

Reactivity of $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\text{CO})_9]$ towards Activated Alkynes and Diynes – Isolation of a Trinuclear Intermediate During the Formation of Bi- and Tetranuclear Products

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Treatment of the trinuclear imido-bridged cluster compound $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\text{CO})_9]$ (**1**) with activated alkynes (methyl propynoate and methyl phenylpropynoate) and diynes (diphenylbutadiyne, 2,4-hexadiyne, 1,6-diphenyloxy-2,4-hexadiyne, and 1-trimethylsilyl-1,4-pentadiyne) in hexanes at reflux temperature leads to separable mixtures of the tetranuclear and binuclear derivatives $[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-RC}\equiv\text{CR}')(\mu\text{-CO})_2(\text{CO})_6]$ and $[\text{Ru}_2\{\mu, \eta^3\text{-RC}\equiv\text{CR}'\text{C}(\text{O})\text{-NPh}\}(\text{CO})_6]$, respectively. While the former complexes feature a phenylimido ligand in a rather rare μ_4 -coordination mode, the binuclear compounds contain acrylamido ligands that result from the coupling of a CO ligand and the original phenylimido ligand of **1** with the incoming alkyne or diyne. Surprisingly, all the products derived from diynes contain a

pendant (non-coordinated) alkyne functionality. The isolation of the trinuclear derivative $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3, \eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_9]$ (**9**) in the reaction of **1** with diphenylbutadiyne and the fact that its thermolysis leads to a mixture of $[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_6]$ and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{C}\equiv\text{CPh})=\text{C}(\text{Ph})\text{C}(\text{O})\text{NPh}\}(\text{CO})_6]$ support the proposal that trinuclear species containing coordinated alkyne or diyne ligands, similar to **9**, are intermediates in the synthesis of all the bi- and tetranuclear products. Only one of the two possible regioisomers of each product (that might have arisen from the asymmetry of the alkyne or diyne reagents used) is formed. The origin of this regioselectivity is also discussed.

Introduction

Carbon–nitrogen bond formation assisted by metal cluster complexes has emerged as a powerful tool for the synthesis of novel organic fragments.^[1–12] The cluster precursors often contain amido (NR_2)^[1,2] or imido (NR)^[4–12] ligands, which constitute the nitrogen source for the synthesis of new N-containing organic fragments. In other cases, C–N bond-forming reactions have been achieved by attack of nitrogen nucleophiles (e.g. RNH_2 , R_2NH) on coordinated unsaturated hydrocarbyls such as alkynyls, allenyls, etc.^[3] In some cases, these assemblies have been successfully separated from the metallic core, yielding interesting heteronuclear organic molecules.^[4–8]

Interesting reactions of face-capping organoimido ligands ($\mu_3\text{-NR}$) in cluster complexes have been reported. These ligands can easily combine with a variety of other ligands such as hydrides,^[13] carbenes,^[5,14] acyls,^[5,8] carbonyls,^[7,10] methoxycarbonyls,^[5] or alkynes^[4,11] to give or-

ganic compounds such as imidates, amides, amines, carbamates, isocyanates, pyridinones, or ureas. In this context, Geoffroy et al. have reported on the reactivity of the trinuclear imido cluster $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\text{CO})_9]$ (**1**) with the internal alkynes diphenylacetylene and methylphenylacetylene.^[4] These reactions afforded, among other noteworthy products, binuclear metallapyrrolidone complexes from which pyridinone or maleimide derivatives could subsequently be obtained by treating them with further alkyne or CO, respectively.^[4]

Recently, our group has been paying attention to the reactivity of diynes with ruthenium carbonyl cluster complexes containing N-donor ligands.^[2,15] To date, only a few reactions of ruthenium clusters with diynes have appeared in the literature,^[2,15–17] though these ligands are expected to be more reactive than monoalkynes and, therefore, to offer a richer derivative chemistry.

The interesting results obtained by Geoffroy et al. in the reactions of **1** with non-activated internal alkynes^[4] prompted us to study its reactivity towards activated alkynes and diynes, the aim being to prepare new derivatives made accessible by the enhanced reactivity expected for these unsaturated molecules as compared to simple non-activated monoalkynes.

We report herein the synthesis and structural characterization of a series of new bi-, tri-, and tetranuclear ruthenium cluster complexes derived from **1** and activated alkynes or diynes. The regioselectivity of the reactions, which

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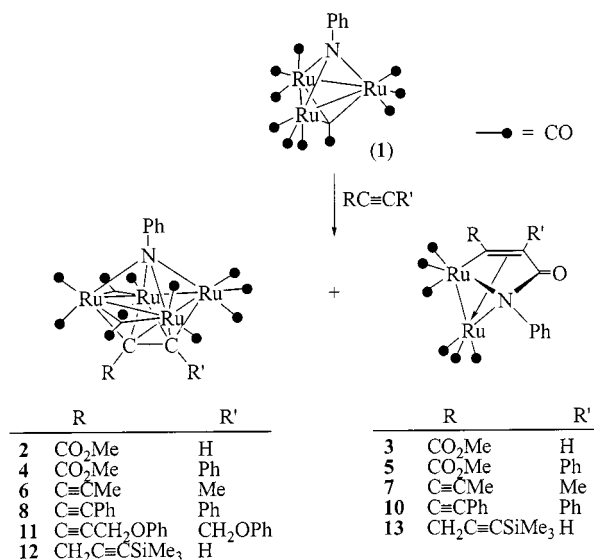
give only one of the two possible regioisomers of each product (that might arise from the asymmetry of the alkyne or diyne reagents used) is discussed. This work also demonstrates that trinuclear alkyne or diyne complexes are intermediates in the synthesis of the final bi- and tetranuclear products.

