

Comparative chemistry of $\mu\text{-}\eta^1\text{:}\eta^2$ -allenyl and $\mu\text{-}\eta^1\text{:}\eta^2$ -acetylide complexes: η^5 -cyclopentadienyl complexes via alkyne-allenyl coupling in the reactions of $\text{PhC}\equiv\text{CPh}$

with $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta_{\beta,\gamma}^2\text{-C}(\text{Ph})=\text{C}=\text{CH}_2\}(\mu\text{-PPh}_2)]$
and $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CPh}\}(\mu\text{-PPh}_2)]$.

X-Ray structures of

$[\{\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^2(\text{C},\text{O}),\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)\}_2]$
and $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^2(\text{C},\text{O}),\eta^5\text{-C}_5\text{HPh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$

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Abstract

The reaction of $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta_{\beta,\gamma}^2\text{-C}(\text{Ph})=\text{C}=\text{CH}_2\}(\mu\text{-PPh}_2)]$ **1** with diphenylacetylene in refluxing toluene provides the new complex $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **2** in good yield. Treatment of $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CPh}\}(\mu\text{-PPh}_2)]$ **4** with diphenylacetylene under the same conditions affords the analogous complex $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HPh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **3**. A reversible decarbonylation of **2** allows access to the novel tetranuclear product $[\{\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)\}_2]$ **5** in high yield. Compounds **3** and **5** were both characterised by single crystal X-ray diffraction analyses which revealed in both cases the presence of an ortho-metallated substituted cyclopentadienyl. Complex **5** is distinguished by two bridging oxygen atoms which connect the dinuclear units.

Complex **2** undergoes quantitative substitution of CO at 60°C in the presence of PPh_3 to give $[\text{Ru}_2(\text{CO})_4(\text{PPh}_3)\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **6**. The reaction between **1** and $\text{PhC}\equiv\text{CH}$ yields a mixture of the isomers $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **7a** and $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **7b**. Similarly, treatment of **4** with $\text{PhC}\equiv\text{CMe}$ generates $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HMePh}(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **8a** and $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HPhMe}(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2)]$ **8b**, confirming the lack of regioselectivity in the coupling of allenyl and alkyne fragments.

Keywords: Ruthenium; $\mu\text{-}\eta^1\text{:}\eta^2$ -allenyl; $\mu\text{-}\eta^1\text{:}\eta^2$ -acetylide; Alkyne–allenyl coupling; Diruthenium complexes; X-ray structures

1. Introduction

The chemistry of σ - and $\sigma\text{-}\eta$ -bound allenyl ligands is developing rapidly due to the emergence of synthetic

routes to mono- and poly-nuclear allenyl complexes [1], evidence of unusual bonding modes [2] and new patterns of chemical reactivity [3]. Our efforts in this area have focussed on bi- and tri-nuclear complexes where the allenyl $-\text{C}(\text{R}^1)=\text{C}=\text{CR}^2\text{R}^3$ is bound as a three-electron $\mu\text{-}\eta^1\text{:}\eta_{\alpha,\beta}^2$ [4], $\mu\text{-}\eta^1\text{:}\eta_{\beta,\gamma}^2$ [5] or five-electron $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ [6] ligand. Access to these multisite bound

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hydrocarbyls via carbon–carbon bond-forming reactions between diazoalkanes and acetylides has allowed a systematic investigation of the chemistry of the allenyl ligands at polynuclear centres.

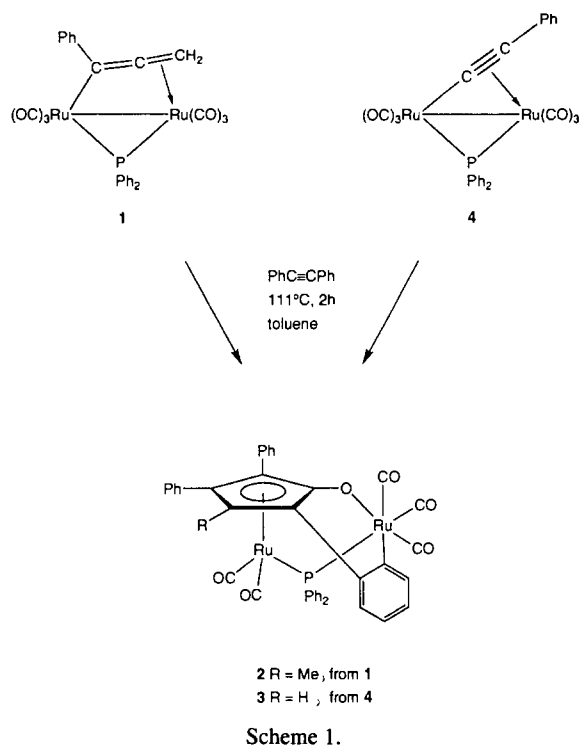
In this paper we describe the reactions of $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1 : \eta^2_{\beta,\gamma}\text{-C(Ph)=C=CH}_2\})(\mu\text{-PPh}_2)]$ **1** with diphenylacetylene investigated in the expectation that the hydrocarbyl group would provide a three-carbon fragment for “3 + 2” coupling reactions with alkynes, leading to chain extension or cyclisation. There is ample precedent in the organometallic literature for the participation of alkynes in hydrocarbon-chain growth at polynuclear centres [7] and in the generation of metallacycles or organic molecules via hydrocarbyl complexes [8].

The major product from the reaction of **1** and PhC_2Ph is the ortho-metallated cyclopentadienyl species $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\})(\mu\text{-PPh}_2)]$ **2**. A closely related product, $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HPh}_2(\text{C}_6\text{H}_4)(\text{O})\})(\mu\text{-PPh}_2)]$ **3** has been obtained from the reaction of the acetylide $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1 : \eta^2\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)]$ **4** with PhC_2Ph under similar conditions. The relationship of these products, the decarbonylation of **2** to the novel tetranuclear cyclopentadienyl complex $[\{\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\})(\mu\text{-PPh}_2)\}_2]$ **5** and the mechanism of alkyne–allenyl coupling are described in this paper. Parts of this work have been the subject of a preliminary communication [9].

2. Results and discussion

Refluxing a toluene solution of the dinuclear allenyl complex **1** or the dinuclear acetylide complex **4** with an excess of diphenylacetylene for 2 h generated in each case, yellow crystals of a major product, **2** and **3** respectively, in good yields (Scheme 1). A close similarity of these species is suggested by the spectroscopic data. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra revealed similar shifts and coupling constants for the two compounds. In the CO regions an identical pattern was found, comprising five signals indicative of an $\text{M}_2(\text{CO})_5$ system, a proposal reinforced by the respective IR data. The $^{31}\text{P}\{^1\text{H}\}$ spectra of complexes **2** and **3** consist of single resonances at 52.5 and 59.0 ppm, respectively, well upfield of the region characteristic of a phosphido group bridging metal–metal bonds, and suggesting the presence of an open phosphido bridge.

