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Reactivity of Alkynes Containing α-Hydrogen Atoms with a Triruthenium Hydrido Carbonyl Cluster: Alkenyl versus Allyl Cluster Derivatives

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

Abstract: The reactions of the hydrido–triruthenium cluster complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(CO)_9]$ (**1**; H_2NNMe_2 = 1,1-dimethylhydrazine) with alkynes that have α-hydrogen atoms give trinuclear derivatives containing edge-bridging allyl or face-capping alkenyl ligands. Under mild conditions (THF, 70 °C) the isolated products are as follows: $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^3\text{-}1\text{-}syn\text{-}Me\text{-}3\text{-}anti\text{-}EtC_3H_3)(\mu\text{-}CO)_2(CO)_6]$ (**2**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^3\text{-}1\text{-}syn\text{-}Me\text{-}3\text{-}syn\text{-}EtC_3H_3)(\mu\text{-}CO)_2(CO)_6]$ (**3**) from 3-hexyne; $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^3\text{-}3\text{-}anti\text{-}PhC_3H_4)(\mu\text{-}CO)_2(CO)_6]$ (**4**), $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}MeCCHPh)(\mu\text{-}CO)_2(CO)_6]$ (**5**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}PhCCHMe)(\mu\text{-}CO)_2(CO)_6]$ (**6**) from 1-phenyl-1-propyne; $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}3\text{-}anti\text{-}PrC_3H_4)(\mu\text{-}CO)_2(CO)_6]$ (**7**), $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}BuCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**8**), and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HCCHBu)(\mu\text{-}CO)_2(CO)_6]$ (**9**) from 1-hexyne; $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}HOH_2CCCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**10**) from propargyl alcohol; and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu_3\text{-}\kappa^2\text{-}MeOCH_2CCH_2)(\mu\text{-}CO)_2(CO)_6]$ (**11**) from 3-methoxy-1-propyne. The regioselectivity of these reactions depends upon the nature of the alkyne reagent, which affects considerably the kinetic barriers of important reaction steps and the stability of the final products. It has been established that the face-capped alkenyl derivatives are not precursors to the allyl products, which are formed via edge-bridged alkenyl intermediates. At higher temperature (toluene, 110 °C), the complexes that have allyl ligands with an *anti* substituent are isomerized into allyl derivatives with that substituent in the *syn* position, for example, **4** into $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^3\text{-}3\text{-}syn\text{-}PhC_3H_4)(\mu\text{-}CO)_2(CO)_6]$ (**14**). The diene complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^4\text{-}trans\text{-}EtC_4H_5)(CO)_7]$ (**13**) has been obtained from the thermolysis of compounds **2** and **7** at 110 °C (**3** and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}3\text{-}syn\text{-}PrC_3H_4)(\mu\text{-}CO)_2(CO)_6]$ (**12**) are also formed in these reactions). A DFT theoretical study has allowed a comparison of the thermodynamic stabilities of isomeric compounds and has helped rationalize the experimental results. Mechanistic proposals for the synthesis of the allyl complexes and their isomerization processes are also provided.

Keywords: alkenyl ligands · allyl ligands · cluster compounds · N ligands · ruthenium

Introduction

Alkenyl groups are important ligands in organometallic chemistry, because they are related to 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,[1–5] despite the fact that some of these clusters have been recognized as intermediates or as catalyst precursors for alkyne–alkene co-dimerization[6] and alkyne hydrogenation,[7] dimerization,[2b] polymerization,[2b] and hydroformylation[2c] processes. Without exception, these alkenyl–triruthenium cluster complexes arise from reactions of alkynes with triruthenium precursors containing hydride ligands.

In this context, we have recently reported the reactivity of the hydrazido-bridged hydrido–carbonyl–triruthenium complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(CO)_9]$[8] (**1**) with a variety of terminal and internal alkynes without α-hydrogen atoms, showing that the products may have their alkenyl ligands in edge-bridging or face-capping positions (Scheme 1) and that

[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) 985103446
E-mail: jac@fq.uniovi.es

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

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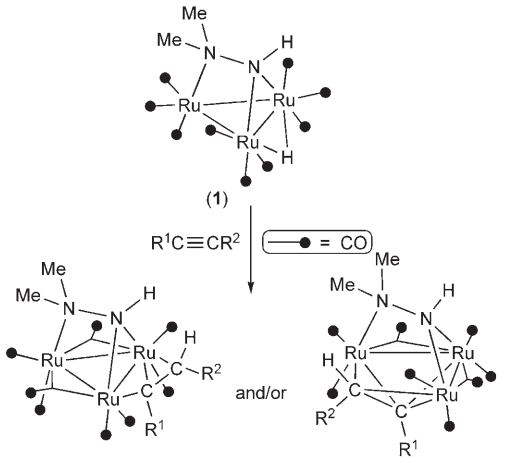


Scheme 1. Reactivity of compound **1** with alkynes having no α-hydrogen atoms.

the nature of the substituents of the alkyne reagent strongly affects the stability of each product.[5]

Carrying out that study,[5] we observed that the use of some alkynes that have α-hydrogen atoms as reagents led not only to alkenyl derivatives, but also to cluster complexes with edge-bridging allyl ligands. As very few reactions of hydrido–carbonyl–triruthenium clusters with alkynes that have α-hydrogen atoms had been hitherto reported and none of them gave allyl derivatives,[3a,b] we decided to perform a thorough study on the reactivity of complex **1** with internal and terminal alkynes that have α-hydrogen atoms, such as 3-hexyne, 1-phenyl-1-propyne, 1-hexyne, propargyl alcohol, and 3-methoxy-1-propyne.

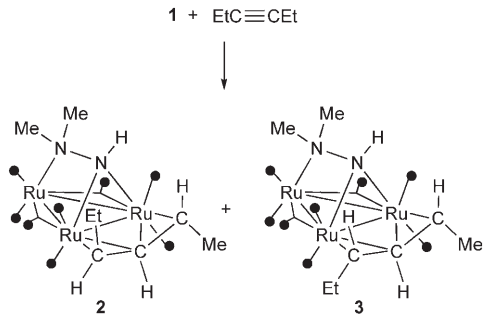
Triruthenium cluster complexes with organic allyl ligands are very rare. To our knowledge, the only precedents are $[Ru_3(\mu\text{-}\kappa^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8]$ and $[Ru_3(\mu_3\text{-}\kappa^5\text{-}HabqCHCHCHR)(\mu\text{-}CO)_2(CO)_6]$ (H_2abqH = 2-amino-7,8-benzoquinoline; R = H, C≡CSiMe$_3$), which contain edge-bridging allyl ligands. The former was prepared by treating the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ with allyl chloride,[9] whereas the H_2abqH-derived clusters were synthesized from $[Ru_3(\mu_3\text{-}\kappa^5\text{-}Habq)(CO)_9]$ and propargyl alcohol or 1-trimethylsilyl-1,4-pentadiyne and contain an edge-bridging allyl fragment attached to a face-capping Habq group.[10] Quite a few cluster complexes containing σ-dimetalated allyl ligands ($MCR^1CR^2CR^3M$) are known. They have been prepared by treating non-hydridic ruthenium clusters with alkynes of the type $R^1CHR^2C{\equiv}CR^3$,[11] and also by inserting alkynes $R^1C{\equiv}CR^2$ into an Ru–CR^3 bond of complexes of the type $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CR^3)(CO)_9]$,[12] but these σ-dimetalated allyl ligands are attached to only one additional metal atom through a typical κ^3-allyl coordination. One penta-[13] and one hexaruthenium[14] cluster have been shown to contain edge-bridging allyl ligands.

We now report that some reactions of complex **1** with alkynes that have α-hydrogen atoms lead to cluster complexes with edge-bridging allyl ligands and that these complexes can be transformed into derivatives containing edge-bridging dienes or isomeric allyl ligands. X-ray diffraction, IR and NMR spectroscopy, and calculations of minimum-energy structures by DFT methods have been used to characterize the products. Comparisons of the absolute energies of isomeric compounds (obtained by DFT calculations) have helped rationalize the experimental results. Mechanistic proposals that account for the observed transformations are also provided.

Results and Discussion

Reactivity studies: The reactivity of compound **1** with 3-hexyne, 1-phenyl-1-propyne, 1-hexyne, propargyl alcohol, and 3-methoxy-1-propyne was studied. All reactions were carried out in a systematic way with THF as solvent and a 1:1.1 cluster-to-alkyne ratio. The reaction solutions were stirred at reflux temperature until the consumption of the starting complex **1** was complete (observed by IR spectroscopy and/or spot TLC). Most reactions gave mixtures of several isomeric products that were separated by chromatographic methods (mostly TLC). Very weak chromatographic bands were not worked up. All isolated products are shown in Schemes 2–5.

