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Reactions of μ_3-Alkenyl Triruthenium Carbonyl Clusters with Alkynes: Synthesis of Trinuclear μ-//-Alkyne, μ-Vinylidene, and μ-Dienoyl Derivatives

Javier A. Cabeza,*[a] Ignacio del Río,[a] Lorena Martínez-Méndez,[a] and Enrique Pérez-Carreño[b]

Abstract: The reactions of doubly face-capped triruthenium cluster complexes of the type $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}R^2CCHR^1)(\mu\text{-}CO)_2(CO)_6]$ ($HNNMe_2$ = 1,1-dimethylhydrazide; R^2CCHR^1 = alkenyl ligand) with terminal and internal alkynes have been studied in refluxing toluene. The following derivatives have been isolated from these reactions: $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}R^2CCHR^1)(\mu\text{-}\kappa^2\text{-}//\text{-}HCCH)(CO)_7]$ ($R^1 = R^2 = H$, **5**; R^1 = Ph, R^2 = H, **6**; $R^1 = CH_2OMe$, R^2 = H, **7a**; R^1 = H, $R^2 = CH_2OMe$, **7b**) from acetylene, $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}\kappa^2\text{-}//\text{-}PhCCPh)(CO)_7]$ (**11**) from diphenylacetylene, and three isomers of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}\kappa^2\text{-}//\text{-}PhCCH)(CO)_7]$ (**14**, **15a**, and **15b**) from phenylacetylene. These products result from substitution of a CO ligand by the alkyne and contain an Ru–Ru edge bridged by the alkyne ligand in a parallel manner. DFT calculations on selected isomeric products have helped to establish that the type of Ru–Ru edge bridged by the alkyne depends more on kinetic factors related to the size of the alkyne substituents than on the thermodynamic stability of the final products. The preparation of triruthenium cluster complexes with μ-//-alkyne ligands is unprecedented and seems to relate to the fact that the starting trinuclear complexes have their two triangular faces protected by capping ligands. The clusters bearing μ-//-acetylene (**5**–**7**) are thermodynamically unstable with respect to their transformation into edge-bridging vinylidene derivatives, $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHR)(\mu\text{-}\kappa^1\text{-}CCH_2)(CO)_7]$ (R = H, **8**; Ph, **9**; CH_2OMe, **10**). DFT calculations have shown that complex **8** is 11.2 kcal mol^{-1} more stable than its precursor **5**. The thermolysis of compound **11** leads to $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^4\text{-}H_2CCHCPhCPhCO)(\mu\text{-}CO)_2(CO)_5]$ (**12**), which contains a novel edge-bridging dienoyl ligand that arises from an unusual coupling of diphenylacetylene, carbon monoxide, and the ethenyl ligand of complex **11**. A chloro-bridged dimer of trinuclear clusters, $[Ru_6(\mu\text{-}Cl)_2(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)_2(\mu_3\text{-}\kappa^2\text{-}HCCH_2)_2(\mu\text{-}\kappa^2\text{-}PhCCHPh)_2(\mu\text{-}CO)_2(CO)_{10}]$ (**13**), has been prepared by treating compound **11** with hydrogen chloride. Therefore, edge-bridging parallel alkynes are susceptible to protonation to give edge-bridging alkenyl ligands. Compound **13** is the first complex to contain two alkenyl ligands on a trinuclear cluster, one face-capping and the other edge-bridging.

Keywords: alkenyl ligands · alkyne ligands · cluster compounds · ruthenium · vinylidene ligands

Introduction

Alkenyl groups are important ligands in organometallic chemistry because they are invoked in many metal-mediated transformations of alkynes and alkenes. However, to date, the number of reports dealing with triruthenium carbonyl cluster complexes containing alkenyl ligands is relatively small,[1–6] despite the fact that some of these clusters have been recognized as intermediates or as catalyst precursors in alkyne–alkene co-dimerization[7] as well as alkyne hydrogenation,[8] dimerization,[2b] polymerization,[2b] and hydroformylation[2c] processes.

In the context of alkenyl triruthenium complexes, we have recently revised the studies of Hansert and Vahren-

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[a] Prof. J. A. Cabeza, Prof. I. del Río, Dr. L. Martínez-Méndez
Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica “Enrique Moles”, Universidad de Oviedo,
33071 Oviedo (Spain)
Fax: (+34) 985-103-446
E-mail: jac@fq.uniovi.es

[b] Prof. E. Pérez-Carreño
Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo (Spain)

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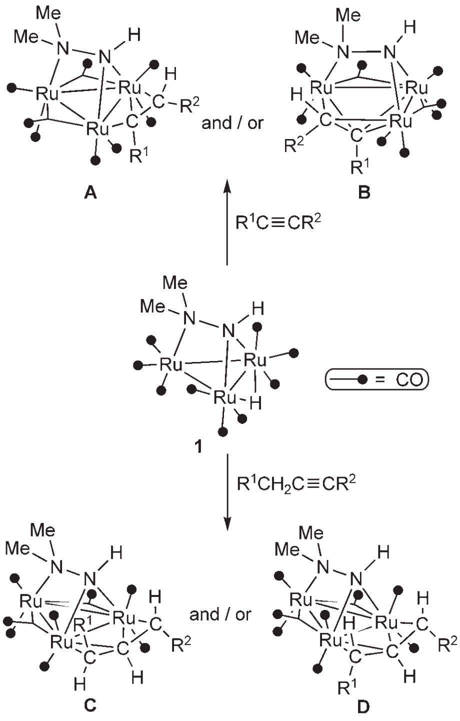
kamp[4] on the reactivity of the Süss-Fink's hydrazido-bridged hydrido carbonyl triruthenium complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(CO)_9]$[9] (**1**) with terminal and internal alkynes without α-hydrogen atoms, showing that the products have alkenyl ligands in edge-bridging or face-capping positions (**A** and **B**, respectively, in Scheme 1) and that the nature of the substituents on the alkyne reagent strongly affects the stability of each product.[5] We have also reported that alkynes with α-hydrogen atoms react with complex **1** to give trinuclear derivatives that contain edge-bridging allyl ligands (**C** and **D** in Scheme 1).[6]



Scheme 1. Reactivity of compound **1** with alkynes.

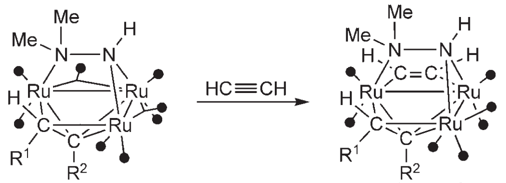
Trimetallic clusters bearing face-capping alkenyl ligands are very rare, not only for ruthenium, but also for other metals. Such ligands have only been found in $[Os_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}CF_3CCHCF_3)(CO)_{10}]$,[10] $[WRu_2Cp^*(\mu\text{-}NPh)(\mu_3\text{-}\kappa^2\text{-}CF_3CCHCF_3)(CO)_7]$,[11] $[Ru_3\{\mu_3\text{-}NS(O)MePh\}(\mu_3\text{-}\kappa^2\text{-}RCCHR)(\mu\text{-}CO)(CO)_7]$,[3a] and in some derivatives of compound **1**.[4–6] Curiously, despite being open (two Ru–Ru bonds) trinuclear clusters, $[Ru_3\{\mu_3\text{-}NS(O)MePh\}(\mu_3\text{-}\kappa^2\text{-}RCCHR)(\mu\text{-}CO)(CO)_7]$ and the μ_3-alkenyl derivatives of compound **1** are 48-electron species.[12,13]

Studying the reactivity of compound **1** towards various alkynes,[5] we observed that the use of high temperatures (> 100 °C) and/or long reaction times led to products that were derived from the incorporation of two alkyne molecules into the starting cluster. This led us to undertake a detailed study on the reactivity of some μ_3-alkenyl derivatives of complex **1** with internal and terminal alkynes, having in mind that no reactions of alkynes with μ_3-alkenyl metallic clusters had hitherto been reported and that these reactions might lead to products containing novel ligands that arise from alkenyl-alkyne couplings.

