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The reaction of $[H_4Ru_4(CO)_{12}]$ with 1-penten-3-yne: dimerization and trimerization through the triple bonds

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Abstract

The clusters $[Ru_4(\mu\text{-}CO)(CO)_{10}(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2\text{-}C_5H_6)_2]$ (**1**), $[Ru_4(CO)_8(\mu_4\text{-}\eta^4{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-}C_{10}H_{12})(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-}C_5H_6)]$ (**2**) and $[Ru_4(CO)_{10}(\mu_4\text{-}\eta^4{:}\eta^1{:}\eta^1{:}\eta^3{:}\eta^1\text{-}C_{15}H_{16})]$ (**3**) have been prepared from the reaction of $[H_4Ru_4(CO)_{12}]$ with 1-penten-3-yne. This reaction is observed to proceed with dimerization and trimerization through the triple bonds. The products were characterized spectroscopically by ^1H- and ^{13}C-NMR. X-ray crystal structures of compounds **1** and **2** are also described. © 2002 Published by Elsevier Science B.V.

Keywords: Oligomerization; Triple bonds; Enynes; Tetraruthenium clusters

1. Introduction

One of the reactions of alkyne-cluster derivatives that has attracted considerable attention is that of the cluster with further amounts to the same, or different, alkyne which yield products where alkyne–alkyne coupling has taken place [1,2]. These reactions have frequently produced metallo-cyclopentadiene clusters [1], or open organic chains coordinated to the metal core [2]. This interest is due to the comparison of these processes with those of chain growth on metal surfaces [3].

More recently, there has been a fast growing interest on the reactivity of carbonyl metal clusters with diynes [4]. Deeming et al. [5] reported the formation of the osmium complexes $[Os_3(\mu_4\text{-}\eta_2\text{-}RC_2CCR')(\mu\text{-}CO)(CO)_9]$, $R = R' = Ph$, ^tBu, $SiMe_3$; $R = Ph$, $R' = SiMe_3$, which on heating suffer cleavage of the diyne ligand to yield complexes with $\mu\text{-}C_2R$ and $\mu_3\text{-}C_2R$ ligands. Reactions of 1,4-diphenylbuta-1,3-diyne with $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{10}(NCMe)_2]$ reported by Bruce et al. [4a] gave mono-, di-, tri- and tetranuclear products which show the diyne to be coordinated only through one of the triple bonds and keeping a phenylethynyl groups as a non-coordinated substituent.

On the other hand, dimerization of the diyne is observed when $[Ru_3(CO)_{12}]$ reacts with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne [4c] while a P–C(diyne) bond is formed in the reaction of $[(\mu\text{-}H)_2Ru_4(CO)_{12}(\mu_3\text{-}PPh)]$ with 1,4-diphenyl butadiyne [4b]. There is one report on the reactivity of $[H_4Ru_4(CO)_{12}]$ with diynes and in these reactions the diyne is observed to dihydrogenate both in a 1,2- and in a 1,4-mode [6].

Only one report was found on the reactivity of an enyne. When $[Ru_3(CO)_{12}]$ reacts with isopropenylacetylene in refluxing heptane, a trinuclear cluster with a coordinated dimerized enyne is formed [7].

In this work, we report the reactions of $[H_4Ru_4(CO)_{12}]$ with 1-penten-3-yne and the spectroscopic characterization of the products including full assignment of the ^1H- and ^{13}C-NMR spectra. X-ray structures of compounds **1** and **2** are also described.

2. Results and discussion

Thermal reaction of $[H_4Ru_4(CO)_{12}]$ with a six-fold excess of 1-penten-3-yne in refluxing octane for 1 h,