The structure of **3**, elucidated by an X-ray diffraction analysis, is shown in Fig. 1. Relevant crystal and data collection parameters are presented in Table 1 and selected bond lengths and angles are given in Table 2. The most striking feature of **3** is the presence of a bridging hydrocarbyl group which may be described as a deprotonated and ortho-metallated 1-hydroxy-2,3,5-triphenylcyclopentadienyl ligand, which connects two



nonbonded Ru atoms (Ru(1) ... Ru(2) 3.956(2) Å). Evidently, linking of one molecule of diphenylacetylene with the alkyne carbons of the original acetylide has occurred, together with the incorporation of a CO to complete the C(6)–C(10) cyclopentadienyl ring. The latter is π -bound to Ru(1) (Ru–C distances 2.209(6)–2.324(6) Å) and is essentially planar, in contrast to η^4 -bound cyclopentadienone complexes where the ketonic CO group is displaced significantly from the plane defined by the other four carbon atoms of the C_5 ring [10]. Carbon–carbon bond lengths range from 1.411(7) to 1.454(9) Å and are typical of such ligands [11]. The π -ligand in **3** is coordinated to Ru(2) via the ring oxygen O(6) and also by a phenyl substituent originat-

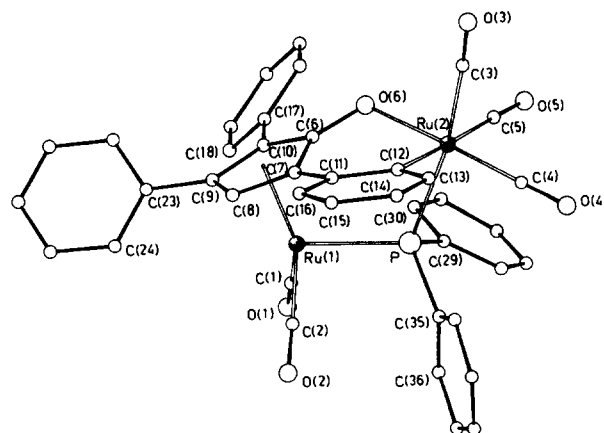


Fig. 1. The molecular structure of $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HPh}_2(\text{C}_6\text{H}_4)(\text{O})\})(\mu\text{-PPh}_2)]$ **3** showing the atomic numbering.

Table 1
X-ray crystallographic and data processing parameters

Complex	3	5
Formula	C ₄₀ H ₂₅ O ₆ PRu ₂	C ₈₀ H ₅₄ O ₁₀ P ₂ Ru ₄ · 2C ₇ H ₈
Molecular weight	834.75	1825.81
Crystal size (mm)	0.20 × 0.25 × 0.32	0.19 × 0.22 × 0.23
Crystal system	triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	10.727(4)	14.123(2)
<i>b</i> (Å)	13.035(6)	20.352(4)
<i>c</i> (Å)	13.706(6)	28.070(4)
α (°)	66.19(2)	—
β (°)	85.91(2)	98.88(1)
γ (°)	79.90(2)	—
<i>V</i> (Å ³)	1726(1)	7971(2)
<i>Z</i>	2	4
<i>D</i> _c (g cm ⁻³)	1.606	1.521
Radiation Mo K α (Å)	0.71073	0.71073
<i>F</i> (000)	832	3680
μ (cm ⁻¹)	9.492	10.31
Scan type	$\theta/2\theta$	ω
2θ range (°)	6–50	3.5–50
Scan width (°)	1.2 ± 0.34 tan θ	1.2
Scan speed (° min ⁻¹)	3–12	2.02–29.30
Reflections measured	6121	7032
Reflections observed	3748 ($I \geq 2\sigma(I)$)	4246 ($I \geq 3\sigma(I)$)
<i>R</i>	0.036	0.036
<i>R</i> _w	0.047	0.040
Goodness of fit	1.01	2.26

ing from the acetylide moiety, which has become metalated in an ortho position through a σ -type interaction [Ru(2)–C(12) 2.123(7) Å].

The metal atoms in **3** are also bridged by an asymmetric phosphido ligand [Ru(1)–P = 2.385(2), Ru(2)–P = 2.476(2) Å] creating an Ru(1)–P–Ru(2) angle of 108.9(1)°, a value much greater than those found in metal–metal bonded systems. Thus in **1** the angle at phosphorus is 75.4(1)° [5] and in a variety of monophosphido-bridged iron group complexes [12],

M–P–M angles lie in the range 69°–77°, whereas in the dianions [Fe₂(CO)₆(μ -PPh₂)₂]²⁻ [13] and in [Fe₂(CO)₆I₂(μ -PMe₂)₂] [14], both characterised by non-bonding Fe ··· Fe distances, the Fe–P–Fe angles are 105.5(1)° and 102.4(2)°, respectively.

The stereochemistry at Ru(1) can be considered tetrahedral, if the centroid of the cyclopentadienyl ring occupies one coordination site (C(1)–Ru(1)–C(2) 89.7(3)°, C(1)–Ru(1)–P 93.9(2)° and C(2)–Ru(1)–P 93.0(2)°) and is consistent with data previously reported

Table 2
Selected bond lengths (Å) and angles (°) for [Ru₂(CO)₅{ μ - η^5 -C₅HPh₂(C₆H₄)O}(μ -PPh₂)] **3**

Bond lengths			
Ru(1) ··· Ru(2)	3.956(2)	Ru(2)–C(4)	1.863(10)
Ru(1)–P	2.385(2)	Ru(2)–C(5)	2.007(9)
Ru(1)–C(1)	1.882(6)	Ru(2)–O(6)	2.099(5)
Ru(1)–C(2)	1.880(8)	Ru(2)–C(12)	2.123(7)
Ru(1)–C ₅ ring (av.)	2.253(6)	C(6)–O(6)	1.302(7)
Ru(1)–Cp ^a	1.895(6)	C(7)–C(11)	1.482(9)
Ru(2)–P	2.476(2)	C(11)–C(12)	1.399(8)
Ru(2)–C(3)	1.938(8)	C ₅ ring: C–C (av.)	1.434(9)
Bond angles			
Ru(1)–P–Ru(2)	108.9(1)	P–Ru(2)–C(5)	91.2(3)
P–Ru(1)–C(1)	93.9(2)	P–Ru(2)–C(12)	90.2(2)
P–Ru(1)–C(2)	93.0(2)	Ru(2)–C(12)–C(11)	121.6(5)
C(1)–Ru(1)–C(2)	89.7(3)	C(7)–C(11)–C(12)	121.0(6)
P–Ru(2)–C(3)	170.2(3)	C ₅ ring: C–C–C (av.)	107.9(6)
P–Ru(2)–C(4)	93.1(3)		

^a Cp^a represents the cyclopentadienyl ring centroid.

for $(\eta^5\text{-C}_5\text{R}_5)\text{RuL}_2\text{X}$ fragments [15]. The three terminal COs at Ru(2), the phosphido bridge and the metallated phenyl and oxygen groups adopt an octahedral geometry. This accounts for the large J_{PC} coupling of 96 Hz apparent for the signal at δ 188.8 in the ^{13}C NMR spectrum which we assign to the CO trans to the phosphido bridge (P-Ru(2)-C(3) $170.2(3)^\circ$) [12b]. The other four carbonyl resonances cannot be unequivocally assigned.

