Reactivity of a Triruthenium Ynenyl Cluster Complex with Diynes: Cluster-Mediated Combination of up to Three Substituted Butadiyne Molecules into a Carbon-Rich Hydrocarbyl Ligand

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The triruthenium ynenyl cluster complex [$Ru_3(\mu_3$-η^2-apyr)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$] (**2**; Hapyr = 2-aminopyrimidine) has been prepared in two steps from [$Ru_3(CO)_{12}$], 2-aminopyrimidine and 2,4-hexadiyne. Its reactivity with two conjugated diynes has been studied. With 2,4-hexadiyne, it affords [$Ru_3(\mu_3$-η^2-apyr){μ-η^5-MeC≡CC=CMeC(=CHMe)-C≡CMe}(μ-CO)$_2$(CO)$_5$] (**3**), which contains a diynedienyl ligand that arises from the coupling of 2,4-hexadiyne with the hex-2-yn-4-en-4-yl ligand of **2**, whereas the reaction of complex **2** with diphenylbutadiyne gives [$Ru_3(\mu_3$-η^2-apyr){μ_3-η^7-PhC≡CC=CPhCMe=CC(=CHMe)C(C≡CPh)=CPh}(μ-CO)-(CO)$_6$] (**4**). Complex **4** contains an unprecedented diynetetraentriyl ligand that arises from the coupling of two diphenylbutadiyne molecules with the hex-2-yn-4-en-4-yl ligand of **2**.

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Introduction

In previous studies, it was observed that 2-amidopyridine-bridged hydrido triruthenium carbonyl complexes[1] activate alkynes, rendering derivatives of the type [$Ru_3(\mu_3$-η^2-apy)(μ-η^2-alkenyl)(μ-CO)$_2$(CO)$_6$] (apy = 2-amidopyridine-type ligand).[2,3] These alkenyl derivatives have been recognized as catalytic precursors for the hydrogenation,[4,5] dimerization,[6] polymerisation[6] and hydroformylation[7] of selected alkynes.

The natural evolution of these investigations led us to study the reactivity of apy-bridged hydrido triruthenium complexes with diynes. In this field, we have already reported that the complex [$Ru_3(\mu$-H)(μ_3-η^2-ampy)(CO)$_9$] (Hampy = 2-amino-6-methylpyridine) reacts with diphenylbutadiyne and 1,6-diphenoxy-2,4-hexadiyne to give ynenyl complexes of the type [$Ru_3(\mu_3$-η^2-ampy)(μ-η^3-RCH=CC≡CR)(μ-CO)$_2$(CO)$_6$] (R = Ph, CH_2OPh). These ynenyl compounds are prone to react with alkynes and diynes to give interesting coupling products, including η^5-cyclopentadienyl and η^5-ruthenacyclopentadienyl derivatives.[8] However, the analogous ynenyl complex derived from [$Ru_3(\mu$-H)(μ_3-η^2-ampy)(CO)$_9$] and 2,4-hexadiyne could not be isolated and, therefore, its reactivity could not be studied.[9]

We report herein that the use of 2-aminopyrimidine (Hapyr) as a ligand precursor, instead of 2-amino-6-methylpyridine, leads to the isolation of a trinuclear ynenyl derivative of 2,4-hexadiyne, [$Ru_3(\mu_3$-η^2-apyr)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$], and allows the study of the reactivity of the latter complex with diynes. We also report that a product of one of these reactions contains an unprecedented hydrocarbyl ligand that arises from the coupling of three diyne molecules.

Results and Discussion

Synthesis of Compounds 1 and 2

The reaction of [$Ru_3(CO)_{12}$] with 2-aminopyrimidine in THF at reflux temperature leads to the trinuclear derivative [$Ru_3(\mu$-H)(μ_3-η^2-apyr)(CO)$_9$] (**1**) (Scheme 1). The compound was characterised by its mass spectrum, which shows the molecular ion, and by its IR and NMR spectra, which are similar to those of [$Ru_3(\mu$-H)(μ_3-η^2-ampy)(CO)$_9$].[10] Thus, the behaviour of 2-aminopyrimidine in its reaction with [$Ru_3(CO)_{12}$] is similar to that of 2-aminopyridines.

