www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 77–85

Journal of Organometallic Chemistry

Alkyne diruthenium chemistry

Joshi Kuncheria, Hameed A. Mirza, Jagadese J. Vittal, Richard J. Puddephatt *

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Received 22 April 1999; accepted 20 July 1999

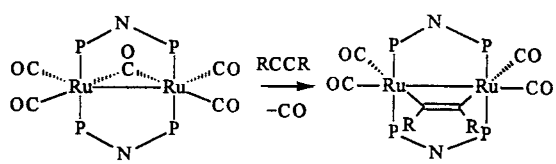
Abstract

The reaction of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (**1**) with alkynes RCCR′ gives the alkyne complexes $[Ru_2(CO)_4(\mu\text{-RC=CR}')(\mu\text{-dppm})_2]$ [**2**, R′ = H; **3**, R′ = CO_2Me or COMe; **4**, R′ = CCR], $[Ru_2(CO)_4H(CCR)(\mu\text{-dppm})_2]$ (**5**) or $[Ru_2(CO)_2(\mu\text{-CO})H(\mu\text{-CCR})(\mu\text{-dppm})_2]$ (**6**), when R = Ph. Complex **6** reacts with chlorinated solvent to give $[Ru_2(CO)_2(\mu\text{-CO})Cl(\mu\text{-CCR})(\mu\text{-dppm})_2]$ (**7**), R = Ph. Complex **1** reacts with excess alkyne RCCH to give $[Ru_2(CO)_2(\mu\text{-CO})\{C(=CH_2)R\}(\mu\text{-CCR})(\mu\text{-dppm})_2]$ (**8**), when R = Ph, Bu or CH_2CH_2CCH, and, when R = Ph, **8** reacts with more PhCCH to give $[Ru_2(CO)_2(\mu\text{-C=CHPh})\{C(=CH_2)Ph\}(\mu\text{-CCPh})(\mu\text{-dppm})_2]$ (**9**), a complex containing three different organic ligands (alkenyl, alkynyl and vinylidene). © 2000 Elsevier Science S.A. All rights reserved.

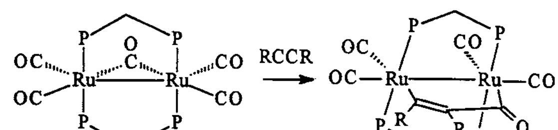
Keywords: Alkyne diruthenium; Metallacyclic compounds; Terminal alkynes

1. Introduction

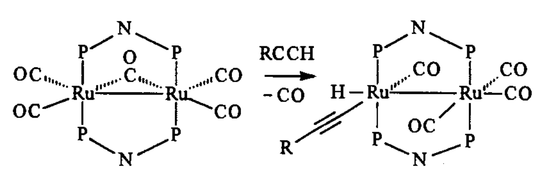
The chemistry of alkynes with ruthenium complexes is varied and interesting and the reaction chemistry of alkynes with diruthenium complexes is particularly rich [1–6]. Internal alkynes typically give bridging alkyne complexes (Eq. (1)) and, by combination with other ligands, they can give metallacyclic compounds (Eq. (2)) [2,3]. Terminal alkynes may behave similarly [4], but they can also undergo oxidative addition to give hydrido(alkynyl) complexes or rearrange to vinylidene complexes (Eqs. (3) and (4)) [5], or couple with excess alkyne to give metallacycles [6–8]. This paper reports new examples of several of these reactions and also describes a new form of reactivity, in which up to three terminal alkyne molecules may react with the binuclear compound $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (**1**), dppm = $Ph_2PCH_2PPh_2$, without alkyne coupling, thus leading to the formation of complexes containing up to three different functional groups derived from the alkyne at the diruthenium centre. A preliminary account of parts of this work has been published [9].



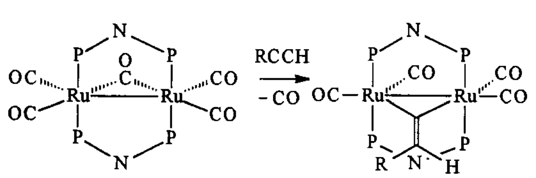
(1)



(2)



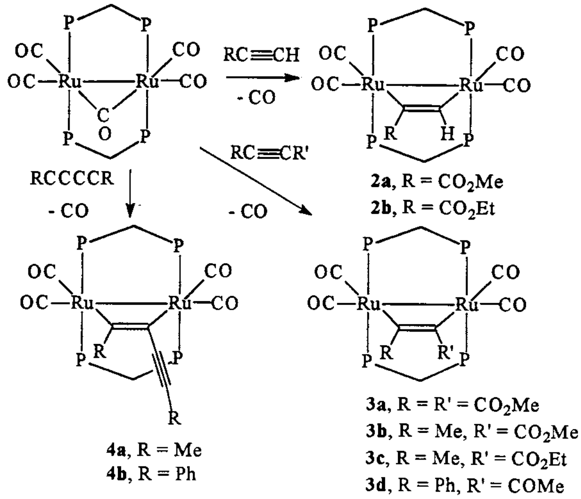
(3)



(4)

* Corresponding author.

0022-328X/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(99)00432-5



Scheme 1.

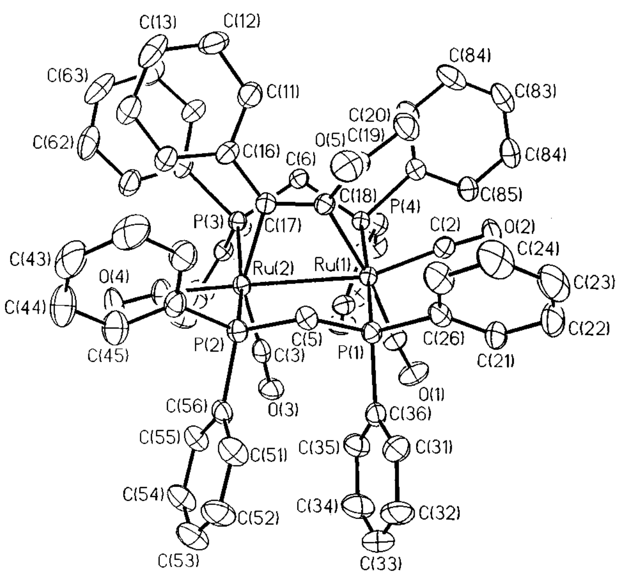


Fig. 1. A view of the structure of complex **3d**.