Results and Discussion

Synthesis and Characterization of the Compounds

It has been reported that compound **1** can be prepared following different synthetic procedures, i.e. by treating $[\text{Ru}_3(\text{CO})_{12}]$ with phenyl isocyanate,^[18] nitrobenzene,^[18,19] or nitrosobenzene,^[20] or by treating the more reactive $[\text{Ru}_3(\text{MeCN})(\text{CO})_{11}]$ with nitrosobenzene.^[8] However, the first three methods afford compound **1** in only moderate to low yields and it is invariably accompanied by considerable amounts of the diimido derivative $[\text{Ru}_3(\mu_3\text{-NPh})_2(\text{CO})_9]$. In our hands, the best yields (up to 40%) were obtained starting from $[\text{Ru}_3(\text{MeCN})(\text{CO})_{11}]$ and nitrosobenzene, following a modification of the published method (see Exp. Section).^[8]

Treatment of a solution of **1** with an excess of methyl propynoate in refluxing hexanes afforded a mixture of compounds, from which the derivatives $[\text{Ru}_4(\mu_4\text{-NPh})\{\mu_4, \eta^2\text{-C}(\text{CO}_2\text{Me})\equiv\text{CH}\}(\mu\text{-CO})_2(\text{CO})_9]$ (**2**) and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{NPh}\}(\text{CO})_6]$ (**3**) could be isolated by column chromatography (Scheme 1). In an analogous reaction, the compounds $[\text{Ru}_4(\mu_4\text{-NPh})\{\mu_4, \eta^2\text{-C}(\text{CO}_2\text{Me})\equiv\text{CPh}\}(\mu\text{-CO})_2(\text{CO})_9]$ (**4**) and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{Ph})\text{C}(\text{O})\text{NPh}\}(\text{CO})_6]$ (**5**) were obtained by reaction of compound **1** with methyl phenylpropynoate.



Scheme 1

The ¹H NMR spectra of the tetranuclear compounds **2** and **4** clearly indicate the absence of hydride ligands and confirm that only one molecule of alkyne is present per phenylimido ligand. Both compounds display the same pat-

tern in the carbonyl stretching region of their IR spectra, showing the presence of terminal and bridging CO ligands. This IR pattern is analogous to that reported previously for the compounds $[\text{Ru}_4(\mu_4\text{-NR})(\mu_4, \eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_9]$ ($\text{R} = \text{Ph}$,^[21] H ^[22]), which were structurally characterized by X-ray diffraction methods.

As the alkyne ligands in **2** and **4** are asymmetric, an X-ray diffraction study was carried out on a single crystal of **4** in order to determine the ligand arrangement within the clusters. A molecular plot is shown in Figure 1. Selected bond lengths are listed in Table 1.

Table 1. Selected interatomic distances [Å] in compounds **4** and **8**

	4	8
Ru(1)–Ru(3)	2.6954(9)	2.6853(9)
Ru(1)–Ru(4)	2.6959(6)	2.684(1)
Ru(2)–Ru(3)	2.7136(6)	2.812(1)
Ru(2)–Ru(4)	2.7951(8)	2.726(1)
Ru(1)–N(3)	2.206(3)	2.201(4)
Ru(1)–C(2)	2.197(4)	2.223(5)
Ru(1)–C(1P)	2.082(4)	2.288(6)
Ru(1)–C(2P)	2.299(4)	2.076(4)
Ru(2)–N(3)	2.145(3)	2.148(4)
Ru(2)–C(1)	2.133(4)	2.114(5)
Ru(3)–N(3)	2.210(3)	2.256(4)
Ru(3)–C(1)	2.397(4)	2.407(5)
Ru(3)–C(2)	2.246(4)	2.299(5)
Ru(3)–C(2P)	1.999(4)	2.034(5)
Ru(4)–N(3)	2.255(3)	2.256(4)
Ru(4)–C(1)	2.333(4)	2.364(5)
Ru(4)–C(2)	2.270(4)	2.281(5)
Ru(4)–C(1P)	2.019(4)	2.004(5)
C(1)–C(2)	1.427(5)	1.424(7)
C(2)–C(3)	1.496(6)	1.427(4)
C(3)–C(4)	—	1.193(7)
C(3)–O(1)	1.190(5)	—
C(3)–O(2)	1.335(6)	—
C(4)–O(2)	1.444(7)	—

The four Ru atoms of **4** define a distorted square, forming a dihedral Ru(1)–Ru(3)–Ru(4)–Ru(2) angle of 19.5°. The Ru–Ru distances range from 2.695 to 2.795 Å. Two CO ligands span the Ru(1)–Ru(3) and Ru(1)–Ru(4) edges. The phenylimido ligand bridges the four metal atoms, while the alkyne ligand is positioned on the opposite face of the metal core, binding the four Ru atoms in an η^2 -fashion, in such a way that it is σ -bonded to Ru(1) and Ru(2) and π -bonded to Ru(3) and Ru(4). The C(2) atom of the alkyne ligand, which bears the CO₂Me group, is attached to the three Ru atoms that bear the bridging carbonyl ligands, while the CPh fragment is bonded to Ru(2), Ru(3), and Ru(4). The cluster shell is completed by nine terminal CO ligands. The structure of **4** resembles those reported previously for the complexes $[\text{Ru}_4(\mu_4\text{-NR})(\mu_4, \eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_9]$ ($\text{R} = \text{Ph}$,^[21] H ^[22]), which contain a symmetrical alkyne ligand.

The μ_4 -coordination mode adopted by the phenylimido ligand in **2** and **4** is rather rare. Apart from the compounds mentioned above, a series of ruthenium compounds containing μ_4 -imido ligands has been prepared by Wong et al.

