

# Synthesis of carbido and related derivatives from calcium carbide and ruthenium carbonyl clusters

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Received 6th March 2002, Accepted 25th July 2002

First published as an Advance Article on the web 13th September 2002

Reactions between a carbido anion ( $C_2^{2-}$ ) source and ruthenium cluster carbonyls are reported for the first time. The reaction between  $CaC_2$  and  $Ru_3(CO)_{12}$ , carried out in thf, affords putative  $Ca[Ru_{10}(C)_2(CO)_{24}]$ , which can be converted into  $[ppn]_2[Ru_{10}(C)_2(CO)_{24}]$  (**1**) in overall 60% yield. The X-ray structure of **1** as its  $2CH_2Cl_2$  solvate is described, together with those of the minor products  $Ru_4(\mu_4-HC_2H)_2(\mu-CO)_2(CO)_9$  (**3**),  $Ru_6C(\mu_3-HC_2Me)(CO)_{15}$  (**4**) and  $Ru_4(\mu_4-CHCHCO)(\mu-CO)(CO)_{10}(tmeda)$  (**5**). The latter contains an Ru-spiked  $Ru_3$  core carrying a CHCHCO ligand; the tmeda chelates the spike Ru atom. The only product from  $Ru_3(\mu-dppm)(CO)_{10}$  and  $CaC_2$  is the known compound  $Ru_6(\mu_4-CCH_2)_2(\mu-dppm)_2(CO)_{12}$  (**6**), formed in 24% yield.

## Introduction

The chemistry of metal cluster carbonyls containing carbido ligands has a long history, the first complex,  $Fe_5C(CO)_{15}$ , being discovered *via* an X-ray structural determination in 1962.<sup>1</sup> These interesting compounds have usually been made by pyrolysis of a simpler precursor carbonyl, the source of the carbido atom being shown to be one of the carbonyl groups.<sup>2,3</sup> In the ruthenium system, extensive studies have revealed several intermediate clusters are formed *en route* from  $Ru_3(CO)_{12}$  to  $Ru_6C(CO)_{17}$ .<sup>4</sup> The chemistry of carbido cluster complexes has been reviewed.<sup>5</sup>

Other synthetic routes have been used to make cluster carbides. For example, condensation of anionic Group 9 cluster carbonyls with halocarbon derivatives results in formation of complexes such as  $[Rh_6C(CO)_{15}]^{2-}$ , from  $CCl_4$  and  $[Rh(CO)_4]^-$ ,<sup>6</sup> or  $[Co_6C(CO)_{15}]^{2-}$ , from  $Co_3(\mu_3-CCl)(CO)_9$  and  $[Co(CO)_4]^-$ .<sup>7</sup> Extensive hydrogenation of a ruthenium cluster-bonded ethynyl group has resulted in the addition of up to three H atoms to one carbon of the  $C_2$  fragment, with a consequent decrease in the C–C bond order. In the last stage, cleavage of the C–C bond afforded a carbido complex, the second carbon atom being fully reduced to a methyl group.<sup>8</sup>

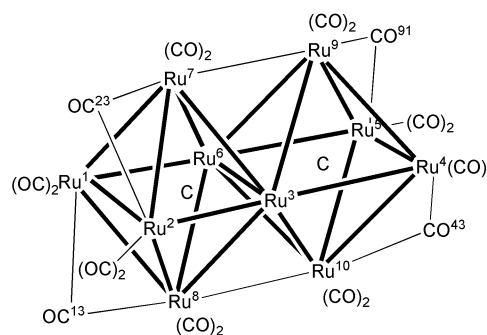
Although several experimental procedures have now been developed to produce carbido clusters in reasonable yield,<sup>9</sup> to the best of our knowledge, there are no reported uses of main group carbides as sources of the carbido carbon atoms. This may be because of (i) the relative difficulties attendant on the production and manipulation of alkali metal acetylides, even though  $Li_2C_2 \cdot en$  is available commercially, or (ii) reports that in reactions with metal carbonyl halides, the acetylides tend to act as one-electron reducing agents. For example, the reaction of  $MnBr(CO)_5$  with  $CaC_2$  is reported to give  $Mn_2(CO)_{10}$ , while  $Fe_3(CO)_{12}$  and  $Co_4(CO)_{12}$  give  $[Fe_3(\mu-H)(CO)_{11}]^-$  and  $[Co_6(CO)_{14}]^{4-}$ , respectively.<sup>10</sup> In addition,  $\{Re(CO)_5\}_2(\mu-C \equiv C)$  cannot be prepared from  $Re(FBF_3)(CO)_5$  and  $Li_2C_2$  or  $Na_2C_2$ .<sup>11</sup> Also relevant is the use of calcium carbide to form transition metal carbides *via* metathesis reactions with halides or oxides in the solid state, which has been reported recently.<sup>12</sup>

We have found that calcium carbide is a useful reagent for the preparation of the anionic dicarbido cluster  $[Ru_{10}(C)_2-$

$(CO)_{24}]^{2-}$ , which was first described in 1982 as the product from thermolysis (210–230 °C, 80 h) of  $[Ru_6C(CO)_{16}]^{2-}$  in refluxing tetraglyme.<sup>13</sup> Several other products have been isolated from the reaction mixture, but these are formed in low yields and probably result from reactions of various cluster complexes with ethyne formed from the calcium carbide reacting with adventitious water.

## Results and discussion

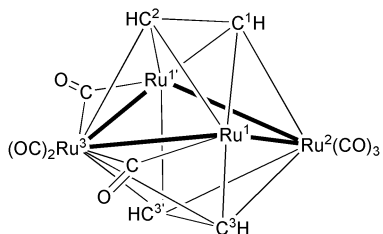
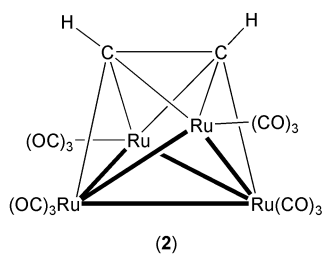
When a 30-fold excess of solid calcium carbide (which is approximately 80% pure) is added to a solution of  $Ru_3(CO)_{12}$  in thf and the mixture heated overnight, a dark-coloured solution containing solid material is obtained. Removal of solvent and filtration of an acetone extract of the residue into a solution of  $[ppn]Cl$  in  $CH_2Cl_2$  produces a dark purple solution, from which the salt  $[ppn]_2[Ru_{10}(C)_2(CO)_{24}]$  (**1**) can be isolated in 60% yield. We have not yet characterised any complexes from the solid; based on the formulation  $Ca[Ru_{10}C_2(CO)_{24}]$ , the yield is *ca.* 70%. The  $\nu(CO)$  band frequencies in the IR spectrum are similar to those reported earlier, while the  $^{13}C$  resonances of the CO groups are found between  $\delta$  185 and 205 as five singlets, the interstitial carbide giving a singlet at  $\delta$  456.89 (*cf.*  $\delta$  456 in the  $[NEt_4]^+$  salt). In the electrospray (ES) mass spectrum, the doubly-charged parent anion is found at  $m/z$  855.