The thermal reaction (refluxing THF) of 2,4-hexadiyne with compound **1**, in a 1:1 mol ratio, leads to a mixture of compounds from which the major product, the ynenyl derivative [$Ru_3(\mu_3$-η^2-apyr)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$] (**2**) (Scheme 1), could be separated by TLC.

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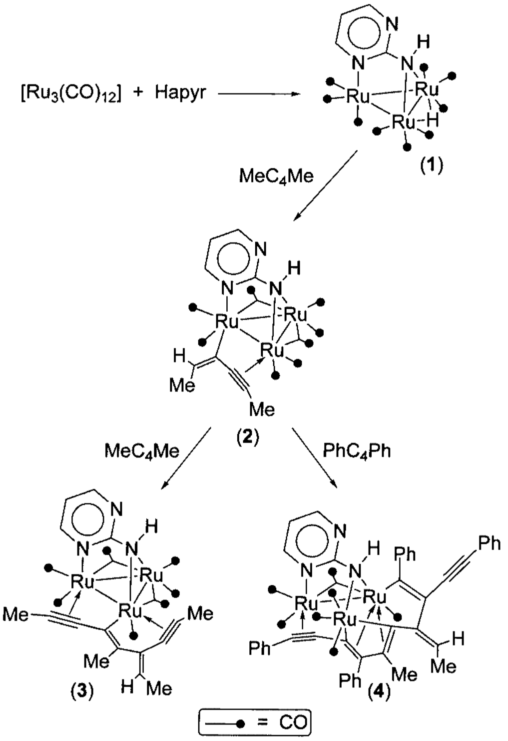

Scheme 1

The mass spectrum of **2** shows the corresponding molecular ion. Its IR spectrum indicates the presence of bridging CO ligands. The ^{1}H NMR spectrum also confirms the insertion of the original diyne into a Ru−hydride bond of **1** to give an ynenyl ligand. The multiplicity of the signal of this hydrogen atom in **2** (quadruplet, J = 6.5 Hz) indicates that it is adjacent to a methyl group. The structure depicted for this compound in Scheme 1, which shows a bridging three-electron donor hex-2-yn-4-en-4-yl ligand, is also supported by the similarity of its spectroscopic data with those of the compounds [Ru$_3$(μ$_3$-η^2-ampy)(μ-η^3-RCH=CC≡CR)(μ-CO)$_2$(CO)$_6$] (R = Ph, CH$_2$OPh), the structures of which have been determined by X-ray diffraction methods.[8]

We have recently reported that the isolation of the 2-amido-6-methylpyridine derivative [Ru$_3$(μ$_3$-η^2-ampy)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$] could not be achieved. Although this complex was spectroscopically detected in the reaction of [Ru$_3$(μ-H)(μ$_3$-η^2-ampy)(CO)$_9$] with 2,4-hexadiyne, mixtures of inseparable products were always obtained, regardless of the ratio of the reactants.[9] This prevented the study of its derivative chemistry. As desired, the slightly different polarity of analogous ampy and apyr derivatives allows the successful TLC separation of complex **2**.

Considering the asymmetry of each triple bond of hexa-2,4-diyne, the insertion of one of its triple bonds into a Ru−H bond of **1** could lead to two different products. As occurred with [Ru$_3$(μ-H)(μ$_3$-η^2-ampy)(CO)$_9$],[9] the reaction is selective in the sense that only the insertion product containing a hex-2-yn-4-en-4-yl ligand, (compound **2**) is formed. The alternative product would have a hex-2-yn-4-en-5-yl ligand. This selectivity has also been observed previously for the reaction of compound **1** with 1,6-diphenoxy-2,4-hexadiyne,[8] but not with diphenylbutadiyne.[9,11] A mechanistic proposal accounting for the formation of compounds similar to **2** from conjugated diynes and hydrido trinuclear clusters has been reported.[8]