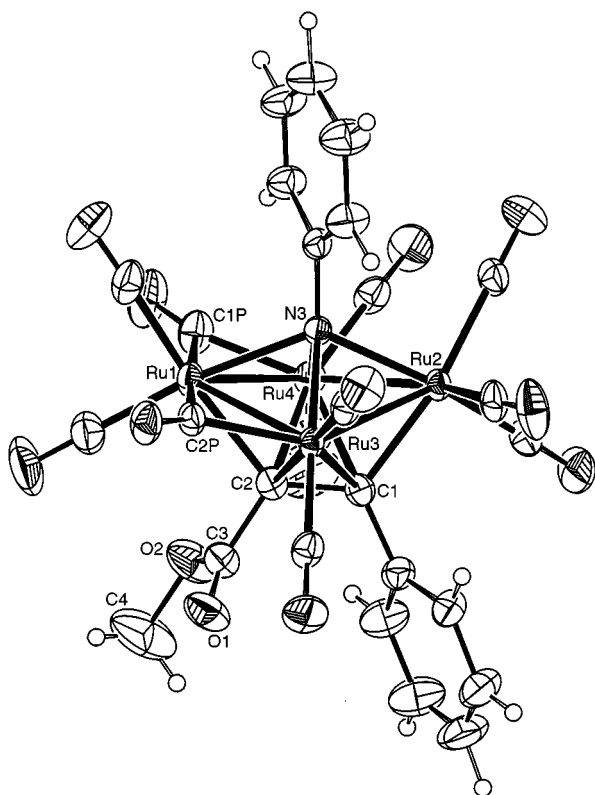


Figure 1. Molecular structure of compound **4**; ellipsoids are drawn at a 50% probability level

by deoxygenation reactions of the methoxyimido precursor $[\text{Ru}_3(\mu_3\text{-NOMe})(\mu_3\text{-CO})(\text{CO})_9]$.^[12] Further examples of μ_4 -imido complexes are the heteronuclear derivative $[\text{WO}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-O})\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-CCPh})(\text{CO})_{10}]$ ^[23] and the iron complex $[\text{Fe}_4(\mu_4\text{-NEt})(\mu, \eta^2\text{-ONeEt})(\text{CO})_{11}]$.^[24]

The other two complexes isolated from the reactions of **1** with monoalkynes are the binuclear derivatives **3** and **5**. Their elemental analyses and mass spectra clearly indicate their binuclear nature, while their ^1H NMR spectra show the incorporation of only one molecule of alkyne per phenylimido ligand. A comparison of the ^1H and ^{13}C NMR spectra of both compounds with those of other related binuclear metallapyrrolidone complexes^[9,11,12a] also indicates that the CO_2Me group is attached to the C_α carbon atom. Both compounds display the same IR pattern in the carbonyl stretching region, suggesting an analogous ligand arrangement. This IR pattern is similar to that reported previously for other binuclear metallapyrrolidone ruthenium^[4,11,12a] and iron^[9,25] compounds. All these data are in accordance with the structures proposed for **3** and **5** in Scheme 1, and are also supported by an X-ray structural characterization of a related compound (*vide infra*).

Similar coupling reactions of imido ligands with CO and alkynes to give binuclear metallapyrrolidone compounds have also been reported for rhodium,^[26] although in this case the coordination sphere of the metal atoms is not completed by carbonyl but by cyclopentadienyl ligands.

The reactivity of **1** towards 2,4-hexadiyne, diphenylbutadiyne, 1,6-diphenyloxy-2,4-hexadiyne, and 1-trimethylsilyl-

1,4-pentadiyne was studied. To our surprise, the diyne ligands exhibited the same reactivity pattern as the monoalkynes, leading to mixtures of the tetranuclear cluster compounds $[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-RC}\equiv\text{CR}')(\mu\text{-CO})_2(\text{CO})_9]$ ($\text{R} = \text{C}\equiv\text{CMe}$, $\text{R}' = \text{Me}$, **6**; $\text{R} = \text{C}\equiv\text{CPh}$, $\text{R}' = \text{Ph}$, **8**; $\text{R} = \text{C}\equiv\text{CCH}_2\text{OPh}$, $\text{R}' = \text{CH}_2\text{OPh}$, **11**; $\text{R} = \text{CH}_2\text{C}\equiv\text{CSiMe}_3$, $\text{R}' = \text{H}$, **12**; Scheme 1) and the binuclear metallapyrrolidones $[\text{Ru}_2\{\mu, \eta^3\text{-RC}\equiv\text{CR}'\text{C}(\text{O})\text{NPh}\}(\text{CO})_6]$ ($\text{R} = \text{C}\equiv\text{CMe}$, $\text{R}' = \text{Me}$, **7**; $\text{R} = \text{C}\equiv\text{CPh}$, $\text{R}' = \text{Ph}$, **10**; $\text{R} = \text{CH}_2\text{C}\equiv\text{CSiMe}_3$, $\text{R}' = \text{H}$, **13**; Scheme 1), which could be separated by chromatographic methods. In the case of 1,6-diphenyloxy-2,4-hexadiyne, only the tetranuclear derivative **11** could be satisfactorily isolated, while the corresponding binuclear compound could not be separated from uncharacterized impurities.

Interestingly, in the reaction of **1** with diphenylbutadiyne, a novel trinuclear derivative, subsequently characterized as $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3, \eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_9]$ (**9**), could be isolated in addition to the aforementioned tetranuclear and binuclear compounds **8** and **10**.

The IR spectra of the tetranuclear compounds **6**, **8**, **11**, and **12** are reminiscent of those of compounds **2** and **4**, indicating a similar ligand arrangement. This was confirmed by an X-ray diffraction study carried out on a single crystal of **8**. A molecular plot is shown in Figure 2 and selected bond lengths are listed in Table 1. For quick comparison purposes, and as far as possible, similar numbering schemes have been used for **4** and **8**. The structure of **8** is entirely analogous to that of compound **4**. Again, the car-

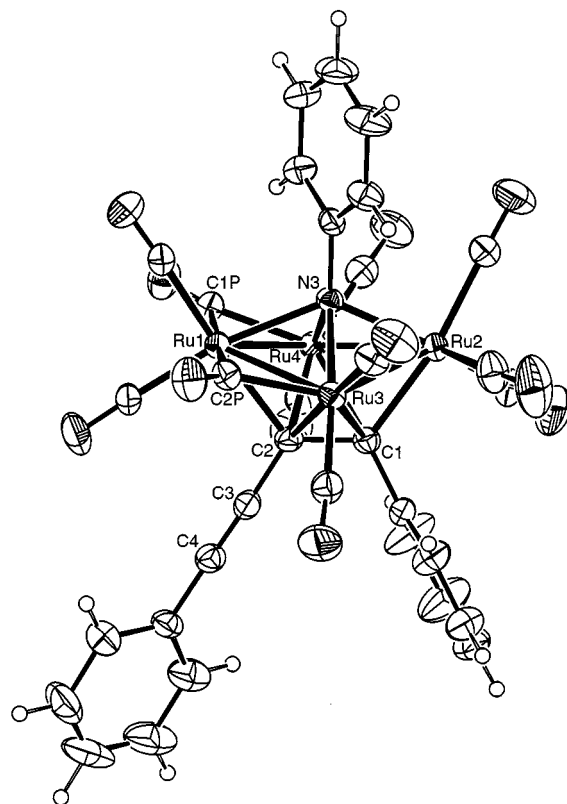


Figure 2. Molecular structure of compound **8**; ellipsoids are drawn at a 50% probability level