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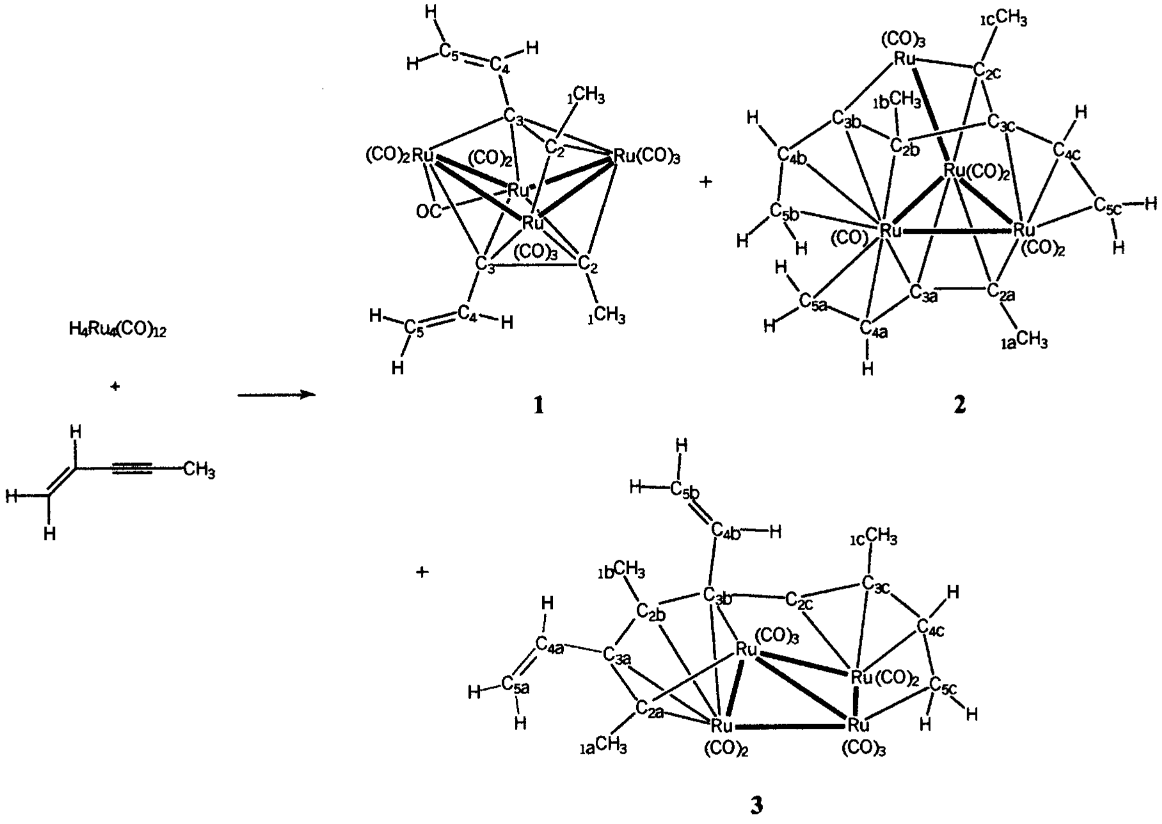
yielded three products, **1**–**3**, Scheme 1. These were separated by chromatographic methods. Spectroscopic data for these compounds are given in Tables 1 and 2. The use of one- and two-dimensional NMR techniques ($^1H-^1H$ NOESY, $^1H-^1H$ COSY, $^1H-^{13}C$ HETCOR and $^1H-^{13}C$ HMBC) allowed assignment of the spectra of all three compounds.

Compound **1**, showed in the mass spectrum, a molecular ion at *m*/*z* 844 and stepwise loss of up to 11 carbonyl groups, thus suggesting the formula $[Ru_4(CO)_{11}(C_{10}H_{12})]$, i.e. two enyne groups bonded to a tetranuclear core. The ^1H-NMR spectrum did not show signals in the hydride region and the infrared spectrum shows the presence of bridging carbonyl groups. The X-ray crystal structure of this compound confirmed the proposal; Fig. 1 shows the molecular structure while selected bond distances and angles are summarized in Table 3.

The structure shows that two independent molecules of enyne have coordinated separately to the tetraruthenium core through the alkyne moiety, in a similar manner to that described for $[Ru_4(CO)_{11}(Ph_2C_2)_2]$ [8]. The olefin fragment shows no interaction with any of the metal atoms. The metal atoms adopt a distorted square geometry, which can be better described as a butterfly where the metal–metal bond forming the



Scheme 1.

Table 1
^1H-NMR data for **1**–**3** [a]

Compound		δ (ppm), *J* (Hz)			
		CH_3	CH [$^3J_{trans}$, $^3J_{cis}$]	CH_{2cis} {$^2J_{gem}$}	CH_{2trans}
1		1.94 (s)	5.40 (dd) [16.6, 10.7]	4.83 (d)	4.70 (d)
2	a	3.53 (s)	4.79 (dd) [11.0, 6.7]	2.73 (d)	1.18 (d)
	b	0.51 (s)	4.95 (dd) [9.5, 7.8]	3.12 (dd) {3.1}	2.47 (dd)
	c	2.51 (s)	3.54 (dd) [12.3, 7.9]	3.43 (dd) {0.9}	1.61 (dd)
3	a	2.55 (s)	6.23 (dd) [17.8, 11.4]	5.48 (dd) {1.0}	5.24 (dd)
	b	2.26 (s)	6.76 (dd) [16.8, 10.5]	4.96 (dd) {1.7}	5.15 (dd)
	c	1.66 (s)	4.12 (dd) [2.0, 2.0]	2.61 (dd) {15.5}	2.02 (dd)

[a] See Scheme 1 for assignment; experiments carried out in $CDCl_3$.