The reaction of **1** with 3-hexyne (Scheme 2) gave two isomeric allyl derivatives (**2** and **3**) that differ in the orientation of the allyl substituents. While the ethyl and methyl groups of complex **2** are in *anti* and *syn* positions, respectively, both



Scheme 2. Reaction of compound **1** with 3-hexyne.

substituents are in *syn* positions in complex **3**. Curiously, under analogous reaction conditions, the reactions with 1-phenyl-1-propyne and 1-hexyne (Schemes 3 and 4) gave mixtures of three products consisting of one allyl derivative with a substituent in *anti* position (**4** and **7**) and two isomeric face-capped alkenyl derivatives (**5**, **6**, **8**, and **9**), while the reactions of compound **1** with propargyl alcohol and 3-methoxy-1-propyne did not afford any allyl derivative, but only a face-capped alkenyl product with the two hydrogen atoms in a *gem* arrangement (**10** and **11**; Scheme 5). In no case did we obtain compounds with edge-bridging alkenyl ligands,

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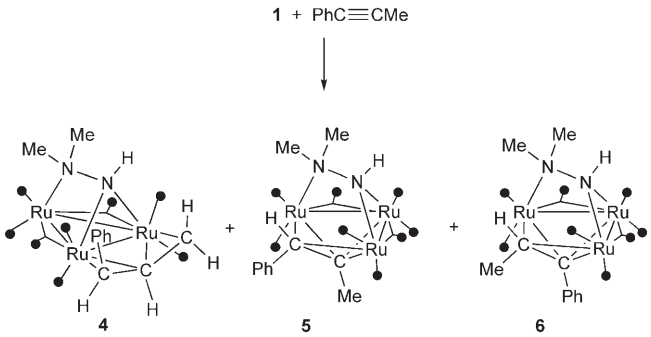
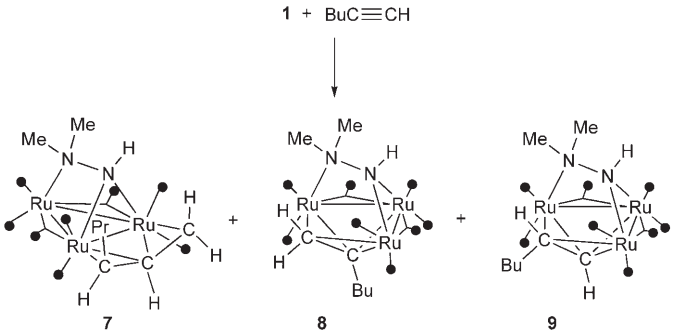


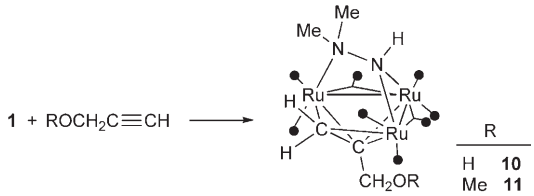
Scheme 3. Reaction of compound **1** with 1-phenyl-1-propyne.



Scheme 4. Reaction of compound **1** with 1-hexyne.

despite the fact that derivatives of this type are generally the products of reactions of hydrido–carbonyl cluster complexes with alkynes that have no α-hydrogen atoms.[1–5]

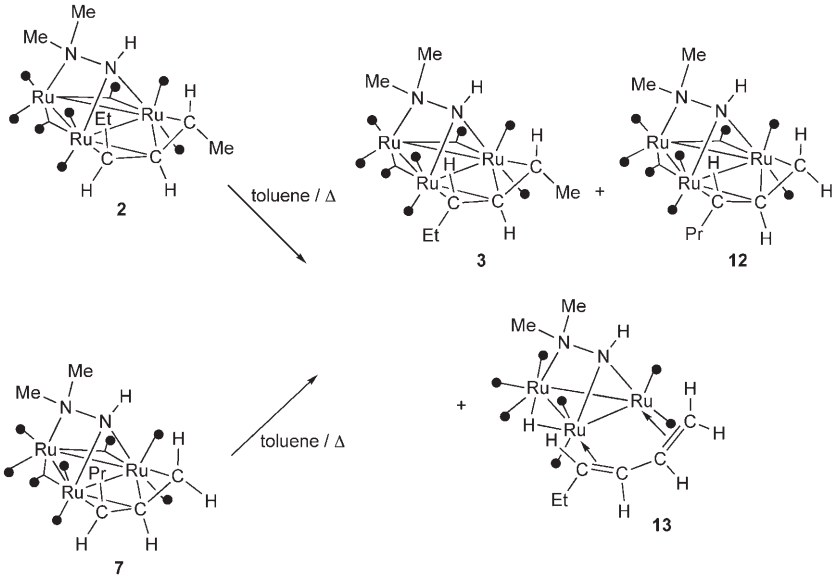
To check whether the face-capped alkenyl products could be transformed into their allyl isomers or not, compounds **8** and **9** (both arising from the reaction of compound **1** with 1-hexyne in refluxing THF, 15 min) were individually heated in refluxing THF. While compound **9** remained unaltered, a complete transformation of the *gem* isomer **8** into the *trans* isomer **9** was observed after 2 h. This long reaction time contrasts with the short reaction time required for the reaction of compound **1** with 1-hexyne, which gave compound **9** as the major product after 15 min in refluxing THF. This implies that the *trans* isomer **9** observed in the reaction of **1** with 1-hexyne should not arise, at least to a great extent, from the *gem* isomer **8**. On the contrary, it is reasonable to propose that both the *gem* and *trans* isomers formed from **1** in short reaction times arise from a common early hydrido–alkyne intermediate that evolves through different pathways (Markonikoff and anti-Markonikoff insertions) to give the observed products.[5] Therefore, the allyl complexes do not arise from their face-capped alkenyl isomers.



Scheme 5. Reactions of compound **1** with propargyl alcohol and 3-methoxy-1-propyne.

The thermolysis of the *anti*-ethyl-*syn*-methyl allyl complex **2** in toluene at reflux temperature for 25 min gave a mixture of the hydrido–diene derivative **13** and two allyl complexes, the *syn*-ethyl-*syn*-methyl complex **3** and the *syn*-propyl complex **12** (Scheme 6). An analogous treatment of the *anti*-propyl allyl complex **7** afforded the same mixture of products. These reactions proceeded very slowly in refluxing THF. Compound **12** was only observed in these thermolysis reactions and could not be obtained pure, because it could not be separated from complex **3** by crystallization or chromatographic methods.

Curiously, the *anti*-phenyl allyl complex **4** underwent a rearrangement process in refluxing toluene that ended in the *syn*-phenyl allyl isomer **14** as the only final product (Scheme 7).



Scheme 6. Thermolysis of compounds **2** and **7**.

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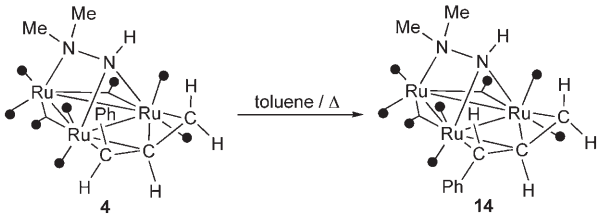

Scheme 7. Isomerization of compound **4** into **14**.

The results shown in Schemes 6 and 7 indicate that the allyl complexes are not involved (as intermediates) in the synthesis of the face-capped alkenyl derivatives. The isomerization of the *anti*-substituted allyl derivatives (**2**, **4**, and **7**) into the *syn*-substituted ones (**3**, **14**, and **12**, respectively) suggests that the latter are more stable than the former. In addition, the transformations of **2** and **7** into **12** and **3**, respectively, imply a 1,4-migration of a hydrogen atom within the corresponding allyl ligand and the slippage of the bridged Ru–Ru edge over the ligand carbon atoms. Such processes may be related to the observation of the diene derivative **13** as a side product accompanying the isomerization products (Scheme 6). Proposals addressing mechanistic aspects of the synthesis of the allyl complexes and their isomerization processes are given and commented below.

X-ray diffraction studies: The structures of compounds **2**, **3**, and **8** were determined by X-ray diffraction. A selection of interatomic distances is given in Table 1. For comparison purposes, a common atomic numbering scheme has been used.

Table 1. Selected interatomic distances (Å) in compounds **2**, **3**, **8**, and **13**.

	2[a]	**3**[a]	**8**[a]	**13**[b]
Ru1–Ru2	2.744(1)	2.7702(6)	2.7141(9)	2.796
Ru1–Ru3	2.760(1)	2.7553(6)	3.7849(2)	3.012
Ru2–Ru3	2.753(1)	2.7477(6)	2.8200(9)	2.763
N1–Ru1	2.106(8)	2.125(5)	2.139(8)	2.108
N1–Ru2	2.107(8)	2.127(4)	2.091(8)	2.111
N2–Ru3	2.207(7)	2.218(4)	2.226(7)	2.220
C3–Ru1			2.44(1)	
C3–Ru2				2.292
C3–Ru3			2.34(1)	
C4–Ru1			2.329(8)	
C4–Ru2	2.21(1)	2.197(6)	2.226(9)	2.311
C4–Ru3			2.280(9)	
C5–Ru1	2.56(2)	2.538(6)		2.423
C5–Ru2	2.60(1)	2.552(6)		
C6–Ru1	2.20(1)	2.177(6)		2.248
C3–C4	1.51(2)	1.509(9)	1.40(1)	1.400
C4–C5	1.37(2)	1.426(9)	1.51(1)	1.446
C5–C6	1.49(2)	1.398(9)	1.52(1)	1.418

[a] X-ray diffraction data. [b] Calculated by DFT methods.