Apart from the above-mentioned ynenyl compounds derived from [Ru$_3$(μ-H)(μ$_3$-η^2-ampy)(CO)$_9$],[8] only a few more ynenyl derivatives have heretofore been reported as products of reactions of carbonylruthenium clusters with diynes, i.e. the compounds [Ru$_2$(μ-N=CPh$_2$)(μ-η^2-CH$_2$=CCH$_2$C≡CSiMe$_3$)(CO)$_6$],[12] [Ru$_3$(μ$_3$-η^2-pyNMe)(μ-η^3-PhCH=CC≡CPh)(μ-CO)$_2$(CO)$_6$],[11] and [Ru$_4$(μ-η^2-dmpz)(μ$_4$-η^4-MeCH=CC≡CMe)(μ-CO)(CO)$_{10}$] (Hdmpz = 3,5-dimethylpyrazole).[13] The cluster complex [Ru$_3${μ-NS(O)MePh}(μ-η^3-PhCH=CC≡CPh)(CO)$_9$] also contains an ynenyl ligand, but in this case the ligand arises from an alkynyl−vinylidene coupling.[14]

Reactions of Compound 2 with Diynes

Treatment of compound **2** with 2,4-hexadiyne in THF at reflux temperature leads to [Ru$_3$(μ$_3$-η^2-apyr){μ-η^5-MeC≡CC=CMeC(=CHMe)C≡CMe}(μ-CO)$_2$(CO)$_5$] (**3**) in quantitative yield (Scheme 1). Its analytical and spectroscopic data, although indicating the presence of the apyr ligand, the existence of bridging and terminal CO ligands, and the incorporation of the new 2,4-hexadiyne molecule, did not reveal its molecular structure, which was determined by X-ray diffraction.

Figure 1 shows a view of compound **3**. A selection of bond lengths is given in Table 1. The new ligand, which can be described as a 5-methyl-6-(ethylidene)nona-2,7-diyn-4-en-4-yl ligand, behaves as a five-electron donor. It spans the longest edge of the metal triangle [Ru(1)−Ru(3): 2.8874(9) Å], and is attached to Ru(1) through a C≡C triple bond (two-electron π-type interaction) and to Ru(3) through the remaining C≡C triple bond (two-electron π-type interac-

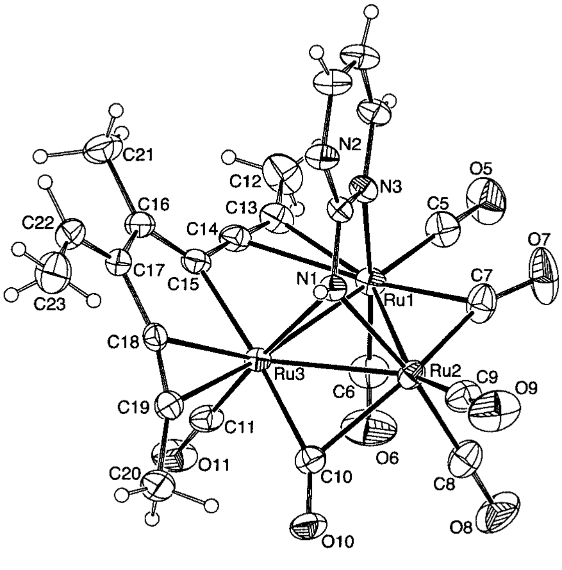

Figure 1. Molecular structure of compound **3**; thermal ellipsoids are drawn at a 40% probability level

tion) and the C(15) carbon atom (one-electron σ-type interaction). The remaining edges of the metal triangle are shorter [Ru(1)−Ru(2): 2.7846(9) Å, Ru(2)−Ru(3): 2.6662(8) Å], and each one is asymmetrically bridged by a CO ligand. The apyr ligand caps the Ru_3 triangle, and is attached to the Ru(2)−Ru(3) edge through the exocyclic N(1) atom and to the Ru(1) atom through the heterocyclic N(3) atom. The cluster shell is completed with five terminal CO ligands. Thus, the compound is a closed-shell 48-electron cluster. Overall, the structure resembles that of the related ampy derivative, which contains an analogous diynedienyl ligand.[9]