2. Results and discussion

2.1. Formation of bridging alkyne complexes

Several alkynes reacted with complex **1** [10] at room temperature (r.t.) to form bridging alkyne complexes $[Ru_2(\mu\text{-RC=CH})(CO)_4(\mu\text{-dppm})_2]$ (**2**) or $[Ru_2(\mu\text{-RC=CR}')(CO)_4(\mu\text{-dppm})_2]$ (**3**), as shown in Scheme 1. Complex **2** with R = H and complex **3** with $R = R' = CO_2Me$ have been previously reported [3] and several related complexes with other bridging diphosphines are also known [2,5]. No intermediates or side-products were observed in the formation of the new complexes **2** (unlike the case when $R = R' = H$ [3]) and they were isolated as air-stable yellow solids. The alkynes 3-hexyne and diphenyl acetylene failed to react with **1** under mild conditions while several terminal alkynes gave more complex products as described below. The diynes RCC-CCR, R = Me or Ph, reacted similarly (Scheme 1) to give complexes $[Ru_2(\mu\text{-RC=CCCR})(CO)_4(\mu\text{-dppm})_2]$ (**4**), with one free alkyne group. Attempts to coordinate the free alkyne group of **4** by reaction with a second equivalent of the diruthenium complex **1** were unsuccessful. In complexes **2**–**4** the coordinated alkyne is present in the μ_2-parallel bonding mode in which it acts a two-electron ligand (dimetalated alkene).

The new complexes were characterized by elemental analysis and by their spectroscopic properties, and the structure of **3d** was confirmed crystallographically. In each case, the IR spectra exhibited terminal carbonyl stretching energies from 2025 to 1880 cm^{-1} but no bridging carbonyl stretch. All compounds gave a weak band at ca. 1600 cm^{-1} due to ν(C=C). Other bands were in similar regions to those in the free ligands. Thus, **2a**, **2b** and **3a**–**3c** gave bands at ca. 1650 cm^{-1} due to ν(C=O) of the ester substituents, complex **3d** showed a medium intensity band at 1700 cm^{-1} due to ν(C=O) of the acetyl substituent and **4a** and **4b** gave bands at 2161 and 2132 cm^{-1} respectively, due to the free alkynyl group.

The symmetrical complex **3a**, having C_{2v} symmetry, gave a singlet in the ^{31}P-NMR but all other complexes have only C_s symmetry and gave rise to AA′BB′ splitting patterns. In the ^{1}H-NMR spectra, the methylene protons of the dppm ligand appear as two resonances since the CH^aH^b protons of each dppm ligand are non-equivalent. Complexes **2a** and **2b** gave δ(=CH) = 8.40 and 8.55, respectively, in the region expected for the proposed structures. If the alkyne had rearranged to a vinylidene complex, the vinyl proton would appear at lower δ [5]. Other resonances due to the alkyne ligands are unremarkable and are listed in Section 3.

The structure of $[Ru_2(\mu\text{-PhC=CCOMe})(CO)_4(\mu\text{-dppm})_2]$ (**3d**) is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The complex contains the *trans,trans*-$Ru_2(\mu\text{-dppm})_2$ unit as in the starting complex **1** [3,11]. Counting the Ru–Ru bond, each metal has slightly distorted octahedral geometry with the major distortion arising as a result of the presence of the Ru2C2 ring [angles RuRuC = 66.0(1) and 70.2(1)°]. The Ru–C distances to the coordinated alkyne [Ru2–C17 = 2.172(4) Å and Ru1–C18 = 2.196(4) Å] are typical of those for other Ru–alkyl and Ru–alkenyl bonds [2–7]. The C17–C18 distance of 1.343(6) Å is in the range expected for a double bond and the distance Ru1–Ru2 = 2.963(5) Å is in the normal range for a single bond [2–11].

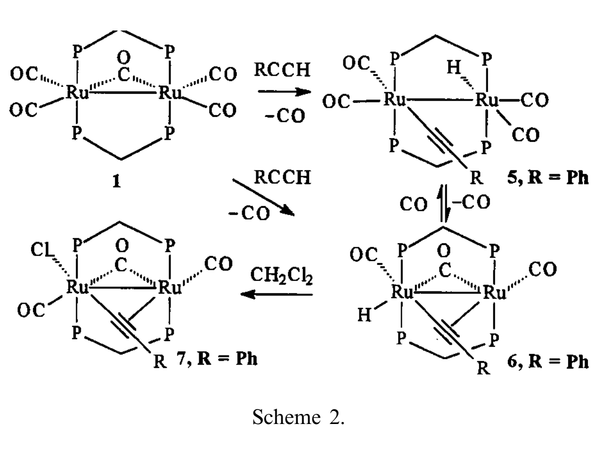
2.2. The initial reactions of complex 1 with phenyl acetylene

The first products observed in the reaction of complex **1** with PhCCH are tentatively characterized by their spectroscopic properties as the hydride complexes **5** and **6** which are formed by C–H oxidative addition (Scheme 2). These complexes survive for several hours at r.t. but attempts to separate them have been unsuccessful. When the reaction was carried out in CH_2Cl_2 solution at r.t., complex **5** and, more slowly, **6** were converted to the chloro derivative **7** on reaction with the solvent. Complex **7** was identified as the μ-η^2-acetylide derivative $[Ru_2(CO)_2(\mu\text{-}CO)Cl(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2]$ by its spectroscopic data and by an X-ray structure determination. The structure is illustrated in Fig. 2 and is closely related to that proposed for the hydride derivative **6**. Selected bond distances and angles for **7** are given in Table 2.

The structure determination was not straightforward as a result of disorder, which is not shown in Fig. 2.

Table 1
Selected bond distances (Å) and angles (°) in $[Ru_2(CO)_4(\mu\text{-}PhC{=}CCOMe)(\mu\text{-dppm})_2]$ (**3d**)

Bond distances (Å)			
Ru(1)–C(2)	1.900(5)	Ru(1)–C(1)	1.924(5)
Ru(1)–C(18)	2.196(4)	Ru(1)–P(1)	2.362(1)
Ru(1)–P(4)	2.370(1)	Ru(1)–Ru(2)	2.9631(5)
Ru(2)–C(4)	1.882(5)	Ru(2)–C(3)	1.918(5)
Ru(2)–C(17)	2.172(4)	Ru(2)–P(3)	2.347(1)
Ru(2)–P(2)	2.383(1)	O(1)–C(1)	1.139(5)
O(2)–C(2)	1.140(5)	O(3)–C(3)	1.155(5)
O(4)–C(4)	1.147(5)	O(5)–C(19)	1.249(6)
C(11)–C(12)	1.389(7)	C(16)–C(17)	1.488(6)
C(17)–C(18)	1.343(6)	C(18)–C(19)	1.488(6)
C(19)–C(20)	1.485(7)		
Bond angles (°)			
C(2)–Ru(1)–C(1)	93.2(2)	C(2)–Ru(1)–C(18)	94.7(2)
C(1)–Ru(1)–C(18)	172.1(2)	C(2)–Ru(1)–Ru(2)	160.7(1)
C(1)–Ru(1)–Ru(2)	106.1(1)	C(18)–Ru(1)–Ru(2)	66.0(1)
C(4)–Ru(2)–C(3)	98.6(2)	C(4)–Ru(2)–C(17)	109.8(2)
C(3)–Ru(2)–C(17)	151.6(2)	C(4)–Ru(2)–Ru(1)	177.3(1)
C(3)–Ru(2)–Ru(1)	81.5(1)	C(17)–Ru(2)–Ru(1)	70.2(1)
O(1)–C(1)–Ru(1)	174.7(4)	O(2)–C(2)–Ru(1)	176.2(4)
O(3)–C(3)–Ru(2)	178.1(4)	O(4)–C(4)–Ru(2)	171.3(5)
C(18)–C(17)–Ru(2)	107.9(3)	C(17)–C(18)–C(19)	123.9(4)
C(17)–C(18)–Ru(1)	115.2(3)	C(19)–C(18)–Ru(1)	120.3(3)
O(5)–C(19)–C(20)	117.6(5)	O(5)–C(19)–C(18)	119.4(5)



Scheme 2.