The structures of compounds **2** and **3** (Figures 1 and 2, respectively) correspond to two isomeric allyl derivatives and are nearly identical. In both cases, the hydrazido group caps the metal triangle in the same way as that found previously

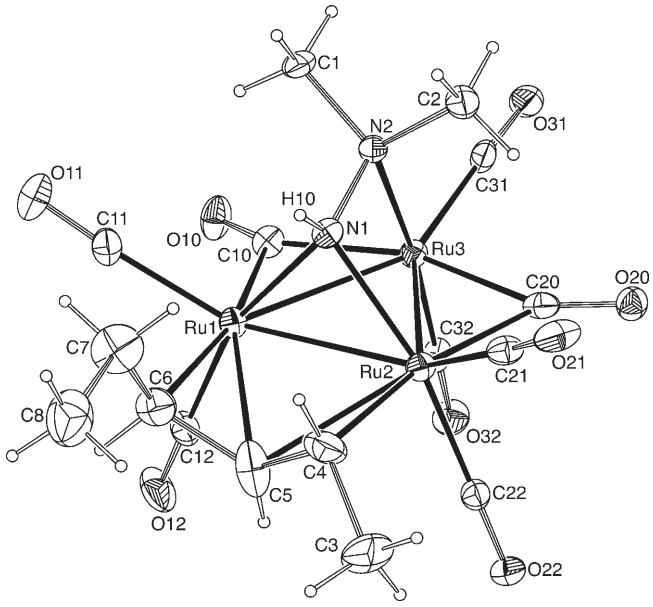

Figure 1. Molecular structure of compound **2**.

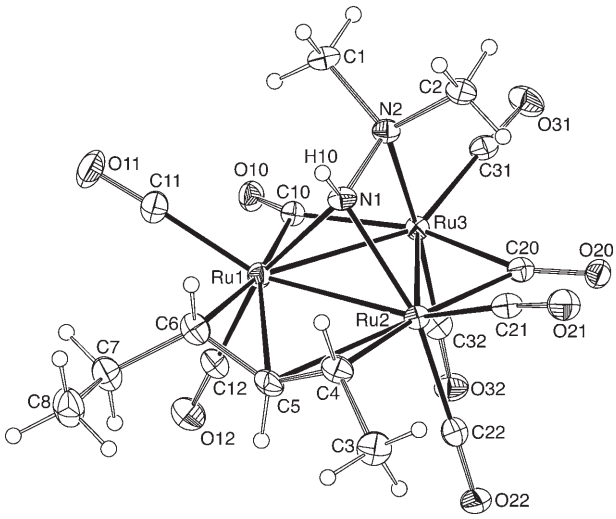

Figure 2. Molecular structure of compound **3**.

in complex **1**[8] and in most of its derivatives.[5,15] The allyl ligand spans the same Ru–Ru edge as the amido fragment of the hydrazido group and is attached to Ru1 through the carbon atoms C5 and C6 and to Ru2 through C4 and C5, the distances from the central carbon atom C5 to Ru1 and Ru2 being 0.35–0.40 Å longer than those from C4 and C6 to Ru2 and Ru1, respectively. The dihedral angle between the planes defined by the allyl C4, C5, and C6 atoms and the Ru_3 triangle is 63.5(9)° in **2** and 61.9(4)° in **3**. Both compounds have eight CO ligands, two of which are bridging and six are terminal. The Ru–Ru distances, ranging from 2.74 to 2.77 Å, confirm the presence of Ru–Ru single bonds.[16] The only noticeable difference between these compounds is the arrangement of the ethyl and methyl groups on the allyl fragment. While the methyl group is in a *syn* po-

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sition in both compounds, the ethyl group is *anti* in **2** and *syn* in **3**.

Figure 3 shows the structure of compound **8**. In this case, two face-capping ligands are placed at either sides of the metal triangle, the hydrazido ligand and an alkenyl ligand.

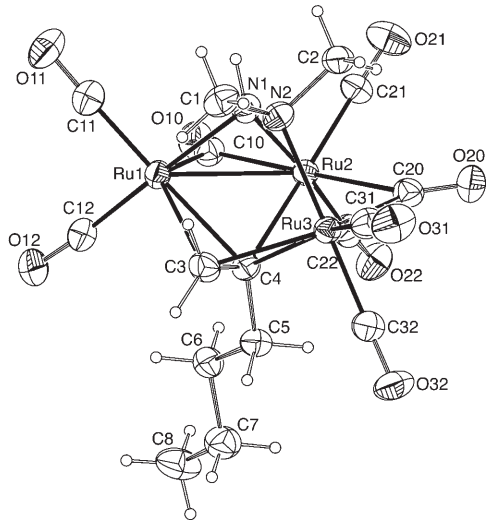

Figure 3. Molecular structure of compound **8**.

The alkenyl ligand has two H atoms on C3 in *gem* positions and one *n*-butyl group on C4, attached to Ru2 through C4 and to Ru1 and Ru3 through both C3 and C4. The cluster shell is completed with six terminal and two bridging CO ligands. The length of the Ru1–Ru3 edge, 3.7849(2) Å, is out of the bonding range for Ru–Ru bonds.[16] Despite being an open triangular cluster, its electron count is 48 and thus disobeys the EAN rules (EAN = effective atomic number).[17] Trimetallic clusters bearing face-capping alkenyl ligands are scarce. While $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CF_3CCHCF_3)(CO)_{10}]$[18] and $[WRu_2(\mu\text{-}NPh)(\mu_3\text{-}\eta^2\text{-}CF_3CCHCF_3)(\eta^5\text{-}C_5Me_5)(CO)_7]$[19] are closed 48-electron triangular clusters, Süss-Fink's complexes $[Ru_3\{\mu_3\text{-}NS(O)MePh\}(\mu_3\text{-}\eta^2\text{-}RCCHR)(\mu\text{-}CO)(CO)_7]$[3a] and the face-capped alkenyl products derived from **1** and alkynes without α-hydrogen atoms[5] are open (two Ru–Ru bonds) 48-electron triangular clusters.

IR spectroscopy: This spectroscopic technique was very useful to assign the type of hydrocarbon ligand contained in each product, because all the face-capped alkenyl derivatives have the same absorption pattern in the carbonyl-stretching region of their IR spectra (Table 2) and an analogous situation occurs for the allyl derivatives (Table 3). The IR spectrum of the unique diene complex **13** (Table 3) is quite different from all the others. Within each group, changes in the nature of the alkenyl or allyl ligand substituents slightly affect the wavenumber of the ν_{CO} bands, but they do not significantly alter the relative transmittance of the absorptions (the band pattern is maintained). Unfortunately, the ν_{CO} absorptions of these complexes are also almost unaffected by the position of the substituents on the alkenyl or allyl ligands and, consequently, the stereochemistry of the alkenyl and allyl ligands could not be established by this spectroscopic technique.

It is curious that all the face-capped alkenyl derivatives reported in this article have two bridging carbonyl ligands (they have analogous IR spectra and complex **8** has been characterized by X-ray diffraction), whereas two types of carbonyl ligand arrangements have been observed in face-capped alkenyl products derived from complex **1** and alkynes without α-hydrogen atoms; one arrangement is analogous to that of the alkenyl products described herein and the other consists of one bridging and seven terminal carbonyl ligands.[5]

Table 2. IR data (recorded in CH_2Cl_2) for the compounds with face-capping alkenyl ligands.

	Alkenyl ligand	ν_{CO} [cm^{-1}]
5	MeC=CHPh	2058 (w), 2017 (vs), 1989 (m), 1957 (m), 1849 (w, br), 1824 (w, br)
6	PhC=CHMe	2060 (w), 2010 (vs), 1991 (m), 1956 (m), 1852 (w, br), 1791 (w, br)
8	BuC=CH_2	2057 (w), 2018 (vs), 1986 (m), 1955 (m), 1948 (w), 1929 (w, br), 1801 (w, br)
9	HC=CHBu	2059 (w), 2017 (vs, br), 1987 (m), 1956 (m), 1925 (w, br), 1802 (w, br)
10	$HOCH_2C$=CH_2	2054 (w), 2018 (vs, br), 1979 (m, sh), 1951 (m), 1828 (w, br), 1799 (w, br)
11	$MeOCH_2C$=CH_2	2060 (w), 2024 (vs, br), 1988 (m, sh), 1956 (m), 1822 (w, br), 1797 (w, br)

Table 3. IR data (recorded in CH_2Cl_2) for the compounds with edge-bridging allyl and diene ligands.

	Hydrocarbon ligand	ν_{CO} [cm^{-1}]
2	1-*syn*-Me-3-*anti*-EtC_3H_3	2059 (m), 2014 (vs), 1984 (s), 1962 (m), 1843 (w), 1799 (m)
3	1-*syn*-Me-3-*syn*-EtC_3H_3	2057 (m), 2013 (vs), 1984 (s), 1962 (m), 1843 (w), 1801 (m)
4	3-*anti*-PhC_3H_4	2060 (m), 2021 (vs), 1989 (s), 1968 (m), 1849 (w), 1805 (m)
7	3-*anti*-PrC_3H_4	2058 (m), 2017 (vs), 1984 (s), 1965 (m), 1846 (w), 1801 (m)
12[a]	3-*syn*-PrC_3H_4	–
13	*trans*-EtCH=CHCH=CH_2	2064 (s), 2000 (s, sh), 1992 (vs), 1936 (m), 1919 (m)
14	3-*syn*-PhC_3H_4	2060 (m), 2019 (vs), 1989 (s), 1968 (m), 1850 (w), 1806 (m)

[a] This compound could not be separated from complex **3**. Therefore, its IR spectrum could not be recorded.

NMR spectroscopy: The ^{1}H NMR data of the compounds with face-capping alkenyl ligands are given in Table 4. All these products contain one hydrogen atom on the C=C fragment of alkenyl ligand that is always *cis* to the Ru atom σ-bonded to the alkenyl ligand and that arises from the original hydride of the starting complex **1**. The resonance of this proton is observed in the range $\delta = 4.62$–2.94 ppm. An additional resonance is observed for alkenyls derived from terminal alkynes. For compounds **8**, **10**, and **11**, which have two

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Table 4. ^{1}H NMR data (recorded in $CDCl_3$ at 20 °C) for the compounds with face-capping alkenyl ligands.