We now communicate the synthesis of triruthenium clusters in which an edge-bridging parallel alkyne coexists with a face-capping alkenyl ligand. The conversion of such an alkyne ligand into an edge-bridging vinylidene ligand and the formation of a dienoyl ligand by a three-component (CO, alkyne, and alkenyl) coupling process are also reported. X-ray diffraction analyses, IR and NMR spectroscopic studies, and calculations of minimum-energy structures by DFT methods have been used to characterize the products. The experimental results have been rationalized in conjunction with DFT calculations, which have allowed us to compare the absolute energies of isomeric reaction products.

Results and Discussion

Reactions of μ_3-alkenyl triruthenium complexes with acetylene: The reaction of compound **1** with acetylene (1 atm) in THF at reflux temperature afforded the μ_3-ethenyl derivative $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**2**) in good yield.[5] However, when these reagents were allowed to react in refluxing toluene, the μ_3-ethenyl-μ-//-acetylene $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}\kappa^2\text{-}//\text{-}HCCH)(CO)_7]$ (**5**) was obtained from a 30 min reaction, while **2** was observed as an intermediate. In an independent experiment, it was proven that complex **2** reacts with acetylene (1 atm) in toluene at reflux temperature (30 min) to give compound **5** (Scheme 2).



	R^1	R^2		R^1	R^2
2	H	H	**5**	H	H
3a	Ph	H	**6**	Ph	H
3b	H	Ph	**7a**	CH_2OMe	H
4	H	CH_2OMe	**7b**	H	CH_2OMe

Scheme 2. Reactions of μ_3-alkenyl clusters with acetylene.

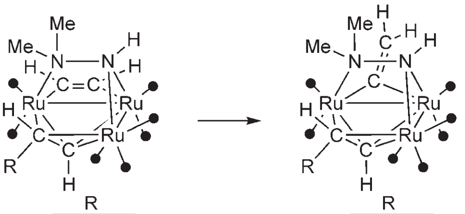
In related experiments (acetylene, 1 atm, refluxing toluene, 30 min), we observed that the phenylacetylene-derived *trans-* and *geminal*-alkenyl isomers $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHPh)(\mu\text{-}CO)_2(CO)_6]$ (**3a**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}PhCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**3b**), respectively, led to the same product, that is, the μ_3-*trans*-alkenyl-μ-//-acetylene derivative $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHPh)(\mu\text{-}\kappa^2\text{-}//\text{-}HCCH)(CO)_7]$ (**6**) (Scheme 2). However, under analogous conditions, the methyl propargyl ether-derived μ_3-*geminal*-alkenyl $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}MeOCH_2CCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**4**) afforded a mixture of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHCH_2OMe)(\mu\text{-}\kappa^2\text{-}//\text{-}HCCH)(CO)_7]$

(**7a**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu_3\text{-}\kappa^2\text{-MeOCH}_2\text{CCH}_2)(\mu\text{-}\kappa^2\text{-//-HCCH})(CO)_7]$ (**7b**), which, in addition to a μ-//-acetylene ligand, contain a μ_3-*trans*- (**7a**) or a μ_3-*geminal*-alkenyl (**7b**) ligand (Scheme 2).

We have previously reported that μ_3-*geminal*-alkenyl derivatives of complex **1** are less stable than their μ_3-*trans*-alkenyl isomers and that μ_3-*geminal*- to μ_3-*trans*-alkenyl isomerization processes are achievable under thermal conditions.[5] These data, coupled with the results of the reactions that led to compounds **6**, **7a**, and **7b**, suggest that the isomerization of **3b** into **3a** is fast in refluxing toluene and that it should take place prior to the reaction of **3b** with acetylene, whereas the isomerization of the μ_3-*geminal*-alkenyl complex **4** into its μ_3-*trans*-alkenyl isomer is slower such that both **4** and its μ_3-*trans*-alkenyl isomer react with acetylene to give the observed mixture of **7a** and **7b**. However, the occurrence of processes involving the isomerization of μ_3-*geminal*-alkenyl-μ-//-acetylene complexes (such as **7b**) into μ_3-*trans*-alkenyl-μ-//-acetylene species (such as **6** and **7a**) cannot be ruled out.

Although there have been quite a number of reports dealing with binuclear complexes that have edge-bridging alkyne ligands with a parallel arrangement of the carbon atoms with respect to the bridged metal atoms (μ-//-alkyne ligands),[14,15] such ligands are unprecedented in transition metal carbonyl cluster chemistry. As far as we are aware, the triplatinum complex $[Pt_3(\mu\text{-//-}Ph_2C_2)(PEt_3)_3]$ is the only previous example of a metal cluster having a μ-//-alkyne ligand.[16]

Isomerization of μ-//-acetylene clusters into μ-vinylidene derivatives: The reactions that led to the μ-//-acetylene clusters **5**–**7** were not clean. The isolation of pure products required the use of chromatographic separations and the final yields were never higher than 60 %. We also observed that reaction times longer than 30 min resulted in lower yields of the μ-//-acetylene clusters, favoring the formation of other products that decomposed on TLC plates but that survived column chromatography. These results led us to investigate the thermolysis of compounds **5**, **6**, and **7a** in toluene at reflux temperature. The edge-bridged vinylidene derivatives $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu_3\text{-}\kappa^2\text{-HCCHR})(\mu\text{-}\kappa^1\text{-CCH}_2)(CO)_7]$ (R = H (**8**), Ph (**9**), CH_2OMe (**10**)) were isolated in good yields (60–75 %), after column chromatography, from 1 h reactions (Scheme 3).



	R
5	H
6	Ph
7a	CH_2OMe

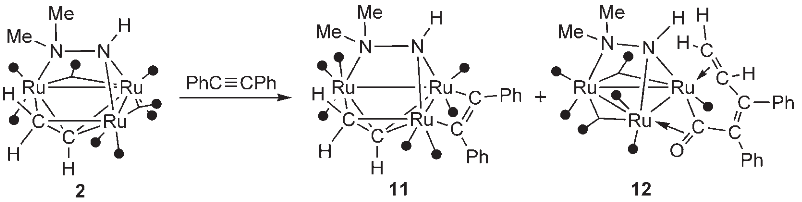
	R
8	H
9	Ph
10	CH_2OMe

Scheme 3. Edge-bridging acetylene to edge-bridging vinylidene isomerization reactions.

In ruthenium cluster chemistry, face-capping vinylidene ligands are well represented,[17] but edge-bridging vinylidene ligands have not been hitherto reported. Only a few diruthenium complexes having bridging vinylidene ligands have been reported.[14c,d,h,18] Although most of them arise from reactions of binuclear precursors with terminal alkynes, it is remarkable that the involvement of μ-//-alkyne species as intermediates in their synthesis has not been unambiguously established. It has been reported that the reactions of $[Ru_2\{\mu\text{-}\kappa^2\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}(\mu\text{-CO})_2(CO)_2]$ with terminal alkynes afford mixtures of μ-//-alkyne and μ-vinylidene derivatives, the ratio of which is insensitive to both the temperature and the reaction time and, therefore, the authors conclude that the two types of complexes should be formed through independent reaction pathways.[14h] It has also been proposed that $[Ru_2Cp_2(\mu\text{-CO})_2(CO)(MeCN)]$ reacts with acetylene to give, via a hydrido-ethynyl intermediate, $[Ru_2Cp_2(\mu\text{-}\kappa^2\text{-HCCHCO})(\mu\text{-CO})(CO)]$, the latter subsequently isomerizing to the vinylidene $[Ru_2Cp_2(\mu\text{-}\kappa^1\text{-CCH}_2)(\mu\text{-CO})(CO)_2]$.[18a] In addition, on the basis of extended Hückel calculations, it has been proposed that the transformation of binuclear μ-//-alkyne complexes into their μ-vinylidene isomers should proceed through a transition state of very high energy and, consequently, the authors conclude that such a process should be highly unlikely.[19] All these data contrast with the clear evidence that the μ-//-alkyne clusters **5**, **6**, and **7a** are precursors to the vinylidene derivatives **8**–**10**, respectively. On the other hand, it has also been proposed that μ-//-alkyne complexes are involved in a reaction by which $[Ru_2CpCp^*\{\mu\text{-}\kappa^1\text{-CC(CO}_2\text{Me)}_2\}(\mu\text{-CO})(CO)_2]$ is formed from dimethylacetylenedicarboxylate and the appropriate diruthenium precursor[14c] and also in reactions that give μ-vinylidene derivatives from terminal alkynes and binuclear complexes of metals other than ruthenium.[20] Therefore, detailed mechanistic studies, including theoretical ones using modern DFT methods, are needed to shed more light on the transformation of alkynes into edge-bridging vinylidene ligands in di- and polynuclear complexes.