Table 2
^{13}C-NMR spectral assignments for **1**–**3** [a]

Compound		δ (ppm)				
		C_1	C_2	C_3	C_4	C_5
1		31.2	154.8	126.0	145.1	117.8
2	a	33.2	134.9	170.4	60.9	66.9
	b	16.9	57.5	124.8	99.6	47.9
	c	32.9	139.1	100.7	61.2	44.3
3	a	31.9	152.3	125.9	130.1	122.3
	b	18.6	89.8	198.5	146.1	112.9
	c	22.1	157.0	118.2	45.5	55.9

[a] See Scheme 1 for assignment; experiments carried out in $CDCl_3$.

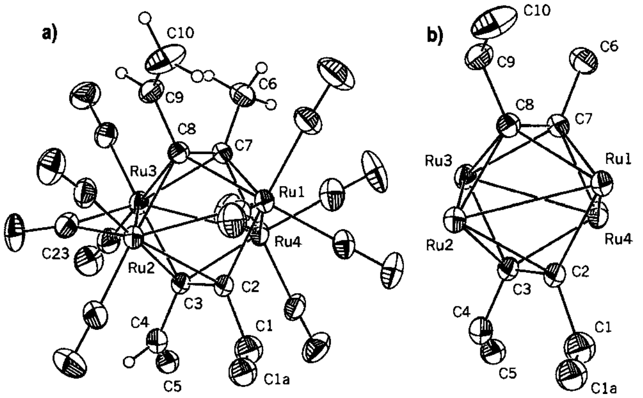


Fig. 1. (a) Molecular structure of $Ru_4(\mu\text{-CO})(CO)_{10}(\mu_4\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{-}C_5H_6)_2$ (**1**). (b) The CO groups have been omitted for clarity. ORTEPS shown at 50% probability.

hinge is broken. The angle between the wings of the butterfly is 138.32(2)°. Each ligand is coordinated through the alkyne side of the molecule to four ruthenium atoms by means of two π-bonds to two metal atoms and two σ-bonds to the other two metal atoms. Therefore all four metal atoms form a π-bond with one alkyne unit and a σ-bond with the other alkyne fragment. A bridging carbonyl group is observed between Ru(2) and Ru(3).

One of the organic ligands, C(1)–C(5), showed some disorder in the position of the free olefinic fragment. Therefore, atoms C(1a) and C(5) were refined with partial occupancy to get values of 0.43 [(C(1a)] and 0.57 [C(5)]. In solution, no evidence was obtained for the presence of two isomers since only one NMR signal is observed for each proton and each carbon atom of the ligand.

Metal–metal bond lengths range between 2.7466(8) and 2.8482(7) Å where the shortest value corresponds to the bond bridged by the carbonyl group.

Ruthenium–carbon π-bonds are in the range between 2.261(6) and 2.361(7) Å. These values are larger than the ones observed in $[HIrRu_3(CO)_{11}(\mu_3\text{-}\eta_2\text{-PhCCPh})]$ [9] and $[Ru_4(\mu_4\text{-}\eta_2\text{-PhC}_2\text{CCPh})(CO)_{12}]$ [4a] but more similar to those observed in $[HIrRu_3(CO)_{11}(\mu_3\text{-}\eta_2\text{-MeCCMe})]$ [9]. There are larger differences in ruthenium–carbon σ-bonds, in the same alkyne fragment, than in $[Ru_4(CO)_{11}(Ph_2C_2)_2]$ [8]. The carbon–carbon distance in the non-coordinated olefin fragment is