	Alkenyl ligand	δ [ppm]
5	MeC=CHPh	7.61 (d, J = 7.1 Hz, 2H; Ph), 7.38 (m, 3H; Ph), 4.62 (s, 1H; C*H*), 2.71 (s, 3H; CH_3), 2.23 (s, 3H; CH_3), 2.20 (s, 3H; CH_3), 1.94 (s, 1H; N*H*)
6	PhC=CHMe	7.21 (m, 5H; Ph), 2.94 (q, J = 5.1 Hz, 1H; C*H*), 2.72 (s, 1H; CH_3), 2.30 (s, 1H; CH_3), 2.25 (d, J = 5.1 Hz, 3H; CH_3), 2.04 (s, 1H; N*H*)
8	BuC=CH_2	4.05 (d, J = 5.3 Hz, 1H; C*H*), 2.61 (s, 1H; CH_3), 2.46 (d, J = 5.3 Hz, 1H; C*H*), 2.39 (m, 2H; CH_2), 2.06 (s, 1H; CH_3), 1.99 (s, 1H; N*H*), 1.18 (m, 4H; 2 CH_2), 0.78 (t, J = 6.7 Hz, 3H; CH_3)
9	HC=CHBu	6.01 (d, J = 13.5 Hz, 1H; C*H*), 3.41 (dt, J = 13.5, 5.1 Hz, 1H; C*H*), 2.61 (s, 1H; CH_3), 2.41 (m, 1H; CH*H*), 2.16 (m, 1H; CH*H*), 1.71 (m, 2H; CH_2), 1.56 (m, 2H; CH_2), 1.01 (t, J = 7.5 Hz, 3H; CH_3)
10	$HOCH_2C$=CH_2	4.16 (dd, J = 12.8, 5.2 Hz, 1H; CH*H*), 4.01 (dd, J = 12.8, 5.2 Hz, 1H; CH*H*), 3.96 (d, J = 4.4 Hz, 1H; CH*H*), 2.66 (s, 3H; CH_3), 2.07(s, 3H; CH_3), 2.05 (d, J = 4.4 Hz, 1H; CH*H*), 1.97 (s, 1H; N*H*), 1.60 (t, J = 4.4 Hz, 1H; O*H*)
11	$MeOCH_2C$=CH_2	3.83 (d, J = 4.9 Hz, 1H, CH*H*), 3.73 (d, J = 10.8 Hz, 1H; C*H*H), 3.63 (d, J = 10.8 Hz, 1H; CH*H*), 3.14 (s, 3H; OCH_3), 2.63 (s, 3H; CH_3), 2.08 (d, J = 4.9 Hz, 1H; CH*H*), 2.03 (s, 3H; CH_3), 1.87 (s, 1H; N*H*)

H atoms in *gem* positions, this resonance always appears at a lower chemical shift (in the range δ = 2.46–2.05 ppm) with a small coupling constant (J in the range 5.3–4.4 Hz). For compound **9**, which has two H atoms in a mutual *trans* arrangement, this resonance is observed at a higher chemical shift (δ = 6.01 ppm) with a greater coupling constant (J = 13.5 Hz). For compounds **5** and **6**, the relative arrangement of their methyl and phenyl substituents was clearly indicated by the multiplicities of the methyl and C=C*H* resonances. Thus, for compound **5** both resonances are singlets, whereas for compound **6** both resonances are coupled to each other (J = 5.1 Hz). This indicates that in **6** the alkenyl hydrogen atom and the methyl group are attached to the same carbon atom. Therefore, the stereochemistry of the alkenyl ligands in these complexes can be assigned by using simple ^{1}H NMR spectroscopy.[5]

The ^{1}H NMR spectra of the allyl derivatives are more complicated (Table 5). The assignments shown in Figure 4 for the allyl protons were made with the help of selective proton-decoupled and COSY experiments. In general, the H_{syn}–$H_{central}$ couplings (range: J = 8.6–7.3 Hz) are greater than the H_{syn}–H_{anti} couplings (range: J = 5.9–2.9 Hz) and smaller than the H_{anti}–$H_{central}$ couplings (range: J = 12.7–11.1 Hz). Their chemical shifts are low, as expected for metal-shielded protons. These trends have also been observed in other tri-[9,10] and binuclear[20] complexes with μ-allyl ligands.

It is noteworthy that some complexes have resonances at unusually low chemical shifts (close to zero or even negative). This occurs for many of the H_{anti} protons of the allyl compounds and for one of the diasterotopic methylene protons of compounds **2** (H_a) and **7** (H_f). Such a great shielding seems to indicate that these protons are close to metal atoms. As commented below, this fact has important mechanistic implications in some isomerization processes in which the allyl complexes are involved.

The stereochemistry of the diene group of compound **13** is *trans*. This was easily deduced from its ^{1}H NMR spectrum, which shows that H_e is coupled to H_d with a large coupling constant (J = 12.4 Hz), typical of a *trans* H_e–H_d arrangement, being also coupled to the methylene group protons. In addition to the signals of the diene and hydrazido groups, the ^{1}H NMR spectrum of **13** also shows a singlet at δ = −11.49 ppm, corresponding to the hydride ligand.

Table 5. ^{1}H NMR data (recorded in $CDCl_3$ at 20 °C) for the compounds with edge-bridging allyl and diene ligands.

	Hydrocarbon ligand	δ [ppm]
2	1-*syn*-Me-3-*anti*-EtC_3H_3	4.42 (ddd, J = 13.1, 8.6, 5.0 Hz, 1H; C*H*), 2.39 (d, J = 5.9 Hz, 3H; CH_3), 1.97 (dd, J = 12.3, 8.6 Hz, 1H; C*H*), 1.93 (s, 3H; CH_3), 1.87 (s, 3H; CH_3), 1.45 (dq, J = 12.3, 5.9 Hz, 1H; C*H*), 1.31 (ddq, J = 13.1, 11.8, 6.8 Hz, 1H; CH*H*), 1.15 (t, J = 6.8 Hz, 3H; CH_3), 0.68 (s, 1H; N*H*), −0.32 (ddq, J = 11.8, 6.8, 5.0 Hz, 1H; CH*H*)
3	1-*syn*-Me-3-*syn*-EtC_3H_3	2.91 (ddq, J = 14.6, 7.4, 3.1 Hz, 1H; CH*H*), 2.28 (d, J = 5.9 Hz, 3H; CH_3), 2.04 (ddq, J = 13.9, 7.4, 3.1 Hz, 1H; CH*H*), 1.92 (m, 1H; CH), 1.87 (s, 6H; 2 CH_3), 1.79 (m, 1H; C*H*), 1.46 (t, J = 7.4 Hz, 3H; CH_3), 0.55 (m, 1H; C*H*), 0.38 (s, 1H; N*H*)
4	3-*anti*-PhC_3H_4	7.11 (m, 3H; Ph), 6.85 (m, 2H; Ph), 5.75 (d, J = 8.9 Hz, 1H; C*H*), 3.43 (dd, J = 8.9, 3.6 Hz, 1H; C*H*), 2.50 (dt, J = 12.7, 8.9 Hz, 1H; C*H*), 1.92 (s, 6H; 2 CH_3), 0.84 (dd, J = 12.7, 3.6 Hz, 1H; C*H*), 0.49 (s, 1H; N*H*)
7	3-*anti*-PrC_3H_4	4.62 (ddd, J = 13.3, 7.3, 4.4 Hz, 1H; C*H*), 3.45 (dd, J = 7.3, 4.4 Hz, 1H; C*H*), 2.13 (dt, J = 11.2, 7.3 Hz, 1H; C*H*), 1.95 (s, 3H; CH_3), 1.78 (s, 3H; CH_3), 1.62 (m, 2H; CH_2), 1.41 (m, 1H; CH*H*), 0.93 (t, J = 7.4 Hz, 3H; CH_3), 0.56 (s, 1H; N*H*), 0.45 (dd, J = 11.2, 4.4 Hz, 1H; C*H*), −0.36 (dtd, J = 13.3, 9.8, 4.4, 1H; CH*H*)
12[a]	3-*syn*-PrC_3H_4	3.61 (dd, J = 7.5, 3.2 Hz, 1H; CH*H*), 2.39 (t, J = 7.2 Hz, 3H; CH_3), −0.27 (dd, J = 11.9, 3.2 Hz, 1H; CH*H*)
13	*trans*-EtCH=CHCH=CH_2	4.20 (dd, J = 12.4, 5.3 Hz, 1H; C*H*), 3.84 (dt, J = 12.4, 8.7 Hz, 1H; C*H*), 3.11 (dd, J = 8.1, 2.6 Hz, 1H; C*H*), 2.66 (m, 1H; CH*H*), 2.50 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 2.14 (m, 1H; CH*H*), 1.19 (t, J = 8.11 Hz, 3H; CH_3), 1.09 (s, 1H; N*H*), 0.70 (ddd, J = 12.8, 8.1, 5.3 Hz, 1H; C*H*), −0.80 (dd, J = 12.8, 2.6 Hz, 1H; C*H*), −11.49 (s, 1H; μ-*H*)
14	3-*syn*-PhC_3H_4	7.36 (m, 4H; Ph), 7.23 (m, 1H; Ph), 3.67 (dd, J = 7.9, 2.9 Hz, 1H; CH*H*), 2.88 (br td, J = 11.1, 7.9 Hz, 1H; C*H*), 1.91 (s, 6H; 2CH_3), 1.84 (d, J = 11.1 Hz, 1H; C*H*), 0.54 (s, 1H; NH), −0.12 (dd, J = 11.1, 2.9 Hz, 1H; CH*H*)

[a] This compound could not be separated from complex **3**. Only the resonances that could be unequivocally assigned to this complex are given.