Table 1. Selected Interatomic Distances [Å] in Compound **3**

Ru(1)−Ru(2)	2.7846(9)	Ru(1)-Ru(3)	2.8874(9)
Ru(2)−Ru(3)	2.6662(8)	Ru(1)−N(3)	2.147(3)
Ru(2)−N(1)	2.156(3)	Ru(3)−N(1)	2.186(3)
Ru(1)−C(5)	1.903(4)	Ru(1)−C(6)	1.862(4)
Ru(1)−C(7)	2.249(4)	Ru(1)−C(13)	2.245(4)
Ru(1)−C(14)	2.434(4)	Ru(2)−C(7)	1.965(4)
Ru(2)−C(8)	1.863(4)	Ru(2)−C(9)	1.895(4)
Ru(2)−C(10)	2.235(4)	Ru(3)−C(10)	2.024(4)
Ru(3)−C(11)	1.839(3)	Ru(3)−C(15)	2.117(3)
Ru(3)−C(18)	2.268(3)	Ru(3)−C(19)	2.388(3)
C(5)−O(5)	1.134(5)	C(6)−O(6)	1.143(5)
C(7)−O(7)	1.157(5)	C(8)−O(8)	1.154(5)
C(9)−O(9)	1.122(5)	C(10)−O(10)	1.154(4)
C(11)−O(11)	1.148(5)	C(12)−C(13)	1.475(6)
C(13)−C(14)	1.242(5)	C(14)−C(15)	1.377(5)
C(15)−C(16)	1.345(5)	C(16)−C(17)	1.463(5)
C(16)−C(21)	1.497(5)	C(17)−C(18)	1.437(5)
C(17)−C(22)	1.342(5)	C(18)−C(19)	1.222(5)
C(19)−C(20)	1.470(5)	C(22)−C(23)	1.481(8)

The reaction of complex **2** with one equivalent of diphenylbutadiyne, in THF at reflux temperature, led only to intractable mixtures. However, the use of a 1:2 ratio of the reactants led to a mixture of compounds from which the trinuclear derivative $[Ru_3(\mu_3\text{-}\eta^2\text{-apyr})\{\mu_3\text{-}\eta^7\text{-PhC}{\equiv}\text{CC}{=}\text{CPhCMe}{=}\text{CC}({=}\text{CHMe})\text{C}(\text{C}{\equiv}\text{CPh}){=}\text{CPh}\}(\mu\text{-CO})(CO)_6]$ (**4**) could be separated by TLC. X-ray diffraction was necessary to determine its structure, since its analytical and spectroscopic data, although suggesting the incorporation of two diphenylbutadiyne molecules to complex **2**, did not allow a structural assignment.

Figure 2 shows a view of compound **4**. A selection of bond lengths is given in Table 2. While the Ru(1)−Ru(3) distance [2.8341(5) Å] corresponds to a metal−metal bond, the Ru(1)−Ru(2) and Ru(2)−Ru(3) distances [4.0288(5) Å and 3.0929(5) Å respectively] are too long to be assigned to Ru−Ru bonds. The new ligand spans the two long Ru−Ru edges and is attached to Ru(1) through a C≡C triple bond (two-electron π-type interaction). It is involved in a ruthenacyclopentadiene fragment with Ru(2), to which it is bonded through the carbon atoms C(18) and C(24) (two one-electron σ-type interactions). It also binds to Ru(3) through both double bonds of the ruthenacyclopentadiene fragment (two two-electron π-type interactions) and the C(12) carbon atom (one-electron σ-type interaction). This hydrocarbyl ligand, which can be systematically named as a 1,4,9-triphenyl-5-methyl-7-ethyliden-8-(phenylethynyl)nona-1-yn-3,5,8-trien-3,6,9-triyl ligand, behaves as a nine-electron donor. The apyr ligand is attached to the Ru(2) and Ru(3) atoms through the exocyclic N(1) atom and to Ru(1) through the heterocyclic N(3) atom. The Ru(1)−Ru(3) edge is asymmetrically bridged by a CO ligand. The complex shell is completed with six terminal CO ligands. Thus, the compound is a 52-electron species.

Although a few hydrocarbyl ligands resulting from the coupling of two diyne molecules at metal cluster cores have