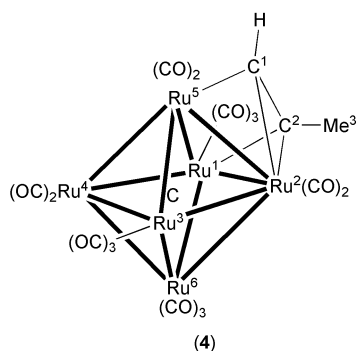
(1) CO groups on Ru(3,6) omitted for clarity

While the formation of **1** can result from thermolysis of smaller ruthenium cluster carbides, we showed independently that heating  $\text{Ru}_3(\text{CO})_{12}$  in thf overnight does not result in any cluster condensation. Consequently, the formation of **1** is a direct result of the interaction of  $\text{CaC}_2$  with the carbonyl, an interesting and unusual cleavage of the  $\text{C}_2^{2-}$  anion taking place. Complex **1** was originally obtained by extended thermolysis of the mono-carbido cluster  $[\text{NET}_4]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ ; it was noted that the yield was dependent on the counter cation, only decomposition resulting when Na,  $[\text{ppn}]^+$  or  $[\text{NET}_3(\text{CH}_2\text{Ph})]^+$  were used.<sup>13</sup> Fusion of two  $\text{Ru}_6$  clusters with concomitant elimination of two  $\text{Ru}(\text{CO})_n$  fragments [or one  $\text{Ru}_2(\text{CO})_n$  fragment] had occurred.

With a similar experiment carried out with only a 10-fold excess of  $\text{CaC}_2$ , the mother liquor from the separation of **1** was evaporated and the residue extracted with dichloromethane. Preparative t.l.c. enabled separation of several minor components, three of which have been purified and characterised initially by single-crystal X-ray crystallography as  $\text{Ru}_4(\mu_4\text{-HC}_2\text{-H})(\text{CO})_{12}$  (**2**),  $\text{Ru}_4(\mu_4\text{-HC}_2\text{H})_2(\mu\text{-CO})_2(\text{CO})_9$  (**3**) and  $\text{Ru}_6\text{C}(\mu_3\text{-HC}_2\text{Me})(\text{CO})_{15}$  (**4**). Subsequent assignments of their spectra (IR, NMR, ES MS) on the bases of their solid-state structures are discussed below. Complex **2** has been described before<sup>14</sup> and **3** is the prototype for a series of substituted complexes  $\text{M}_4(\mu_4\text{-RC}_2\text{R}')_2(\text{CO})_{11}$  ( $\text{M} = \text{Fe}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Et}$ ;  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{Me}$ ,  $\text{Ph}$ ) which have been reported earlier and which contain two alkyne molecules attached to opposite sides of a buckled  $\text{M}_4$  rhomb.<sup>15</sup> It was characterised only by a single-crystal X-ray structural determination, while the pattern of  $\nu(\text{CO})$  peaks in its IR spectrum is similar to those reported for the substituted analogues.

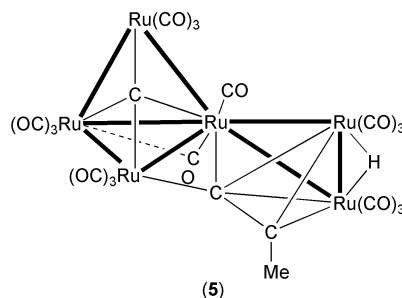


(3) CO groups on Ru(1,1') omitted for clarity

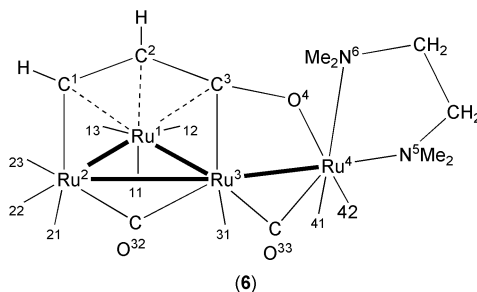


Complex **4** is a simple  $\mu_3$ -propyne complex of the hexanuclear carbido carbonyl  $\text{Ru}_6\text{C}(\text{CO})_{17}$ . A range of analogous complexes, including the but-2-yne complex, has been described by others.<sup>16,17</sup> In **4**, the propyne ligand is attached in the usual

$\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$  mode to one triangular face of the octahedral  $\text{Ru}_6\text{C}$  cluster, with bond parameters similar to those found for the but-2-yne analogue.<sup>16</sup> All the CO ligands are terminal, as found in the solid-state structure, and give rise to  $\nu(\text{CO})$  bands between 2088 and 1982  $\text{cm}^{-1}$  in the IR spectrum. In the  $^1\text{H}$  NMR spectrum, the Me and H protons of the alkyne resonate at  $\delta$  1.67 and 6.97, respectively. We have described in an earlier account the formation of  $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$  (**5**) during the reaction between  $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$  and ethyne.<sup>18</sup> Disproportionation of two molecules of  $\text{C}_2\text{H}_2$  to give a carbide and propyne ligands occurred, and we suggest that a similar reaction takes place here.



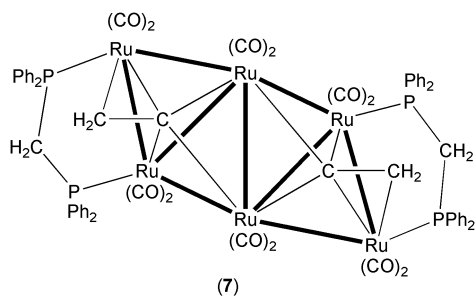
In an effort to facilitate the initial reaction between  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{CaC}_2$ , we added some tetramethyldiaminoethane (tmeda) to the reaction mixture, hoping that the calcium cations would be complexed by the diamine. As described in the Experimental section, little change was observed in the formation of **1**, but among the minor products, the cluster  $\text{Ru}_4(\mu_4\text{-CHCHCO})(\mu\text{-CO})(\text{CO})_{10}(\text{tmeda})$  (**6**) was characterised. We believe this to be the first example of a ruthenium cluster containing the tmeda ligand.