Clearly, in the formation of **2** an analogous coupling sequence has occurred, involving linking of the $\text{C}_\alpha\text{-C}_\beta$ unit of the allenyl in **1** with a molecule each of diphenylacetylene and carbon monoxide. The methylene group picks up an H atom, presumably liberated from the *ortho*-position of the now-metallated phenyl group, thus generating the methyl substituent of the cyclopentadienyl ring. This is shown by the doublet at δ 2.4 ($J_{\text{PC}} = 1.5$ Hz) in the ^1H NMR spectrum, and a high field ^{13}C singlet (δ 15.2).

A solution of **3** in toluene was heated to 80°C and purged with dinitrogen. Monitoring reaction progress by IR spectroscopy showed the disappearance of starting material and the formation of a new compound characterised spectroscopically and by X-ray diffraction as the tetranuclear species $[(\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2))_2]$ **5**. A perspective view of the molecular structure of complex **5** is shown in Fig. 2. Some selected bond lengths and angles are listed in Table 3.

The molecule has crystallographically imposed C_2 symmetry, with the two-fold axis passing through the centre of the Ru(2), Ru(2a), O(5), O(5a) parallelogram. The metal-metal separations Ru(1) \cdots Ru(2) (3.831(1) Å) and Ru(2) \cdots Ru(2a) (3.450(1) Å) are too long to be considered as bonding interactions and therefore, remarkably, the two halves of the molecule are held

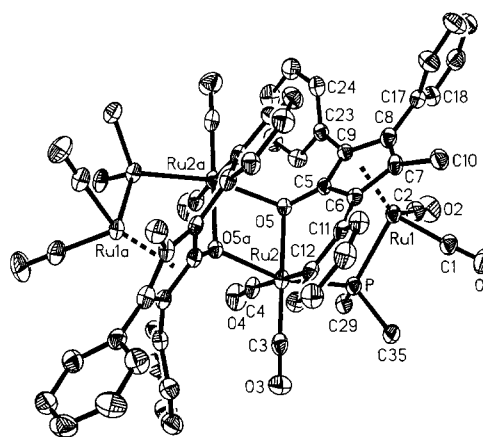


Fig. 2. The molecular structure of $[(\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2))_2]$ **5** showing the atomic numbering. For clarity, the *P*-phenyl rings have been omitted.

together only by the two bridging oxygen atoms, O(5) and O(5a). These serve as three-electron donating bridging ligands to the Ru(2) \cdots Ru(2a) system allowing an 18-electron count for all four metal atoms. The open oxygen bridges lead to an Ru(2)–O(5)–Ru(2a) angle of $105.0(1)^\circ$, a value of similar magnitude to that observed at phosphorus.

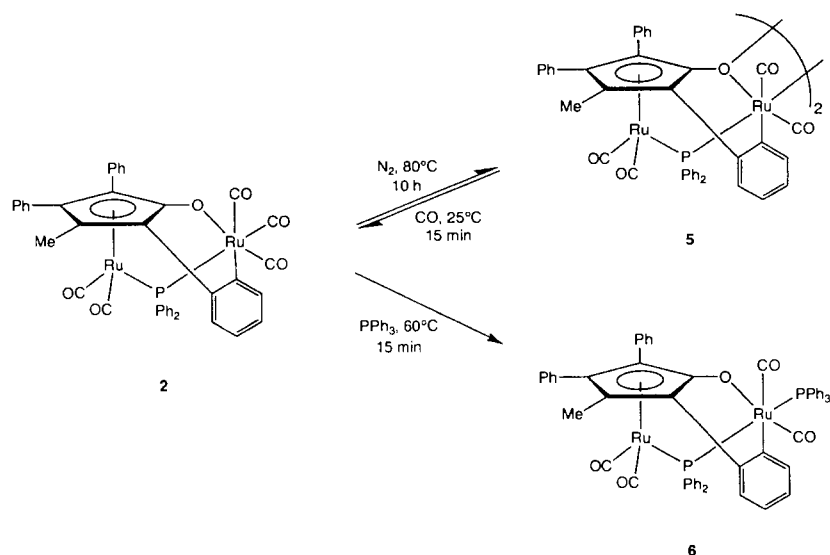
As expected, the structural characteristics of each of the dinuclear fragments closely match those obtained for complex **3**. Thus the two ruthenium atoms are bridged by a deprotonated and *ortho*-metallated 1-hydroxy-2,4,5-triphenyl-3-methylcyclopentadienyl ligand, analogous to that present in **3**. A bridging phosphido also links the two metals, again asymmetrically (Ru(1)–P 2.409(2), Ru(2)–P 2.346(2) Å), creating a characteristically large Ru(1)–P–Ru(2) angle of $107.36(3)^\circ$. As with **3**, the stereochemistry at Ru(1) may be considered tetrahedral, (C(1)–Ru(1)–C(2) $89.2(3)^\circ$, C(1)–Ru(1)–P

Table 3

Selected bond lengths (Å) and angles ($^\circ$) for $[(\text{Ru}_2(\text{CO})_4\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)(\text{O})\}(\mu\text{-PPh}_2))_2]$ **5**

Bond lengths			
Ru(1) \cdots Ru(2)	3.831(1)	Ru(2)–C(4)	1.985(6)
Ru(2) \cdots Ru(2a)	3.450(1)	Ru(2)–O(5)	2.119(3)
Ru(1)–P	2.409(2)	Ru(2)–O(5a)	2.229(3)
Ru(1)–C(1)	1.897(6)	Ru(2)–C(12)	2.115(6)
Ru(1)–C(2)	1.893(6)	C(5)–O(5)	1.318(6)
Ru(1)–C ₅ ring (av.)	2.260(5)	C(6)–C(11)	1.483(8)
Ru(1)–Cp ^a	1.900(5)	C(11)–C(12)	1.421(8)
Ru(2)–P	2.346(2)	C ₅ ring: C–C (av.)	1.438(7)
Ru(2)–C(3)	1.838(6)		
Bond angles			
Ru(1)–P(1)–Ru(2)	107.36(3)	P–Ru(2)–O(5a)	163.5(1)
P–Ru(1)–C(1)	91.6(2)	Ru(2)–O(5)–Ru(2a)	105.0(1)
P–Ru(1)–C(2)	97.7(2)	O(5)–Ru(2)–O(5a)	73.7(1)
C(1)–Ru(1)–C(2)	89.2(3)	P–Ru(2)–C(12)	92.2(2)
P–Ru(2)–C(3)	89.7(2)	Ru(2)–C(12)–C(11)	121.9(2)
P–Ru(2)–C(4)	91.8(2)	C(6)–C(11)–C(12)	120.6(3)
P–Ru(2)–O(5)	89.9(1)	C ₅ ring: C–C–C (av.)	108.0(3)

^a Cp^a represents the cyclopentadienyl ring centroid.



Scheme 2.

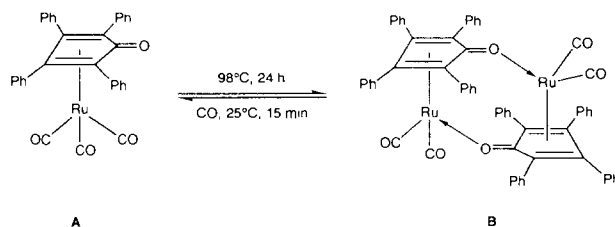
91.6(2)°, C(2)–Ru(1)–P 97.7(2)°, while that found at Ru(2) is octahedral. In the latter case, octahedral coordination is achieved by the substitution of a CO in the monomeric parent complex **2** by the oxygen atom attached to the cyclopentadienyl.