Reactions of complex 2 with diphenylacetylene and phenylacetylene: To compare the behavior of di- and monosubstituted alkynes with that of acetylene in their reactions with face-capped alkenyl triruthenium clusters, we studied the reactions of complex **2** with diphenylacetylene and phenylacetylene. As compound **2** was prepared in good yield and as all of the face-capped alkenyl clusters **2**–**4** showed a similar reactivity with acetylene (Scheme 2), we decided to utilize compound **2** as a starting material for further reactivity studies, considering it a representative face-capped alkenyl cluster.

Two complexes, the edge-bridged alkyne derivative $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu_3\text{-}\kappa^2\text{-HCCH}_2)(\mu\text{-}\kappa^2\text{-//-PhCCPh})(CO)_7]$ (**11**) and the edge-bridged dienoyl cluster $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-}\kappa^4\text{-H}_2\text{CCHCPhCPhCO})(\mu\text{-CO})_2(CO)_5]$ (**12**), were isolated from a reaction in which complex **2** and diphenylacetylene were heated in toluene at reflux temperature for 1 h (Scheme 4). From a subsequent experiment, in which

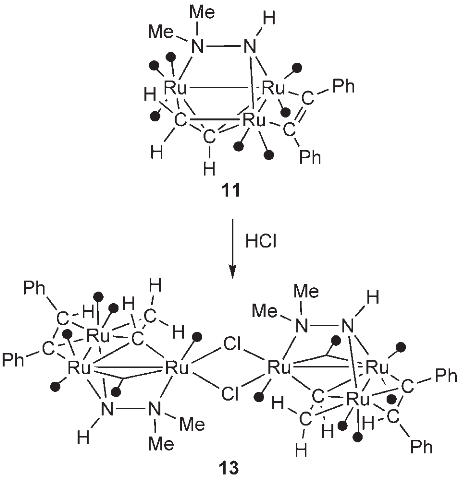


Scheme 4. Reaction of compound **2** with diphenylacetylene.

complex **11** was heated in refluxing toluene for 1 h, we concluded that **11** is a precursor to complex **12**.

Interestingly, the Ru–Ru edge bridged by the diphenylacetylene ligand in **11** is different from that bridged by acetylene in **6** and **7**, and that the formation of the 2,3-diphenylpenta-2,4-dienoyl ligand of complex **12** implies an unusual three-component coupling, namely that of carbon monoxide with an alkyne and an alkenyl ligand, for which there is only one precedent, that is, the formation of a 2,3,4-trimethylhexa-2,4-dienoyl ligand by treatment of [Ru_3(μ-H){μ_3-NS(O)MePh}$(CO)_9$] with 2-butyne.[3c]

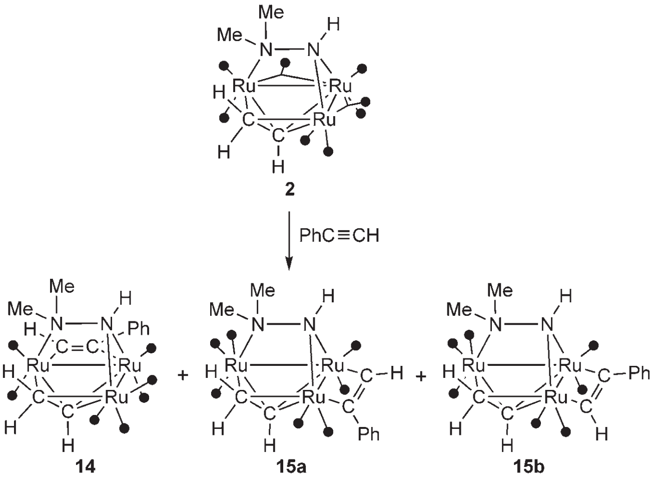
In an attempt to prepare single crystals of compound **11** from a solution of this complex in chloroform, we obtained some crystals of a different complex, which was subsequently identified as [Ru_6(μ-Cl)$_2$(μ_3-κ^2-$HNNMe_2$)$_2$(μ_3-κ^2-$HCCH_2$)$_2$(μ-κ^2-PhCCHPh)$_2$(μ-CO)$_2$$(CO)_{10}$] (**13**). As this complex seemed to arise from a reaction of **11** with hydrogen chloride and it is well known that chloroform produces small amounts of hydrogen chloride when it is exposed to light for long periods of time,[21] we subsequently treated compound **11** with a solution of hydrogen chloride in diethyl ether. The hexanuclear product **13** was thereby obtained in excellent yield (Scheme 5).



Scheme 5. Reaction of compound **11** with hydrogen chloride.

The formation of compound **13** seems to involve the protonation of one of the alkyne carbon atoms of **11** to give an edge-bridging alkenyl ligand. The thus formed cationic intermediate seems to be electrophilic enough to undergo substitution of a CO ligand by chloride.[22] The unsaturation of the resulting trinuclear chloro complex is alleviated by dimerization. As far as we are aware, there are no previous examples of hexaruthenium clusters with two halogen atoms bridging two trinuclear units. The presence of two alkenyl ligands in a triruthenium cluster is also unprecedented.

The fact that the Ru–Ru edge spanned by the diphenylacetylene ligand in **11** is different from that spanned by acetylene in **6** and **7** led us to investigate the reactivity of compound **2** with phenylacetylene. In this case, we obtained a mixture of three isomeric products, [Ru_3(μ_3-κ^2-$HNNMe_2$)(μ_3-κ^2-$HCCH_2$)(μ-κ^2-//-HCCPh)$(CO)_7$] (**14**, **15a**, and **15b**), one of which (**14**) could be separated from the other two by chromatographic methods (Scheme 6). While the Ru–Ru edge spanned by the alkyne ligand in compound **14** is different from that spanned in **15a** and **15b**, **15a** differs from **15b** in the position of the alkyne phenyl group.



Scheme 6. Reaction of compound **2** with phenylacetylene.

X-ray diffraction studies: The crystal structures of **6**·CH_2Cl_2, **12**·0.25(CH_2Cl_2), and **13**·$CHCl_3$ have been determined by X-ray diffraction analysis. A selection of interatomic distances is given in Table 1. For comparison purposes, a common atom numbering scheme has been used. The molecular structure of compound **6** is shown in Figure 1. The 1,1-dimethylhydrazido ligand caps three ruthenium atoms in the same way as previously found in complex **1**[9] and most of its derivatives.[5,6,23] The alkenyl ligand bears one phenyl group on C6 and two H atoms in a *trans* arrangement, one on C5 and one on C6. It also caps the metal triangle in the same manner as found in other complexes bearing μ_3-alkenyl ligands,[5,6] being attached to Ru2 through C5 and to Ru1 and Ru3 through both C5 and C6. The acetylene ligand spans

Table 1. Selected interatomic distances [Å] in compounds **6**, **12**, and **13** (X-ray diffraction data).