Table 3
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths									
C(1a)–C(1)	0.987(17)	C(9)–C(10)	1.298(10)	Ru(2)–C(3)	2.298(6)	Ru(3)–C(8)	2.290(6)		
C(1)–C(2)	1.534(9)	Ru(1)–Ru(2)	2.8482(7)	Ru(3)–C(3)	2.198(6)	Ru(2)–C(23)	2.068(7)		
C(2)–C(3)	1.409(9)	Ru(2)–Ru(3)	2.7466(8)	Ru(4)–C(3)	2.261(6)	Ru(3)–C(23)	2.053(8)		
C(3)–C(4)	1.528(9)	Ru(3)–Ru(4)	2.8279(7)	Ru(1)–C(7)	2.342(6)	C(23)–O(23)	1.157(8)		
C(4)–C(5)	1.156(13)	Ru(4)–Ru(1)	2.8039(7)	Ru(3)–C(7)	2.314(6)	Ru–Cco (av)	1.898		
C(6)–C(7)	1.547(9)	Ru(1)–C(2)	2.150(6)	Ru(4)–C(7)	2.155(6)	C–O (av)	1.140		
C(7)–C(8)	1.386(9)	Ru(2)–C(2)	2.303(6)	Ru(1)–C(8)	2.274(6)	Ru(1)···Ru(3) [a]	3.8353(8)		
C(8)–C(9)	1.507(8)	Ru(4)–C(2)	2.361(7)	Ru(2)–C(8)	2.203(6)	Ru(2)···Ru(4) [a]	3.8304(9)		
Bond angles									
Ru(1)–Ru(2)–Ru(3)	86.53(2)	Ru(2)–C(3)–Ru(4)	114.3(2)	C(2)–C(3)–C(4)	119.3(6)				
Ru(2)–Ru(3)–Ru(4)	86.79(2)	Ru(1)–C(7)–Ru(3)	110.9(3)	C(3)–C(4)–C(5)	130.6(10)				
Ru(3)–Ru(4)–Ru(1)	85.85(2)	Ru(1)–C(8)–Ru(3)	114.4(2)	C(6)–C(7)–C(8)	120.5(5)				
Ru(4)–Ru(1)–Ru(2)	85.32(2)	C(1a)–C(1)–C(2)	127.9(13)	C(7)–C(8)–C(9)	119.9(5)				
Ru(2)–C(2)–Ru(4)	110.4(3)	C(1)–C(2)–C(3)	119.9(6)	C(8)–C(9)–C(10)	125.7(6)				
Dihedral angles									
Ru(1)–Ru(2)–Ru(3) vs Ru(3)–Ru(4)–Ru(1)	138.32(2)	C(7)–C(8)–Ru(1) vs C(7)–C(8)–Ru(3)	121.6(2)						
Ru(2)–Ru(3)–Ru(4) vs Ru(4)–Ru(1)–Ru(2)	138.34(2)	C(2)–C(3) vs C(7)–C(8)	82.2(2)						
C(2)–C(3)–Ru(2) vs C(2)–C(3)–Ru(4)	121.5(2)								

[a] No bond distances.

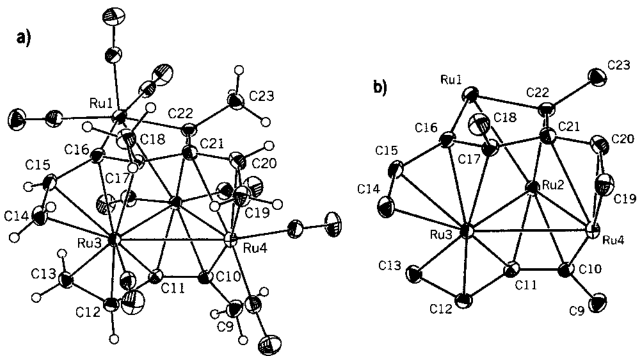


Fig. 2. (a) Molecular structure of $Ru_4(CO)_8(\mu_4\text{-}\eta^4{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-}C_{10}H_{12})(\mu_3\text{-}\eta^3{:}\eta^2{:}\eta^1\text{-}C_5H_6)$ (**2**). (b) The CO groups have been omitted for clarity. ORTEPs shown at 50% probability.

1.298(10) Å, a normal value for a C=C bond as described in the dates of crystallographic database [10]. The C–C bond coordinated to the Ru_4 moiety shows a larger distance (1.386(9)Å).

The mass spectrum of compound **2** indicated the presence of three molecules of enyne coordinated to a tetraruthenium core. The presence of three organic ligands is also observed in the ^1H- and ^{13}C-NMR spectra which show three signals for each of the different groups (Tables 1 and 2).

Single crystals of compound **2** were obtained from a chloroform solution and they were studied by X-ray crystallography. A perspective view of the molecular structure, together with the atomic numbering scheme is shown in Fig. 2 and some selected interatomic distances and angles are given in Table 4.

The structure shows a spiked triangular tetraruthemium metal framework with two separated carbon chains coordinated to the metal core. The first chain is the result of the dimerization of the enyne through head-to-tail coupling of the triple bonds. The second chain is a single enyne molecule. The dimerized chain is bonded to all four ruthenium atoms in $\eta^4{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3$ fashions. The C_5 chain is coordinated to Ru(3), Ru(2) and Ru(4) in $\eta^3{:}\eta^2{:}\eta^1$ modes.

The spiked triangle framework has been observed in several Os_4 clusters [11] and has also been observed in a Ru_4–diyne complex [12]. Metal–metal distances are within the same range than those observed previously. Ru(1) (the spike) has three carbonyl groups bonded while Ru(2) and Ru(4) have two carbonyls each and Ru(3) is only bonded to one carbonyl group. Angles in the metal core show the spike to be bent towards one of the edges of the triangle [Ru(1)–Ru(2)–Ru(3) 86.343(12) vs. Ru(1)–Ru(2)–Ru(4) 121. 832(14)°].