Since the preliminary publication of the X-ray structure of **5**, [9] we have found that optimum yields are obtained by heating a toluene solution of **2** at 80°C for 10 h while removing liberated CO with a dinitrogen purge.

Thus in **2** we observe thermally-assisted decarbonylation at Ru(CO)₃ to generate a free coordination site, which allows the coupling of two dinuclear fragments via oxygen bridges. The structure shows the loss of the CO *trans* to the phosphido bridge, the site now being employed to link the two halves of the dimer together. This is borne out by the disappearance of the ¹³C NMR signal with its characteristic phosphorus–carbon coupling (*J*_{PC} 95.3 Hz). There is close correspondance between the ¹³CO data and the structure of **5**. As expected, four terminal CO signals are observed; δ 201.9(d, *J*_{PC} 7.8 Hz), 201.1 (d, *J*_{PC} 6.1 Hz), 200.1 (d, *J*_{PC} 80.6 Hz) and 190.9 (s). The large coupling apparent for the signal at δ 200.1 can be reconciled in terms of the weak *trans* influence of the bridging oxygen atoms. The presence of an oxygen donor O(5a), which has a weak *trans* influence, *trans* to phosphorus produces an Ru(2)–P bond length (2.346(2) Å) which is significantly shorter than the P–Ru(1) contact (2.409(2) Å). Similarly the very short Ru(2)–C(3) distance of 1.838(6) Å, by far the shortest Ru–CO bond in **5**, can be ascribed to the weak *trans* influence of O(5). The combined effect of this is a significant contraction of the P–Ru(2)–C(3) unit. Since *J*_{P–M–X} couplings may reflect the bond strengths of the P–M and M–X interactions [16], a large *J*_{P–Ru(2)–C(3)} is not unexpected. It

seems likely that the resonance occurring as a singlet at δ 190.9 is associated with C(4)O(4) which is bound to Ru(2) via an elongated Ru–C bond of 1.985(6) Å, considerably longer than the other metal–carbonyl distances observed. The two remaining carbonyl ligands are approximately equidistant from the metal (Ru(1)–C(1) 1.897(6), Ru(1)–C(2) 1.893(6) Å) and represent signals found at δ 201.9 (d, *J*_{PC} 7.8 Hz) and 201.1 (d, *J*_{PC} 6.1 Hz) which have correspondingly similar coupling constants.

The decarbonylation reaction is reversed on exposure to carbon monoxide at ambient temperature and allows the quantitative regeneration of the Ru₂(CO)₅ monomeric complex **2** after 15 min (Scheme 2). This equilibrium, consisting of a rapid room-temperature carbonylation and a much slower decarbonylation–dimerization process, closely resembles the behaviour of a related ruthenium system reported by Mays and Shvo (Scheme 3). The mononuclear complex [(η⁴-C₄Ph₄CO)Ru(CO)₃] **A**, synthesised in high yields from [Ru₃(CO)₁₂] and three equivalents of tetraphenylcyclopentadieneone (tetracyclone) in refluxing benzene [17] or heptane [18], will undergo decarbonylation under conditions similar to those employed for **2** to afford the dinuclear derivative [(η⁴-C₄Ph₄CO)Ru(CO)₂]₂ **B** [18]. The latter consists of two nonmetal–metal bonded 16-

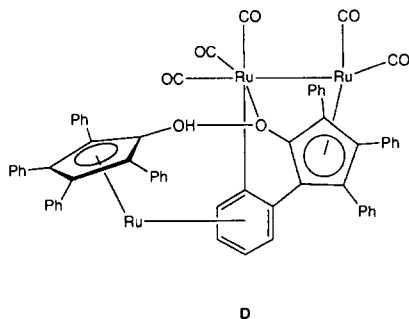


Scheme 3.

electron ($\eta^4\text{-C}_4\text{Ph}_4\text{CO}$)Ru(CO)₂ units in which each metal atom achieves electronic saturation by coordination to the ketonic oxygen of the other tetracyclone ligand. In common with complex **2**, exposure of a solution of **B** to CO at room temperature causes rapid carbonylation, reforming the tricarbonyl complex **A**. Mays et al. have demonstrated the dissociation of **B** into the 16-electron monomeric species [($\eta^4\text{-C}_4\text{Ph}_4\text{CO}$)Ru(CO)₂] which reacts readily with other 2-electron donors to give complexes of the type [($\eta^4\text{-C}_4\text{Ph}_4\text{CO}$)Ru(CO)₂L] (L = PPh₃, P(OMe)₃, or BuⁿNH₂) [18]. In the presence of moisture or protic compounds, **B** is transformed into the hydrido complex [($\mu\text{-H}$)Ru₂(CO)₄($\mu\text{-}\eta^5, \eta^5\text{-C}_4\text{Ph}_4\text{COHOC}_4\text{Ph}_4$)] **C** [19].

One other report of the ortho-metallation of a phenyl-substituted cyclopentadienone has appeared in the literature [20]. In this case, pyrolysis of the reaction mixture from [Ru₃(CO)₁₂] and tetracyclone provided a 20% yield of the cyclometallated trinuclear complex **D**. In common with **2** and **3**, **D** bears a cyclopentadienone η^5 -bound to the first Ru atom and linked to a second by ortho-metallation of a Ph substituent, with dative coordination of the adjacent ketonic oxygen. Clearly, the cyclic ligand in **D** is formed from intact tetracyclone starting material, unlike the C–C coupling reaction evident in the formation of **2** and **3**. As expected, the structural data associated with the hydrocarbyl fragments of complexes **5** and **D** are very similar. The C–O bond length of the ring carbonyl in **5** at 1.318(6) Å compares with a value of 1.327(10) Å for **D**, while the related metal–oxygen interactions are 2.119(3) and 2.148(5) Å, respectively. Although η^6 -coordination of the ortho-metallated phenyl ring to a third Ru atom in **D** causes its expansion, the Ru–C(σ -ortho) bond distance of 2.138(8) Å is similar to that observed in **5** (2.115(6) Å).

In the presence of triphenylphosphine, complex **2** undergoes smooth and quantitative conversion to a single monosubstituted product **6**, formulated as [Ru₂(CO)₄(PPh₃)($\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)\text{O}$)]($\mu\text{-PPh}_2$) on the basis of spectroscopic and analytical data. The ³¹P NMR spectrum consists of doublets at δ 59.7 and 22.9, with an observed P–P coupling of 281.6 Hz. The



magnitude of the coupling constant suggests substitution of the PPh₃ *trans*- to the phosphido bridge [12b]. This hypothesis is also confirmed by ¹³C NMR spectroscopy which shows the absence of a large J_{PC} normally characteristic of *trans* carbonyls. Thus the four ¹³C signals suggest coordination in *cis* positions relative to the phosphorus ligands: δ 202.5 (d, J_{PC} 6.3 Hz), 201.3 (dd, J_{PC} 8.6 Hz, J_{PC} 8.6 Hz), 199.4 (d, J_{PC} 6.5 Hz), 191.0 (dd, J_{PC} 7.6 Hz, J_{PC} 3.8 Hz). The absence of any *cis* substitutional isomers is perhaps not entirely unexpected as it is the *trans* carbonyl site (C(3)O(3) in **3**) which is involved in the formation of **5**.