	6	12	13
Ru1–Ru2	2.7299(7)	2.6633(8)	2.715(2)
Ru1–Ru3	3.5783(6)	2.7626(9)	3.868(2)
Ru2–Ru3	2.9594(7)	2.7136(8)	2.740(1)
N1–Ru1	2.033(5)	2.096(7)	2.14(1)
N1–Ru2	2.124(6)	2.120(7)	2.09(1)
N2–Ru3	2.229(5)	2.210(6)	2.26(1)
C3–Ru1			2.21(1)
C3–Ru2	1.989(7)		2.11(1)
C4–Ru1			2.32(1)
C4–Ru3	2.073(7)		
C5–Ru1	2.217(6)		2.38(1)
C5–Ru2	2.213(6)	2.292(8)	2.35(1)
C5–Ru3	2.123(6)		2.07(1)
C6–Ru1	2.281(6)		2.15(1)
C6–Ru2		2.259(8)	
C6–Ru3	2.316(6)		2.97(2)
C21–Ru1		2.708(8)	
C21–Ru2		2.020(8)	
C3–C4	1.327(11)	1.35(1)	1.40(2)
C3–C21		1.48(1)	
C4–C5		1.47(1)	
C5–C6	1.439(9)	1.38(1)	1.44(2)
C21–O21		1.245(9)	
O21–Ru1		2.188(5)	
Cl1–Ru3			2.475(4)
Cl1′–Ru3			2.524(3)

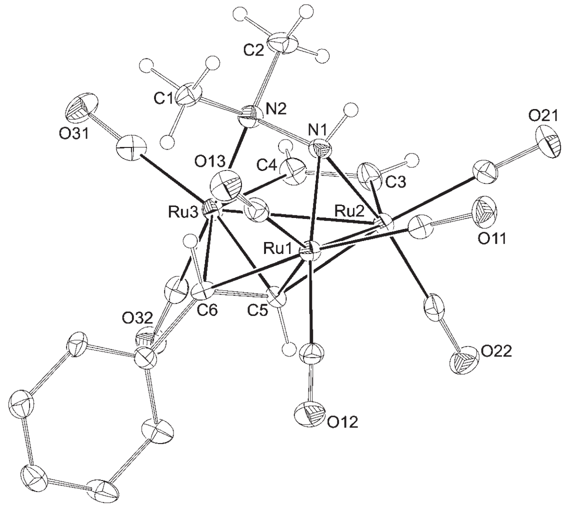


Figure 1. Molecular structure of compound **6**.

the Ru2–Ru3 edge in such a way that both metal atoms and the C3 and C4 carbon atoms are coplanar, thus behaving as a 1,2-dimetalated ethene.[14] The cluster shell is completed with seven terminal CO ligands. The length of the Ru1–Ru3 edge, 3.5783(6) Å, is out of the bonding range for Ru–Ru bonds.[24] Despite being an open triangular cluster, the electron count of this arrangement is 48 and thus it disobeys the EAN rule.[13] This has previously been observed in other triruthenium cluster complexes having face-capping alkenyl ligands[5,6] and has been rationalized by theoretical calculations.[12]

The most remarkable feature of the molecular structure of compound **12** (Figure 2) is the presence of a novel 2,3-diphenylpentadienoyl ligand bridging the same Ru–Ru edge as the amido fragment of the capping 1,1-dimethylhydrazido ligand. The carbonyl fragment of this dienoyl ligand spans the Ru1–Ru2 edge, while the C atoms of its terminal CC double bond are attached to Ru2, and thus overall it behaves as a five-electron donor ligand.[13] The cluster shell is completed with two bridging and five terminal CO ligands. The three Ru–Ru distances are within the Ru–Ru bonding range,[24] as expected for a 48-electron trinuclear cluster. Only a few examples of acyl-bridged triruthenium clusters, in addition to those formed by insertion of CO groups into Ru–C bonds of alkenyl[2b,c] and alkyne[3c] derivatives, have been structurally characterized.[25]

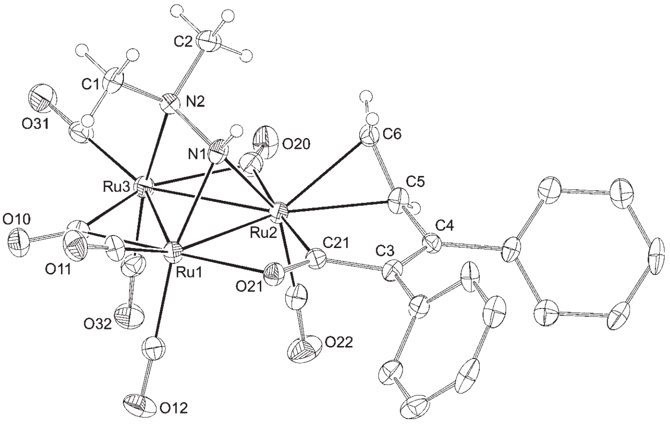


Figure 2. Molecular structure of compound **12**.

Figure 3 shows the molecular structure of compound **13**. The molecule is centrosymmetric and consists of two open triruthenium clusters interconnected by two bridging chlorine atoms. While one face of the metallic triangle is capped by a 1,1-dimethylhydrazido ligand, the opposite face is capped by an ethenyl ligand. Curiously, the terminal C atom of this ethenyl ligand, C6, is attached to only one metal atom, Ru1, instead of being attached to two metal atoms, as previously found in other clusters having face-capping alkenyl ligands.[5,6] The Ru1–Ru2 edge is also spanned by a 1,2-diphenylethenyl ligand. The cluster shell is completed by one edge-bridging and five terminal CO ligands. The electron count for each trinuclear fragment is 50 and, therefore, the cluster obeys the EAN rule.[13] This, in fact, represents an exception for trinuclear complexes containing face-capping alkenyl ligands, which are frequently open 48-electron clusters (see above).[5,6,12]

Knowledge of the position of the 1,2-diphenylethenyl ligand in compound **13** allowed us to propose that the diphenylacetylene ligand of its precursor, compound **11**, also spans the same Ru–Ru edge as the amido fragment of the hydrazido group (Scheme 4).

IR spectroscopy: This spectroscopic technique (Table 2) proved very useful for making structural assignments be-

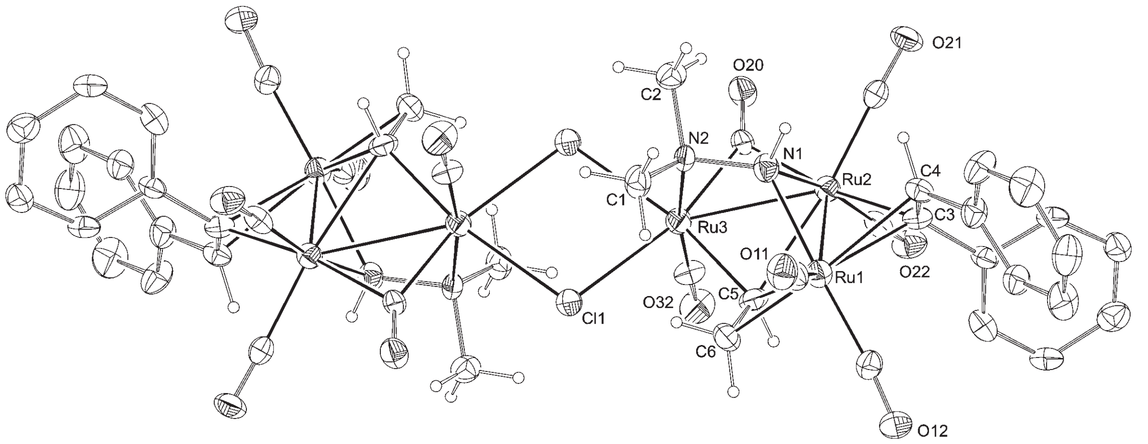


Figure 3. Molecular structure of compound **13**.

Table 2. IR data (recorded in CH_2Cl_2) for the isolated compounds.