The first ligand molecule in the dimerized chain [atoms C(14) to C(18)], is bonded to Ru(3) in the η^4-mode and to Ru(1) by a σ bond with C(16), the second part of the dimer [atoms C(19) to C(23)] is bonded η^3 to Ru(4) and $\eta^1{:}\eta^1$ to Ru(2) and Ru(1). Coordination of one part of the chain, produces a five-membered metallacyclic ring [Ru(1)–C(16)–C(17)–C(21)–C(22)] similar to the one observed in diyne

Table 4
Select bond lengths (Å) and bond angles (°) for **2**

Bond lengths							
C(14)–C(15)	1.416(6)	C(9)–C(10)	1.506(5)	Ru(3)–C(15)	2.217(4)	Ru(2)–C(10)	2.206(4)
C(15)–C(16)	1.433(5)	C(10)–C(11)	1.351(5)	Ru(3)–C(16)	2.233(4)	Ru(4)–C(10)	2.084(4)
C(16)–C(17)	1.459(6)	C(11)–C(12)	1.413(5)	Ru(3)–C(17)	2.163(4)	Ru(2)–C(11)	2.131(4)
C(17)–C(18)	1.532(5)	C(12)–C(13)	1.378(6)	Ru(4)–C(19)	2.255(4)	Ru(3)–C(11)	2.148(4)
C(17)–C(21)	1.497(5)	Ru(1)–Ru(2)	2.7942(5)	Ru(4)–C(20)	2.201(4)	Ru(3)–C(12)	2.273(4)
C(21)–C(20)	1.439(6)	Ru(2)–Ru(3)	2.8342(4)	Ru(4)–C(21)	2.467(4)	Ru(3)–C(13)	2.291(4)
C(20)–C(19)	1.379(7)	Ru(3)–Ru(4)	2.9796(4)	Ru(2)–C(22)	2.181(4)	Ru–Cco (av)	1.904
C(21)–C(22)	1.467(6)	Ru(4)–Ru(2)	2.7299(4)	Ru(1)–C(16)	2.096(4)	C–O (av)	1.139
C(22)–C(23)	1.529(5)	Ru(3)–C(14)	2.222(4)	Ru(1)–C(22)	2.083(4)	C–H (av)	0.948
Bond angles							
Ru(1)–Ru(2)–Ru(3)	86.343(12)	Ru(1)–C(16)–C(17)	117.3(3)	C(21)–C(22)–C(23)	116.1(3)		
Ru(1)–Ru(2)–Ru(4)	121.832(14)	C(16)–C(17)–C(21)	110.3(3)	Ru(1)–C(22)–C(21)	115.4(2)		
Ru(2)–Ru(3)–Ru(4)	55.943(10)	C(16)–C(17)–C(18)	119.0(3)	Ru(1)–C(22)–C(23)	123.4(3)		
Ru(2)–Ru(4)–Ru(3)	59.333(10)	C(18)–C(17)–C(21)	115.8(3)	C(9)–C(10)–C(11)	127.3(3)		
Ru(3)–Ru(2)–Ru(4)	54.724(11)	C(17)–C(21)–C(20)	119.7(4)	C(10)–C(11)–C(12)	146.9(4)		
C(14)–C(15)–C(16)	123.1(4)	C(17)–C(21)–C(22)	115.6(4)	C(11)–C(12)–C(13)	118.6(5)		
C(15)–C(16)–C(17)	113.3(4)	C(20)–C(21)–C(22)	124.4(3)	C(16)–Ru(1)–C(22)	78.8(2)		
Ru(1)–C(16)–C(15)	129.2(3)	C(21)–C(20)–C(19)	123.8(4)				
Dihedral angles							
C(14)–C(15)–C(16)–C(17)	−2.0(6)	C(16)–C(17)–C(21)–C(22)	11.3(5)	C(16)–C(17)–C(21)–C(20)	175.5(4)		
C(14)–C(15)–C(16)–Ru(1)	172.9(4)	Ru(1)–C(16)–C(17)–C(21)	−17.9(4)	C(17)–C(21)–C(22)–Ru(1)	0.0(5)		
C(15)–C(16)–C(17)–C(21)	157.6(4)	C(19)–C(20)–C(21)–C(22)	162.3(4)	C(21)–C(22)–Ru(1)–C(16)	−7.5(3)		

dimerization reactions [4c]. As it can be appreciated from the torsion angle values (Table 4), the metallacycle adopts an envelope conformation with C(17)–C(21)–C(22)–Ru(1) being in a plane and C(16) somewhat below that plane. Two of the atoms of that ring, C(17) and C(16), together with C(15) and C(14), are bonded to Ru_3 in a η^4-mode. Several η^4-hydrocarbon bonded clusters have been described [13] but they generally show a double–single–double bond character alternation in the chain whereas an analysis of bond distances in **2** does not follow the same trend. The two carbon–carbon bond distances involved in the η^3-bond, an allylic type of fragment, are different too (1.379(7) and 1.439(6) Å) and show a larger difference than that is observed in other compounds with a similar structure [14].