2.1. Allenyl–alkyne and alkynyl–alkyne coupling

In the formation of **2**, the allenyl fragment of **1** provides two ring carbon atoms and a substituent methyl group of the cyclopentadienone ring, while in generating **3** the acetylide of **4** contributes both of its sp carbon atoms to the ring system. Although the formation of cyclopentadienone and metallacyclopentadiene ring systems from transition metal-mediated alkyne coupling reactions is well known, there are fewer examples of the synthesis of η^5 -cyclopentadienyl organometallic complexes. The trinuclear relative of **1**, [Ru₃(CO)₈($\mu_3\text{-}\eta^1, \eta^2, \eta^2\text{-H}_2\text{C}=\text{C}=\text{C}\text{-Pr}^i$)]($\mu\text{-PPh}_2$), exhibits distinctly different behaviour towards alkynes [3f]. The major product is [Ru₃(CO)₇($\mu_3\text{-}\eta^2, \eta^2, \eta^3\text{-H}_2\text{C}=\text{C}\text{-CPr}^i\text{-CR}^i$)]($\mu\text{-PPh}_2$) which features a metallacyclic component derived from an alkyne, the C _{α} –C _{β} unit of the allenyl and a ruthenium atom. Other metallacyclopentadiene complexes are frequently obtained in alkyne-coupling reactions of metal carbonyls [21]. Wojcicki et al. found no reaction between the heterodinuclear species [(CO)₃Fe($\mu\text{-}\eta^2, \eta^3\text{-PhC}=\text{C}=\text{CH}_2$)]WCp(CO)₂] and either MeO₂CC \equiv CCO₂Me or Me₃SiC \equiv CH [22]. However, “3 + 2” metal-assisted cycloaddition reactions have been reported for [CpFe(CO)₂($\eta^1\text{-HC}=\text{C}=\text{CH}_2$)] [23] and [CpW(CO)₃($\eta^1\text{-HC}=\text{C}=\text{CH}_2$)] [24] on treatment with tetracyanoethylene, to afford σ -bound cyclopentenes. Cyclopentadienyl and cyclopentadienone complexes have been isolated from the direct reaction of metal carbonyls with alkynes [25], although the former occur only sporadically and in very low yields, usually being accompanied by a host of other products. Thus the synthesis of the dinuclear cyclopentadienyl complexes **2** and **3** in good yields from the allenyl **1** and the acetylide **4**, respectively, and alkynes is rather remarkable and represents an unprecedented route to cyclopentadienyl systems.

An investigation of the reactivities of **1** and **4** towards unsymmetrical alkynes was undertaken in order to detect any regioselectivity in the C–C coupling sequence. Clearly, symmetrical alkynes RC \equiv CR' (R = R') facilitate the formation of a single regioisomer. However, where R \neq R' the cyclopentadienyl moiety may be

formed in two possible ways. Employing the conditions used to obtain **2** and **3**, complexes **1** and **4** were treated with $\text{PhC}\equiv\text{CH}$ and $\text{MeC}\equiv\text{CPh}$, respectively (Scheme 4). In both cases a mixture of two compounds was obtained, which IR, ^{31}P and ^1H spectroscopies show to be analogues of **2** and **3**. Thus allenyl **1** provides a mixture of the regioisomers $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}(\text{C}_6\text{H}_4)\text{O}\}(\mu\text{-PPh}_2)]$ **7a** and $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}(\text{C}_6\text{H}_4)\text{O}\}(\mu\text{-PPh}_2)]$ **7b** while acetylide **4** yields $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HMePh}(\text{C}_6\text{H}_4)\text{O}\}(\mu\text{-PPh}_2)]$ **8a** and $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{HPhMe}(\text{C}_6\text{H}_4)\text{O}\}(\mu\text{-PPh}_2)]$ **8b**. Attempts to separate mixtures of either **7a,b** or **8a,b** by chromatography or fractional crystallisation proved unsuccessful. The ^{31}P NMR spectra of **7a,b** and **8a,b** showed approximately equimolar mixtures of isomers, confirming the lack of any selective coupling in the formation of the *ortho*-metallated products. In the synthesis of the metallacycle $[\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^2,\eta^2,\eta^3\text{-H}_2\text{C}=\text{C}-\text{CPr}^i\text{-CR}^i\text{CR}^i)(\mu\text{-PPh}_2)]$ mentioned above, the alkyne insertion step also proceeds randomly to give a mixture of the two regioisomers [3f].

3. Experimental

3.1. Materials and instrumentation

Complexes **1** [4] and **4** [26] were prepared by reported procedures. All manipulations were carried out on a double manifold by using standard Schlenk techniques under dry di-nitrogen. Toluene was stored over LiAlH_4 and distilled under di-nitrogen prior to use. Diphenylacetylene, phenylacetylene and 1-phenyl-1-propyne were purchased from Aldrich, triphenylphosphine from Strem, and used as received. Purification of

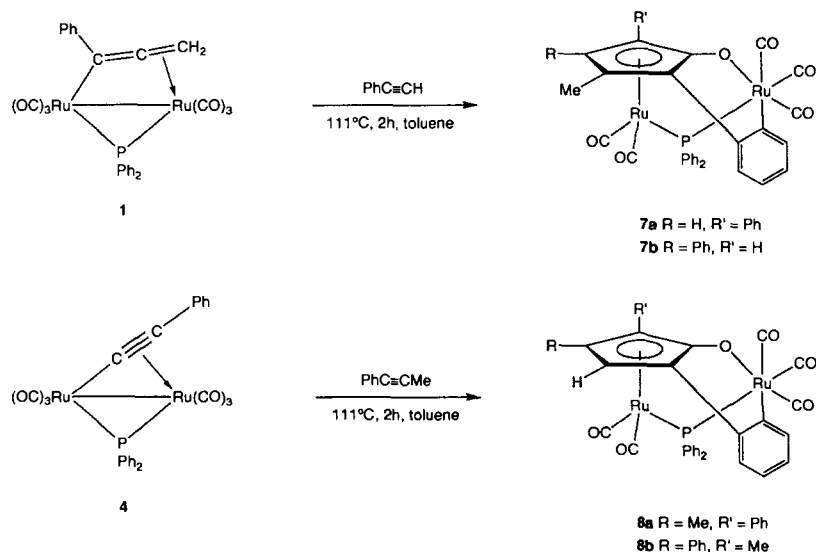
products was performed by column chromatography using Florisil (100–200 mesh).