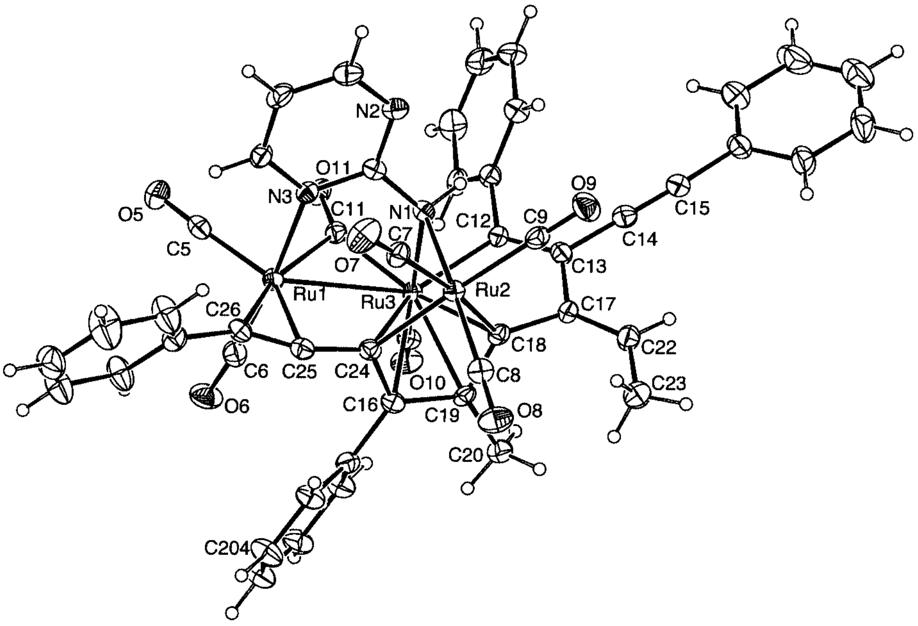

Figure 2. Molecular structure of compound **4**; thermal ellipsoids are drawn at a 40% probability level

Table 2. Selected interatomic distances [Å] in compound **4**

Ru(1)−Ru(2)	4.0288(5)	Ru(1)−Ru(3)	2.8341(5)
Ru(2)−Ru(3)	3.0929(5)	Ru(1)−N(3)	2.161(4)
Ru(2)−N(1)	2.170(4)	Ru(3)−N(1)	2.232(4)
Ru(1)−C(5)	1.875(6)	Ru(1)−C(6)	1.889(6)
Ru(1)−C(11)	2.226(5)	Ru(1)−C(25)	2.263(5)
Ru(1)−C(26)	2.253(5)	Ru(2)−C(7)	1.974(6)
Ru(2)−C(8)	1.892(6)	Ru(2)−C(9)	1.956(5)
Ru(2)−C(18)	2.133(5)	Ru(2)−C(24)	2.125(5)
Ru(3)−C(10)	1.853(5)	Ru(3)−C(11)	1.995(5)
Ru(3)−C(12)	2.106(4)	Ru(3)−C(16)	2.457(5)
Ru(3)−C(18)	2.227(5)	Ru(3)−C(19)	2.372(5)
Ru(3)−C(24)	2.547(5)	C(5)−O(5)	1.131(7)
C(6)−O(6)	1.139(7)	C(7)−O(7)	1.127(7)
C(8)−O(8)	1.129(7)	C(9)−O(9)	1.138(6)
C(10)−O(10)	1.138(6)	C(11)−O(11)	1.176(6)
C(12)−C(13)	1.356(7)	C(13)−C(14)	1.439(7)
C(13)−C(17)	1.483(7)	C(14)−C(15)	1.199(9)
C(16)−C(19)	1.438(7)	C(16)−C(24)	1.448(7)
C(17)−C(18)	1.489(6)	C(17)−C(22)	1.326(7)
C(18)−C(19)	1.404(7)	C(19)−C(20)	1.517(7)
C(22)−C(23)	1.489(8)	C(24)−C(25)	1.399(7)
C(25)−C(26)	1.258(7)		

been reported,[8,9,15] complex **4** is the first example of a hydrocarbyl ligand resulting from the coupling of three diyne molecules.

The compounds [Ru$_3$(μ_3-η^2-ampy)(μ-η^3-RCH=CC≡CR)(μ-CO)$_2$(CO)$_6$] (R = Ph, CH$_2$OPh), structurally analogous to **2**, are the only ynenyl derivatives whose reactivity with alkynes and diynes has been studied. They systematically give trinuclear products containing η^5-ruthenacyclopentadienyl fragments which arise from the coupling of the coordinated ynenyl ligands with a C≡C triple bond of the new reagent (alkyne or diyne).[8] It is noteworthy that the reactions of **2** with 2,4-hexadiyne and diphenylbutadiyne do not give related products, but instead give compounds **3** and **4**. At this stage, it seems that this different reactivity is not due to steric reasons, but it is not yet clear whether it may be caused by the different substituents of the ynenyl ligands, the different capping *N*-donor ligands or a combination of both.