The molecular structure of **6** is based on an Ru-spiked  $\text{Ru}_3$  triangle, which carries a  $\text{CHCHCO}$  ligand, formed by combination of a CO ligand with an ethyne molecule (again, presumably formed from the  $\text{CaC}_2$ ). The chelating tmeda ligand is attached to the Ru spike. Complex **6** contains the familiar allylic ligand  $\text{CHCHCO}^-$  which is closely related to that found in  $\text{Ru}_3(\mu\text{-H})\{\mu_3\text{-CHCHC}(\text{OH})\}(\text{CO})_8(\text{PPh}_3)_3$ .<sup>19</sup> In the reactions which lead to **6**, deprotonation of the hydroxy group has occurred and the resulting anion has become attached to the fourth Ru atom. The origin of the latter is not clear at this stage—one possibility is that an intermediate mononuclear species, such as  $\text{Ru}(\text{CO})_3(\text{tmeda})$ , may be formed. The proximity of the fourth Ru atom results in Ru–Ru bond formation, giving the spiked cluster. The new bond is bridged by one CO group, which gives rise to the  $\nu(\text{CO})$  band found at 1864  $\text{cm}^{-1}$  in the IR spectrum. In the  $^1\text{H}$  NMR spectrum, the two protons on the  $\text{CHCHCO}$  ligand give two doublets at  $\delta$  6.28 and 7.85, while those of the tmeda ligand occur at  $\delta$  3.14 ( $\text{CH}_2$ ), and 2.37 and 2.60 (Me). Surprisingly, the oxo anion has not attacked a CO, as found in the formation of  $\text{Au}_3\text{Ru}_3\{\mu_3\text{-OC}(\text{O})\text{CPh}_2\text{CHC}\}(\text{CO})_8(\text{PPh}_3)_3$ .<sup>20</sup>

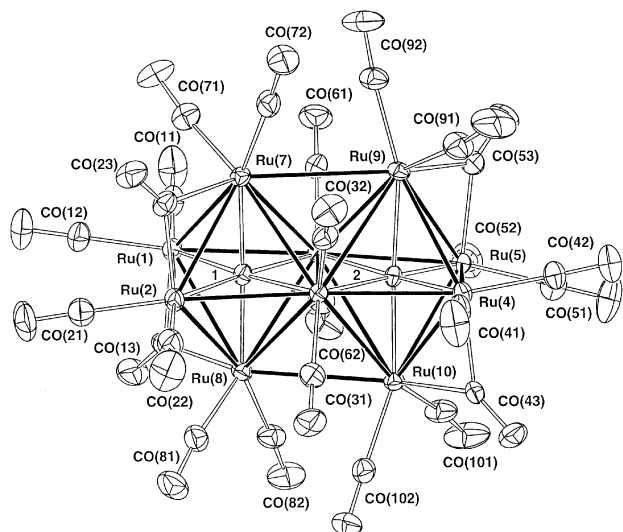
We have also examined the reaction between  $\text{CaC}_2$  and  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ , which often affords products different in structure from those obtained from the parent carbonyl. In this

instance, the sole product that we have been able to characterise is the hexanuclear vinylidene cluster  $\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\mu\text{-dppm})_2(\text{CO})_{12}$  (**7**), isolated in only 18–24% yield, which we earlier obtained serendipitously and characterised as the benzene solvate from the reaction of  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{SiMe}_3)(\mu\text{-dppm})(\text{CO})_7$  with KF in MeOH.<sup>21</sup> The present structure determination was carried out with a mixed  $\text{CHCl}_3\text{-MeCN}$  solvate, which showed considerable disorder (see Experimental section).

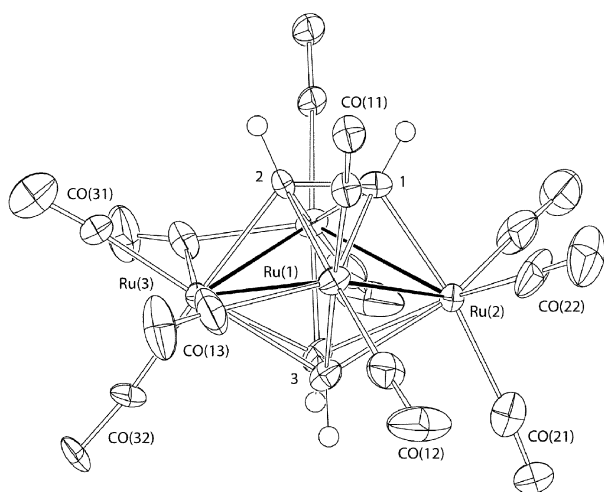


### Molecular structures

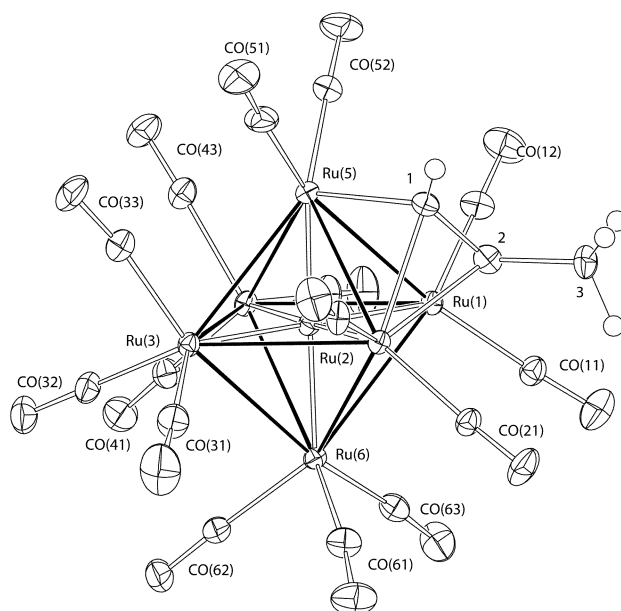
Fig. 1–4 contain plots of the cation of **1** and molecules of **3**, **4** and **6**, respectively; significant bond parameters are given in Tables 1–4.