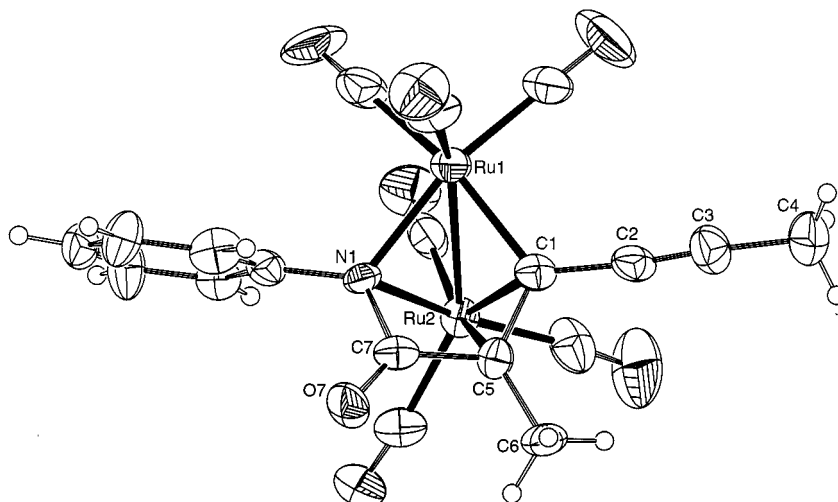


Figure 3. Molecular structure of compound **7**; ellipsoids are drawn at a 50% probability level

bon atom bearing the most electron-withdrawing substituent of the coordinated alkyne, the $\text{C}\equiv\text{CPh}$ group, is bonded to the three metal atoms that bear the bridging carbonyl ligands.

The structures of the binuclear ruthenapyrrolidones **7**, **10**, and **13** are analogous to those described above for compounds **3** and **5**. The positions of the substituents attached to the C_α and C_β carbon atoms of the metallapyrrolidone fragments were unambiguously determined on the basis of their ^{13}C and ^1H NMR spectra (Scheme 1). These data also compare well with those reported previously for related iron^[9] and ruthenium^[11,12a] compounds. This structural assignment was also supported by an X-ray structure determination carried out on a single crystal of **7**.

The structure of **7** is shown in Figure 3. Selected bond lengths are listed in Table 2. The compound consists of two ruthenium atoms bridged by an acrylamido ligand, which stems from the coupling of the original imido ligand, one of the $\text{C}\equiv\text{C}$ bonds of the incoming diyne, and a carbonyl ligand. The molecule can be described as a ruthenapyrrolidone fragment attached to a ruthenium atom through the Ru, N, and both C atoms of the double bond,

C(1) and C(5). The carbon atom C(1), bearing the non-coordinated $\text{C}\equiv\text{CMe}$ group, is also σ -bonded to Ru(1). The coordination sphere of each metal atom is completed by three terminal CO ligands. The C(1)–C(5) distance, 1.42(2) Å, is within the range typical of coordinated double bonds, while the C(1)–Ru(1) bond length, 2.05(2) Å, is shorter than that corresponding to C(1)–Ru(2), 2.26(2) Å, reflecting σ - and π -interactions, respectively. The Ru(1)–Ru(2) distance, 2.682(2) Å, is appropriate for a single metal–metal bond.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the trinuclear compound **9** show the presence of the imido ligand and indicate the incorporation of one molecule of diyne into the cluster shell. Its trinuclear nature was revealed by its elemental analysis and mass spectrum, which shows the appropriate molecular ion isotopomers. The presence of nine carbonyl ligands was also deduced from its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The 50-electron count of the cluster is consistent with the presence of only two metal–metal bonds. Unfortunately, despite many attempts, we could not obtain crystals of **9** suitable for an X-ray diffraction study and the coordination mode of the diyne could not be unambiguously determined. However, its IR spectrum compares well with that reported previously for the imido-bridged cluster $[\text{Ru}_3(\mu_3\text{-NOPh})(\mu_3, \eta^2\text{-PhC}\equiv\text{CH})(\text{CO})_9]$,^[12a] which was structurally characterized by X-ray diffraction methods and which features the same ligand arrangement as that depicted for **9** in Scheme 2.

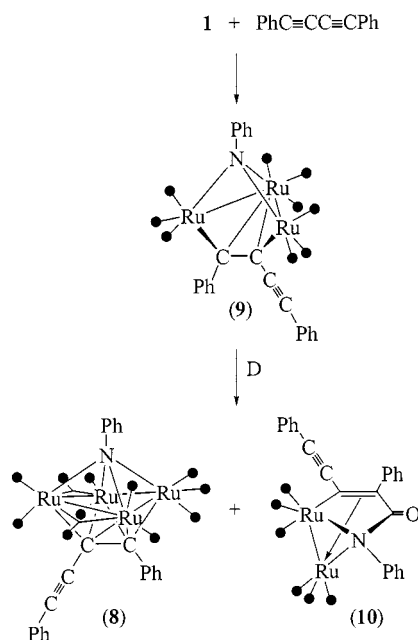
Regioselectivity of the Products

In all the reactions reported in this article, the use of asymmetric alkynes could have led to the formation of two regioisomers for each compound. However, *only one of the two possible regioisomers is selectively formed*. Dienes can also be considered as asymmetric alkynes, since all the isolated products derived from them contain a pendant (non-coordinated) alkyne fragment.