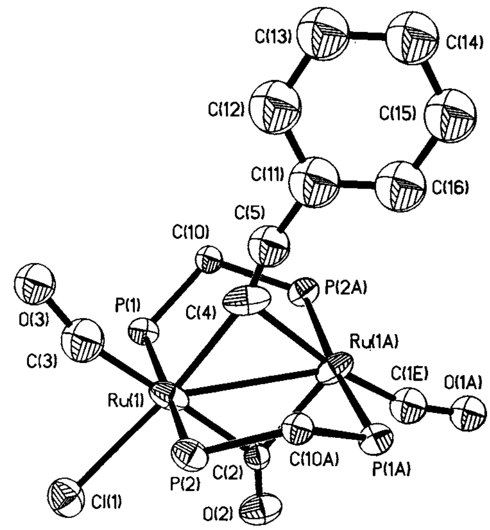


Fig. 2. A view of the structure of complex **7**. There is a crystallographic two-fold axis passing through the μ-CO group and only one of the resulting disorder forms is shown.

Table 2
Selected bond distances (Å) and angles (°) in $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCPh)Cl(\mu\text{-dppm})_2]\cdot 0.25C_6H_6$ (**7**)

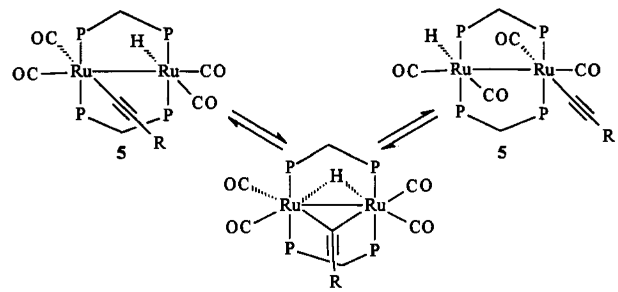
Bond distances (Å)			
Ru(1)–Ru(1A)	2.914(3)	Ru(1)–P(1)	2.370(5)
Ru(1)–P(2)	2.366(5)	Ru(1)–Cl(1)	2.54(2)
Ru(1A)–C(1E)	1.74(4)	Ru(1)–C(2)	2.13(2)
Ru(1)–C(3)	1.85(4)	Ru(1)–C(4)	2.16(2)
Bond angles (°)			
P(2)–Ru(1)–P(1)	172.7(2)	Ru(1)–C(4)–Ru(1A)	85(1)
C(5)–C(4)–Ru(1A)	112(2)	C(5)–C(4)–Ru(1)	164(3)
O(2)–C(2)–Ru(1)	137.0(4)	O(1)–C(1)–Ru(1A)	163(5)
O(3)–C(3)–Ru(1A)	164(4)	C(5)–C(4)–Ru(1)	164(3)

There is a crystallographic two-fold axis running through the atoms C4–C2–O2 (Fig. 2) and this imposes 50:50 disorder of the other ligand atoms in the $Ru_2C_4C_2O_2$ plane, with the result that these atoms are not accurately located. Nevertheless the main features of the structure are clearly defined. The structure of **7** is based on the *trans*,*trans*-$Ru_2(\mu\text{-dppm})_2$ unit with a Ru–Ru single bond (Ru–Ru = 2.914(3) Å). One ruthenium atom (Ru1 in Fig. 2) is also bonded to terminal chloride and carbonyl ligands, and to bridging carbonyl and alkynyl ligands; Ru1 achieves an 18-electron configuration if the alkynyl group acts as a one-electron σ-bonded ligand at this centre. The second ruthenium atom (Ru1A in Fig. 2) is bound to a terminal carbonyl ligand and to the bridging carbonyl and alkynyl ligands; Ru1A achieves the 18-electron configuration if the alkynyl group acts as a two-electron ligand to this ruthenium atom. The angles at C4, namely Ru1–C4–C5 = 164(3)° and Ru1A–C4–C5 = 112(2)°, support the assignment of the alkynyl group as a three-electron σ,π-bonded ligand, though the distance

Ru1A–C5 = 2.70(2) Å is considerably longer than Ru1A–C4 = 2.16(2) Å. Complex **7** can then be considered as a Ru(II)Ru(0) complex.

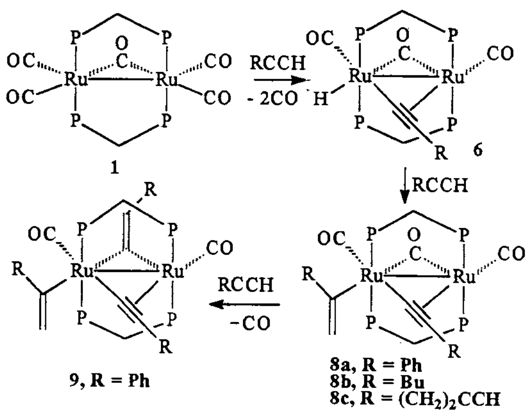
The spectroscopic properties of **7** are consistent with the solid state structure. Thus, the IR spectrum contains two terminal carbonyl bands at 1970 and 1865 cm^{-1} and one bridging carbonyl band at 1770 cm^{-1}. The ^{31}P-NMR spectrum contained two multiplets due to the phosphorus atoms bonded to the two different ruthenium centres, and the ^{1}H-NMR spectrum contained two multiplets due to non-equivalent CH^aH^b protons on each dppm ligand.

Complex **5** gives a broad single resonance in the ^{31}P-NMR spectrum at r.t. at $\delta = 24.5$ and two broad carbonyl resonances in the ^{13}C-NMR spectrum at $\delta = 196$ and 205. The ^{1}H-NMR spectrum gave a quintet resonance at $\delta = -10.35$, $J_{PH} = 14$ Hz, due to the RuH group. The IR spectrum contained four terminal carbonyl bands in the range 1896–1985 cm^{-1} and a sharper band assigned to ν(RuH) of a terminal hydride at 2028 cm^{-1}. These spectra indicate a structure with only C_2 symmetry which then achieves effective C_{2v} symmetry through stereochemical non-rigidity. The structure **5**, with easy exchange of the hydride and alkynyl groups between ruthenium centres as shown in Eq. (5), is consistent with the spectroscopic data.



(5)

Complex **6** is formed from **5** by loss of a carbonyl ligand and formation of a bridging alkynyl ligand. The ^{31}P-NMR spectrum contains two resonances at $\delta = 27.5$ and 28.5, and the hydride resonance is observed at $\delta = -10.46$ as a multiplet due to coupling to non-equivalent phosphorus atoms. The complex was always formed in the presence of **5** and the stereochemistry assigned in Scheme 2 is tentative. Complexes **6** and **7** are closely related but the hydride in **6** is tentatively suggested to be *cis* to the alkynyl group, compared to the *trans* stereochemistry of chloride and alkynyl ligands in **7**.