Compd	ν_{CO} [cm^{-1}]
5	2069 (w), 2030 (s), 2006 (vs), 1997 (m, sh), 1958 (m), 1942 (w, sh)
6	2067 (w), 2029 (s), 2008 (vs), 1997 (m, sh), 1959 (m), 1944 (w, sh)
7a	2068 (w), 2031 (s), 2007 (vs), 1993 (w, sh), 1958 (m), 1942 (w, sh)
7b	2067 (w), 2029 (s), 2005 (vs), 1994 (w, sh), 1955 (m), 1938 (w, sh)
8	2064 (m), 2027 (s), 2006 (vs), 1993 (m, sh), 1956 (m)
9	2061 (w), 2027 (s), 2008 (vs), 1994 (m, sh), 1958 (m)
10	2064 (w), 2027 (s), 2005 (vs), 1989 (w, sh), 1956 (m)
11	2072 (m), 2023 (m), 2006 (vs), 1978 (w, sh), 1954 (m, br), 1942 (w, sh)
12	2046 (s), 2010 (s), 1997 (m, sh), 1968 (m), 1946 (m), 1898 (w, br), 1781 (m, br)
13[a]	2050 (m), 2011 (s), 2000 (s), 1955 (m, br), 1942 (w, sh), 1842 (w), 1827 (w, br)
14	2067 (m), 2020 (m), 2005 (vs), 1975 (w, sh), 1953 (m), 1940 (w, sh)
15a + **15b**[b]	2067 (m), 2027 (s), 2006 (vs), 1974 (w, sh), 1957 (m, br), 1944 (w, sh)

[a] Recorded in THF. [b] Inseparable mixture.

cause all of the acetylene-bridged complexes (**5**–**7**) exhibit the same absorption pattern in the carbonyl stretching region of their IR spectra, and an analogous situation arises for the vinylidene derivatives (**8**–**10**). The IR spectrum of the diphenylacetylene-bridged complex **11** differs slightly from those of **5**–**7**, indicating that the structures of **11** and **5**–**7** are not alike. On the basis of these IR absorption patterns, we surmise that the Ru–Ru edge bridged by phenylacetylene in the isomeric derivatives **15a** and **15b** is the same as that bridged by diphenylacetylene in complex **11**, whereas the phenylacetylene ligand of compound **14** is on the same edge as the alkyne ligand of **5**–**7**. As expected, the IR spectra of complexes **12** and **13** are quite different from those of all the other compounds.

NMR spectroscopy: The ^1H NMR data of the isolated compounds are collected in Table 3. These data confirm the presence of the respective ligands, but provide no information on the location of these ligands on the clusters.

The compounds having face-capping alkenyl ligands have one H atom on the C=C fragment that is always *cis* to the σ-bonded Ru atom and that arises from the original hydride of the starting complex **1**. The resonance of this proton is observed in the range $\delta = 4.24$ to 2.46 ppm. The compounds that contain a face-capping ethenyl ligand have two additional H atoms on the C=C fragment, both in a reciprocal *cis* arrangement, whereas those with face-capping alkenyl ligands derived from other terminal alkynes have only one additional hydrogen atom. In these compounds, the H atom that is *trans* to σ-bonded Ru on the terminal C atom resonates in the range $\delta = 2.11$ to -0.25 ppm, and couples to its *geminal* H atom with a smaller coupling constant ($J = 6.9$–4.4 Hz) than that resulting from their coupling to the *cis* H atom ($J = 9.8$–8.4 Hz), whereas the H atom on the C atom σ-bonded to the Ru atom resonates at a much higher chemical shift, in the range $\delta = 8.12$ to 6.53 ppm, being strongly coupled to its *trans* H atom ($J = 14.2$–11.6 Hz).[5,6] Therefore, the position of the substituents of the face-capping alkenyl ligands can be straightforwardly assigned by means of ^1H NMR spectroscopy.

It is curious that the resonances of the protons of the edge-bridging acetylene ligands (compounds **5**–**7**) are observed as singlets (in the range $\delta = 7.89$ to 7.80 ppm), despite being in a mutual *cis* arrangement on a formal alkene moiety (as noted above, coupling constants of $J = 9.8$–8.4 Hz are observed for the *cis* H atoms of face-capping alkenyl ligands), whereas those of the edge-bridging vinylidene ligands (compounds **8**–**10**) appear at doublets ($J = 7.6$–7.9 Hz) at lower chemical shifts ($\delta = 6.32$–6.21 ppm).

The $^{13}C\{^1H\}$ NMR spectra of representative examples of edge-bridging acetylene and vinylidene clusters were obtained. In addition to the resonances of the alkenyl and 1,1-dimethylhydrazido ligands, the spectrum of compound **5** shows the acetylene resonances at $\delta = 101.2$ and 101.0 ppm, and that of compound **8** shows the vinylidene resonances at $\delta = 248.4$ and 126.2 ppm. These chemical shifts are compa-

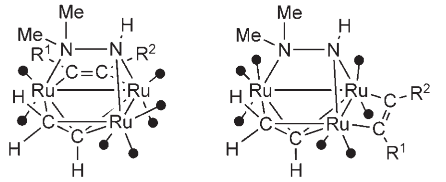
Table 3. ^{1}H NMR data (recorded in [D]chloroform at 20 °C) for the isolated compounds.

Compd	Alkyne-derived ligands	δ [ppm]
5	μ_3-HCCH$_2$, μ-HCCH	7.84 (s, 1H; HCC*H*), 7.80 (s, 1H; *H*CCH), 7.60 (dd, J = 11.8, 9.3 Hz, 1H; CH), 2.54 (dd, J = 9.3, 6.9 Hz, 1H; CH*H*), 2.18 (s, 3H; Me), 2.07 (s, 3H; Me), 1.79 (s, 1H; NH), 0.11 (dd, J = 11.8, 6.9 Hz, 1H; C*H*H)
6	μ_3-HCCHPh, μ-HCCH	8.12 (d, J = 12.7 Hz, 1H; CH), 7.89 (s, 1H; HCC*H*), 7.82 (s, 1H; *H*CCH), 7.35 (m, 5H; Ph), 2.43 (d, J = 12.7 Hz, 1H; CH), 2.35 (s, 3H; Me), 2.27 (s, 3H; Me), 1.69 (s, 1H; NH)
7a	μ_3-HCCHCH$_2$OMe, μ-HCCH	7.84 (s, 1H; HCC*H*), 7.81 (s, 1H; *H*CCH), 7.53 (d, J = 11.3 Hz, 1H; CH), 3.78 (dd, J = 9.8, 5.4 Hz, 1H; CH*H*), 3.62 (dd, J = 9.8, 5.4 Hz, 1H; C*H*H), 3.43 (s, 3H; OMe), 2.23 (s, 3H; Me), 2.14 (s, 3H; Me), 1.68 (s, 1H; NH), 0.80 (dt, J = 11.3, 5.4 Hz, 1H; CH)
7b	μ_3-MeOCH$_2$CCH$_2$, μ-HCCH	7.94 (s, 1H; HCC*H*), 7.87 (s, 1H; *H*CCH), 4.31 (d, J = 11.3 Hz, 1H; OCH*H*), 4.21 (d, J = 11.3 Hz, 1H; OC*H*H), 3.11 (s, 3H; OMe), 3.09 (d, J = 7.4 Hz, 1H; CCH*H*), 2.21 (s, 3H; Me), 2.08 (s, 3H; Me), 1.61 (s, 1H; NH), −0.25 (d, J = 7.4 Hz, 1H; CC*H*H)
8	μ_3-HCCH$_2$, μ-CCH$_2$	7.13 (dd, J = 12.2, 9.8 Hz, 1H; C*H*), 6.26 (d, J = 7.6 Hz, 1H; CCH*H*), 6.21 (d, J = 7.6 Hz, 1H; CCH*H*), 3.00 (dd, J = 9.8, 5.9 Hz, 1H; CH*H*), 2.60 (s, 3H; CH$_3$), 2.03 (s, 3H; Me), 1.63 (s, 1H; NH), 1.60 (dd, J = 12.2, 5.9 Hz, 1H; CH*H*)
9	μ_3-HCCHPh, μ-CCH$_2$	7.56 (d, J = 12.8 Hz, 1H; CH), 7.13 (m, 5H; Ph), 6.32 (d, J = 7.9 Hz, 1H; CCH*H*), 6.26 (d, J = 7.9 Hz, 1H; CC*H*H), 4.24 (d, J = 12.8 Hz, 1H; CH), 2.78 (s, 3H; Me), 2.30 (s, 3H; Me), 1.74 (s, 1H; NH)
10	μ_3-HCCHCH$_2$OMe, μ-CCH$_2$	7.05 (d, J = 11.6 Hz, 1H; CH), 6.25 (d, J = 7.9 Hz, 1H; CCH*H*), 6.21 (d, J = 7.9 Hz, 1H; CC*H*H), 3.96 (dd, J = 9.8, 5.1 Hz, 1H; CH*H*), 3.61 (dd, J = 9.8, 5.1 Hz, 1H; C*H*H), 3.47 (s, 3H; OMe), 2.70 (s, 3H; Me), 2.46 (dt, J = 11.6, 5.1 Hz, 1H; CH), 2.09 (s, 3H; Me), 1.76 (s, 1H; NH)
11	μ_3-HCCH$_2$, μ-PhCCPh	8.05 (dd, J = 14.2, 9.4 Hz, 1H; CH), 7.32 (m, 10H; 2Ph), 3.20 (dd, J = 9.4, 6.7 Hz, 1H; CH*H*), 3.02 (s, 3H; Me), 2.42 (s, 3H; Me), 2.40 (s, 1H; NH), −0.21 (dd, J = 14.2, 6.7 Hz, 1H; C*H*H)
12[a]	μ-H$_2$CCHCPhCPhCO	7.5–6.9 (m, 10H; 2*Ph*), 6.48 (dd, J = 11.8, 8.4 Hz, 1H; CH), 5.88 (s, 1H; NH), 4.71 (dd, J = 8.4, 1.2 Hz, 1H; CH*H*), 3.75 (dd, J = 11.8, 1.2 Hz, 1H; C*H*H), 2.81 (s, 3H; Me), 2.65 (s, 3H; Me)
13[b]	μ_3-HCCH$_2$, μ-PhCCHPh	7.2–7.0 (m, 10H; 2Ph), 6.53 (dd, J = 8.8, 8.6 Hz, 1H; CH), 4.71 (s, 1H; CH), 3.70 (s, 1H; NH), 3.59 (dd, J = 8.6, 4.4 Hz, 1H; CH*H*), 3.41 (dd, J = 8.8, 4.4 Hz, 1H; C*H*H), 2.31 (s, 3H; Me), 1.85 (s, 3H; Me)
14	μ_3-HCCH$_2$, μ-HCCPh	7.5–7.3 (m, 5H; Ph), 7.18 (s, 1H; PhCC*H*), 7.11 (dd, J = 11.8, 8.6 Hz, 1H; CH), 3.61 (dd, J = 9.6, 5.2 Hz, 1H; CH*H*), 2.69 (s, 3H; Me), 2.05 (s, 3H; Me), 1.81 (s, 1H; NH), 1.26 (dd, J = 11.8, 5.2 Hz, 1H; C*H*H)