For the metallapyrrolidone complexes, electronic rather than steric effects seem to govern the exclusive formation

Table 2. Selected interatomic distances [Å] in compound **7**

Ru(1)–Ru(2)	2.681(2)
Ru(1)–C(1)	2.05(2)
Ru(1)–N(1)	2.12(2)
Ru(2)–C(1)	2.26(2)
Ru(2)–C(5)	2.28(2)
Ru(2)–C(7)	2.57(2)
Ru(2)–N(1)	2.16(2)
N(1)–C(7)	1.48(2)
C(1)–C(2)	1.45(3)
C(1)–C(5)	1.42(2)
C(2)–C(3)	1.15(3)
C(3)–C(4)	1.48(3)
C(5)–C(6)	1.48(3)
C(5)–C(7)	1.48(3)
C(7)–O(7)	1.20(2)



Scheme 2

of one of the two possible isomers in each case, since the group attached to the pyrrolidone C_α atom is always more electron-withdrawing than that attached to C_β , regardless of their volumes. This proposal is also in agreement with the results obtained by Geoffroy et al. for analogous derivatives, for which no explanations were given.^[4]

In the case of the tetranuclear derivatives, again only one of the two possible isomers was observed in each case. In these complexes, the two alternative coordination modes of the alkynes or diynes are not expected to lead to marked differences in the spectroscopic data, and only in the compounds studied by X-ray diffraction methods could the ligand disposition be unambiguously determined. For the X-ray-characterized compounds **4** and **8**, it is found that the ruthenium atom that bears the two bridging CO ligands is attached to the carbon atom of the alkyne moiety that bears the most electron-withdrawing group, but, coincidentally, this group is also the smallest one in each case. It is also unfortunate that the two previously reported structures of related compounds are of complexes containing a symmetrical alkyne ligand, $[\text{Ru}_4(\mu_4\text{-NR})(\mu_4, \eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_9]$ ($\text{R} = \text{Ph}$,^[21] H ^[22]). However, careful examination of the X-ray structures of all these tetranuclear complexes indicates that there is sufficient space at both ends of the $\text{C}\equiv\text{C}$ moiety to accommodate the bulkier substituent. Therefore, electronic rather than steric effects must account for the observed regioselectivity. Accordingly, the assignment of the substituents shown in Scheme 1 for the tetranuclear derivatives is such that the most electron-withdrawing substituent of the alkyne is close to the ruthenium atom that bears the two bridging CO ligands, as found in the structurally characterized compounds **4** and **8**.

Insights into the Formation of the Bi- and Tetranuclear Compounds

The synthesis of the bi- and tetranuclear complexes appears to be initiated by coordination of the alkyne or diyne reagents to compound **1**, to generate trinuclear intermediates analogous to complex **9**. These 50-electron trimetallic intermediates seem to be highly unstable as they could only be isolated in the reaction with diphenylbutadiyne. In subsequent steps, the alkyne coordination must be followed by cluster fragmentation and C–C and C–N bond formations to afford the corresponding binuclear ruthenapyrrolidone complexes. The $\text{Ru}(\text{CO})_x$ fragments arising from this cluster degradation would be readily trapped by the remaining trimetallic intermediates to afford the corresponding tetranuclear derivatives (Scheme 2).

This proposal is supported by the fact that compound **9** is readily converted into an approximately 1:1 mixture of compounds **8** and **10** upon heating in hexanes or after long periods in solution at room temperature. In fact, all attempts to obtain single crystals of **9** afforded compound **8** as the only crystallized species, while the IR spectrum of the remaining solution indicated the presence of the binuclear derivative **10** as the major product.

Concluding Remarks

The present work describes the synthesis of a series of bi- and tetranuclear ruthenium derivatives by treatment of a trinuclear imido-bridged compound with activated alkynes and diynes. In each case, only one of the two possible regioisomers of the product is formed. This selectivity has been rationalized on the basis of electronic effects of the groups attached to the $\text{C}\equiv\text{C}$ moiety. The μ_4 -coordination mode adopted by the imido ligand in the tetranuclear compounds reported herein is rather rare for ligands of this type, the number of examples hitherto reported being very limited.^[12,21–24]

Surprisingly, the diynes studied in the present work invariably behaved as simple monoalkynes, leading to metal complexes containing a pendant, non-coordinated alkyne fragment. These results are to some extent at variance with those found for other triruthenium clusters in their reactions with diynes, where these ligands lead to a richer derivative chemistry than that of simple monoalkynes.^[2,15–17] The isolation, characterization, and observed reactivity of the trinuclear derivative **9** has shed light on the general reaction pathway followed by trinuclear imido-bridged cluster complexes in their reactions with alkynes and diynes since compounds analogous to **9** are intermediates in the formation of the final bi- and tetranuclear products.

Experimental Section

General Remarks: Solvents were dried with sodium diphenyl ketyl (THF, hydrocarbons) or calcium hydride (dichloromethane, acetonitrile) and were 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.

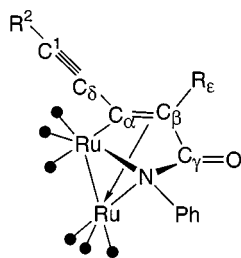


Figure 4. Carbon atom labeling scheme for the binuclear derivatives

(carbonyl stretching region) and by spot TLC (silica gel). – All reagents were purchased as analytically pure samples, except for anhydrous Me_3NO , which was obtained by azeotropic distillation of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in toluene. – IR: Perkin–Elmer Paragon 1000 FT. – NMR: Bruker AC-200, AC-300, or DPX-300, room temperature, SiMe_4 as internal standard; carbon atom labeling scheme see Figure 4. – Microanalyses were obtained from the University of Oviedo Analytical Service. – FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Synthesis of $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3\text{-CO})(\text{CO})_9]$ (1): A solution of Me_3NO (70 mg, 0.936 mL) in dichloromethane (50 mL) was added dropwise to a solution of $[\text{Ru}_3(\text{CO})_{12}]$ (500 mg, 0.782 mmol) in dichloromethane/acetonitrile (400 mL:15 mL) at -78°C . An instantaneous color change from yellow to brown was observed. Once the addition was complete, the mixture was allowed to warm to room temperature and a solution of nitrosobenzene (100 mg, 0.934 mmol) in dichloromethane (10 mL) was added dropwise. After stirring for 15 min, the mixture was concentrated under reduced pressure to a volume of ca. 2 mL and the residue was transferred to a column of silica gel (10×2 cm). Elution with hexanes afforded first a yellow band, which contained some unchanged $[\text{Ru}_3(\text{CO})_{12}]$, followed by a second yellow band containing 210 mg (40%) of complex **1**. – $\text{C}_{16}\text{H}_5\text{NO}_{10}\text{Ru}_3$ (674.46): calcd. C 28.50, H 0.75, N 2.08; found C 28.70, H 0.80, N 1.99. – FAB-MS: $m/z = 675$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2102$ (d), 2070 (vs), 2029 (m), 1721 (w, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 7.20\text{--}7.00$ (m, 5 H, Ph).