Scheme 3.

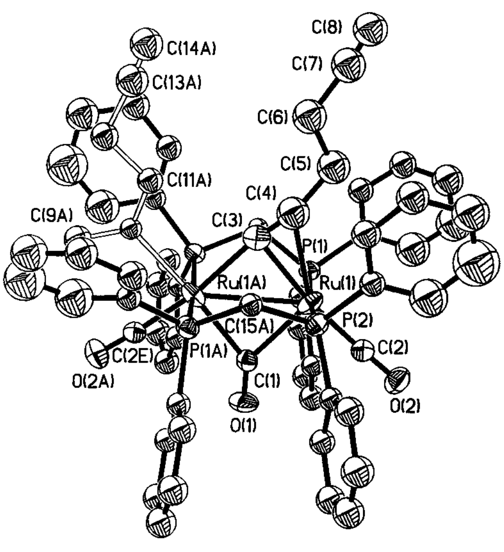


Fig. 3. A view of the structure of complex **8c**. There is a crystallographic two-fold axis passing through the μ-CO group and only one of the resulting disorder forms is shown.

2.3. Formation of alkenyl(alkynyl)diruthenium complexes

The initial reactions of **1** with PhCCH are similar in acetone or benzene solution to give **5** and **6**, but further reactions with excess alkyne then occur to give **8a** and then **9**, R = Ph, as shown in Scheme 3. It has not been possible to isolate **8a** in pure form since it was always formed in mixtures with **5**, **6** and **9**, but it was characterized spectroscopically and by its subsequent reaction to give **9**. In addition, the reactions of **1** with 1-hexyne or with 1,5-hexadiyne in acetone give the corresponding complexes **8b**, R = Bu, and **8c**, R = CH_2CH_2CCH, respectively and, since these complexes did not react further with excess alkyne, it was possible to isolate them in pure form. Complex **8c** contains two free alkyne groups but it did not react further, either intramolecularly or by reaction with excess complex **1**. Complex **8c** was characterized by a structure determination and a view of the molecular structure is shown in Fig. 3 with selected bond parameters listed in Table 3. The same type of crystallographic disorder was found as for complex **7**, so the disordered ligand atoms are not accurately located.

Table 3
Selected bond distances (Å) and angles (°) in $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{\equiv}C(CH_2)_2C{\equiv}CH\}\{C({=}CH_2)(CH_2)_2C{\equiv}CH\}(\mu\text{-dppm})_2]\cdot 0.5$ acetone (**8c**)

Bond distances (Å)			
Ru(1)–C(2)	1.80(2)	Ru(1)–C(3)	2.17(2)
Ru(1)–C(1)	2.19(2)	Ru(1)–C(4)	2.33(4)
Ru(1A)–C(10A)	2.34(3)	Ru(1)–P(2)	2.346(4)
Ru(1)–P(1)	2.347(4)	Ru(1)–Ru(1A)	2.914(3)
O(1)–C(1)	1.12(2)	O(2)–C(2)	1.16(2)
Bond angles (°)			
P(2)–Ru(1)–P(1)	170.8(2)	C(4)–C(3)–Ru(1)	85(3)
O(1)–C(1)–Ru(1)	138.2(4)	C(4)–C(3)–Ru(1A)	163(3)
O(2)–C(2)–Ru(1)	176(1)	C(9A)–C(10A)–Ru(1A)	116(2)
Ru(1A)–C(1)–Ru(1)	83.6(8)	C(11A)–C(10A)–Ru(1A)	119(2)
Ru(1)–C(3)–Ru(1A)	84.2(8)		

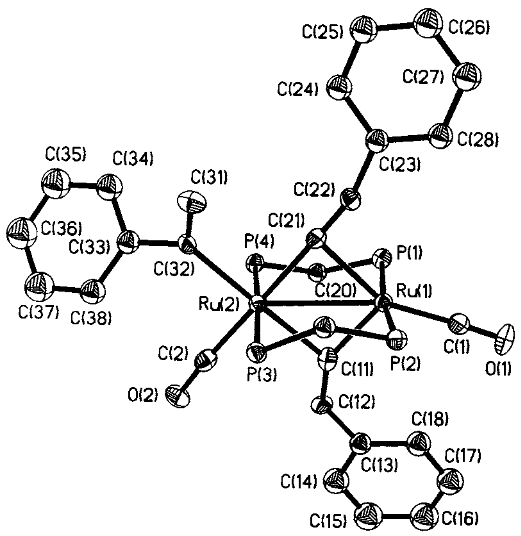


Fig. 4. A view of the structure of complex **9**, with phenyl groups of the dppm ligands omitted for clarity.

The structure of **8c** is based on the *trans,trans*-$Ru_2(\mu\text{-dppm})_2$ unit with a Ru–Ru distance of 2.914(3) Å, identical with that in complex **7**. The equatorial plane contains two terminal and one bridging CO ligand, a bridging acetylide ligand and a σ-bonded alkenyl unit $C({=}CH_2)(CH_2)_2C{\equiv}CH$. The structure is clearly similar to that of **7**, except that the chloride ligand in **7** is *trans* to the alkynyl ligand, whereas in **8c** the alkenyl and alkynyl ligands are mutually *cis*, as also suggested for **6**. Another difference between **8c** and **7** is in the geometry of the bridging alkynyl group, which is more symmetrically π-bonded to Ru1 in **8c** [Ru1–C3 = 2.17(2) Å; Ru1–C4 = 2.33(4) Å] than in **7**. This difference can be attributed to greater steric hindrance in the phenylethynyl derivative **7**, as discussed later. The structure of **8c**, and by analogy **8a** and **8b**, is that expected by insertion of a second equivalent of alkyne into the Ru–H bond of alkynyl(hydrido) complex intermediates analogous to **6**. The insertion is regioselective since only the isomer $-C({=}CH_2)R$ is formed in each case, with no evidence for the alternate –CH=CHR unit.

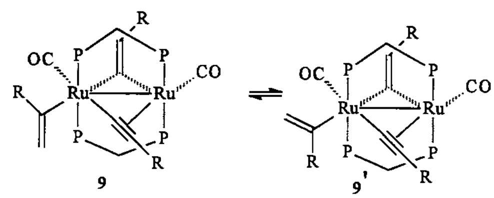
The spectroscopic properties of complexes **8a**–**8c** are similar and will be discussed for **8c** only. The IR spectrum of **8c** contained three carbonyl bands, two due to terminal carbonyls at 1918 and 1857 cm^{-1} and one due to the bridging carbonyl at 1755 cm^{-1}. There were also weak bands at 2150 and 2200 cm^{-1} which, since they were not present in the spectrum of **8b**, are assigned to the $\nu(C{\equiv}C)$ stretches of the free alkyne units. The ^1H-NMR spectrum of **8c** contained two vinyl resonances at $\delta = 4.70$ and 5.70 [m, $^2J(H^aH^b) = 2$ Hz, $=CH^aH^b$], as expected for the $RuC(R){=}CH_2$ group, as well as other bands of the dppm and alkynyl, alkenyl ligands (see Section 3). The ^{31}P-NMR spectrum contained an AA′BB′ pattern at $\delta = 31.5$ and 35.0 [m, dppm].