[a] Recorded in [D$_6$]Me$_2$CO. [b] Recorded in [D$_6$]Me$_2$SO.

rable to those found for these bridging ligands in binuclear complexes.[14,18]

Theoretical calculations: Minimum-energy structure calculations were carried out by DFT methods. Calculations were performed on selected real molecules (products isolated in the present work) and on hypothetical ones with the aim of not only comparing their thermodynamic stabilities (important to rationalize the experimental results), but also to assign or confirm the structures of compounds for which no X-ray diffraction data were available. No simplified model compounds were used for the calculations. Calculated structures are assigned Roman numbers, irrespective of whether they correspond to real (also designated with Arabic numbers) or hypothetical compounds. Computer-generated images of all these structures and their atomic coordinates are given as Supporting Information.



	Energy	Structure	Energy	Structure
$R^1 = R^2$ = H	3.0	**Ia** (**5**)	0.0	**IIa** (-)
$R^1 = R^2$ = Ph	3.6	**Ib** (-)	0.0	**IIb** (**11**)
R^1 = H, R^2 = Ph	3.5	**Ic** (**14**)	0.0	**IIc** (**15a**)
R^1 = Ph, R^2 = H	2.1	**Id** (-)	0.1	**IId** (**15b**)

Figure 4. Relative energies (kcal mol^{-1}) of DFT-optimized structures of three families of isomeric products formally derived from compound **2** and acetylene (first line), diphenylacetylene (second line), or phenylacetylene (third and fourth lines). For each alkyne, 0.0 kcal mol^{-1} is the energy assigned to the most stable isomer.

Figure 4 shows the relative energies of optimized structures of members of three families of isomeric clusters formally derived from reactions of acetylene, diphenylacetylene, or phenylacetylene with complex **2**. The isomers result from the existence of two different Ru–Ru edges that can be bridged by the alkyne ligand and, additionally in the case of phenylacetylene, from the existence of two possible alternative positions of the phenyl group on the coordinated alkyne ligand. For the three families, the most stable isomers have the alkyne on the same Ru–Ru edge as the NH fragment (structures **IIa**, **IIb**, and **IIc**), but they are only 2.1–3.6 kcal mol^{-1} more stable than those having the alkyne on the other Ru–Ru edge (structures **Ia**–**Id**). Structures **IIc** and **IId** have approximately the same energy.

These data are not only compatible with the experimental results obtained from the reactions of compound **2** (and the other face-capped alkyne clusters) with alkynes, but also shed some light on mechanistic aspects of these reactions.

As the products of the reactions of **2** with acetylene and diphenylacetylene are **5** (not the most stable product) and **11** (the most stable product), respectively, we propose that the activation of compound **2** generates a vacant site on the Ru atom attached to the NMe$_2$ fragment of the hydrazido ligand, the methyl groups of which partially protect the metal atom from external attack. As acetylene is a very small alkyne, it can reach this metal atom without obstruction to give the observed product (**5**) after cyclization. The isomerization process that would give the product of structure **IIa** from **5** must have a very high activation energy because it is not observed under the experimental reaction conditions. This activation energy must be higher than that for the process that leads to the vinylidene derivative **8** (which is the product formed when **5** is heated). However, in the case of diphenylacetylene, the greater volume of this alkyne impedes its approach to the activated metal atom, Ru3. Under the reaction conditions, a CO ligand migration could transfer the vacant site to the adjacent metal atom, Ru2, which would then be attacked by the alkyne. In this case, the alkyne-bridged edge should be that corresponding to the most stable product (**11**).

This reasoning is also consistent with the fact that the reaction of compound **2** with phenylacetylene gives a mixture of three compounds (**14**, **15a**, and **15b**). Although we have no analytical data to help us assign the position of the phenyl group on the alkyne ligand of **14** (the location of the alkyne in the cluster is assigned on the basis of IR spectroscopy), the above-described analysis of the results obtained with acetylene and diphenylacetylene supports the view that this complex has structure **Ic** (Figure 4) and not **Id**, because the formation of the latter complex would be hampered by steric hindrance between the phenyl ring of the alkyne and an N-methyl group of the hydrazido ligand.

The structure of the vinylidene derivative **8** was optimized by DFT methods (structure **III** in the Supporting Information) in order to compare its absolute energy with that of its precursor, the acetylene complex **5**. This calculation indicated that **8** is 11.2 kcal mol^{-1} more stable than **5**, in agreement with the experimentally observed irreversible transformation of **5** to **8**.

As commented above, we have also used DFT methods to shed light on structural aspects of compounds for which no X-ray diffraction data were available. Of the structures of compounds of this kind reported in this article, we have chosen to describe those of the vinylidene and diphenylacetylene derivatives **8** (structure **III**) and **11** (structure **IIb**), respectively, as the most representative examples.

The DFT-optimized structure of compound **8** (**III**) is shown in Figure 5. A selection of interatomic distances is given in Table 4. This structure is very similar to that of compound **6** (Figure 1), except for the absence of a phenyl ring on the face-capping alkenyl ligand of **8** and the presence of a vinylidene in **8** spanning the Ru–Ru edge that is bridged by the acetylene ligand in compound **6**. As far as interatomic distances are concerned, the most remarkable differences between compounds **6** and **8** are the Ru2–Ru3 distance, which is 0.16 Å shorter in the vinylidene complex, and the C6–Ru3 distance, which is 0.36 Å longer in the vinylidene complex. As commented above, the C6–Ru3 distance in compound **13** is also very long, at 2.97(2) Å. The vinylidene C3–C4 distance, 1.330 Å, is typical of a double bond.

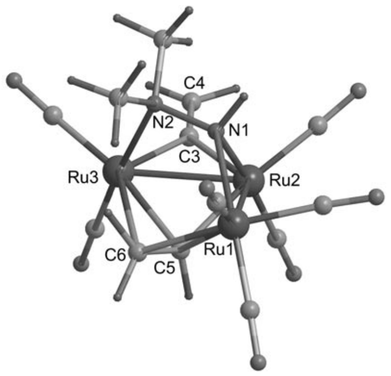


Figure 5. DFT-optimized molecular structure of compound **8** (structure **III**).