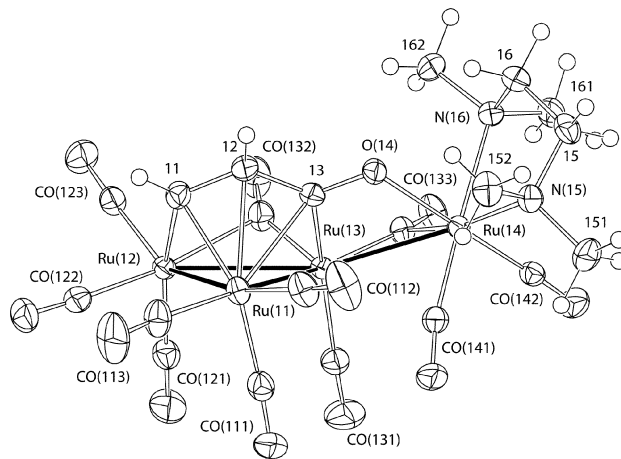
**Fig. 1** Plot of the anion in  $[\text{ppn}]_2[\text{Ru}_{10}(\text{C})_2(\text{CO})_{24}]$  (**1**), showing atom numbering scheme.



**Fig. 2** Plot of a molecule of  $\text{Ru}_4(\mu_4\text{-HC}_2\text{H})_2(\mu\text{-CO})_2(\text{CO})_9$  (**3**). A crystallographic mirror plane passes through Ru(2,3) and carbonyls 21, 31, 32 and the C(1,2) alkyne group.



**Fig. 3** Plot of a molecule of  $\text{Ru}_6\text{C}(\mu_3\text{-HC}_2\text{Me})(\text{CO})_{15}$  (**4**).



**Fig. 4** Plot of molecule 1 of  $\text{Ru}_4(\mu_4\text{-CHCHCO})(\mu\text{-CO})(\text{CO})_{10}(\text{tmeda})$  (**6**).

**Table 1** Selected bond distances (Å) for  $[\text{ppn}]_2[\text{Ru}_{10}(\text{C})_2(\mu\text{-CO})_4(\text{CO})_{20}]$  (**1**)<sup>a</sup>

Ru(1)–Ru(2)	2.9575(6)	Ru(4)–Ru(10)	2.8117(6)
Ru(4)–Ru(5)	2.9659(5)	Ru(5)–Ru(9)	2.8126(6)
Ru(3)–Ru(6)	2.8670(5)	Ru(3)–Ru(7)	2.8350(5)
Ru(1)–Ru(6)	2.9047(5)	Ru(3)–Ru(10)	2.8511(6)
Ru(2)–Ru(3)	2.8962(5)	Ru(6)–Ru(8)	2.8246(6)
Ru(3)–Ru(4)	2.8813(5)	Ru(6)–Ru(9)	2.8231(6)
Ru(5)–Ru(6)	2.9023(5)	Ru(3)–Ru(8)	3.1228(6)
Ru(1)–Ru(7)	2.9537(6)	Ru(3)–Ru(9)	3.1152(6)
Ru(2)–Ru(8)	3.0081(6)	Ru(6)–Ru(7)	3.0888(6)
Ru(4)–Ru(9)	2.9712(6)	Ru(6)–Ru(10)	3.1472(6)
Ru(5)–Ru(10)	2.9526(6)	Ru(7)–Ru(9)	3.2279(5)
Ru(1)–Ru(8)	2.8198(6)	Ru(8)–Ru(10)	3.1020(5)
Ru(2)–Ru(7)	2.8353(6)		

<sup>a</sup> Ru–Ru bond distances have been grouped by type. Ru–C distances 2.025–2.102(5); C(1)–C(2) 3.015(5) Å.

In the structure of the anion in  $[\text{ppn}]_2[\mathbf{1}]$ , very similar to but more precisely defined than that found in  $[\text{NEt}_4]_2[\text{Ru}_{10}(\text{C})_2(\text{CO})_{24}]$  ( $[\text{NEt}_4]_2[\mathbf{1}]$ ),<sup>13</sup> the core comprises two octahedra sharing an edge, one carbido atom being encapsulated in each. The Ru–Ru separations form several sets. The shortest are those bridged by CO ligands [2.8117–2.8353(6) Å], while Ru(3)–Ru(6), at 2.8670(5) Å, is shared between the octahedra. Of the non-bridged Ru–Ru vectors, those on the outside of the cluster

are longer [2.9526–3.0081(6) Å] than the inner Ru(eq)–Ru(eq) separations [2.8813–2.9047(6) Å]. Several Ru–Ru distances are longer than 3 Å, ranging from Ru(2)–Ru(8) [3.0081(6) Å] to Ru(6)–Ru(10) [3.1472(6) Å], while the separations between the two pairs of apical Ru atoms are of the same order [Ru(7)–Ru(9) 3.2279(5), Ru(8)–Ru(10) 3.1020(5) Å]. Of some interest are the diagonal Ru(ap)–Ru(eq) distances involving atoms Ru(3,6); both atoms are involved in short [2.8231–2.8511(6) Å] and long interactions [3.1152–3.1472(6) Å], resulting in a twist being imparted to the bioctahedral cluster [torsion angles Ru(1,2,4,5) and Ru(2,1,5,4) –8.13 and –8.09(2)°]. The C(1) ··· C(2) separation is 3.015(5) Å. The two [ppn]<sup>+</sup> cations are bent, with N–P distances of 1.569–1.586(5) Å; P–N–P 141.7, 143.1(3)°.

Several reactions of **1** with unsaturated hydrocarbons have given derivatives in which the apical Ru atoms are considered to be either bonded or non-bonded.<sup>13,22</sup> This feature has been discussed previously in terms of the cluster valence electron (c.v.e.) count for this anion (138 c.v.e.) and the occupation of both bonding and anti-bonding MOs as the HOMOs.<sup>13,22</sup> This c.v.e. count arises from the presence of two edge-sharing octahedra, for which the Mingos procedure<sup>23</sup> gives 2 × 86 (Ru<sub>6</sub> octahedra) – 34 (Ru<sub>2</sub> edge) = 138 c.v.e. It seems to us that there is a continuum of Ru–Ru bonding interactions in all these complexes, the relative separations of the bonding and

anti-bonding orbitals being determined by the electron density within the cluster, which is, in turn, determined by the nature of the other ligands present.

Of interest is the presence of two C atoms within the cluster, rather than the initial C<sub>2</sub> species present in the CaC<sub>2</sub> precursor. In closely related Group 9 carbido clusters, the presence of C or C<sub>2</sub> ligands has been related to the size of the cluster, the latter required a (larger) trigonal prismatic cavity.<sup>24</sup> However, the final geometry is not a simple consequence of electron count. In the isoelectronic [Rh<sub>12</sub>(C)<sub>2</sub>(CO)<sub>24</sub>]<sup>2–25</sup> and Rh<sub>12</sub>(C<sub>2</sub>)(CO)<sub>25</sub><sup>26</sup> clusters, different cluster geometries are adopted as a result of 2e in the former being replaced by the sterically more demanding CO ligand in the neutral complex. In the present case, the more electron-rich Ru atoms result in octahedral cavities being formed, with resulting cleavage of the C–C bond. Further discussion of the electronic structures of these and related complexes is deferred until DFT studies have been completed.