2.4. The complex $[Ru_2(CO)_2(\mu\text{-}C{=}CHPh)\{C({=}CH_2)\text{-}Ph\}(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2]$ (9)

The reaction of complex **1** with excess phenyl acetylene slowly gave complex **9**, as shown in Scheme 3. Complex **9** is unique in that it contains alkynyl, alkenyl and vinylidene groups in the same molecule. The structure of **9** was established by a structure determination; a view of the structure is shown in Fig. 4 and selected bond distances and angles are in Table 4. There was no disorder in the structure of **9** so the atoms of the organic ligands are more accurately located than in **7** and **8c**.

The structure of **9** is again based on the *trans,trans*-$Ru_2(\mu\text{-dppm})_2$ unit with a Ru–Ru distance of 2.853(1) Å, slightly shorter than in the carbonyl-bridged complexes **7** and **8c**. The equatorial plane contains two terminal carbonyl ligands, bridging phenyl acetylide and styrenylidene ligands and a σ-bonded styrenyl ligand $-C({=}CH_2)Ph$. The structure is clearly similar to that of **8a**, except that the bridging carbonyl ligand in **8a** is replaced by the bridging C=CHPh group in **9** (Scheme 3). The phenyl substituent of the styrenylidene group is directed *syn* to the less sterically hindered ruthenium center Ru1 and the distance Ru1–C11 = 1.99(1) Å is shorter than Ru2–C11 = 2.24(1) Å. The angle C11–C12–C13 = 135(1)° is significantly greater than the ideal angle of 120°, so as to minimize steric hindrance between the *ortho* hydrogen atom and the carbonyl ligand C1O1. In addition, the angle Ru1–C11–C12 = 146(1)° is significantly higher than Ru2–C11–C12 = 129(1)°, again to reduce this steric hindrance. The angle C31–C32–C33 = 118(1)° of the alkenyl ligand is close to the ideal value. Of the ligands derived from phenylacetylene, the CC distance in the alkynyl ligand (C21–C22 = 1.22(2) Å) is shorter than in the vinylidene (C11–C12 = 1.37(2) Å) or alkenyl (C31–C32 = 1.35(2) Å) ligand. The bridging phenylethynyl ligand is only slightly distorted from linearity (Ru2–C21–C22 = 175(1)°) and, while C21 is clearly bonded to both ruthenium atoms (Ru1–C21 = 2.22(1), Ru2–C21 = 2.07(1) Å), the distance Ru1–C22 = 2.69(1) Å indicates a very weak bonding interaction. The orientation of this bridging alkynyl group is similar to that in **7** and appears to be a result of steric effects of the phenyl substituent. The molecule is sterically congested as shown in Fig. 5, and the phenyl group lies approximately parallel to and coplanar with the Ru–Ru axis in a narrow region between phenyl substituents of the dppm ligands. It is probably this ability of the planar phenyl substituents to be accommodated in the $Ru_2(CO)_2$ plane that allows the incorporation of three units derived from the PhCCH reagent, whereas a maximum of two such groups can be formed from alkyl acetylenes.

Complex **9** is stereochemically non-rigid and its NMR spectra are temperature dependent. Thus, at r.t., the ^{31}P-NMR spectrum contained an $[AB]_2$ multiplet with $\delta = 15$ and 19 but, at -90°C, this split to give major resonances at $\delta = 18$ and 21 due to **9** and minor ones at $\delta = 12$ and 20 due to **9′**. At r.t., the vinyl protons were observed at $\delta = 5.33$ and 5.90 but at low temperature, each split to give major resonances at $\delta = 5.10$ and 6.00 and minor ones at $\delta = 4.95$ and 5.15. Finally, the vinylidene resonance at r.t. $\delta = 7.75$ split at low temperature to give $\delta = 7.8$ and 7.7. A likely explanation for these observations is that there is restricted rotation about the ruthenium–vinyl bond, leading to equilibration with **9′** as shown in Eq. (6). However, the data do not rule out other exchange processes such as the inversion of the extended chair conformation of the $Ru_2(P_2C)_2$ unit. The relative rigidity of the core structure of **9** is attributed to steric rather than to electronic effects (see Fig. 5).



(6)

Table 4
Selected bond distances (Å) and angles (°) in $[Ru_2(CO)_2(\mu\text{-CCPh})(\mu\text{-C=CHPh})\{C(=CH_2)Ph\}(\mu\text{-dppm})_2]\cdot C_6H_6\cdot 0.5C_2H_5OH$ (**9**)

Bond distances (Å)			
Ru(1)–Ru(2)	2.853(1)	Ru(1)–P(1)	2.361(4)
Ru(1)–P(2)	2.365(4)	Ru(2)–P(3)	2.373(4)
Ru(2)–P(4)	2.362(4)	Ru(1)–C(1)	1.85(1)
Ru(2)–C(2)	1.89(1)	Ru(1)–C(11)	1.99(1)
Ru(2)–C(11)	2.24(1)	Ru(1)–C(21)	2.22(1)
Ru(2)–C(21)	2.07(1)	Ru(2)–C(32)	2.17(1)
C(1)–O(1)	1.15(1)	C(2)–O(2)	1.15(2)
C(11)–C(12)	1.37(2)	C(12)–C(13)	1.45(2)
C(21)–C(22)	1.22(2)	C(22)–C(23)	1.45(1)
C(31)–C(32)	1.35(2)	C(32)–C(33)	1.50(2)
Bond angles (°)			
		C(21)–Ru(1)–Ru(2)	46.2(3)
P(2)–Ru(1)–P(1)	171.3(1)	P(4)–Ru(2)–P(3)	176.7(1)
C(11)–Ru(1)–Ru(2)	51.4(4)	C(21)–Ru(1)–C(11)	97.4(5)
C(11)–Ru(1)–C(1)	110.1(5)	C(11)–Ru(2)–Ru(1)	43.9(3)
C(21)–Ru(2)–Ru(1)	50.6(3)	C(13)–C(12)–C(11)	135(1)
C(22)–C(21)–Ru(2)	175(1)	C(12)–C(11)–Ru(1)	146(1)
Ru(1)–C(11)–Ru(2)	84.7(5)	C(12)–C(11)–Ru(2)	129(1)
Ru(1)–C(21)–Ru(2)	83.2(4)	C(31)–C(32)–Ru(2)	123(1)
C(22)–C(21)–Ru(1)	98(1)	C(31)–C(32)–C(33)	112(1)
C(32)–Ru(2)–C(11)	176.4(5)	O(1)–C(1)–Ru(1)	177(1)
C(21)–Ru(2)–C(2)	179.2(5)	O(2)–C(2)–Ru(2)	176(1)

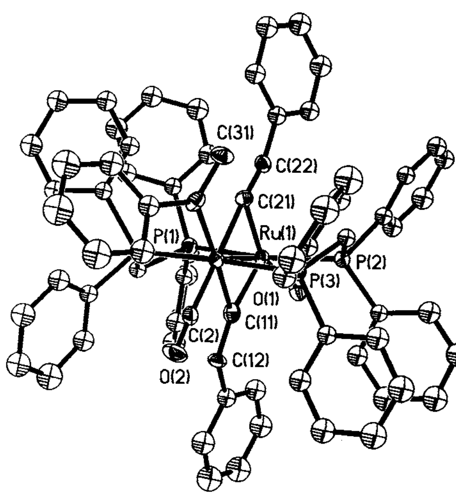


Fig. 5. A view of the structure of complex **9**, with phenyl groups of the dppm ligands included to illustrate the steric congestion. Note the orientation of the PhC substituents which are roughly coplanar with the $Ru_2(CO)_2$ unit.