Table 4. Selected interatomic distances [Å] in compounds **8** and **11** (data from DFT calculations).

	8	11
Ru1–Ru2	2.838	2.844
Ru1–Ru3	3.894	3.856
Ru2–Ru3	2.791	2.935
N1–Ru1	2.201	2.166
N1–Ru2	2.156	2.151
N2–Ru3	2.327	2.321
C3–Ru2	2.049	2.128
C3–Ru3	2.041	
C4–Ru1		2.094
C5–Ru1	2.279	2.300
C5–Ru2	2.207	2.189
C5–Ru3	2.310	2.332
C6–Ru1	2.278	2.558
C6–Ru3	2.674	2.245
C3–C4	1.330	1.329
C5–C6	1.428	1.431

The DFT-optimized structure of compound **11** (**IIb**) is shown in Figure 6. A selection of interatomic distances is given in Table 4. This structure is also similar to that of compound **6**, but compound **11** does not have the phenyl group on the face-capping alkenyl ligand and has the alkyne ligand, in this case diphenylacetylene, bridging the Ru1–Ru2 edge instead of the Ru2–Ru3 edge. The coordination

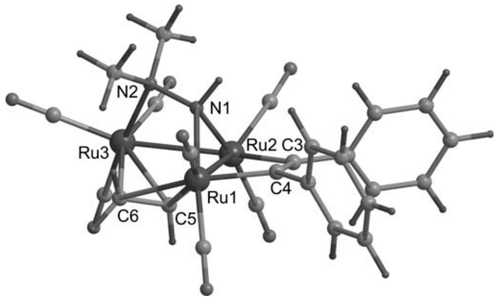


Figure 6. DFT-optimized molecular structure of compound **11** (structure **IIb**).

of the alkyne to the Ru1–Ru2 edge does not significantly affect the distance between these two metal atoms, which is comparable to that in **8** and only 0.11 Å longer than that found by X-ray diffraction in complex **6**, but it provokes a marked lengthening of the C6–Ru1 distance, which is 0.28 Å longer than in complex **8** and 0.26 Å longer than in complex **6**. The C3–C4 distance, 1.329 Å, is typical of a double bond.

Conclusion

In this article, we have described reactions of compounds **2**–**4** with terminal and internal alkynes giving products that result from the substitution of a CO ligand by the alkyne and that contain an Ru–Ru edge bridged by the alkyne ligand in a parallel manner (**5**–**7**). DFT calculations on selected isomeric products have helped to establish that the regiochemistry of these reactions is more influenced by the size of the alkyne substituents than by the thermodynamic stability of the final products. The preparation of triruthenium cluster complexes with parallel edge-bridging alkyne ligands is unprecedented and seems to relate to the fact that the starting trinuclear complexes have their two triangular faces protected by capping ligands. Actually, the reactions of alkynes with non-hydrido triruthenium clusters having at least one face of the metallic triangle free of capping ligands generally afford derivatives that have face-capping alkyne ligands.[26]

We have demonstrated experimentally and by theoretical calculations that the clusters having acetylene as a parallel edge-bridging ligand are thermodynamically unstable with respect to their transformation into derivatives that contain an edge-bridging vinylidene ligand (**8**–**10**). Such derivatives were hitherto unknown in ruthenium cluster chemistry.

The formation of the novel edge-bridging dienoyl ligand of compound **12** involves the unusual thermally-induced coupling of three ligands of **11**, that is, diphenylacetylene, carbon monoxide, and the ethenyl ligand.

A chloro-bridged dimer of trinuclear clusters (**13**) has been prepared by treating compound **11** with hydrogen chloride. This compound represents the first instance of two alkenyl ligands being present on a trinuclear cluster, one face-capping and the other edge-bridging. Therefore, edge-bridging alkynes are susceptible to protonation to give edge-bridging alkenyl ligands.

The results reported in this article on the reactivity of alkynes with the non-hydrido cluster complex **2**, taken together with those recently reported on the reactions of these reagents with the hydrido cluster **1**,[5,6] offer a rather broad picture of the reactivity of alkynes with hydrazido-bridged triruthenium carbonyl cluster complexes and significantly complement previous data on the reactivity of alkynes with triruthenium carbonyl cluster complexes bearing other face-capping ligands.

Experimental Section

General: Solvents were dried over $Na[Ph_2CO]$ (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC on silica gel. Compounds **1**[9] and **2**–**4**[5] were prepared as described elsewhere. The remaining reagents were purchased from commercial sources. IR: Perkin-Elmer FT Paragon 1000X. NMR: Bruker AV-400 and DPX-300, room temperature, TMS as internal standard ($\delta = 0$). Microanalyses: Perkin-Elmer 2400. MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun at about 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. All isolated products gave satisfactory C, H, N, microanalyses (Supporting Information). Their FAB+ mass spectra showed the respective molecular ion in each case (Supporting Information). All chromatographic separations (TLC and column) were carried out using silica gel as solid support.

Reaction of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (2) with acetylene: synthesis of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}\kappa^2\text{-}/\!/\text{-}HCCH)(CO)_7]$ (5): Acetylene was slowly bubbled through a solution of compound **2** (50 mg, 0.081 mmol) in toluene (10 mL) at reflux temperature for 30 min. The color changed from yellow to light brown. The solvent was removed under reduced pressure and the residue was separated on TLC plates, using hexane/dichloromethane (1:1) as eluent. Extraction of the first band (yellow) allowed the isolation of compound **5** as a yellow solid (24 mg, 48 %). A brown residue remained uneluted. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): $\delta = 209.9, 201.5, 200.1, 198.3, 196.4, 196.0, 192.5$ (7CO), 125.3 (CH), 101.2 (CH), 101.0 (CH), 57.4 (Me), 56.7 (Me), 23.6 ppm (CH_2).

Reaction of $[Ru_3(\mu_3\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(CO)_9]$ (1) with acetylene: alternative synthesis of compound 5: A similar procedure to that described above, using complex **1** (50 mg, 0.081 mmol) as starting material, also afforded complex **5** (26 mg, 52 %).

Reaction of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHPh)(\mu\text{-}CO)_2(CO)_6]$ (3a) with acetylene: synthesis of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHPh)(\mu\text{-}\kappa^2\text{-}/\!/\text{-}HCCH)(CO)_7]$ (6): Acetylene was slowly bubbled through a solution of compound **3a** (50 mg, 0.072 mmol) in toluene (10 mL) at reflux temperature for 30 min. The color changed from yellow to brown. The solvent was removed under reduced pressure and the residue was separated on TLC plates, using hexane/dichloromethane (3:2) as eluent. Extraction of the first band (yellow) allowed the isolation of compound **6** as a yellow solid (32 mg, 65 %). A brown residue remained uneluted.

Reaction of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}PhCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (3b) with acetylene: alternative synthesis of compound 6: An analogous procedure to that described above, using complex **3b** (50 mg, 0.072 mmol) as starting material, also afforded complex **6** in a similar yield.

Reaction of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}MeOCH_2CCH_2)(\mu\text{-}CO)_2(CO)_6]$ (4) with acetylene: synthesis of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHCH_2OMe)(\mu\text{-}\kappa^2\text{-}/\!/\text{-}HCCH)(CO)_7]$ (7a) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}MeOCH_2CCH_2)(\mu\text{-}\kappa^2\text{-}/\!/\text{-}HCCH)(CO)_7]$ (7b): Acetylene was slowly bubbled through a solution of compound **4** (50 mg, 0.072 mmol) in toluene (10 mL) at reflux temperature for 30 min. The color changed from yellow to brown. The solvent was removed under reduced pressure and the residue was separated on TLC plates, using hexane/dichloromethane (1:1) as eluent. Extraction of the first and second bands (both yellow) allowed the isolation of compounds **7b** (10 mg, 20 %) and **7a** (15 mg, 30 %), respectively, as yellow solids. A brown residue remained uneluted.