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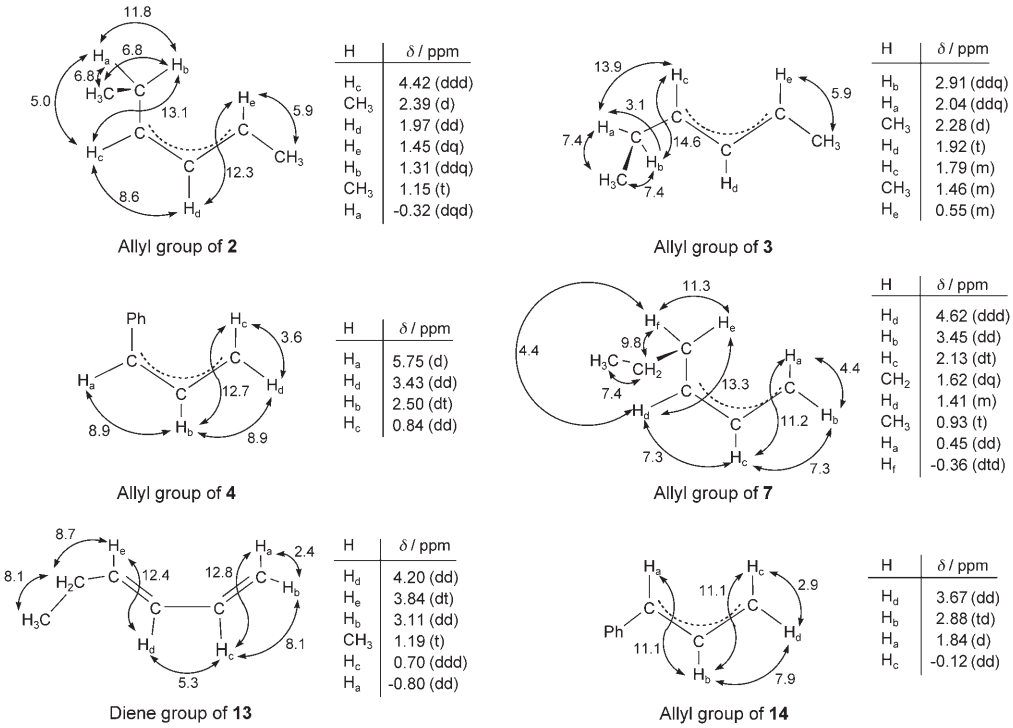

Figure 4. ^{1}H NMR assignments of the allyl and diene protons of compound **2**, **3**, **4**, **7**, **13**, and **14**. The arrows connect protons coupled to each other. The numbers nearby the arrows represent coupling constants (Hz).

Theoretical calculations: Minimum-energy structure calculations were carried out by using 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 stability (important in order 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, irrespectively 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.

For the cases in which both experimental (X-ray diffraction) and theoretical (DFT calculations) structural data were obtained, the structural parameters given by both methods are practically identical. This fact validates the calculations.

Figure 5 shows the relative energies of a family of isomeric clusters formally derived from complex **1** and 3-hexyne. Without exception, the allyl derivatives (**I**–**IV**) are more stable than the alkenyl derivatives (**V**, **VI**). Within the group of allyl derivatives, structure **I**, which has the ethyl and methyl substituents in *syn* positions, is the most stable, and structure **IV**, which has these substituents in *anti* positions, the least stable. The face-capped alkenyl complex (**VI**) is overall the least stable isomer, being 2.87 kcal mol^{-1} less stable than the edge-bridged alkenyl isomer (**V**).

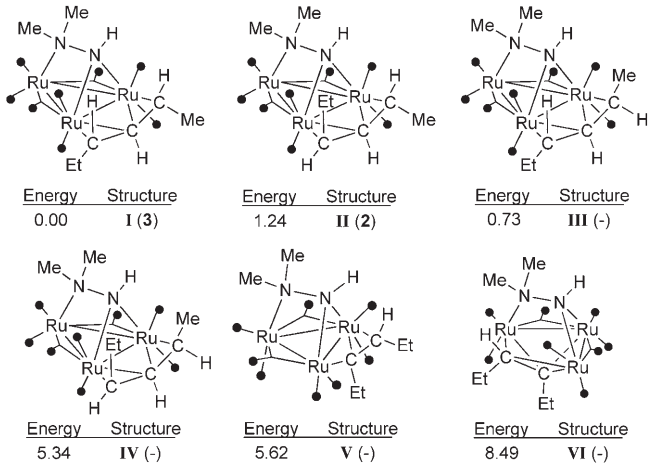

Figure 5. Relative energies (kcal mol^{-1}) of DFT-calculated minimum-energy structures of isomeric products formally derived from compound **1** and 3-hexyne. The energy of the most stable structure is assigned as 0.00 kcal mol^{-1}.

Compounds **14** and **4** are the only two possible allyl derivatives of 1-phenyl-1-propyne. However, the asymmetry of this alkyne provokes an increase of the number of possible alkenyl isomers (Figure 6). Again, the allyl derivatives are the most stable isomers, with the *syn* isomer (structure **VII**) being 3.60 kcal mol^{-1} more stable than the *anti* isomer (structure **VIII**). Within the group of alkenyl derivatives, the edge-bridged products (**IX** and **X**) are more stable than the face-capped ones (**XI** and **XII**), with those that have the hy-

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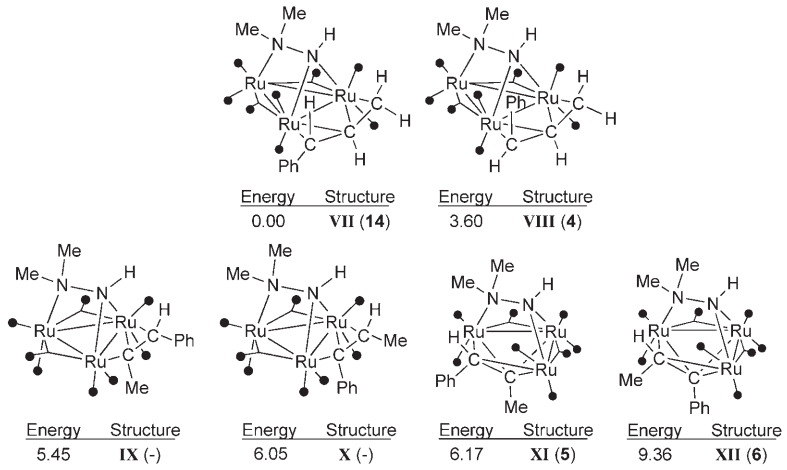

Figure 6. Relative energies (kcal mol^{-1}) of DFT-calculated minimum-energy structures of isomeric products formally derived from compound **1** and 1-phenyl-1-propyne. The energy of the most stable structure is assigned as 0.00 kcal mol^{-1}.

drogen and phenyl groups in *gem* arrangement (**IX** and **XI**) being more stable than those that have these groups in *trans* arrangement (**X** and **XII**).

For the derivatives of 1-hexyne, the energetic situation (Figure 7) is analogous to that found for the derivatives of 1-phenyl-1-propyne (Figure 6). In this case, for both the edge-bridged and face-capped alkenyl derivatives, those with the alkenyl hydrogen atoms in a *gem* arrangement (**XV** and **XVII**) are less stable than those with these hydrogen atoms in a *trans* arrangement (**XVI** and **XVIII**, respectively). This trend has also been observed for alkenyl complexes derived from compound **1** and terminal alkynes with no α-hydrogen atoms.[5] The face-capped *trans*-alkenyl complex **9** (**XVIII**) is even more stable than the edge-bridged *trans*-alkenyl derivative (**XVI**). It is also interesting to note that all the allyl and alkenyl derivatives of 3-hexyne (Figure 5) and 1-hexyne (Figure 7) are isomers and that compound **3** (structure **I**) is 0.94 kcal mol^{-1} less stable than **12** (structure **XIII**).

Figure 7 also shows the relative energies computed for products formally derived from compound **1** and propargyl alcohol. In this case, although the number and type of isomers coincide with those derived from 1-hexyne, the energies do not follow the trends found for the alkynes commented above, probably due to the presence of the oxygen atom. Thus, although the allyl derivatives (**XIX** and **XX**) are again more stable than the alkenyl ones (**XXI**-**XXIV**), the most stable structure corresponds to the *anti* isomer **XX**, and the *trans* face-capped alkenyl **XXIV** is more stable than any of the edge-bridged isomers (**XXI** and **XXII**).