2.5. Mechanisms of the reactions

In terms of mechanism, the vinyl group in complex **8a** arises by insertion of alkyne into the Ru–H bond of **6**. This step is likely to be preceded by migration of carbonyl ligands in **6** to create a vacant site for alkyne coordination *cis* to the hydride. It is interesting that the regiochemistry of the insertion reaction to give the Ru–CR=CH$_2$ unit in **8** (and hence also in **9**) is different from that observed with mononuclear ruthenium complexes which normally give the *E*-Ru–CH=CHR unit [11]. Formation of **9** requires replacement of the μ-CO ligand of **8** by the phenylvinylidene group and this is likely to be preceded by C–H activation of a third equivalent of phenylacetylene followed by rearrangement of the intermediate hydrido(alkynyl) intermediate, which is too short-lived to be detected by spectroscopic monitoring. There are precedents for the formation of complexes analogous to **2**–**6** [2–4] but complexes **8** and **9** are new structural types. Complex **9** is particularly remarkable since it contains three different ligands, each derived from phenylacetylene.

3. Experimental

NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer and referenced to TMS (^{1}H, ^{13}C) or phosphoric acid (^{31}P). IR spectra were recorded as Nujol mulls by using a Perkin–Elmer IR2000 spectrometer. Complex **1** was prepared as described elsewhere [10].

3.1. *[$Ru_2(CO)_4$(μ-HC=CCOOCH$_3$)(μ-dppm)$_2$] (**2a**)*

A solution of [$Ru_2(CO)_4$(μ-CO)(μ-dppm)$_2$] (0.11 g, 0.1 mmol) in THF (20 ml) was treated with a slight excess of methyl propiolate (10 μl, 0.11 mmol). The reaction mixture was stirred under nitrogen for about 1 h. The solvent was then removed under reduced pressure to yield the product (0.093 g, 81%). A crystalline, analytically pure sample of this complex was obtained from a concentrated acetone solution by slow evaporation. Anal. Calc. for $C_{58}H_{48}O_6P_4Ru_2$: C, 59.64; H, 4.11. Found: C, 59.10; H, 4.25%. IR: ν(CO) = 2016, 1987, 1947, 1923; 1654 (C=O); 1600 (C=C). NMR (acetone-d_6): δ(^{1}H) = 4.55, 3.70 [m, each 2H, CH_2P_2]; 3.1 [s, 3H, CH_3]; 8.4 [s, 1H, CH]; δ(^{31}P) = 29.3, 30.5 [m, dppm]; δ(^{13}C) = 217, 211, 202, 198 (CO). FAB-MS: m/z = 1167 [M]$^+$, 1139 [M−CO]$^+$, 1111 [M−2CO]$^+$, 1057 [M−4CO]$^+$ amu.

Similarly prepared were: [$Ru_2(CO)_4$(μ-H_3CC=CC-OOCH$_3$)(μ-dppm)$_2$] (**3b**), (yield: 69%). Anal. Calc. for $C_{59}H_{50}O_6P_4Ru_2$: C, 59.94; H, 4.23. Found: C, 59.20; H, 4.23%. IR: ν(CO) = 1984, 1962, 1954, 1920; 1636 (C=C). NMR (acetone-d_6): δ(^{1}H) = 4.50, 3.40 [m, each 2H, CH_2P_2]; 2.75 [s, 3H, MeO]; 2.00 [s, 3H, MeC]; δ(^{31}P) = 26.0 (unresolved m, dppm). FAB-MS: m/z = 1181 [M]$^+$, 1153 [M−CO]$^+$, 1125 [M−2CO]$^+$, 1096 [M−3CO]$^+$ amu. [$Ru_2(CO)_4$(μ-HC=CCOOC$_2$H$_5$)(μ-dppm)$_2$] (**2b**); yield: 90%. Anal. Calc. for $C_{59}H_{50}O_6P_4Ru_2$: C, 59.94; H, 4.23. Found: C, 59.10; H, 4.00%. IR: ν(CO) = 2064, 2025, 1981, 1942; 1674 (C=O). NMR (acetone-d_6): δ(^{1}H) = 4.50, 3.70 [m, each 2H, CH_2P_2]; 3.60 [q, 2H, CH_2]; 0.70 [t, 3H, CH_3]; 8.55 [s, 1H, CH]; δ(^{31}P) = 29.0, 30.2 [m, dppm]; δ(^{13}C) = 214, 211, 206, 201 [CO]. [$Ru_2(CO)_4$(μ-MeC=CC-OOEt)(μ-dppm)$_2$] (**3c**); yield: 72%. Anal. Calc. for $C_{60}H_{52}O_6P_4Ru_2$: C, 60.25; H, 4.35. Found: C, 59.50; H, 4.20%. IR: ν(CO) = 1990, 1937, 1917, 1876, 1641. NMR (acetone-d_6): δ(^{1}H) = 4.50, 3.40 [m, each 2H, CH_2P_2]; 3.30 [q, 2H, CH_2]; 2.10 [s, 3H, MeC]; 0.45 [t, 3H, COOCH$_2$Me]; δ(^{31}P) = 26.0 (unresolved multiplet, dppm). FAB-MS: m/z = 1195 [M]$^+$, 1167 [M−CO]$^+$, 1139 [M−2CO]$^+$, 1111 [M−3CO]$^+$ amu. [$Ru_2(CO)_4$(μ-EtO$_2$CC=CCO$_2$Et)(μ-dppm)$_2$]; yield: 65%. Anal. Calc. for $C_{62}H_{54}O_8P_4Ru_2$: C, 59.37; H, 4.30. Found: C, 58.76; H, 4.17%. IR: ν(CO) = 1998, 1951, 1925, 1897,1662, 1650. NMR (acetone-d_6): δ(^{1}H) = 4.80, 3.40 [m, each 2H, CH_2P_2]; 3.30 [q, 4H, CH_2]; 0.40 [t, 6H, CH_3]; δ(^{31}P) = 26.0 [s, dppm]. [$Ru_2(CO)_4$(μ-PhC=CCOMe)(μ-dppm)$_2$] (**3d**); yield: 72%. Anal. Calc. for $C_{64}H_{52}O_5P_4Ru_2 \cdot 3C_3D_6O$: C, 62.52; H, 4.99. Found: C, 62.64; H, 4.54%. IR: ν(CO) = 1982, 1937, 1929, 1884, 1700. NMR (benzene-d_6): δ(^{1}H) = 5.20, 3.15 [m, each 2H, CH_2P_2]; 1.9 [s, 3H, CH_3]; δ(^{31}P) = 25.0 (unresolved multiplet, dppm); δ(^{13}C) = 216.5, 211.5, 209.5, 202.5 [CO]. FAB-MS: m/z = 1227 [M]$^+$, 1199 [M−CO]$^+$, 1171 [M−2CO]$^+$, 1143 [M−3CO]$^+$ amu. [$Ru_2(CO)_4$(μ-MeC=CC≡CMe)(μ-dppm)$_2$] (**4a**); yield: 58%. Anal. Calc. for $C_{60}H_{50}O_4P_4Ru_2$: C, 62.01; H, 4.30. Found: C, 61.82; H, 4.38%. IR: ν(CO) = 1979, 1947, 1915, 1894; 1673 (C=C); 2161 (C≡C). NMR (acetone-d_6): δ(^{1}H) = 4.30, 3.50 [m, each 2H, CH_2P_2]; 1.9, 1.7 [s, each 3H, Me]; δ(^{31}P) = 28.5, 27.0 [m, dppm]. [$Ru_2(CO)_4$(μ-PhC=CC≡CPh)(μ-dppm)$_2$] (**4b**); yield: 62%. Anal. Calc. for $C_{70}H_{54}O_4P_4Ru_2$: C, 65.36; H, 4.20. Found: C, 65.10; H, 4.31%. IR: ν(CO) = 2001, 1948, 1924, 1881; 2132 (C≡C). NMR (CD_2Cl_2): δ(^{1}H) = 4.40, 3.40 [m, each 2H, CH_2P_2]; δ(^{31}P) = 26.5, 27.5 [m, dppm]. δ(^{13}C) = 215, 212, 202, 197 (CO); 145, 140 (C=C); 103, 93 (C≡C).

