 5.378$ and $\zeta_2 = 2.303$ with the weighting coefficients $c_1 = 0.5340$ and $c_2 = 0.6365$ was used to represent the Ru 4d atomic orbitals. The experimental structures of compounds **2** and **3** were idealised for the calculations. The SR and $PR_2$ groups have been replaced by SH and $PH_2$ groups for the calculations.

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