As commented above, DFT methods were also used to shed light on structural aspects of compounds for which no X-ray diffraction data were available. Among the compounds of this kind reported in this work, the diene complex **13** is the most noticeable one, because is different from all the others. The *trans* stereochemistry of the internal C=C bond of the diene ligand was inferred from the ^{1}H NMR spectrum of the compound and was imposed in the input used for the calculation. The position of the hydride ligand, spanning the Ru1−Ru3 edge, was also included in the calculation input model. The DFT-optimized structure is shown in Figure 8. A selection of interatomic distances is given in Table 1. A closed triruthenium unit is capped by the Me_2NNH ligand in the same way as that found in the allyl compounds **2** and **3** (see above). The metal atoms of the edge bridged by the amido fragment are also spanned by the diene ligand in such a way that each metal atom is attached to two carbon atoms, Ru1 to C5 and C6, and Ru2 to C3 and C4. The distances between the carbon atoms of the butadiene fragment are consistent with the coordination of both alkene moieties, the central C4−C5 distance being slightly longer (1.446 Å) than the C3−C4 and C5−C6 distances (1.400 and 1.418 Å, respec-

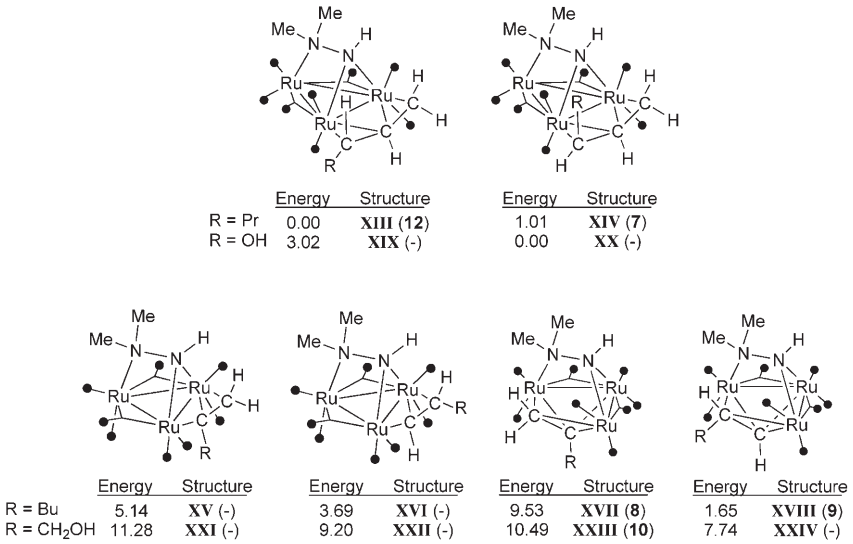

Figure 7. Relative energies (kcal mol^{-1}) of DFT-calculated minimum-energy structures of two families of isomeric products formally derived from compound **1** and 1-hexyne (**XIII**–**XVIII**) or propargyl alcohol (**XIX**–**XXIV**). The energy of the most stable structure of each family of isomers is assigned as 0.00 kcal mol^{-1}.

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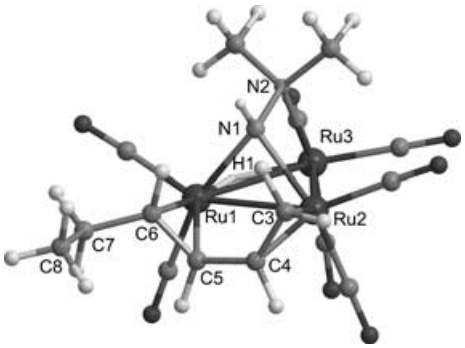


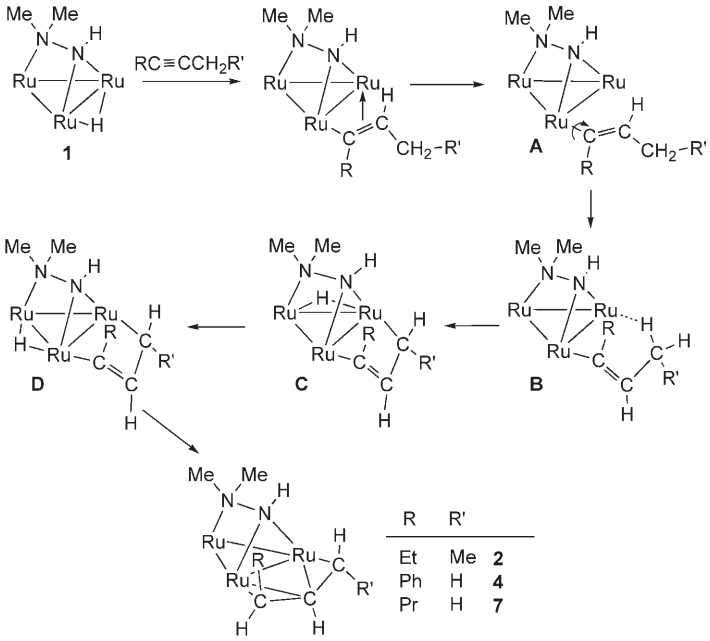
Figure 8. DFT-optimized molecular structure of compound **13**.

tively). As a consequence of the presence of the hydride ligand, the Ru1–Ru3 edge is about 0.23 Å longer than the other two edges. As far as we are aware, there is only one previous example of a complex with a conjugated diene ligand bridging two metal atoms, namely, the 1,3-cyclohexadiene derivative $[Ru_5(\mu_5\text{-}C)(\kappa^6\text{-}C_6H_6)(\kappa^4\text{-}C_6H_8)(CO)_{10}]$.[21]

Mechanistic considerations on the synthesis of the allyl derivatives and their isomerization processes: In a previous work with alkynes lacking α-hydrogen atoms,[5] we showed that their reactions with complex **1** follow an associative mechanism and that the initially formed hydrido–alkyne intermediate evolves toward edge-bridged and face-capped alkenyl products through two different reactions pathways, whose activation energies depend upon the alkyne substituents. The results of the DFT calculations shown in Figures 5–7 demonstrate that, for alkynes with α-hydrogen atoms, the allyl derivatives are the most stable isomers and that the edge-bridged alkenyl derivatives are generally more stable than their isomers with face-capped alkenyl ligands. However, it is curious that no edge-bridged alkenyl derivatives have been observed as products of any of the reactions of compound **1** with alkynes with α-hydrogen atoms, although this type of alkenyl derivative is often the product of reactions of compound **1** with alkynes without α-hydrogen atoms.[5]

All these facts led us to propose that the allyl derivatives arise from a rapid transformation of edge-bridged alkenyl clusters. If this is true, and taking into account that we have experimentally checked that the face-capped alkenyl products are not precursors to the allyl complexes, even at high temperature (toluene, 110 °C), the regioselectivity of the reactions shown in Schemes 2–5 should be directly related to the rates of formation of the edge-bridged and the face capped alkenyl complexes from the initial hydrido–alkyne intermediate. In other words, the regioselectivity of the reactions depends upon the nature of the alkyne R groups, because this factor seems to affect to a great extent the kinetic barriers of important reaction steps. Thus, for the reaction of **1** with 3-hexyne (Scheme 2), we propose that the face-capped alkenyl products should be formed at a much slower rate than the edge-bridged ones (or not formed at all) and that the transformation of the latter into the allyl derivatives (which are the only observed products) should take place immediately. In contrast, in the reactions of **1** with propargyl alcohol and 3-methoxy-1-propyne (Scheme 5), the rates of formation of edge-bridged alkenyl derivatives should be negligible compared with that of the face-capped *gem*-alkenyl complexes (which are the only observed products). Comparable reaction rates would lead to mixtures of allyl and face-capped alkenyl products, as occurs in the reactions shown in Schemes 3 and 4.

Scheme 8 shows a mechanistic proposal that accounts for the transformation of edge-bridged alkenyl derivatives into allyl products with an R group in the *anti* position (compounds **2**, **4**, and **7**). It involves the activation of a C_α–H bond of the alkenyl ligand (**B**→**C**) and the migration of the so formed hydride ligand to the σ-bonded vinyl C atom (**C**→**2**, **4**, or **7**). An alternative proposal in which the hydride is transferred through the NH-bridged Ru–Ru edge may also be possible.



Scheme 8. Proposal of reaction pathway for the synthesis of the allyl derivatives **2**, **4**, and **7** from their corresponding edge-bridged alkenyl isomers (carbonyl ligands have been omitted for clarity).

As demonstrated by DFT calculations (Figures 5–7), the allyl derivatives **2**, **4**, and **7**, which have an R substituent in the *anti* position, are thermodynamically less stable than their isomers **3**, **14**, and **12**, respectively, which have the R substituent in the *syn* position. In fact, all *anti*-R allyl complexes can be isomerized into the corresponding *syn*-R allyl derivatives when heated in toluene at reflux temperature. Scheme 9 contains a mechanistic proposal for such a rearrangement. It involves the 1,3-migration of the H_{anti} hydrogen atom (via the hydrido intermediates **E** and **F**, or via the NH-bridged Ru–Ru edge) from the C^1 to the C^3 carbon atom (**G**). Rotation of the RH_2C–CH bond would facilitate