The molecule of **3** has a crystallographic plane of symmetry passing through Ru(2,3)C(21,31,32) and the midpoint of the C(3)–C(3') vector. The four Ru atoms form a rhomb bent along the Ru(1) ··· Ru(1') vector, with two different bonded Ru–Ru distances: Ru(1)–Ru(2) [2.834(1) Å] and Ru(1)–Ru(3), bridged by CO(13) [2.773(1) Å]. Angles subtended at one Ru atom by the others are 85.25–87.57(5)°. The two ethyne molecules lie on opposite sides of the Ru<sub>4</sub> core, each being attached by two σ [Ru(1)–C(3) 2.14(2), Ru(3)–C(2) 2.14(2) Å] and two π [Ru–C 2.27–2.31(1) Å] bonds, the differences arising because only Ru(2) is not attached to a μ-CO ligand. The C(1)–C(2) separation is 1.39(3) Å. Unlike previous structurally characterised examples which contain only one,<sup>15</sup> **3** contains two bridging CO ligands. This cluster contains 62 c.v.e.

For **4**, the octahedral Ru<sub>6</sub>C cluster has Ru–Ru separations [2.9088–2.9905(4) Å] in the non-alkyne bridged faces and internal Ru–C(carbide) distances [2.028–2.069(4), av. 2.05(1) Å] which are similar to those found in the parent cluster<sup>27</sup> and the but-2-yne analogue.<sup>16</sup> The Ru<sub>3</sub> face [Ru(1,2,5)] supporting the alkyne is slightly contracted [Ru–Ru 2.7718–2.8532(4) Å], as is the opposite face [Ru(3,4,6): Ru–Ru 2.8547–2.8943(4) Å]. The Ru–C(alkyne) distances [Ru(1)–C(2) 2.059(4), Ru(5)–C(1) 2.046(4); Ru(2)–C(1,2) 2.189, 2.217(4) Å] are similar to those found in Ru<sub>3</sub>(μ<sub>3</sub>-HC<sub>2</sub>Me)(μ-CO)(CO)<sub>9</sub> and related Ru<sub>6</sub>C clusters containing μ<sub>3</sub>-alkynes. The C(1)–C(2) separation is 1.400(6) Å and the bend-back angle for the Me substituent is 56.0(3)°. All CO groups are terminal, a configuration that is preserved in solution.

Comparison of the structure of **6** with that of Ru<sub>3</sub>(μ-H)-{μ<sub>3</sub>-CHCHC(OH)}(CO)<sub>8</sub>(PPh<sub>3</sub>) (**8**)<sup>18</sup> shows similar Ru–Ru separations in the Ru<sub>3</sub> triangle, with the exception of Ru(2)–Ru(3) [2.8910, 2.8627(2) Å; values for molecules 1, 2 given], which here is bridged by CO rather than by H as in **8**. The Ru(3)–Ru(4) distance is 2.8259, 2.8111(3) Å, and this vector is bridged both by an η<sup>1</sup>-CO ligand and by the η<sup>2</sup>(C,O)-CO portion of the CHCHCO ligand [Ru(3)–C(3) 2.030, 2.027(2), Ru(4)–O(4) 2.075, 2.073(2) Å]. The tmeda ligand chelates

**Table 2** Selected bond distances (Å) and angles (°) for Ru<sub>4</sub>(μ<sub>4</sub>-HC<sub>2</sub>-H)<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>9</sub> (**3**)<sup>a</sup>

Ru(1)–Ru(2)	2.834(1)	Ru(2)–C(1)	2.11(2)
Ru(1)–Ru(3)	2.773(1)	Ru(2)–C(3)	2.31(1)
Ru(1)–Ru(1')	3.838(1)	Ru(3)–C(2)	2.14(2)
Ru(2)–Ru(3)	3.843(1)	Ru(3)–C(3)	2.28(1)
Ru(1)–C(1)	2.31(1)	C(1)–C(2)	1.39(3)
Ru(1)–C(2)	2.27(1)	C(3)–C(3')	1.37(2)
Ru(1)–C(3)	2.14(1)		
Ru(2)–Ru(1)–Ru(3)	86.53(4)	Ru(2)–C(1)–C(2)	125(1)
Ru(1)–Ru(2)–Ru(1')	85.25(5)	Ru(3)–C(2)–C(1)	126(1)
Ru(1)–Ru(3)–Ru(1')	87.57(5)	Ru(1)–C(3)–C(3')	125.2(9)

<sup>a</sup> Primed atoms are related by the intramolecular plane.

**Table 3** Selected bond distances (Å) for Ru<sub>6</sub>C(μ<sub>3</sub>-HC<sub>2</sub>Me)(CO)<sub>15</sub> (**4**)<sup>a</sup>

Ru(1)–Ru(2)	2.8056(4)	Ru(2)–Ru(3)	2.9699(4)
Ru(1)–Ru(5)	2.8532(4)	Ru(1)–Ru(4)	2.9340(4)
Ru(2)–Ru(5)	2.7718(4)		
Ru(1)–Ru(6)	2.9423(4)	Ru(1)–C(2)	2.059(4)
Ru(2)–Ru(6)	2.9293(4)	Ru(2)–C(1)	2.189(4)
Ru(3)–Ru(5)	2.9088(5)	Ru(2)–C(2)	2.217(4)
Ru(4)–Ru(5)	2.9905(4)	Ru(5)–C(1)	2.046(4)
Ru(3)–Ru(4)	2.8943(4)		
Ru(3)–Ru(6)	2.8547(4)	C(1)–C(2)	1.400(6)
Ru(4)–Ru(6)	2.8882(4)	C(2)–C(3)	1.505(6)

<sup>a</sup> Ru–C(carbide) 2.028–2.069(4), av. 2.05(1) Å. C(1)–C(2)–C(3) 124.0(3)°.