General Procedure for the Reactions of 1 with Alkynes and Diynes: In a typical reaction, a solution of **1** in hexanes (30 mL) was stirred at reflux temperature with an excess of the appropriate alkyne or diyne until complete consumption of the starting material **1** (IR monitoring). The color of the solution changed from yellow to brown. The solution was then transferred to a column of silica gel (2×15 cm). In each case, elution with hexanes afforded a first band that contained some unchanged starting material **1**. Subsequent elution with the appropriate eluent gave the products.

$[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-C}(\text{CO}_2\text{Me})\equiv\text{CH})(\mu\text{-CO})_2(\text{CO})_9]$ (2) and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{NPh}\}(\text{CO})_6]$ (3): Reactants: **1** (52 mg, 0.077 mmol); methyl propynoate (50 μL , 0.562 mmol). Reaction time: 2 h.

Data for 2: Eluted with hexanes/diethyl ether (10:1). Second band (yellow). Yield: 7 mg (10%). – $\text{C}_{21}\text{H}_9\text{NO}_{13}\text{Ru}_4$ (887.30): calcd. C 28.42, H 1.02, N 1.58; found C 28.56, H 1.05, N 1.61. – FAB-MS: $m/z = 859$ [$\text{M}^+ - \text{CO}$]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2097$ (m), 2061 (s), 2041 (vs), 2001 (m), 1982 (m, sh), 1907 (w), 1844 (m, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 6.90\text{--}6.30$ (m, 5 H, Ph), 6.21 (s, 1 H, CH), 3.93 (s, 3 H, CH_3).

Data for 3: Eluted with hexanes/diethyl ether (3:1). Third band (pale green). Yield: 12 mg (27%). – $\text{C}_{17}\text{H}_9\text{NO}_9\text{Ru}_2$ (573.42): calcd.

C 35.61, H 1.58, N 2.44; found C 35.98, H 1.69, N 2.35. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2102$ (m), 2076 (s), 2032 (s), 2014 (m), 1693 (m, br), 1659 (w, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 7.33\text{--}7.10$ (m, 3 H, Ph), 6.70 (d, $J = 7.4$ Hz, 2 H, Ph), 6.12 (s, 1 H, CH), 3.78 (s, 3 H, CH_3).

$[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-C}(\text{CO}_2\text{Me})\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_9]$ (4) and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{CO}_2\text{Me})=\text{CPhC}(\text{O})\text{NPh}\}(\text{CO})_6]$ (5): Reactants: **1** (51 mg, 0.076 mmol); methyl phenylpropynoate (39 μL , 0.263 mmol). Reaction time: 2 h.

Data for 4: Eluted with hexanes/diethyl ether (10:1). Second band (yellow). Yield: 22 mg (30%). – $\text{C}_{27}\text{H}_{13}\text{NO}_{13}\text{Ru}_4$ (963.40): calcd. C 33.65, H 1.36, N 1.45; found C 33.50, H 1.29, N 1.40. – FAB-MS: $m/z = 965$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2095$ (m), 2064 (s), 2041 (vs), 2006 (m), 1989 (m, sh), 1901 (w), 1845 (m, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 7.20\text{--}6.60$ (m, 7 H, Ph), 6.51 (t, $J = 7.5$ Hz, 1 H, Ph), 5.42 (d, $J = 7.5$ Hz, 2 H, Ph), 3.03 (s, 3 H, CH_3).

Data for 5: Eluted with hexanes/diethyl ether (3:1). Third band (pale green). Yield: 22 mg (45%). – $\text{C}_{23}\text{H}_{13}\text{NO}_9\text{Ru}_2$ (649.52): calcd. C 42.53, H 2.02, N 2.16; found C 42.65, H 2.13, N 2.09. – FAB-MS: $m/z = 651$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2100$ (m), 2075 (vs), 2031 (s), 2013 (m), 1712 (m, br), 1698 (m, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 7.38\text{--}7.08$ (m, 8 H, Ph), 6.80 (d, $J = 7.4$ Hz, 2 H, Ph), 3.45 (s, 3 H, CH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 194.3, 190.9, 189.2$ (CO's); 173.3 (C_γ), 172.1 (C_α), 167.5 (C_δ), 146.6 (NC), 133.9 (C_ϵ); 130.0, 128.3, 127.6, 127.4, 126.1, 126.0 (Ph); 100.5 (C_β); 18.7 (C_1).

$[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-MeC}\equiv\text{CC}\equiv\text{CMe})(\mu\text{-CO})_2(\text{CO})_9]$ (6) and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{C}\equiv\text{CMe})=\text{CMeC}(\text{O})\text{NPh}\}(\text{CO})_6]$ (7): Reactants: **1** (50 mg, 0.074 mmol); 2,4-hexadiyne (15 mg, 0.192 mmol). Reaction time: 55 min.

Data for 6: Eluted with hexanes. Second band (orange). Yield: 30 mg (46%). – $\text{C}_{23}\text{H}_{11}\text{NO}_{11}\text{Ru}_4$ (881.66): calcd. C 31.33, H 1.26, N 1.59; found C 31.29, H 1.30, N 1.48. – FAB-MS: $m/z = 881$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2090$ (m), 2058 (s), 2034 (vs), 2001 (m), 1982 (m, sh), 1895 (w, br), 1840 (m, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 6.60$ (t, $J = 7.5$ Hz, 2 H, Ph), 6.44 (t, $J = 7.5$ Hz, 1 H, Ph), 5.24 (d, $J = 7.5$ Hz, 2 H, Ph), 1.83 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3).