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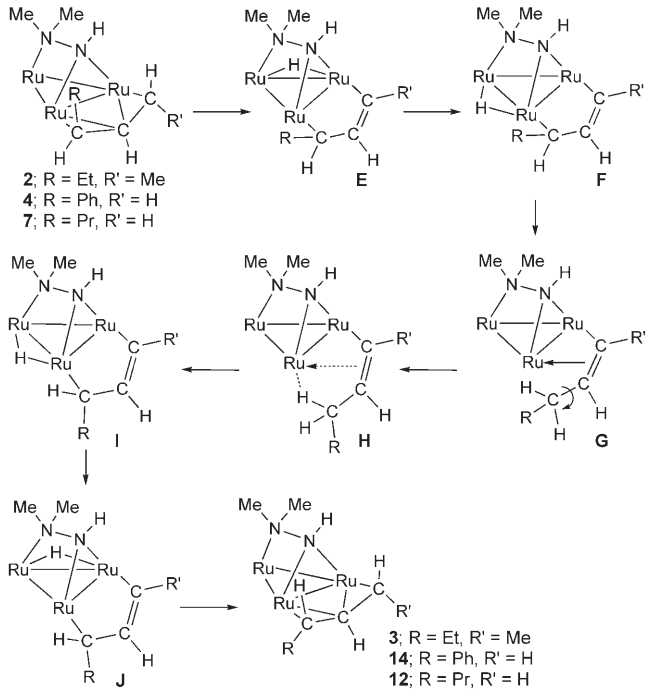
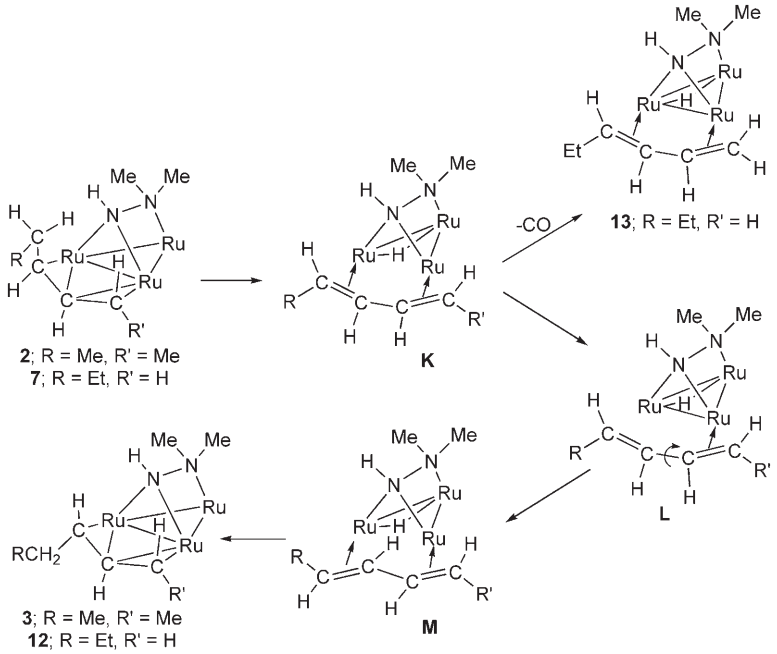


Scheme 9. Mechanistic proposal for the *anti* to *syn* rearrangement of the R groups of edge-bridging allyl derivatives through edge-bridging alkenyl intermediates (carbonyl ligands have been omitted for clarity).

the activation of the appropriate C–H bond (**H**). A subsequent migration of the so formed hydride to the C^1 carbon atom (via the hydrido intermediates **I** and **J**, or via the NH-bridged Ru–Ru edge) would render the corresponding isomer with the R group in the *syn* position. This proposal is valid for any R group and is supported by the fact that the chemical shifts of the H_{anti} protons of the allyl complexes are very low (see above), indicating short Ru···H_{anti} distances.

An alternative reaction pathway that would also account for the *anti* to *syn* rearrangement of CH_2R groups of allyl complexes is depicted in Scheme 10. It involves the activation of one of the C–H bonds of the CH_2R group in the *anti* position to give a 50-electron hydrido–diene intermediate (**K**) that may release a CO ligand to give **13** or may decoordinate one of its alkene moieties (**L**). Rotation about the diene C–C single bond in **L** and subsequent recoordination of the pendant alkene moiety (**M**) would allow the transfer of the hydride to the adjacent terminal CHR fragment of the diene to render a product with an allyl ligand with a CH_2R group in a *syn* position. This reaction pathway is supported by the isolation of the diene complex **13** from thermolysis reactions of compounds **2** and **7** in refluxing toluene and by the fact that the ^{1}H NMR signals of one of the protons of the *anti* CH_2R group of compounds **2** and **7** appear are very low chemical shifts (see above), indicating short Ru···H distances.

As commented above, the thermolysis of complex **2** in refluxing toluene gave the same mixture of products as the thermolysis of complex **7** (compounds **3**, **12**, and **13**, in a ca. 1.4:1.3:1 molar ratio). This implies that, in these reactions, most steps are reversible and that the *anti* to *syn* rearrangement processes shown in Scheme 10 (and/or Scheme 9) are concomitant with processes that involve a 1,4-migration of a hydrogen atom and a movement of the bridged Ru–Ru edge over the hydrocarbon chain. Scheme 11 shows a mechanistic proposal for the transformation of complex **7** into complex **3**. The activation of one of the C–H bonds of the CH_2Et group (**K**) and the edge-to-edge migration of the so formed hydride ligand would lead to intermediate **N**. Decoordination of the appropriate alkene moiety (**O**), followed by rotation about its single C–C bond and recoordination of the pendant alkene moiety (**P**) would promote the migration of the hydride ligand onto the diene terminal C atom that bears the Me group, rendering complex **3**. An analogous reaction pathway starting from complex **2** would also lead to complex **3** (Scheme 11). The transformation of **2** into **12** would imply the reaction sequence **2**→**3** (Scheme 9, 10, and/or 11), **3**→**7** (Scheme 11, reverse way), and **7**→**12** (Scheme 9 and/or 10).



Scheme 10. Mechanistic proposal for the *anti* to *syn* rearrangement of CH_2R groups of edge-bridging allyl derivatives through edge-bridging alkene intermediates (carbonyl ligands have been omitted for clarity).

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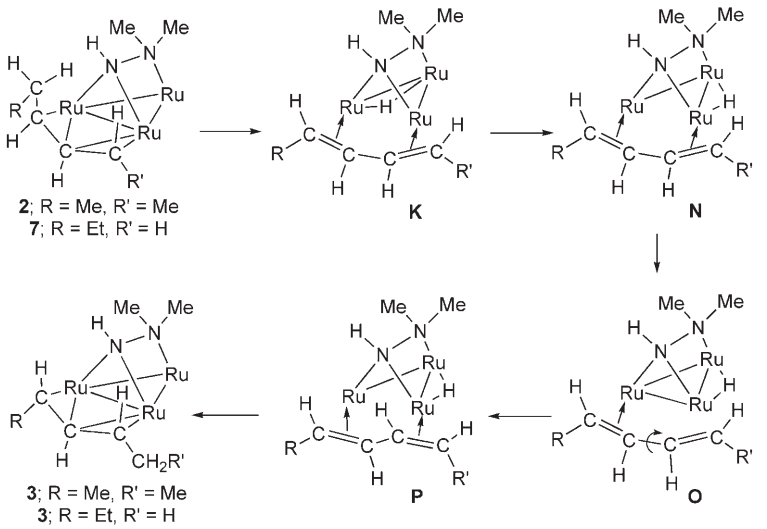

Scheme 11. Mechanistic proposal for the isomerization of compounds **2** and **7** into complex **3** through the slippage of the bridged Ru-Ru edge over the ligand chain (carbonyl ligands have been omitted for clarity).

Conclusion

As stated in the Introduction, all the hitherto published reports devoted to reactions of alkynes with face-capped hydrido–triruthenium cluster complexes,[1–5] including those dealing with alkynes that have α-hydrogen atoms,[3a,b] describe that the products of these reactions are alkenyl derivatives. This contribution demonstrates for the first time that hydrido–triruthenium cluster complexes may be transformed into allyl derivatives when treated with alkynes that have α-hydrogen atoms.

We have shown that the selectivity of the reactions is influenced by the nature of the alkyne reagents and that the allyl derivatives arise from edge-bridged alkenyl intermediates. DFT calculations have demonstrated that the allyl derivatives are thermodynamically more stable than both their edge-bridged and face-capped alkenyl isomers. However, in some instances (e.g., the cases of propargyl alcohol and 3-methoxy-1-propyne), the formation of allyl derivatives is kinetically disfavored and the reactions end in face-capped alkenyl products, because they are formed with lower energy barriers than the corresponding edge-bridged alkenyl intermediates. Therefore, the kinetic aspects of the migratory insertion processes (formation of the alkenyl ligand from the corresponding hydrido–alkyne intermediate complex) have crucial influence on the selectivity of the reactions. DFT calculations have also shown that allyl complexes that have R substituents in *anti* positions are less stable than those in which these substituents are in *syn* positions. This also rationalizes the isomerization processes that have been observed at 110 °C, for which reasonable reaction pathways have been proposed.

The results reported in this article, coupled to those reported recently on reactions of complex **1** with alkynes that do not have α-hydrogen atoms,[5] represent a rather wide picture of the reactivity of alkynes with hydrazido-bridged hydrido–carbonyl–triruthenium cluster complexes and complement previous data on the reactivity of alkynes with hydrido–carbonyl–triruthenium cluster complexes containing other face-capping ligands.

Experimental Section

General: Solvents were dried over Na-[Ph_2CO] (THF, diethyl ether, hydrocarbons), or CaH_2 (dichloromethane, 1,2-dichloroethane) 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. Compound **1** was prepared as described elsewhere.[4,8] Alkyne 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 ($\delta = 0$ ppm). 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). All their FAB+ mass spectra showed the corresponding molecular ion (Supporting Information).

Reaction of 1 with 3-hexyne—synthesis of [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ-κ^3-1-*syn*-Me-3-*anti*-EtC$_3$H$_3$)(μ-CO)$_2$(CO)$_6$] (2) and [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ-κ^3-1-*syn*-Me-3-*syn*-EtC$_3$H$_3$)(μ-CO)$_2$(CO)$_6$] (3): A solution of compound **1** (50 mg, 0.081 mmol) and 3-hexyne (10 μL, 0.089 mmol) in THF (30 mL) was stirred at reflux temperature for 20 min. The color changed from dark to bright yellow. The solvent was removed under reduced pressure and the residue was separated by TLC (silica gel), by using hexane/dichloromethane/acetone (10:2:0.5) as eluant. Extraction of the first band (dark yellow) allowed the isolation of compound **2** as a dark yellow solid (17 mg, 28 %). Extraction of the second dark yellow band afforded a 1:10 mixture of compounds **2** and **3**. Slow diffusion of hexane layered onto a solution of this mixture in dichloromethane (1 mL) afforded dark yellow crystals of compound **3** (6 mg, 10 %).