3.2. *[$Ru_2(CO)_2$(μ-CO)(μ-CCBu){C(=CH$_2$)-Bu}(μ-dppm)$_2$] (**8b**)*

A slight excess of 1-hexyne (35 μl, 0.30 mmol) was added to a stirred solution of [$Ru_2(CO)_4$(μ-CO)(μ-dppm)$_2$] (0.15 g, 0.135 mmol) in THF (15 ml) at r.t., resulting in an immediate change in color of the solution to orange–yellow. After 3 h, the solvent was removed under reduced pressure to give the product as a yellow solid; yield 90%. It was recrystallized from acetone by slow evaporation to give orange crystals. Anal. Calc. for $C_{65}H_{64}O_3P_4Ru_2$: C, 63.98; H, 5.25. Found: C, 63.40; H, 5.08%. IR: ν(CO) = 1916, 1855, 1755; NMR (CD_2Cl_2): δ(^{1}H) = 3.95, 2.80 [m, 2H, CH_2P_2]; 5.60, 4.60 [br s, each 1H, C=CH$_2$]; 1.10 [m, 4H, α-CH$_2$]; 0.90 [t, 4H, γ-CH$_2$]; 0.10 [q, 4H, β-CH$_2$]; 0.70, 0.60 [t, each 3H, CH_3]; δ(^{31}P) = 36.0, 31.5 [m, dppm]. FAB-MS: m/z = 1165, 1083, 1055, 1027, 999 amu.

3.3. *[$Ru_2(CO)_2$(μ-CO){C≡C-(CH$_2$)$_2$C≡CH}{C(=CH$_2$)(CH$_2$)$_2$C≡CH}(μ-dppm)$_2$]·0.5 acetone (**8c**)*

This was prepared similarly, but the reaction took 9 h to complete. The product (yield, 82%) was crystallised from a CH_2Cl_2 solution by slow diffusion of ethanol. Anal. Calc. for $C_{66.5}H_{59}O_{3.5}P_4Ru_2$: C, 64.34; H, 4.75. Found: C, 65.10; H, 4.71%. IR: $\nu(CO) = 1918$, 1857, 1755; 2200, 2150 (C≡C) NMR (CD_2Cl_2): $\delta(^1H) = 4.00$, 2.80 [m, each 2H, CH_2P_2]; 5.70, 4.70 [br s, each 1H, C=CH_2]; 4.1 [s, 1H, CH]; 0.90, 0.80 [t, each 2H, γ-CH_2]; 1.30 [m, 4H, β-CH_2]; 0.70, 0.60 [t, each 3H, CH_3]; $\delta(^{31}P) = 35.0$, 31.5 [m, dppm]. FAB-MS: $m/z = 1133$, 1055, 1027, 999, 971 amu.

3.4. Intermediates in reaction of [$Ru_2(CO)_4(\mu$-CO)(μ-dppm)$_2$] with PhCCH

To a solution of [$Ru_2(CO)_4$(μ-CO)(μ-dppm)$_2$] (0.05 g, 0.05 mmol) in CD_2Cl_2 (0.6 ml) in an NMR tube was added phenyl acetylene (5.1 μl, 0.05 mmol). The following intermediates were detected by their NMR spectra: **5**, R = Ph; $\delta(H) = 3.25$, 4.10 [m, each 2H, CH_2P_2]; − 10.37 [quin, $J_{PH} = 14$ Hz, RuH]; $\delta(P) = 24.5$ [br s, dppm]; $\delta(C) = 196$, 205 [br s, CO]. **6**, R = Ph; $\delta(H) =$ 3.47, 4.44 [m, each 2H, CH_2P_2]; − 10.46 [m, 1H, RuH]; $\delta(P) = 27.5$, 28.5 [m, dppm].

3.5. [$Ru_2(CO)_2$(μ-CO)(μ-CCPh)Cl(μ-dppm)$_2$]·0.25 benzene (**7**)

To a solution of [$Ru_2(CO)_4$(μ-CO)(μ-dppm)$_2$] (0.11 g, 0.1 mmol) in CH_2Cl_2 (20 ml) was added phenyl acetylene (10.2 μl, 0.1 mmol). The reaction mixture was then stirred at r.t. for 10 h. Removal of the solvent under reduced pressure yielded an orange solid, which was crystallized by slow evaporation of a solution in benzene. Anal. Calc. for $C_{62.5}H_{50.5}O_3P_4ClRu_2$: C, 61.93; H, 4.17. Found: C, 61.40; H, 4.20. IR: $\nu(CO) = 1970$, 1865, 1770; NMR (CD_2Cl_2): $\delta(^1H) = 3.82$, 2.92 [m, each 2H, CH_2P_2]; $\delta(^{31}P) = 19.0$, 29.3 [m, dppm]; $\delta(C) = 197$, 208 [m, *t*-CO]; 229 [m, μ-CO].