Data for 7: Eluted with hexanes/diethyl ether (10:1). Third band (pale green). Yield: 14 mg (33%). – $\text{C}_{19}\text{H}_{11}\text{NO}_7\text{Ru}_2$ (567.46): calcd. C 40.22, H 1.95, N 2.47; found C 40.01, H 1.86, N 2.39. – FAB-MS: $m/z = 569$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2210$ (w), 2094 (m), 2067 (vs), 2022 (s), 1998 (m), 1686 (m, br) cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 7.30\text{--}7.13$ (m, 3 H, Ph), 6.72 (d, $J = 7.0$ Hz, 2 H, Ph), 2.36 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 195.6, 191.7, 189.9$ (CO's); 175.2 (C_γ), 154.4 (C_α), 147.0 (NC), 128.0, 126.2, 125.7 (Ph); 108.3 (C_δ), 98.3 (C_β), 82.2 (C_1), 16.2 (C_ϵ), 4.1 (C_2).

$[\text{Ru}_4(\mu_4\text{-NPh})(\mu_4, \eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_9]$ (8), $[\text{Ru}_3(\mu_3\text{-NPh})(\mu_3, \eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_8]$ (9), and $[\text{Ru}_2\{\mu, \eta^3\text{-C}(\text{C}\equiv\text{CPh})=\text{CPhC}(\text{O})\text{NPh}\}(\text{CO})_6]$ (10): Reactants: **1** (50 mg, 0.074 mmol); diphenylbutadiyne (25 mg, 0.124 mmol). Reaction time: 35 min.

Data for 8: Eluted with hexanes/diethyl ether (30:1). Second band (orange). Yield: 10 mg (13%). – $\text{C}_{33}\text{H}_{15}\text{NO}_{11}\text{Ru}_4$ (1005.81): calcd. C 39.41, H 1.50, N 1.39; found C 39.82, H 1.52, N 1.40. – FAB-MS: $m/z = 1005$ [M^+]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2091$ (m), 2061 (s), 2036 (vs), 2006 (m), 1985 (m), 1892 (w), 1843 (m, br) cm^{-1} . –

¹H NMR (CDCl₃): δ = 7.20–6.45 (m, 13 H, Ph), 5.41 (d, *J* = 7.8 Hz, 2 H, Ph).

Data for 9: Eluted with hexanes/diethyl ether (30:1). Third band (yellow). Yield: 20 mg (32%). – C₃₁H₁₅NO₉Ru₃ (848.46): calcd. C 43.88, H 1.78, N 1.65; found C 44.01, H 1.90, N 1.68. – FAB-MS: *m/z* = 850 [M⁺]. – IR (CH₂Cl₂): ν(CO) = 2095 (w), 2076 (s), 2053 (s), 2026 (s), 2006 (m), 1995 (m, sh) cm⁻¹. – ¹H NMR (CDCl₃): δ = 7.40–6.70 (m, 15 H, Ph). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 200.0 (1 CO), 199.5 (3 CO), 195.1 (2 CO), 191.3 (1 CO), 177.3 (2 CO), 161.7, 153.7, 148.4 (Ru–C), 136.0 (Ru–C), 132.2–117.9 (m, 15 CH), 111.2 (C_{ipso}), 102.3 (C_{ipso}), 97.0 (C_{ipso}).

Data for 10: Eluted with hexanes/diethyl ether (3:1). Fourth band (pale green). Yield: 14 mg (27%). – C₂₉H₁₅NO₇Ru₂ (691.60): calcd. C 50.36, H 2.19, N 2.03; found C 50.18, H 2.04, N 1.99. – FAB-MS: *m/z* = 693 [M⁺]. – IR (CH₂Cl₂): ν(CO) = 2188 (w), 2094 (m), 2069 (vs), 2026 (s), 2007 (m), 1696 (m, br) cm⁻¹. – ¹H NMR (CDCl₃): δ = 7.74 (d, *J* = 7.3 Hz, 2 H, Ph), 7.49–7.16 (m, 11 H, Ph), 6.81 (d, *J* = 7.3 Hz, 2 H, Ph). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 196.1 (CO's); 175.1 (C_γ), 151.8 (C_α), 147.8 (NC), 153.4 (C_ε); 131.5, 131.4, 129.3, 129.1, 128.5, 128.3, 128.1, 127.1, 126.8, 122.8 (Ph); 110.6 (C_δ), 104.2 (C_β), 93.0 (C₁).

[Ru₄(μ₄-NPh)(μ₄,η²-PhOCH₂C≡CC≡CCH₂OPh)(μ-CO)₂(CO)₉] (11): Reactants: **1** (75 mg, 0.111 mmol); 1,6-diphenyloxy-2,4-hexadiyne (58 mg, 0.222 mmol). Reaction time: 45 min. Silica gel TLC eluting with hexanes/CH₂Cl₂ (5:1), second band (orange). Yield: 14 mg (12%). – C₃₅H₁₉NO₁₃Ru₄ (1065.54): calcd. C 39.45, H 1.80, N 1.31; found C 39.61, H 1.88, N 1.26. – FAB-MS: *m/z* = 1065 [M⁺]. – IR (CH₂Cl₂): ν(CO) = 2094 (m), 2062 (s), 2036 (vs), 2005 (m), 1983 (m), 1895 (w), 1846 (m, br) cm⁻¹. – ¹H NMR (CDCl₃): δ = 7.30–6.40 (m, 15 H, Ph), 4.67 (s, 2 H, CH₂), 3.38 (s, 2 H, CH₂).

[Ru₄(μ₄-NPh){μ₄,η²-C(CH₂C≡CSiMe₃)=CH}(μ-CO)₂(CO)₉] (12) and [Ru₂{μ,η³-C(CH₂C≡CSiMe₃)=CHC(O)NPh}(CO)₆] (13): Reactants: **1** (52 mg, 0.077 mmol); 1-trimethylsilyl-1,4-pentadiyne (20 μL, 0.117 mmol). Reaction time: 35 min.