**Table 4** Selected bond parameters for Ru<sub>4</sub>(μ<sub>4</sub>-CHCHCO)(μ-CO)(CO)<sub>10</sub>(tmeda) (**6**; values for molecules 1, 2)

Ru(1)–Ru(2)	2.7699, 2.7656(3)	Ru(4)–O(4)	2.075, 2.073(2)
Ru(1)–Ru(3)	2.8613, 2.8702(3)	Ru(4)–N(5)	2.232, 2.230(2)
Ru(2)–Ru(3)	2.8910, 2.8627(2)	Ru(4)–N(6)	2.247, 2.250(2)
Ru(3)–Ru(4)	2.8259, 2.8111(3)		
		C(1)–C(2)	1.401, 1.401(3)
Ru(1)–C(1)	2.224, 2.235(2)	C(2)–C(3)	1.431, 1.435(3)
Ru(1)–C(2)	2.273, 2.286(2)	C(3)–O(4)	1.319, 1.312(2)
Ru(1)–C(3)	2.387, 2.383(2)	C(5)–N(5)	1.490, 1.487(3)
Ru(2)–C(1)	2.069, 2.089(3)	C(5)–C(6)	1.503, 1.499(3)
Ru(3)–C(3)	2.030, 2.027(3)	C(6)–N(6)	1.493, 1.483(3)
C(1)–C(2)–C(3)	120.4, 119.8(3)	C(3)–O(4)–Ru(4)	107.5, 107.9(1)
C(2)–C(3)–O(4)	119.2, 119.8(2)	N(5)–Ru(4)–N(6)	81.11, 81.68(7)

Ru(4), with Ru(4)–N(5,6) 2.232, 2.230; 2.247, 2.250(2) Å and an N(5)–Ru(4)–N(6) bite angle of 81.11, 81.68(7)°. The N atoms are *trans* to the Ru–Ru bond and to CO(41) and the *tmeda* takes up an envelope conformation. The geometry of the CHCHCO fragment is similar to that found in **8**, with C(1)–C(2) 1.401, 1.401(3), C(2)–C(3) 1.431, 1.435(3) and C(3)–O(4) 1.319, 1.312(2) Å; the angles C(1)–C(2)–C(3) and C(2)–C(3)–O(4) are 120.4, 119.8(3) and 119.2, 119.8(2)°, respectively. Normal  $\sigma$  [Ru(2)–C(1) 2.069, 2.089(3); Ru(3)–C(3) 2.030, 2.027(2) Å] and  $\pi$  bonds [Ru(1)–C(1,2,3) 2.224–2.387(2) Å] are found to the Ru<sub>3</sub> triangle.

## Conclusion

We have shown for the first time that it is possible to use calcium carbide as a source of carbido carbons in ruthenium clusters, the major product from its reaction with Ru<sub>3</sub>(CO)<sub>12</sub> being the decanuclear dicarbido anion [Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>]<sup>2-</sup>. An unusual feature of this reaction is the cleavage of the C<sub>2</sub><sup>2-</sup> anion present in crystalline CaC<sub>2</sub>. Some minor products have also been characterised: these contain ethyne or derived ligands and we are inclined to suggest that these complexes are formed from traces of ethyne present in the reaction mixture, possibly generated by the reaction of CaC<sub>2</sub> with water or another proton source.

## Experimental

### General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by Chemical and Micro-analytical Services p/l, Melbourne. Preparative t.l.c. was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF<sub>254</sub>, 0.5 mm thickness).

### Instrumentation

IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (<sup>1</sup>H at 300.13 MHz, <sup>13</sup>C at 75.47 MHz) or Varian Gemini 200 (<sup>1</sup>H at 199.8 MHz, <sup>13</sup>C at 50.29 MHz) spectrometers. Unless otherwise stated, spectra were recorded using solutions in CDCl<sub>3</sub> in 5 mm sample tubes. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required.<sup>28</sup>

### Reagents

Ru<sub>3</sub>(CO)<sub>12</sub><sup>29</sup> and Ru<sub>3</sub>( $\mu$ -dppm)(CO)<sub>10</sub><sup>30</sup> were prepared according to the cited methods. CaC<sub>2</sub> (Aldrich) was a commercial sample, used as received. It appeared to be about 80% pure, the major impurity being Ca(OH)<sub>2</sub>.

### Reactions of CaC<sub>2</sub>

(a) **With Ru<sub>3</sub>(CO)<sub>12</sub>**. A suspension of Ru<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.16 mmol) and CaC<sub>2</sub> (100 mg, 1.6 mmol) in thf (20 ml) was heated at reflux point overnight to give a brown solution above a dark coloured precipitate. After removal of solvent (rotary evaporator), the residue was extracted separately with CH<sub>2</sub>Cl<sub>2</sub> (fraction A) and acetone (fraction B). Fraction A was separated by preparative t.l.c. (hexane–acetone 7:3) to give several coloured bands: (a) a brown band (*R<sub>f</sub>* 0.74) contained Ru<sub>6</sub>C-( $\mu_3$ -HC<sub>2</sub>Me)(CO)<sub>15</sub> (**4**) (2.3 mg, 2.7%), isolated as dark red crystals (from CH<sub>2</sub>Cl<sub>2</sub>–MeOH). IR (cyclohexane):  $\nu$ (CO) 2088w, 2062vw, 2043s, 2057m, 2022m, 2015m, 1994vw, 1982vw cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.67 (s, 3H, Me), 6.97 (s, 1H, CH); (b) a red band (*R<sub>f</sub>* 0.71) yielded Ru<sub>4</sub>( $\mu_4$ -HC<sub>2</sub>H)(CO)<sub>12</sub> (**2**)

(4.8 mg, 5.3%), identified by comparison [IR  $\nu$ (CO)] with an authentic sample; (c) a yellow band (*R<sub>f</sub>* 0.68) contained Ru<sub>4</sub>( $\mu_4$ -HC<sub>2</sub>H)<sub>2</sub>( $\mu$ -CO)<sub>2</sub>(CO)<sub>9</sub> (**3**) (1.1 mg, 1.0%), obtained as dark yellow crystals (from CH<sub>2</sub>Cl<sub>2</sub>–pentane), identified by single-crystal X-ray diffractometry. IR (cyclohexane):  $\nu$ (CO) 2093w, 2063m, 2040s, 2030vs, 2019 (sh), 1985m, 1954vw, 1848w (br) cm<sup>-1</sup>.