Reaction of 1 with 1-phenyl-1-propyne—synthesis of [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ-κ^3-3-*anti*-PhC$_3$H$_4$)(μ-CO)$_2$(CO)$_6$] (4), [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ$_3$-κ^2-MeCCHPh)(μ-CO)$_2$(CO)$_6$] (5), and [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ$_3$-κ^2-PhCCHMe)(μ-CO)$_2$(CO)$_6$] (6): A solution of compound **1** (50 mg, 0.081 mmol) and 1-phenyl-1-propyne (11 μL, 0.089 mmol) in THF (30 mL) was stirred at reflux temperature for 20 min. The color changed from yellow to orange. The solvent was removed under reduced pressure and the residue was supported onto TLC plates (silica gel). Hexane/acetone (10:1) eluted three bands. The bands were extracted and the corresponding solutions were evaporated to dryness, giving, in order of elution, compounds **4** (yellow solid, 12 mg, 21 %), **5** (yellow solid, 9 mg, 16 %) and **6** (orange solid, 8 mg, 14 %).

Reaction of 1 with 1-hexyne—synthesis of [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ-κ^2-3-*anti*-PrC$_3$H$_4$)(μ-CO)$_2$(CO)$_6$] (7) and [$Ru_3(\mu_3$-κ^2-HNNMe$_2$)(μ$_3$-κ^2-BuCCH$_2$)(μ-CO)$_2$(CO)$_6$] (8): A solution of compound **1** (50 mg, 0.081 mmol) and 1-hexyne (10 μL, 0.089 mmol) in THF (30 mL) was stirred at reflux temperature for 15 min. The color changed from yellow to orange. The solvent was removed under reduced pressure and the residue was separated by TLC (silica gel). Repeated elution with hexane/dichloromethane (5:1) allowed the separation of two bands. The first band afforded compound **7** as a yellow solid (9 mg, 15 %). The second band

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contained a 2.5:1 mixture of compounds **8** and **9** (^{1}H NMR spectroscopic identification). Slow diffusion of a 3:1: hexane/toluene solvent mixture layered onto a solution of the complex mixture in dichloromethane (1 mL) allowed the isolation of compound **8** as orange crystals (11 mg, 20%).

Reaction of 1 with propargyl alcohol—synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$HOCH_2CCH_2)(\mu$-$CO)_2(CO)_6$] (10): A solution of compound **1** (50 mg, 0.081 mmol) and propargyl alcohol (5 μL, 0.089 mmol) in THF (30 mL) was stirred at reflux temperature for 20 min. The color changed from yellow to orange. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and the resulting solution was supported onto a silica gel chromatographic column (3×10 cm) packed in hexane. Hexane/dichloromethane (1:1) eluted compound **10**, which was isolated as an orange solid after solvent removal (39 mg, 65%).

Reaction of 1 with 3-methoxy-1-propyne—synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$MeOH_2CCCH_2)(\mu$-$CO)_2(CO)_6$] (11): A solution of compound **1** (50 mg, 0.081 mmol) and 3-methoxy-1-propyne (7 μL, 0.089 mmol) in THF (30 mL) was stirred at reflux temperature for 20 min. The color changed from yellow to orange. The solvent was removed under reduced pressure and the residue was separated by TLC (silica gel), by using hexane/dichloromethane (3:2) as eluant. Extraction of the major band (first, orange) allowed the isolation of compound **11** as an orange solid (18 mg, 34%).

Thermolysis of compound 8 at 110°C—synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu_3$-κ^2-$HCCHBu)(\mu$-$CO)_2(CO)_6$] (9): Compound **8** (10 mg) was stirred in THF (20 mL) at reflux temperature for 2 h. Solvent removal under reduced pressure and crystallization of the residue from dichloromethane/hexane afforded compound **9** as yellow crystals (6 mg, 66%).

Thermolysis of compound 7 at 110°C—synthesis of [$Ru_3(\mu$-$H)(\mu_3$-κ^2-$HNNMe_2)(\mu$-κ^4-*trans*-$EtC_4H_5)(CO)_7$] (13): A solution of compound **7** (20 mg, 0.027 mmol) in toluene (20 mL) was stirred at reflux temperature for 25 min to give a 1.4:1.2:1 mixture of compounds **3**, **12**, and **13** (^{1}H NMR spectroscopy of the crude reaction mixture). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (2 mL). The resulting solution was separated by TLC (silica gel). Hexane/dichloromethane (3:1) eluted two yellow bands, which were extracted with dichloromethane. The corresponding solutions were evaporated to dryness, giving, in order of elution, compound **13** (orange solid, 4 mg, 22%) and a mixture of compounds **3** and **12**, which could not be separated.

Thermolysis of compound 4 at 110°C—synthesis of [$Ru_3(\mu_3$-κ^2-$HNNMe_2)(\mu$-κ^3-3-*syn*-$PhC_3H_4)(\mu$-$CO)_2(CO)_6$] (14): A solution of compound **4** (15 mg, 0.021 mmol) in toluene (10 mL) was stirred at reflux temperature for 30 min. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and the resulting solution was supported onto a silica gel chromatographic column (3×5 cm) packed in hexane. Hexane/dichloromethane (1:1) eluted compound **14**, which was isolated as a yellow solid after solvent removal (13 mg, 87%).

X-ray structures of 2, 3, and 8: Diffraction data were collected on a Nonius Kappa-CCD diffractometer by using graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54180$ Å). Data were reduced to F_o^2 values. Absorption corrections were applied using XABS2[22] (for **2** and **3**) or SORTAV[23] (for **8**). The structures were solved by Patterson interpretation using the program DIRDIF-96.[24] Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL-97.[25] All non-H atoms were refined anisotropically. Refinement of the model proposed for **8** converged with a high discrepancy index. A difference Fourier synthesis showed two sets of three peaks forming two triangles identical to that defined by the Ru atoms of the main fragment. After obtaining analogous results from six different data sets, we concluded that, due to disorder or twining, the molecule was situated in the crystal in three different independent positions. We included the six peaks in the final model as Ru atoms with a site-occupancy factor of 0.05 and the atoms of the main Ru_3 fragment with a site-occupancy factor of 0.9. This treatment resulted in good final discrepancy indexes. This unusual crystallographic problem has previously been observed on a few occasions.[12c,26] The molecular plots were made with the PLATON program package.[27] The WINGX program system[28] was used throughout the structure determinations. Details of the data collection and refinement parameters are given in Table 6.

CCDC-269582 (**2**), CCDC-269583 (**3**), and CCDC-269584 (**8**) 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.

Theoretical calculations: All the structure optimizations were performed by hybrid DFT, within the Gaussian 98 program suite,[29] by using the Becke's three-parameter hybrid exchange-correlation functional[30] containing the B3LYP non-local gradient correction.[31] The LANL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[32] The basis set used for the remaining atoms was the 6-31G with addition of (d,p)-polarization for all atoms. All optimized structures were confirmed as minima by calculation of analytical frequencies. For each calculation, the input model molecule was based on one of the X-ray-determined structures reported in this article, conveniently modified by changing the appropriate R groups.

Table 6. Crystal, measurement, and refinement data for the compounds studied by X-ray diffraction.

	2	**3**	**8**
formula	$C_{16}H_{18}N_2O_8Ru_3$	$C_{16}H_{18}N_2O_8Ru_3$	$C_{16}H_{18}N_2O_8Ru_3$
M_r	669.53	669.53	669.53
color	yellow-orange	yellow-orange	yellow
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$	$C2/c$
a [Å]	13.1609(11)	10.6332(4)	30.2736(13)
b [Å]	10.8710(9)	16.1546(7)	9.3745(4)
c [Å]	16.0299(15)	13.1513(5)	18.4076(8)
β [°]	104.296(5)	110.581(2)	124.634(3)
V [Å^3]	2222.4(3)	2114.88(15)	4298.4
Z	4	4	8
$F(000)$	1296	1296	2592
ρ_{calcd} [g cm^{-3}]	2.001	2.103	2.069
μ [mm^{-1}]	16.690	17.538	17.258
crystal size [mm]	0.10×0.08×0.05	0.13×0.10×0.10	0.15×0.10×0.75
T [K]	120(2)	120(2)	293(2)
θ range [°]	2.84–68.62	4.52–68.33	3.55–68.39
min/max h, k, l	−15/15, −13/12, −19/19	0/12, 0/19, −15/14	−36/29, 0/11, 0/22
collected reflns	18404	13902	16676
unique reflns	3804	3872	3922
reflns with $I > 2\sigma(I)$	2183	3572	3269
absorption correction	XABS2	XABS2	SORTAV
max/min transmission	0.452/0.225	0.176/0.150	0.272/0.160
parameters/restraints	265/1	268/2	296/2
GOF on F^2	0.937	1.064	1.013
R_1 [on F, $I > 2\sigma(I)$]	0.0558	0.0409	0.0854
wR_2 (on F^2, all data)	0.1575	0.1043	0.1993
Max/min $\Delta\rho$ [e Å^{-3}]	0.872/−0.975	1.177/−0.883	2.155/−2.796

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