Solution IR spectra were recorded on a Perkin Elmer 180 instrument, using sodium chloride cells of 0.5 mm path length. NMR spectra were recorded on Bruker AC 200 ($^{13}\text{C}\{^1\text{H}\}$ 50.3 MHz), AM 250 (^1H , 250 MHz; $^{31}\text{P}\{^1\text{H}\}$ 103.1 MHz) or WH 400 (^1H , 400 MHz; $^{13}\text{C}\{^1\text{H}\}$ 100.6 MHz; $^{31}\text{P}\{^1\text{H}\}$ 162.0 MHz) instruments in CDCl_3 solution at room temperature. The $^{31}\text{P}\{^1\text{H}\}$ spectra are referenced externally to 85% H_3PO_4 and ^1H , ^{13}C to solvent sources. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario or M-H-W Laboratories, Phoenix, Arizona.

3.2. Preparation of $[\text{Ru}_2(\text{CO})_5\{\mu\text{-}\eta^5\text{-C}_5\text{MePh}(\text{C}_6\text{H}_4)\text{O}\}(\mu\text{-PPh}_2)]$ **2**

$[\text{Ru}_2(\text{CO})_6(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1:\eta^2\text{-C}(\text{Ph})=\text{C}=\text{CH}_2\}]$ **1** (0.25 g, 0.37 mmol) and $\text{PhC}\equiv\text{CPh}$ (0.10 g, 0.56 mmol) were dissolved in toluene (35 ml) and the solution was heated under reflux for 2 h after which monitoring of the CO absorptions in the IR spectrum revealed the complete consumption of starting material. Removal of the solvent in vacuo yielded a yellow residue which was chromatographed on a Florisil column. Elution with heptane–toluene (5:1) gave a single yellow band of complex **2** (0.17 g, 0.20 mmol, 54%). A microanalytical sample was obtained by crystallisation from heptane–toluene at -10°C .

2: IR ($\nu(\text{CO})$, C_7H_{16}): 2100s, 2051m, 2025vs, 1999s, 1976s cm^{-1} . ^1H NMR: δ 8.03–6.96 (m, 24H, C_6H_5 , C_6H_4); 2.39 (d, J_{PH} 1.5 Hz, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 201.7 (d, J_{PC} 7.1 Hz, CO); 198.6 (d, J_{PC} 6.9 Hz, CO); 196.4 (d, J_{PC} 9.5 Hz, CO); 188.5 (d, J_{PC} 95.3, CO); 185.1 (d, J_{PC} 5.1 Hz, CO); 171.4 (d, J_{PC} 5.6 Hz,



Scheme 4.

CpCO); 162.1–124.5 (m, Ph); 102.0 (s, Cp); 98.4 (d, J_{PC} 4.3 Hz, Cp); 91.3 (d, J_{PC} 2.6 Hz, Cp); 86.2 (s, Cp); 15.1 (s, Me). $^{31}P\{^1H\}$ NMR: δ 52.5 (s). Anal. Calc. for $C_{41}H_{27}O_6PRu_2 \cdot 0.5C_7H_8$: C, 59.73; H, 3.49; P, 3.46%. Found: C, 59.87; H, 3.81; P, 3.56%.

3.3. Preparation of $[Ru_2(CO)_5\{\mu-\eta^5-C_5HPh_2-(C_6H_4)O\}(\mu-PPh_2)]$ **3**

Following a procedure identical to that detailed in Section 3.2 above, treatment of $Ru_2(CO)_6(\mu-\eta^1:\eta^2-C\equiv CPh)(\mu-PPh_2)$ **4** (0.25 g, 0.38 mmol) with diphenylacetylene (0.10 g, 0.56 mmol) led to the isolation of complex **3** as a microcrystalline solid (0.17 g, 0.20 mmol, 53%).

3: IR ($\nu(CO)$, C_7H_{16}): 2100s, 2051m, 2028vs, 2001s, 1978s cm^{-1} . 1H NMR: δ 8.02–6.99 (m, 24H, C_6H_5 , C_6H_4); 6.32 (d, J_{PH} 1.8 Hz, 1H, Cp-H). $^{13}C\{^1H\}$ NMR: δ 201.4(d, J_{PC} 7.3 Hz, CO); 197.6 (d, J_{PC} 7.2 Hz, CO); 196.1 (d, J_{PC} 9.2 Hz, CO); 188.8 (d, J_{PC} 96.0 Hz, CO); 184.9 (d, J_{PC} 5.1 Hz, CO); 170.8 (d, J_{PC} 5.1 Hz, CpCO); 159.6–124.2 (m, Ph); 97.4 (d, J_{PC} 4.1 Hz, CpCPh); 89.8 (d, J_{PC} 3.6 Hz, CPCPh); 89.0 (d, J_{PC} 2.0 Hz, CpCPh); 82.5 (s, CpCH). $^{31}P\{^1H\}$ NMR: δ 59.0 (s). Anal. Calc. for $C_{40}H_{25}O_6PRu_2$: C, 57.55; H, 3.02; P, 3.71%. Found: C, 57.41; H, 3.32; P 3.57%.

3.4. Preparation of $[\{Ru_2(CO)_4\{\mu-\eta^5-C_5MePh_2-(C_6H_4)O\}(\mu-PPh_2)\}_2]$ **5**

Complex **2** (0.084 g, 0.099 mmol) was dissolved in toluene (40 ml) and purged with dinitrogen while heating at 80°C. The reaction was monitored by IR spectroscopy which showed the gradual diminution of **2** and the production of **5**. After 10 h the heating was stopped and the solvent evaporated under reduced pressure to give an orange oily solid which was passed through a 1" Florisil plug using toluene–heptane (2 : 1) as eluant. The resulting yellow solution was concentrated by evaporation and cooled overnight at $-10^\circ C$ to give yellow crystals of complex **5** (0.024 g, 0.014 mmol). Further reduction in volume of the supernatant afforded a second batch of crystals (0.043 g, 0.025 mmol, total yield: 78%).

5: IR ($\nu(CO)$, C_6H_{14}): 2047w, 2032w, 2024vs, 1977s, 1962m, cm^{-1} . 1H NMR: δ 8.08–6.73 (m, 48H, C_6H_5 , C_6H_4); 2.41 (d, J_{PH} 1.7 Hz, 6H, Me). $^{13}C\{^1H\}$ NMR: δ 201.9 (d, J_{PC} 7.8 Hz, CO); 201.1 (d, J_{PC} 6.1 Hz, CO); 200.1 (d, J_{PC} 80.6 Hz, CO); 190.9 (s, CO); 172.6 (s, CpCO); 165.8–123.5 (m, Ph); 102.9 (s, Cp); 98.0 (s, Cp); 97.1 (s, Cp); 95.5 (s, Cp); 16.0 (s, Me). $^{31}P\{^1H\}$ NMR: δ 48.1 (s). Anal. Calc. for $C_{80}H_{54}O_{10}P_2Ru_4 \cdot C_7H_8$: C, 60.27; H, 3.60; P, 3.57%. Found: C, 59.87; H, 3.81; P 3.56%.

3.5. Carbonylation of tetranuclear **5** to dinuclear **2**

Complex **5** (0.050 g, 0.029 mmol) was dissolved in toluene (5 ml) and the solution was purged with a slow stream of carbon monoxide. After 15 min, an IR spectrum revealed the complete conversion of **5** to **2**. Partial evaporation of the solvent, addition of hexane (3 ml) and overnight refrigeration at $-10^\circ C$ gave pale yellow crystals of **2** (0.048 g, 0.054 mmol, 93%).