C–C bond distances of the other separated organic ligand, show a diene character with C(10)–C(11) and C(12)–C(13) showing shorter bond lengths than C(9)–C(10) and C(11)–C(12).

The C_{10} chain in compound **2**, donates a total of ten electrons to the cluster while the C_5 chain donates six electrons. These 16 electrons together with the 48 electrons from the $Ru_4(CO)_8$ core yield a total of 64 electrons, consistent with the structure observed.

Mass spectrometry of compound **3** also suggests the presence of three molecules of the ligand in the cluster but, in contrast with compound **2**, ten carbonyl groups are retained in this compound. Both the ^{1}H- and ^{13}C-NMR show signals for three distinct fragments, although there are differences in chemical shifts and in coupling constants with those observed for compound **2**.

One difference is observed in the coupling constant values of the *cis* and *trans* protons of the olefinic CH_2 groups which are larger in two of the CH_2 groups of compound **3** than in **2** suggesting that these fragments are not directly coordinated to the metal atoms. The third olefinic CH and CH_2 groups not only show smaller ^{1}H–^{1}H coupling constants but also chemical shifts more similar to those observed in compound **2** indicating this fragment is directly bonded to the metal core.

Analysis of the correlation patterns of the different protons and carbons, suggests two of the enynes to be coupled in a head-to-tail fashion as observed in compound **2**. A correlation can also be observed between one of the quaternary carbons of the third enyne ligand with one of the CH_2 protons of the dimerized organic chain. We believe this interaction indicates the third enyne molecule is also bonded to the organic chain, i.e. the ligands have really trimerized.

Another important observation is that the methyl group of the third enyne fragment is interacting with the CH_2 group of the same molecule. This methyl group was originally located five bonds away from the CH_2 group, too far away to allow a correlation. We thus propose that this methyl group has migrated to the next carbon atom to allow the coupling of this group to the dimeric chain. Migration of methyl groups has been previously observed in the reaction of *tert*-butylacetylene with an iron methylidyne complex [15].

Comparison of chemical shifts with those reported in the literature [1–4] and with those obtained in our laboratory in the products of the reaction of $[Ru_3(CO)_{12}]$ with the same enyne ligands [16], make us propose the structure shown in Scheme 1for **3**. In this structure the carbon chain donates 10 electrons, which together with the 52 electrons coming from a $Ru_4(CO)_{10}$ fragment, would give a total of 62 electrons which suggest a butterfly geometry for the metal core.

When the reaction of $[H_4Ru_4(CO)_{12}]$ was carried out with 2-methyl-1-buten-3-yne under the same conditions described above, it yielded a large number of products in very small yields. This could be due to the presence of a terminal alkyne function which could lead to several different mechanistic routes. Further studies on this reaction will be investigated.

It is important to underline that no hydrogenation of the unsaturated ligand was detected in these reactions as had been observed in the reaction of the same cluster with diynes [6]. It also seems that the coordination of the alkyne group to the cluster is preferred to the bonding of the alkene moiety. Dimerization of the alkyne may be taking place on the coordinated alkyne, since we only isolated products where the coupling takes place through the triply bonded carbon atoms.

3. Conclusions

Reactions of the ligand 1-penten-3-yne with $[H_4Ru_4(CO)_{12}]$ yields products that suggest that coordination initially takes place through the triple bond, which then reacts with further amounts of enyne to give products where dimerization and trimerization of the ligand has taken place.

4. Experimental

4.1. General procedures and materials

Reactions were carried out using octane purchased from Aldrich Chemicals and dried by standard procedures. All reactions were carried out under nitrogen atmosphere. The cluster $[H_4Ru_4(CO)_{12}]$ was prepared from $[Ru_3(CO)_{12}]$ purchased from Strem Chemicals, according to the literature method [17]. Both enynes were purchased also from Strem Chemicals and used without further purification. Products are given in the order of decreasing R_f values.