3.6. [$Ru_2(CO)_2(\mu$-$C_2Ph)(\mu$-C=CHPh)-{C(=CH_2)Ph}(μ-dppm)$_2$]·C_6H_6·0.5C_2H_5OH (**9**)

A solution of [$Ru_2(CO)_4$(μ-CO)(μ-dppm)$_2$] (0.20 g, 0.18 mmol) in benzene (20 ml) was stirred with a large excess of phenyl acetylene (100 μl, 1 mmol) for 5 h. After the removal of solvent under vacuum, the residue was redissolved in benzene (3 ml). Crystals of X-ray quality were obtained from this solution by slow diffusion of ethanol (yield, 25%). Anal. Calc. for $C_{83}H_{71}O_{2.5}P_4Ru_2$: C, 69.43; H, 4.94. Found: C, 69.07; H, 5.00%. IR: $\nu(CO) = 1946$, 1886, (CO); NMR (CD_2Cl_2): $\delta(^1H) = 4.52$, 3.78 [m, each 2H, CH_2P_2]; 5.33, 5.90 [d, each 1H, C=CH_2]; 7.75 [s, 1H, C=CH]; $\delta(^{31}P) =$ 15.3, 19.3 [m, dppm]. FAB-MS: $m/z = 1334$ $[M]^+$, 1306, 1204, 999 amu.

3.7. X-ray structure determinations

Orange crystals of [$Ru_2(CO)_4$(μ-PhC=CCOMe)-(μ-dppm)$_2$] were obtained from an acetone solution by slow evaporation. Data were collected using a Siemens diffractometer fitted with a CCD detector; in

Table 5
Experimental details and crystal data

Complex	**3d**·3Me_2CO	**7**·0.25C_6H_6	**8c**·0.5Me_2CO	**9**·C_6H_6·0.5Me_2CO
Formula	$C_{73}H_{70}O_8P_4Ru_2$	$C_{62.5}H_{50.5}ClO_3P_4Ru_2$	$C_{66.5}H_{59}O_{3.5}P_4Ru_2$	$C_{83}H_{71}O_{2.5}P_4Ru_2$
Temperature (K)	298(2)	298(2)	296(2)	296(2)
λ(Mo–K_α) (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Tetragonal	Tetragonal	Triclinic
Space group	$P\bar{1}$	$P4_12_12$	$P4_32_12$	$P\bar{1}$
Cell dimensions				
a (Å)	11.9452(4)	15.178(2)	15.315(2)	14.753(2)
b (Å)	12.3679(4)			19.691(4)
c (Å)	25.5382(9)	26.739(5)	26.977(4)	14.55(5)
α (°)	84.308(1)			94.96(2)
β (°)	80.905(1)			77.12(2)
γ (°)	70.693(1)			105.00(1)
V (A^3)	3511.5(2)	6160(2)	6327(2)	3979(2)
Z	2	4	4	2
D_c (Mg m^{-3})	1.325	1.306	1.302	1.217
μ (mm^{-1})	0.573	0.678	0.622	0.44
Independent reflections	8947	3624	5492	5375
Data	8935	1794	2752	5375
Restraints	0	11	44	0
Parameters	784	140	212	329
Goodness-of-fit on F^2	1.060	1.017	1.062	
R_1 [$I>2\sigma(I)$]	0.0425	0.0788	0.0869	0.0695
wR_2	0.0970	0.1880	0.1887	0.0789

this case a semi-empirical absorption correction was applied using psi scans. Orange–yellow crystals of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCPh)Cl(\mu\text{-}dppm)_2]\cdot 0.25$ benzene were grown by slow evaporation of a solution in benzene at r.t. A crystal of size $0.44 \times 0.32 \times 0.29$ mm was wedged inside a Lindemann capillary tube, flame-sealed and used for the diffraction experiments. Dark red crystals of $[Ru_2(CO)_2(\mu\text{-}CO)\{C{\equiv}C(CH_2)_2C{\equiv}CH\}\{C({=}CH_2)(CH_2)_2C{\equiv}CH\}(\mu\text{-}dppm)_2]\cdot 0.5$ acetone were grown by slow evaporation of solution in acetone at room temperature. A crystal of size $0.47 \times 0.46 \times 0.38$ mm was wedged inside a Lindemann capillary tube, flame-sealed and used for the diffraction experiments. Orange crystals of $[Ru_2(CO)_2(\mu\text{-}CCPh)(\mu\text{-}C{=}CHPh)\{C({=}CH_2)Ph\}(\mu\text{-}dppm)_2]\cdot C_6H_6\cdot 0.5C_2H_5OH$ were obtained by slow diffusion of ethanol into a benzene solution at r.t. A crystal was cut along (100), (0–10) and (−11–2) to the size $0.25 \times 0.26 \times 0.21$ mm, wedged inside a Lindemann capillary tube, flame sealed and used for single crystal diffraction experiments. In these cases, data were collected by using a Siemens P4 diffractometer and an analytical absorption correction was applied. In all cases, refinement was by full-matrix least-squares on F^2. Crystal data are given in Table 5.

4. Supplementary material

Full X-ray data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. XXXXX. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the NSERC (Canada) for financial support.

References

[1] H. El Amouri, M. Gruselle, Chem. Rev. 96 (1996) 1077.
[2] (a) K.A. Johnson, W.L. Gladfelter, Organometallics 11 (1992) 2534. (b) K.A. Johnson, W.L. Gladfelter, Organometallics 8 (1989) 2366.
[3] (a) H.A. Mirza, J.J. Vittal, R.J. Puddephatt, J. Coord. Chem. 37 (1996) 131. (b) H.A. Mirza, J.J. Vittal, R.J. Puddephatt, Organometallics 13 (1994) 3063.
[4] G.Y. Kiel, J. Takats, Organometallics 8 (1989) 841.
[5] (a) K.J. Edwards, J.S. Field, R.J. Haines, B.D. Homann, M.W. Stewart, J. Sundermeyer, S.F. Woollam, J. Chem. Soc. Dalton Trans. 4171 (1996). (b) J.S. Field, R.J. Haines, J. Sundermeyer, S.F. Woollam, J. Chem. Soc. Dalton Trans. 3749 (1993).
[6] (a) L.A. Brady, A.F. Dyke, S.E. Garner, S.A.R. Knox, A. Irving, S.M. Nicholls, A.G. Orpen, J. Chem. Soc. Dalton Trans. 487 (1993). (b) S.A. R. Knox, Pure Appl. Chem. 56 (1984) 81.
[7] (a) H. Matsuzaka, Y. Takagi, M. Hidai, Organometallics 13 (1994) 13. (b) M. Nishio, H. Matsuzaka, Y. Mizobe, M. Hidai, Organometallics 15 (1996) 965.
[8] (a) P. Blenkiron, G.D. Enright, N.J. Taylor, A.J. Carty, Organometallics 15 (1996) 2855. (b) A.J. Carty, Pure Appl. Chem. 54 (1982) 113.
[9] J. Kuncheria, H.A. Mirza, J.J. Vittal, R.J. Puddephatt, Inorg. Chem. Commun. 2 (1999) 197.
[10] (a) H.A. Mirza, J.J. Vittal, R.J. Puddephatt, Inorg. Chem. 32 (1993) 1327. (b) D.W. Engel, K.G. Moodly, L. Subramony, R.J. Haines, J. Organomet. Chem. 349 (1988) 393.
[11] A. Santos, J. Lopez, A. Galan, J.J. Gonzalez, P. Tinoco, A.M. Echavarren, Organometallics 16 (1997) 3482.