3.6. Preparation of $[Ru_2(CO)_4(PPh_3)\{\mu-\eta^5-C_5MePh_2-(C_6H_4)O\}(\mu-PPh_2)]$ **6**

A solution of complex **2** (0.20 g, 0.24 mmol) and PPh_3 (0.074 g, 0.282 mmol) in toluene (10 ml) was heated at 60°C. After 15 min an IR spectrum revealed the complete consumption of starting material and the presence of only one product. Evaporation of the solvent and washing with pentane afforded **6** as a yellow powdery solid (0.25 g, 0.23 mmol, 98%). An analytically pure sample was obtained by recrystallisation from hexane–toluene at $-10^\circ C$.

6: IR ($\nu(CO)$, C_6H_{14}): 2039w, 2020vs, 1971s, cm^{-1} . 1H NMR: δ 7.70–6.48 (m, 39H, C_6H_5 , C_6H_4); 2.35 (d, J_{PH} 0.9 Hz, Me). $^{13}C\{^1H\}$ NMR: δ 202.5 (d, J_{PC} 6.3 Hz, CO); 201.3 (dd, J_{PC} 8.6 Hz, J_{PC} 8.6 Hz, CO); 199.4 (d, J_{PC} 6.5 Hz, CO); 191.0 (dd, J_{PC} 7.6 Hz, J_{PC} 3.8 Hz, CO); 174.2 (dd, J_{PC} 11.0 Hz, J_{PC} 11.0 Hz, CpCO); 147.9–122.9 (m, Ph); 101.4 (s, Cp); 97.3 (d, J_{PC} 3.7 Hz, Cp); 92.0 (s, Cp); 86.5 (s, Cp); 15.1 (s, Me). $^{31}P\{^1H\}$ NMR: δ 59.7 (d, J_{PP} 281.6 Hz, PPh_2); 22.9 (d, J_{PP} 281.6 Hz, PPh_3). Anal. Calc. for $C_{58}H_{42}O_5P_2Ru_2 \cdot 0.5C_7H_8$: C, 65.42; H, 4.11; P, 5.50%. Found: C, 65.40; H, 4.14; P, 5.42%.

3.7. Preparation of the isomers $[Ru_2(CO)_5\{\mu-\eta^5-C_5MeHPh(C_6H_4)O\}(\mu-PPh_2)]$ **7a** and $[Ru_2(CO)_5\{\mu-\eta^5-C_5MePhH(C_6H_4)O\}(\mu-PPh_2)]$ **7b**

A solution of complex **1** (0.200 g, 0.298 mmol) in toluene (35 ml) was treated with a small excess of phenylacetylene (0.049 ml, 0.446 mmol) and heated under reflux for 2 h. After cooling and evaporation of the solvent, the resulting residue was chromatographed on a Florisil column. Elution with hexane–toluene (1 : 1) yielded a yellow product subsequently identified as a mixture of the isomers **7a** and **7b** (0.085 g, 0.110 mmol, 37%).

7a, 7b: IR ($\nu(CO)$, C_7H_{16}): 2100s, 2051m, 2027vs, 1998s, 1971m, 1974sh, cm^{-1} . 1H NMR: δ 8.06–6.55 (m, 38H, C_6H_5 , C_6H_4); 6.16 (s, 1H, Cp-H); 6.10 (s, 1H, Cp-H); 2.57 (s, 3H, Me); 2.33 (s, 3H, Me). $^{31}P\{^1H\}$ NMR: δ 57.9 (s), 54.5 (s). Anal. Calc. for $C_{35}H_{23}O_6PRu_2$: C, 54.41; H, 3.00%. Found: C, 54.24; H, 2.73%.

3.8. Preparation of the isomers $[Ru_2(CO)_5\{\mu-\eta^5-C_5HMePh(C_6H_4)(O)\}(\mu-PPh_2)]$ **8a** and $[Ru_2(CO)_5\{\mu-\eta^5-C_5HPhMe(C_6H_4)(O)\}(\mu-PPh_2)]$ **8b**

Following the procedure outlined in Section 3.7 above, complex **4** (0.200 g, 0.298 mmol) was allowed to react with 1-phenyl-1-propyne (0.056 ml, 0.447 mmol). Purification afforded a mixture of the isomers **8a** and **8b** (0.075 g, 0.097 mmol, 33%).

8a, 8b: IR ($\nu(CO)$, C_7H_{16}): 2099s, 2050m, 2023vs, 1998s, 1971s cm^{-1} . 1H NMR: δ 8.06–6.57 (m, 38H, C_6H_5 , C_6H_4); 6.16 (s, 1H, Cp-H); 6.15 (s, 1H, Cp-H); 2.57 (s, 3H, Me); 2.35 (s, 3H, Me). $^{31}P\{^1H\}$ NMR: δ 57.5 (s), 54.1 (s).

3.9. Crystal structure determination of complex **3**

Yellow crystals of **3** were grown from a saturated toluene/heptane solution at $-10^\circ C$. Data were col-

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^4$) for $[Ru_2(CO)_5\{\mu-\eta^5-C_5HPh_2(C_6H_4)(O)\}(\mu-PPh_2)]$ **3**

	x	y	z	U^a
Ru(1)	846(1)	2636(1)	1922(1)	416(2)
Ru(2)	3440(1)	-67(1)	3295(1)	595(3)
P	2679(1)	1494(1)	1587(1)	468(7)
O(1)	1507(5)	4829(4)	241(4)	765(24)
O(2)	-759(5)	2430(4)	303(5)	891(30)
O(3)	3813(7)	-1929(6)	5551(5)	1289(39)
O(4)	4498(5)	-1659(5)	2243(5)	1011(33)
O(5)	6124(6)	654(7)	3038(6)	1309(47)
O(6)	2751(4)	1142(3)	3932(3)	559(19)
C(1)	1259(6)	4000(5)	875(5)	519(28)
C(2)	-135(6)	2491(5)	914(5)	546(28)
C(3)	3748(8)	-1232(7)	4721(8)	877(43)
C(4)	4097(7)	-1054(6)	2643(7)	767(38)
C(5)	5124(8)	458(7)	3119(7)	854(44)
C(6)	1610(5)	1694(5)	3657(5)	487(26)
C(7)	547(5)	1250(4)	3481(4)	451(23)
C(8)	-507(5)	2125(5)	3259(4)	468(25)
C(9)	-133(5)	3137(5)	3205(5)	469(24)
C(10)	1215(5)	2898(5)	3406(4)	474(25)
C(11)	541(6)	64(5)	3616(4)	480(24)
C(12)	1660(6)	-633(5)	3536(5)	548(27)
C(13)	1529(8)	-1741(5)	3647(5)	689(32)
C(14)	378(8)	-2102(6)	3780(5)	718(34)
C(15)	-713(8)	-1403(6)	3865(5)	687(33)
C(16)	-629(6)	-331(5)	3792(5)	563(28)
C(17)	2038(6)	3698(6)	3432(5)	574(31)
C(18)	1729(7)	4866(6)	2786(6)	706(36)
C(19)	2497(8)	5617(7)	2797(7)	858(45)
C(20)	3564(9)	5234(9)	3411(9)	1046(60)
C(21)	3863(7)	4117(9)	4025(8)	987(58)
C(22)	3108(6)	3320(7)	4045(7)	734(40)
C(23)	-1075(5)	4141(5)	3148(5)	514(26)
C(24)	-2071(6)	4550(5)	2434(6)	662(32)
C(25)	-3019(7)	5402(6)	2469(7)	810(38)
C(26)	-2937(8)	5879(7)	3184(8)	924(46)
C(27)	-1938(7)	5508(6)	3873(7)	769(38)
C(28)	-1010(6)	4640(5)	3863(5)	622(31)
C(29)	4002(5)	2270(5)	1051(6)	607(31)
C(30)	4201(7)	3076(6)	1411(7)	798(42)
C(31)	5260(7)	3608(8)	1104(9)	1112(61)
C(32)	6083(7)	3387(8)	361(9)	1165(64)
C(33)	5915(8)	2592(8)	27(9)	1165(61)
C(34)	4895(7)	2023(7)	365(7)	876(44)
C(35)	2323(5)	1044(5)	546(5)	503(28)
C(36)	2290(8)	1797(7)	-513(6)	792(39)
C(37)	1940(9)	1468(8)	-1288(6)	948(46)
C(38)	1617(9)	413(8)	-996(7)	926(48)
C(39)	1590(8)	-294(7)	25(7)	834(42)
C(40)	1950(7)	4(5)	807(5)	638(31)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