Table 5
Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{21}H_7O_{11}Ru_4$	$C_{23}H_{18}O_8Ru_4$
Molecular weight	844.6	826.7
Temperature (K)	193(2)	193(2)
System	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.1503(7)	9.4254(5)
b (Å)	10.4985(6)	9.7536(5)
c (Å)	19.4776(12)	14.6312(8)
α (°)	90.00	99.2910(10)
β (°)	90.9420(10)	93.6960(10)
γ (°)	90.00	107.8000(1)
V (Å^3)	2484.2(3)	1254.57(12)
Z	4	2
ρ_{calc} (Mg m^{-3})	2.245	2.188
F(000)	1588	792
λ (Mo–K$_\alpha$) (Å)	0.71073	0.71073
μ (Mo–K$_\alpha$) (mm^{-1})	2.442	2.407
2θ range (°)	3.36–58.92	2.84–58.44
Index ranges (h_{min}/h_{max}, k_{min}/k_{max}, l_{min}/l_{max})	−13/16, −13/13, −24/24	−12/12, −12/12, −18/17
Measured reflections	14 235	7310
Observed reflections	3484	3454
($F>4\sigma(F)$) unique reflections [R_{int}]	4935 [0.0387]	3838 [0.0188]
R_1 [$F>4\sigma(F)$]	0.0385	0.0243
wR_2 (on F^2 all data) [a]	0.0901	0.0643
Goodness-of-fit on F^2	1.021	1.044

[a] $w^{-1}=\sigma^2F_o^2+(0.1275P)^2+0.000P$, where $P=(F_o^2+2F_c^2)/3$.

4.2. Spectra

Infrared spectra were recorded in solution in a Perkin–Elmer 16FPC Fourier transform instrument. NMR spectra were recorded in $CDCl_3$ using Me_4Si as external reference in a JEOL Eclipse-400, ^{1}H-NMR field strength was 399.7782 and ^{13}C was 100.5354 MHz. Mass spectra were obtained in a JEOL JMS-SX102A using Xenon. Microanalyses were performed in Oneida Research Services, Inc., NY.

*4.3. Synthesis of [Ru$_4$(μ-CO)(CO)$_{10}$-(μ$_4$-η^1:η^2:η^1:η^2-C$_5$H$_6$)$_2$] (**1**), [Ru$_4$(CO)$_8$-(μ$_4$-η^4:η^1:η^1:η^1:η^3-C$_{10}$H$_{12}$)(μ$_3$-η^3:η^2:η^1-C$_5$H$_6$)] (**2**) and [Ru$_4$(CO)$_{10}$(μ$_4$-η^4:η^1:η^1:η^3:η^1-C$_{15}$H$_{18}$)] (**3**)*

A solution of $[H_4Ru_4(CO)_{12}]$ (50 mg, 0.067 mmol) in octane (30 ml) containing an excess of 1-penten-3-yne (0.036 ml, 0.402 mmol) was heated to reflux for 1 h. During this period the reaction was monitored by spot TLC, which indicated that the majority of the starting material had been consumed and that several new products were present. The solvent was removed from the reaction mixture under reduced pressure. The residue was redissolved in the minimum amount of $CHCl_3$ and passed trough a column of silica using a solution of chloroform–hexane (2:8, v/v) as eluent. The three main products were found in the second red fraction. This fraction was separated by TLC. Elution with chloroform–hexane (1:9, v/v) gave orange [Ru$_4$(CO)$_{10}$(μ$_4$-η^4:η^1:η^1:η^3:η^1-C$_{15}$H$_{18}$)] (**3**) (5.9 mg, 10%). Anal. Calc. for $C_{25}H_{18}O_{10}Ru_4$: C, 34.02; H, 2.06. Found: C, 34.32; H, 2.11%. FABMS: 882 [M$^+$]. IR (hexane, cm^{-1}): ν(CO) 2076(w), 2060(s), 2034(w), 2018(s), 2002(m), 1988(m), 1958(w). Red [Ru$_4$(CO)$_8$(μ$_4$-η^4:η^1:η^1:η^1:η^3-C$_{10}$H$_{12}$)(μ$_3$-η^3:η^2:η^1-C$_5$H$_6$)] (**2**) (12.8 mg, 23%) Anal. Calc. for $C_{23}H_{18}O_8Ru_4$: C, 33.42; H, 2.19. Found: C, 33.89; H, 2.63%. FABMS: 826 [M$^+$]. IR (hexane, cm^{-1}): ν(CO) 2070(s), 2036(vs), 2004(vs), 1996(vs), 1990(vs), 1974(s), 1948(s), 1914(m). And orange–yellow [Ru$_4$(μ-CO)(CO)$_{10}$(μ$_4$-η^1:η^2:η^1:η^2-C$_5$H$_6$)$_2$] (**1**) (8.5 mg, 15%). Anal. Calc. for $C_{21}H_{12}O_{11}Ru_4$: C, 29.86; H, 1.43. Found: C, 30.11; H, 1.98. FABMS: 844 [M$^+$]. IR (hexane, cm^{-1}): ν(CO) 2084(w), 2066(w,sh), 2053(m,sh), 2038(s), 2026(s), 2012(m), 1994(m), 1986(m), 1964(w), 1944(w).