Data for 12: Eluted with hexanes/diethyl ether (10:1). Second band (orange). Yield: 16 mg (22%). – C₂₅H₁₇NO₁₁Ru₄Si (939.49): calcd. C 31.96, H 1.82, N 1.49; found C 32.02, H 1.88, N 1.41. – FAB-MS: *m/z* = 939 [M⁺]. – IR (CH₂Cl₂): ν(CO) = 2091 (m), 2057 (s), 2035 (vs), 2000 (m), 1982 (m), 1897 (w), 1841 (m, br) cm⁻¹. – ¹H NMR (CDCl₃): δ = 6.61 (t, *J* = 7.5 Hz, 2 H, Ph), 6.45 (t, *J* = 7.5 Hz, 1 H, Ph), 5.27 (d, *J* = 7.5 Hz, 2 H, Ph), 4.24 (s, 1 H, CH), 2.55 (s, 2 H, CH₂), 0.21 (s, 9 H, CH₃).

Data for 13: Eluted with hexanes/diethyl ether (3:1). Third band (pale green). Yield: 12 mg (26%). – C₂₁H₁₇NO₇Ru₂Si (625.24): calcd. C 40.32, H 2.74, N 2.24; found C 40.41, H 2.99, N 2.22. – IR (CH₂Cl₂): ν(CO) = 2186 (w), 2095 (m), 2069 (vs), 2022 (s), 1996 (m), 1696 (m, br) cm⁻¹. – ¹H NMR (CDCl₃): δ = 7.21–7.16 (m, 3 H, Ph), 6.78–6.71 (m, 2 H, Ph), 6.00 (s, 1 H, CH), 3.84 (d, *J* = 19.1 Hz, 1 H, CH₂), 3.68 (d, *J* = 19.1 Hz, 1 H, CH₂), 0.16 (s, 9 H, SiMe₃). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 192.2, 181.7 (CO's); 179.1 (C_α), 175.2 (C_γ), 156.2 (C_β), 147.7 (NC), 129.3, 127.3, 127.0 (Ph); 103.2 (C₂), 82.7 (C₁), 37.7 (C_δ), 1.2 (SiMe₃).

Thermolysis of 9: A solution of **9** (40 mg, 0.047 mmol) in hexanes (20 mL) was heated at reflux temperature for 3 h, whereupon the color changed from yellow to brown. It was then concentrated under reduced pressure to a volume of ca. 2 mL and applied to the top of a column of silica gel. Elution with hexanes/diethyl ether (30:1) afforded 13 mg (27%) of compound **8** as an orange solid. Subsequent elution with hexanes/diethyl ether (3:1) afforded a pale-green band, which was found to contain 10 mg (31%) of compound **10**.

Table 3. Relevant crystal and refinement data for compounds **4**, **7**, and **8**

Compound	4	7	8
Empirical formula	C ₂₇ H ₁₃ NO ₁₃ Ru ₄	C ₁₉ H ₁₁ NO ₇ Ru ₂	C ₃₃ H ₁₅ NO ₁₁ Ru ₄
Molecular mass	963.66	567.43	1005.74
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pcab</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.727(2)	11.403(3)	10.031(2)
<i>b</i> [Å]	18.576(4)	16.531(4)	13.239(3)
<i>c</i> [Å]	15.721(3)	22.41(2)	13.523(3)
<i>α</i> [°]	90	90	78.85(3)
<i>β</i> [°]	99.39(3)	90	79.28(3)
<i>γ</i> [°]	90	90	68.95(3)
<i>V</i> [Å ³]	3090.7(11)	4225(5)	1631.0(6)
<i>Z</i>	4	8	2
<i>F</i> (000)	1848	2208	968
<i>D</i> _{calcd.} [g cm ⁻³]	2.071	1.784	2.048
<i>λ</i> (Mo- <i>K</i> _α) [Å]	0.71073	0.71073	0.71073
Crystal size [mm ³]	0.45 × 0.35 × 0.32	0.26 × 0.17 × 0.10	0.40 × 0.30 × 0.40
<i>T</i> [K]	293(2)	293(2)	293(2)
<i>μ</i> [mm ⁻¹]	1.983	1.468	1.879
<i>θ</i> max [°]	24.98	25.97	24.99
Min./max. <i>h</i> , <i>k</i> , <i>l</i>	–11/12, 0/22, –18/18	–14/0, 0/20, 0/27	–11/11, –15/15, –16/0
Measured reflns.	11225	4135	5859
Unique reflns.	5431	4135	5607
Reflns. with [<i>I</i> > 2σ(<i>I</i>)]	4694	1800	4478
Parameters	406	262	439
GoF on <i>F</i> ²	1.076	1.086	1.109
<i>R</i> ₁ [on <i>F</i> , <i>I</i> > 2σ(<i>I</i>)]	0.0353	0.0916	0.0306
<i>wR</i> ₂ (on <i>F</i> ² , all data)	0.0869	0.3462	0.0832
Min., max Δρ, [e·Å ⁻³]	–1.385, 1.388	–1.466, 2.148	–0.657, 0.768

X-ray Crystallographic Studies: Crystal data and refinement details are summarized in Table 3. Single crystals of compounds **4**, **7**, and **8** were analyzed on a Nonius CAD4 diffractometer, equipped with a graphite crystal monochromator, using the ω -2 θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. In all cases, Lorentz and polarization corrections were applied and data were reduced to F_o^2 values. A semiempirical absorption correction was applied based on ψ scans,^[27] with correction factors in the range 0.53 to 0.40 for **4**, 0.977 to 1.011 for **7**, and 0.987 to 0.995 for **8**. The structures were solved by Patterson interpretation using the program DIRDIF-96.^[28] Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL-97.^[29] All non-H atoms were refined anisotropically. Hydrogen atom positions were geometrically calculated and refined as riding on their parent atoms. Molecular plots were generated with the EUCLID program package.^[30]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-164215 (**4**), CCDC-164216 (**7**), and CCDC-164217 (**8**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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