Thermolysis of 5: synthesis of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCH_2)(\mu\text{-}\kappa^1\text{-}CCH_2)(CO)_7]$ (8): A solution of compound **5** (15 mg, 0.024 mmol) in toluene (10 mL) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (1 mL), and the resulting solution was applied to the top of a chromatographic column (7×3 cm) packed in hexane under nitrogen. Elution with hexane/dichloromethane (1:1) separated a yellow band that subsequently afforded compound **8** as a yellow solid (9 mg, 61 %).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 248.4 (C), 204.5 (br), 201.2, 200.1, 198.8, 197.1 (br), 195.7, 195.5 (br; 7 CO), 126.2 (CH_2), 114.9 (CH), 58.1 (Me), 55.9 (Me), 31.3 ppm (CH_2).

Thermolysis of 6: synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-HCCHPh)(μ-κ^1-$CCH_2)(CO)_7$] (9): A solution of compound **6** (15 mg, 0.022 mmol) in toluene (10 mL) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (1 mL), and the resulting solution was applied to the top of a chromatographic column (7 × 3 cm) packed in hexane under nitrogen. Elution with hexane/dichloromethane (1:1) separated a yellow band that subsequently afforded compound **9** as a yellow solid (11 mg, 73 %).

Thermolysis of 7a: synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$HCCHCH_2OMe)(\mu$-κ^1-$CCH_2)(CO)_7$] (10): A solution of compound **7a** (15 mg, 0.023 mmol) in toluene (10 mL) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (1 mL), and the resulting solution was applied to the top of a chromatographic column (7 × 3 cm) packed in hexane under nitrogen. Elution with hexane/dichloromethane (1:1) separated a yellow band that subsequently afforded compound **10** as a yellow solid (10 mg, 66 %).

Reaction of 2 with diphenylacetylene: synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$HCCH_2)(\mu$-κ^2-//-PhCCPh)$(CO)_7$] (11) and [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu$-κ^4-$H_2CCHCPhCPhCO)(\mu$-$CO)_2(CO)_5$] (12): A solution of diphenylacetylene (16 mg, 0.091 mmol) and compound **2** (50 mg, 0.081 mmol) in toluene (20 mL) was stirred at reflux temperature for 40 min. The color changed from yellow to brown. The solvent was then removed under reduced pressure and the residue was separated on TLC plates, using hexane/dichloromethane (1:1) as eluent. Three bands were eluted. The second contained a trace amount of starting material **2**. Extraction of the first (yellow-orange) and third (orange) bands allowed the isolation of compounds **11** (12 mg, 19 %) and **12** (15 mg, 24 %), respectively. A brown residue remained uneluted.

Reaction of 11 with hydrogen chloride: synthesis of [$Ru_6(\mu$-$Cl)_2(\mu_3$-κ^2-$HNNMe_2)_2(\mu_3$-κ^2-$HCCH_2)_2(\mu$-κ^2-$PhCCHPh)_2(\mu$-$CO)_2(CO)_{10}$] (13): A solution of hydrogen chloride in diethyl ether (25 μL, 1 M, 0.025 mmol) was injected into a solution of compound **11** (10 mg, 0.013 mmol) in diethyl ether (10 mL). A color change from yellow to orange was accompanied by the precipitation of an orange solid. The suspension was stirred for 24 h. The solvent was then removed under reduced pressure and the residue was washed with diethyl ether (2 × 5 mL) to give compound **13** as an orange solid (8 mg, 80 %).

Reaction of 2 with phenylacetylene: synthesis of three isomers of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$HCCH_2)(\mu$-κ^2-//-HCCPh)$(CO)_7$] (14, 15a, and 15b): A solution of phenylacetylene (10 μL, 0.091 mmol) and compound **2** (50 mg, 0.081 mmol) in toluene (20 mL) was stirred at reflux temperature for 65 min. The color changed from yellow to brown. The solvent was then removed under reduced pressure and the residue was separated on TLC plates, using hexane/dichloromethane (1:1) as eluent. Three bands were eluted. The third contained a trace amount of starting material **2**. The first band (yellow) afforded a 1:1 mixture (by ^1H NMR integration) of compounds **15a** and **15b** (21 mg, 38 %). The third band (yellow) afforded compound **14** (8 mg, 14 %). A brown residue remained uneluted.

X-ray structures of 6·CH_2Cl_2, 12·0.25(CH_2Cl_2), and 13·$CHCl_3$: Selected crystal, measurement, and refinement data are given in Table 5. Diffraction data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated $Cu_{K\alpha}$ radiation. Data were reduced to F_o^2 values. Absorption corrections were applied using XABS2[27] (for **6**·CH_2Cl_2 and **12**·0.25(CH_2Cl_2)) or SORTAV[28] (for **13**·$CHCl_3$). The structures were solved by Patterson interpretation using DIRDIF-96.[29] Isotropic and full-matrix anisotropic least-squares refinements were carried out with SHELXL-97.[30] All non-H atoms were refined anisotropically. Only the carbon and chlorine atoms of the disordered solvent molecules of **12**·0.25(CH_2Cl_2) and **13**·$CHCl_3$ were included in the final models. The structure of **13**·$CHCl_3$ contains a crystallographic inversion center located in the middle point of the Cl1–Cl1′ vector. The molecular plots were constructed with the PLATON program package.[31] The WINGX program system[32] was used throughout the structure determinations. CCDC-600375 (**6**·CH_2Cl_2), CCDC-600376 (**12**·0.25(CH_2Cl_2)), and CCDC-600377 (**13**·$CHCl_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystal, measurement, and refinement data for the compounds studied by X-ray diffraction.

	6·CH_2Cl_2	**12**·0.25(CH_2Cl_2)	**13**·$CHCl_3$
formula	$C_{19}H_{16}N_2O_7Ru_3\cdot CH_2Cl_2$	$C_{26}H_{20}N_2O_8Ru_3\cdot 0.25(CH_2Cl_2)$	$C_{48}H_{42}Cl_2N_4O_{12}Ru_6\cdot CHCl_3$
M_r	772.47	812.38	1662.54
color	yellow	orange	orange
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pbcn$	$C2/c$
a [Å]	14.5534(4)	27.0420(10)	30.038(2)
b [Å]	8.2718(2)	16.0163(6)	7.6276(6)
c [Å]	21.9018(6)	13.5505(5)	26.349(2)
β [°]	112.416(1)	90	112.237(4)
V [Å^3]	2437.4(1)	5868.9(4)	5588.1(7)
Z	4	8	4
$F(000)$	1496	3168	3236
ρ_{calcd} [g cm^{-3}]	2.105	1.839	1.976
radiation (λ, Å)	$Cu_{K\alpha}$ (1.54180)	$Cu_{K\alpha}$ (1.54180)	$Cu_{K\alpha}$ (1.54180)
μ [mm^{-1}]	17.275	13.191	15.531
crystal size [mm]	0.15 × 0.13 × 0.10	0.23 × 0.10 × 0.05	0.08 × 0.05 × 0.05
T [K]	150(2)	150(2)	150(2)
θ range [°]	3.18 to 81.27	3.21 to 68.33	3.18 to 68.14
min./max. h, k, l	−18/18, −10/10, −28/28	−32/32, −19/19, −16/16	−35/36, −7/8, −31/31
collected reflections	17993	20603	13002
unique reflections	4618	5382	4980
reflections with $I > 2\sigma(I)$	4155	3802	4275
parameters/restraints	315/0	378/1	341/2
GoF on F^2	1.127	1.035	1.060
R_1 [on F, $I > 2\sigma(I)$]	0.0453	0.0505	0.0690
wR_2 (on F^2, all data)	0.2031	0.1522	0.2064
max./min. $\Delta\rho$ [e Å^{-3}]	1.962/−1.776	1.928/−1.580	1.449/−1.486

Theoretical calculations: All structure optimizations were performed by hybrid DFT, within the Gaussian-98 program suite,[33] by using Becke's three-parameter hybrid exchange-correlation functional[34] with the B3LYP non-local gradient correction.[35] The LANL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[36] The 6–31G basis set with addition of (d,p)-polarization was used for all the remaining atoms. All optimized structures were confirmed as minima by the calculation of analytical frequencies. For each calculation, the input model molecule was based on the X-ray-determined structure of complex **6**, suitably modified by variation of the ligands.

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