5. Crystallography

Crystal data and details of the structures are listed in Table 5. The selected crystals were covered with perfluoropolyether oil, attached to the tip of a glass fiber and then mounted on the Euler cradle of a Siemens P4 four-circle diffractometer equipped with a CCD area detector and an LT2 low temperature device. Unit cell dimensions were calculated from four sets of data collected at 193 K, with different crystal orientations over 15 frames, each with $\Delta\Psi=0.3°$. Data collection was carried out in the hemisphere mode at 193 K, at two different X settings with $\Delta\Psi=0.3°$ for each series over a total of 100 frames. Structure solution was performed by the Patterson method, followed by successive difference Fourier cycles [18]. Non-hydrogen atoms were refined anisotropically while hydrogen positions for methyl-groups protons were calculated while those not in methyl groups were found in difference maps and refined freely. In compound **1**, the occupancy of atoms C(1A) and C(5) was calculated and refined finishing with a value of about 0.5 for each. Hydrogen atoms bonded to these carbon atoms were not calculated.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167642 and 167641 for compounds **1** and **2**. 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).

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References

[1] (a) M.I. Bruce, J.R. Hinchliffe, P.A. Humphrey, R.J. Surynt, B.W. Skelton, A.H. White, J. Organomet. Chem. 552 (1998) 109;
(b) E. Sappa, A.M. Manotti, A. Tiripicchio, Inorg. Chim. Acta 42 (1980) 255;
(c) A.A. Koridze, N.M. Astakhova, F.M. Dolgushin, A.I. Yanovskii, Y.T. Struchkov, P.J. Petrovskii, Organometallics 14 (1995) 2167;
(d) R.D. Adams, W. Fu, B. Qu, J. Cluster Sci. 11 (2000) 55;
(e) E. Rosenberg, S. Aime, L. Milone, E. Sappa, A. Tiripicchio, A.M. Manotti, J. Chem. Soc. Dalton Trans. (1981) 2023;
(f) E. Sappa, J. Cluster Sci. 5 (1994) 211;
(g) E. Sappa, J. Organomet. Chem. 573 (1999) 139.

[2] (a) E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203;
(b) E. Sappa, A.M. Manotti, G. Predieri, A. Tiripicchio, Inorg. Chim. Acta 61 (1982) 217;
(c) S. Aime, G. Gervasio, L. Milone, E. Sappa, A. Franchini, Inorg. Chim. Acta 26 (1978) 223;
(d) J.P.H. Charmant, G. Davies, P.J. King, J.R. Wigginton, E. Sappa, Organometallics 19 (2000) 2330.

[3] A.M. Boldi, J. Anthony, C.B. Knobler, F. Diederich, Angew. Chem. Int. Ed. Engl. 31 (1992) 1240.

[4] (a) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Inorg. Chim. Acta 250 (1996) 129;
(b) J.F. Corrigan, N.J. Taylor, A.J. Carty, Organometallics 13 (1994) 3778;
(c) C.S.-W. Lou, W.-T. Wong, J. Chem. Soc. Dalton Trans. (1999) 2511.

[5] A.J. Deeming, M.S.B. Felix, D. Nuel, Inorg. Chim. Acta 213 (1993) 3.

[6] L.P. Clarke, J.E. Davies, P.R. Raithby, G.P. Shields, J. Chem. Soc. Dalton Trans. (2000) 4527.

[7] O. Gambino, E. Sappa, A.M. Manotti-Lanfredi, A. Tiripicchio, Inorg. Chim. Acta 36 (1979) 169.

[8] J.E. Davies, B.F.G. Johnson, C.M. Martin, R.H.H. Pearson, P.J. Dyson, J. Organomet. Chem. 550 (1988) 431.

[9] V. Ferrand, G. Süss-Fink, A. Neels, H. Stoeckli-Evans, J. Chem. Soc. Dalton Trans. (1998) 3825.

[10] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1998) 3825.

[11] R.K. Pomeroy, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry 2, vol. 7, Pergamon, Oxford, 1995, p. 35 (and references therein).

[12] J.A. Cabeza, M. Moreno, V. Riera, M.J. Rosales, Inorg. Chem. Commun. 4 (2001) 57.

[13] A.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry 2, vol. 7, Pergamon, Oxford, 1995, p. 747 (and references therein).

[14] J.P.H. Charmant, P.J. King, R. Quesada-Pato, E. Sappa, C. Schaefer, J. Chem. Soc. Dalton Trans. (2001) 46.

[15] C.P. Cassey, L.K. Woo, P.J. Fagan, R.E. Palermo, B.R. Adams, Organometallics 6 (1987) 447.

[16] F.J. Zuno-Cruz, G. Sánchez-Cabrera, M.J. Rosales, unpublished results.

[17] M.I. Bruce, M.L. Williams, Inorg. Synth. 28 (1990) 219.

[18] G.M. Sheldrick, shelx-93, University of Göttingen, Göttingen, Germany, 1993.