lected at room temperature (295 K) on a Philips PW 1100 diffractometer. One standard reflection was monitored every 50 measurements; no significant decay was

detected during data collection. The individual profiles have been analysed following Lehmann and Larsen [27]. Intensities were corrected for Lorentz and polarisa-

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[\{\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^5\text{-C}_5\text{MePh}_2(\text{C}_6\text{H}_4)\text{O})(\mu\text{-PPH}_2)_2\}]_5$

	x	y	z	U^a
Ru(1)	2111.1(3)	2259.9(2)	3738.9(2)	39.8
Ru(2)	-342.9(3)	1743.8(2)	3063.8(2)	38.8
P	646.6(11)	1690.5(8)	3815.2(5)	42.1
O(1)	2054(4)	3052(2)	4642(1)	69
O(2)	3505(4)	1317(3)	4305(2)	85
O(3)	-2051(3)	1627(3)	3564(2)	75
O(4)	-442(4)	229(2)	2973(2)	74
O(5)	883(2)	1856(2)	2721(1)	37
C(1)	2068(4)	2736(3)	4316(2)	51
C(2)	2973(5)	1660(3)	4092(2)	56
C(3)	-1401(4)	1660(3)	3367(2)	48
C(4)	-344(5)	773(3)	2996(2)	49
C(5)	1527(4)	2275(3)	2932(2)	37
C(6)	1355(4)	2894(2)	3151(2)	34
C(7)	2280(4)	3175(3)	3323(2)	40
C(8)	3012(4)	2729(3)	3228(2)	43
C(9)	2536(4)	2158(2)	2992(2)	37
C(10)	2491(5)	3837(3)	3566(3)	54
C(11)	387(4)	3187(3)	3124(2)	40
C(12)	-437(4)	2779(3)	3097(2)	41
C(13)	-1322(4)	3084(3)	3039(2)	47
C(14)	-1422(5)	3755(3)	3020(2)	58
C(15)	-622(5)	4148(3)	3056(2)	55
C(16)	277(5)	3863(3)	3099(2)	48
C(17)	4053(4)	2865(3)	3300(2)	46
C(18)	4730(5)	2427(3)	3520(2)	56
C(19)	5693(5)	2564(4)	3565(2)	64
C(20)	6004(5)	3134(4)	3388(3)	70
C(21)	5343(6)	3576(4)	3162(3)	75
C(22)	4378(5)	3435(3)	3117(3)	63
C(23)	2949(4)	1602(3)	2752(2)	41
C(24)	3638(4)	1707(3)	2461(2)	51
C(25)	3938(5)	1206(4)	2188(2)	65
C(26)	3557(5)	591(3)	2205(3)	68
C(27)	2871(5)	467(3)	2491(3)	58
C(28)	2563(4)	970(3)	2759(2)	51
C(29)	748(5)	821(3)	4001(2)	50
C(30)	1498(5)	429(3)	3916(2)	63
C(31)	1540(7)	-238(4)	4034(3)	82
C(32)	793(9)	-498(4)	4228(3)	94
C(33)	38(8)	-134(4)	4316(3)	89
C(34)	14(6)	527(4)	4200(3)	71
C(35)	161(4)	2036(3)	4329(2)	51
C(36)	537(5)	1838(4)	4797(2)	61
C(37)	241(6)	2112(5)	5197(2)	75
C(38)	-441(7)	2602(5)	5138(3)	93
C(39)	-805(7)	2819(5)	4683(3)	94
C(40)	-503(6)	2530(4)	4283(2)	70
C(41)S ^b	415(12)	4906(8)	4336(5)	166
C(42)S ^b	1064(15)	4587(7)	4624(5)	175
C(43)S ^b	1988(15)	4825(10)	4731(5)	179
C(44)S ^b	2304(12)	5435(11)	4554(6)	214
C(45)S ^b	1519(15)	5741(7)	4207(7)	216
C(46)S ^b	633(12)	5447(7)	4104(5)	167
C(47)S ^b	-568(14)	4615(9)	4252(6)	253

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

^b S = toluene of solvation.

tion effects. No correction for absorption was applied. Relevant crystal and data collection parameters for the present study are given in Table 1.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all nonhydrogen atoms. All hydrogen atoms of the complex, excepting HC(8) clearly localised in the final ΔF map and refined, were placed at their geometrically calculated positions ($C-H = 1.00 \text{ \AA}$) and refined "riding" on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.5933 and 0.0028, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from Ref. [28]. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 of the "Centro di Studio per la Strutturistica Diffattometrica" del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [29]. Final atomic coordinates for the nonhydrogen atoms and equivalent isotropic displacement coefficients are presented in Table 4.

3.10 Crystal structure determination of complex 5

Yellow crystals of **5** were grown from a saturated toluene/heptane solution at -10°C . Data were collected at room temperature (294 K) on a Syntex P2₁ diffractometer. Background measurements using the stationary crystal, stationary counter method were made at the beginning and end of each scan, each for 25.0% of the total scan time. Two standard reflections were monitored every 100 measurements; no significant decay was detected during data collection. Data were corrected for Lorentz and polarisation effects but not for absorption. Relevant crystal and data collection parameters for the present study are given in Table 1.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all nonhydrogen atoms. A difference Fourier map revealed the positions of the hydrogen atoms (except those of the solvent) and were included in the refinement. In the final cycles of refinement a weighting scheme, $w = 1.25 - 0.0093F_o + 0.00008F_o^2$ was used. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from Ref. [28]. Programs used are described elsewhere [30]. Final atomic coordinates for the nonhydrogen atoms and equivalent isotropic displacement coefficients are presented in Table 5.

Additional crystallographic data for both **3** and **5**

including H-atom coordinates, displacement coefficients and full lists of bond parameters have been deposited at the Cambridge Crystallographic Data Centre. Lists of structure factors are available from the authors.

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