Fraction B was also purified by t.l.c. (acetone–hexane 2:1) to give a dark purple band (*R<sub>f</sub>* 0.33), probably containing [Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>]<sup>2-</sup> as its solvated Ca<sup>2+</sup> salt (43 mg). IR (thf):  $\nu$ (CO) 2049vw, 2004vs, 1960w, 1930w cm<sup>-1</sup>. The compound is moderately stable in air, both in solution and as a solid. It was further characterised by conversion to the [ppn]<sup>+</sup> salt by dissolving 20 mg in acetone (5 ml) and adding [ppn]Cl (1.4 mg, 0.025 mmol). After stirring at r.t. for 30 min, evaporation and extraction of the residue with CH<sub>2</sub>Cl<sub>2</sub> and further purification by preparative t.l.c. (acetone–hexane 2:1) gave [ppn]<sub>2</sub>[Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>] (**1**) (27 mg, 84%) as dark purple crystals (from CH<sub>2</sub>Cl<sub>2</sub>–MeOH). Anal. found: C, 42.30; H, 2.04; N, 0.97; C<sub>98</sub>H<sub>60</sub>N<sub>2</sub>O<sub>24</sub>P<sub>4</sub>Ru<sub>10</sub> calc.: C, 42.28; H, 2.17; N, 1.01%. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 2055vw, 2003vs, 1960w, 1927w, 1783m (br) cm<sup>-1</sup> [*cf.* 2046w, 2003vs, 1962w (sh), 1922w (sh), 1798m cm<sup>-1</sup> (thf)<sup>13g</sup>]. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.24–7.623 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  125.91–133.59 (m, Ph), 185.40, 193.97, 202.36, 203.38, 205.29 (5 × s, CO), 456.89 (s, C). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  22.33 (s, PPh<sub>3</sub>). ES MS (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, positive ion, *m/z*): 538, [ppn]<sup>+</sup>; (negative ion, *m/z*): 855, [Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>24</sub>]<sup>2-</sup> (isotopic peaks separated by 0.5 units).

A later experiment was carried out using Ru<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.16 mmol) and CaC<sub>2</sub> (300 mg, 4.7 mmol) in thf (20 ml) as above, to give a dark brown solution over a dark coloured precipitate. The thf solution gave Ca[Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>] (9 mg), while extraction of the precipitate with acetone gave the same compound (46 mg). The combined product was dissolved in acetone (5 ml) and [ppn]Cl (43 mg, 0.075 mmol) was added. After 30 min at r.t., evaporation and crystallisation of the residue (CH<sub>2</sub>Cl<sub>2</sub>–MeOH) gave [ppn]<sub>2</sub>[Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>] (**1**) (75 mg, 57%) as dark purple crystals.

(b) **With Ru<sub>3</sub>(CO)<sub>12</sub> and *tmeda***. A similar reaction was carried out between Ru<sub>3</sub>(CO)<sub>12</sub> (150 mg, 0.24 mmol) and CaC<sub>2</sub> (150 mg, 2.4 mmol) in thf (20 ml) containing *tmeda* (6 drops, ~40 mg). After removal of solvent, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (fraction A) and acetone (fraction B). Separation of fraction A by preparative t.l.c. (acetone–hexane 2:1) gave a major red band (*R<sub>f</sub>* 0.63) from which dark red crystals of Ru<sub>4</sub>( $\mu_4$ -CHCHCO)-(CO)<sub>11</sub>(*tmeda*) (**6**) (26 mg, 16.7%) were isolated. Anal. found: C, 27.11; H, 2.09; N, 3.25; C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>12</sub>Ru<sub>4</sub> calc.: C, 27.75; H, 2.06; N, 3.17%. IR (cyclohexane):  $\nu$ (CO) 2075m, 2032s, 2022vs, 2007w, 1998w (br), 1993w (br), 1972w, 1959w, 1949w, 1864w (br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.37, 2.60 (2 × s, 2 × 6H, Me), 3.14 (m, 4H, CH<sub>2</sub>), 6.28 [d, *J*(HH) 6.9, 1H, CH], 7.85 [d, *J*(HH) 6.9 Hz, 1 H, CH]. Other bands were separated but not identified.

Fraction B was purified by preparative t.l.c. (as above) to give putative Ca[Ru<sub>10</sub>(C)<sub>2</sub>(CO)<sub>24</sub>] (41 mg, 33%).

(c) **With Ru<sub>3</sub>( $\mu$ -dppm)(CO)<sub>10</sub>**. *Tmeda* (6 drops) was added to a suspension of Ru<sub>3</sub>( $\mu$ -dppm)(CO)<sub>10</sub> (100 mg, 0.1 mmol) and CaC<sub>2</sub> (64 mg, 1 mmol) in thf (10 ml). The mixture was heated at reflux point overnight, after which the solvent was removed and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Separation by preparative t.l.c. (acetone–hexane 3:7) afforded dark red Ru<sub>6</sub>( $\mu_4$ -CCH<sub>2</sub>)<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>(CO)<sub>12</sub> (**7**) (22 mg, 24%), identified by comparison (IR, NMR) with an authentic sample<sup>21</sup> and also by single-crystal X-ray structure determination of a disordered CHCl<sub>3</sub>–MeCN solvate (the previous determination was carried out with a C<sub>6</sub>H<sub>6</sub> solvate). Several minor products were also present but not characterised.

A similar reaction was carried out in the presence of Me<sub>3</sub>NO instead of *tmeda* and produced **7** in 18% yield.

## Structure determinations

Full spheres of data were measured at *ca.* 153 K using a Bruker AXS CCD area-detector instrument.  $N_{\text{total}}$  data merging after “empirical”/multiscan corrections (proprietary software) to  $N$  unique ( $R_{\text{int}}$  quoted),  $N_o$  with  $F > 4\sigma(F)$  being used in the refinements. All data were measured using monochromatic Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å. In the refinements, anisotropic thermal parameter forms were used for the non-hydrogen atoms, ( $U_{\text{iso}}\text{H}$ ) being constrained at estimated values. Conventional residuals  $R$ ,  $R_w$  on  $|F|$  are quoted, statistical weights being employed. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system.<sup>31</sup> Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and tables.

## Crystal and refinement data

(1)  $[\text{ppn}]_2[\text{Ru}_{10}(\text{C})_2(\text{CO})_{24}] \cdot 2\text{CH}_2\text{Cl}_2 \equiv \text{C}_{98}\text{H}_{60}\text{N}_2\text{O}_{24}\text{P}_4\text{Ru}_{10} \cdot 2\text{CH}_2\text{Cl}_2$ ,  $M = 2954.0$ . Triclinic, space group  $P\bar{1}$ ,  $a = 12.313(1)$ ,  $b = 18.211(2)$ ,  $c = 23.540(2)$  Å,  $\alpha = 101.622(3)$ ,  $\beta = 94.226(3)$ ,  $\gamma = 94.918(2)^\circ$ ,  $V = 5129$  Å<sup>3</sup>,  $D_c$  ( $Z = 2$ ) = 1.913 g cm<sup>-3</sup>. Crystal  $0.32 \times 0.30 \times 0.13$  mm,  $\mu(\text{Mo-K}\alpha) = 1.7$  mm<sup>-1</sup>,  $T_{\text{min,max}} = 0.56, 0.73$ .  $2\theta_{\text{max}} = 65^\circ$ ;  $N_{\text{total}} = 103731$ ,  $N = 37560$  ( $R_{\text{int}} = 0.044$ ),  $N_o = 27340$ ,  $R = 0.052$ ,  $R_w = 0.073$ .

(3)  $\text{Ru}_4(\mu_4\text{-HC}_2\text{H})_2(\mu\text{-CO})_2(\text{CO})_9 \equiv \text{C}_{15}\text{H}_4\text{O}_{11}\text{Ru}_4$ ,  $M = 764.5$ . Orthorhombic, space group  $Cmc2_1$ ,  $a = 11.337(2)$ ,  $b = 13.456(2)$ ,  $c = 12.805(2)$  Å,  $V = 1953$  Å<sup>3</sup>,  $D_c$  ( $Z = 4$ ) = 2.599 g cm<sup>-3</sup>. Crystal  $0.30 \times 0.10 \times 0.08$  mm,  $\mu(\text{Mo-K}\alpha) = 3.1$  mm<sup>-1</sup>,  $T_{\text{min,max}} = 0.69, 0.86$ .  $2\theta_{\text{max}} = 62.5^\circ$ ;  $N_{\text{total}} = 14802$ ,  $N = 1733$  ( $R_{\text{int}} = 0.051$ ),  $N_o = 1631$ ,  $R = 0.050$ ,  $R_w = 0.107$ .  $x_{\text{abs}} = 0.07(18)$ .

(4)  $\text{Ru}_6\text{C}(\mu_3\text{-HC}_2\text{Me})(\text{CO})_{15} \equiv \text{C}_{19}\text{H}_4\text{O}_{15}\text{Ru}_6$ ,  $M = 1078.7$ . Monoclinic, space group  $C2/c$ ,  $a = 16.9560(9)$ ,  $b = 9.4025(5)$ ,  $c = 32.929(2)$  Å,  $\beta = 93.079(1)^\circ$ ,  $V = 5242$  Å<sup>3</sup>,  $D_c$  ( $Z = 8$ ) = 2.733 g cm<sup>-3</sup>. Crystal  $0.28 \times 0.24 \times 0.13$  mm,  $\mu(\text{Mo-K}\alpha) = 3.4$  mm<sup>-1</sup>,  $T_{\text{min,max}} = 0.58, 0.84$ .  $2\theta_{\text{max}} = 75^\circ$ ;  $N_{\text{total}} = 52942$ ,  $N = 13654$  ( $R_{\text{int}} = 0.042$ ),  $N_o = 11414$ ,  $R = 0.038$ ,  $R_w = 0.071$ .

(6)  $\text{Ru}_4(\mu_4\text{-CHCHCO})(\mu\text{-CO})(\text{CO})_{10}(\text{tmeda}) \cdot 0.5\text{CH}_2\text{Cl}_2 \equiv \text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_{12}\text{Ru}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ ,  $M = 925.1$ . Triclinic, space group  $P\bar{1}$ ,  $a = 13.2174(6)$ ,  $b = 14.5234(9)$ ,  $c = 16.5710(7)$  Å,  $\alpha = 73.859(1)$ ,  $\beta = 82.855(1)$ ,  $\gamma = 68.495(1)^\circ$ ,  $V = 2842$  Å<sup>3</sup>,  $D_c$  ( $Z = 4$ ) = 2.162 g cm<sup>-3</sup>. Crystal  $0.26 \times 0.14 \times 0.06$  mm,  $\mu(\text{Mo-K}\alpha) = 2.2$  mm<sup>-1</sup>,  $T_{\text{min,max}} = 0.60, 0.78$ .  $2\theta_{\text{max}} = 75^\circ$ ;  $N_{\text{total}} = 59267$ ,  $N = 29321$  ( $R_{\text{int}} = 0.031$ ),  $N_o = 20247$ ,  $R = 0.031$ ,  $R_w = 0.026$ . ( $x, y, z, U_{\text{iso}}\text{H}$ ) were refined.

(7)  $\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\mu\text{-dppm})_2(\text{CO})_{12} \cdot 0.5\text{CHCl}_3 \cdot 2\text{MeCN} \equiv \text{C}_{66}\text{H}_{48}\text{O}_{12}\text{P}_4\text{Ru}_6 \cdot 0.5\text{CHCl}_3 \cdot 2\text{CH}_3\text{CN}$ ,  $M = 1905.2$ . Triclinic, space group  $P\bar{1}$ ,  $a = 13.079(1)$ ,  $b = 15.254(1)$ ,  $c = 19.114(2)$  Å,  $\alpha = 90.636(2)$ ,  $\beta = 99.454(2)$ ,  $\gamma = 105.195(2)^\circ$ ,  $V = 3624$  Å<sup>3</sup>,  $D_c$  ( $Z = 2$ ) = 1.746 g cm<sup>-3</sup>. Crystal  $0.49 \times 0.36 \times 0.30$  mm,  $\mu(\text{Mo-K}\alpha) = 1.42$  mm<sup>-1</sup>,  $T_{\text{min,max}} = 0.57, 0.80$ .  $2\theta_{\text{max}} = 65^\circ$ .  $N_{\text{total}} = 72818$ ,  $N = 25430$  ( $R_{\text{int}} = 0.035$ ),  $N_o = 19208$ ,  $R = 0.061$ ,  $R_w = 0.113$ .

## Variata

(4) ( $x, y, z, U_{\text{iso}}\text{H}$ ) were refined. (6) The dichloromethane was modelled with the chlorine atoms disordered over two sets of sites, occupancies set at 0.7 and complement after trial refinement; ( $x, y, z, U_{\text{iso}}\text{H}$ ) were refined. (7) Molecular parameters determined from this structure are less precise than those of the original determination, which was carried out on a tris-benzene solvate, as a result of the presence of a disordered component, which can be described in terms of the heavy atom component being modelled as distributed over a pair of sites, population *ca* 1:9, displaced on average by *ca* 0.5 Å. It is not possible to define the light atom array associated with the minor component, so that we cannot say whether the two molecules are the same, one possibly displaced in concert with some component of solvent disorder, or whether there is a second component. However, we do not find any evidence for the latter in

the NMR spectra. The chloroform solvent is modelled in terms of residues of occupancy 0.318(3), 1/2 – 0.318(3).

CCDC reference numbers 181260–181264.

See <http://www.rsc.org/suppdata/dt/b2/b202364b/> for crystallographic data in CIF or other electronic format.

## Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey plc, Reading, UK, for a generous loan of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ . We thank Professor B. K. Nicholson (University of Waikato, Hamilton, New Zealand) for some mass spectra.

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