We also studied the reactions of **2** with some monoalkynes, but complex mixtures, from which we could not isolate and characterise any product, were formed in all cases.

Experimental Section

General Remarks: Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or calcium hydride (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk and vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). All reagents were purchased as analytically pure samples. IR: Perkin−Elmer Paragon 1000 FT spectrometer. NMR: Bruker AC-200, AC-300 or DPX-300 spectrometers, room temperature, SiMe$_4$ as internal standard. Microanalyses were obtained from the University of Oviedo's Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela's Mass Spectroscopic Service; data given refer to the most abundant molecular ion isotopomer.

[Ru$_3$(μ-H)(μ_3-η^2-apyr)(CO)$_9$] (1): A mixture of [Ru$_3$(CO)$_{12}$] (300 mg, 0.468 mmol) and 2-aminopyrimidine (71 mg, 0.749 mmol) in THF (50 mL) was stirred at reflux temperature for 90 min. After concentration under reduced pressure to approximately 2 mL, the solution was applied to the top of a chromatography column (10 × 2 cm) packed with activity I neutral alumina in hexane. Hexane/dichloromethane (1:1) eluted two bands. The first, yellow, contained some [Ru$_4$H$_4$(CO)$_{12}$] product (IR identification). The second band, yellow-orange, afforded compound **2** after solvent removal (150 mg, 48%). C$_{13}$H$_5$N$_3$O$_9$Ru$_3$ (650.44): calcd. C 24.01, H 0.77, N 6.46; found C 23.85, H 0.76, N 6.38. FAB-MS: *m/z* = 652 [M$^+$]. IR (CH$_2$Cl$_2$): ν(CO) = 2084 (m), 2054 (s), 2030 (vs), 1998 (s), 1964 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.42 (dd, *J* = 5.1, 2.4 Hz, 1 H), 8.20 (dd, *J* = 5.1, 2.4 Hz, 1 H), 6.76 (t, *J* = 5.1 Hz, 1 H), 4.55 (br. s, 1 H), −11.31 (s, 1 H) ppm.

[Ru$_3$(μ_3-η^2-apyr)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$] (2): A solution of complex **1** (150 mg, 0.230 mmol) and 2,4-hexadiyne (20 mg, 0.256 mmol) in THF (20 mL) was stirred at reflux temperature for 60 min. The colour changed from yellow to red. After concentration under reduced pressure to approximately 2 mL the solution was applied to preparative silica gel TLC plates. Repeated elution with hexane/dichloromethane (3:1) allowed the separation of two bands. The second band, orange, contained a small amount of compound **3** (9 mg, 5%). The first band, orange, gave compound **2** (51 mg, 30%) upon extraction with dichloromethane. C$_{18}$H$_{11}$N$_3$O$_8$Ru$_3$ (700.54): calcd. C 30.86, H 1.58, N 6.00; found C 30.91, H 1.63, N 5.84. FAB-MS: *m/z* = 702 [M$^+$]. IR (CH$_2$Cl$_2$): ν(CO) = 2064 (s), 2030 (vs), 2022 (vs), 1994 (s), 1969 (w), 1873 (w), 1820 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.00 (m, 2 H), 6.50 (t, *J* = 5.4 Hz, 1 H), 6.43 (q, *J* = 6.5 Hz, 1 H), 4.05 (br. s, 1 H), 2.94 (s, 3 H), 2.45 (d, *J* = 6.5 Hz, 3 H) ppm.

[Ru$_3$(μ_3-η^2-apyr){μ-η^5-MeC≡CC=CMeC(=CHMe)C≡CMe}(μ-CO)$_2$(CO)$_5$] (3): A solution of complex **2** (15 mg, 0.021 mmol) and 2,4-hexadiyne (2 mg, 0.025 mmol) in THF (10 mL) was stirred at reflux temperature for 60 min. The original yellow colour of the solution darkened slightly. The solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give compound **3** (14 mg, 89%) as a yellow-orange solid. C$_{23}$H$_{17}$N$_3$O$_7$Ru$_3$ (750.65): calcd. C 36.80, H 2.28, N 5.60; found C 36.76, H 2.12, N 5.59. FAB-MS: *m/z* = 752 [M$^+$]. IR (CH$_2$Cl$_2$): ν(CO) = 2064 (vs), 2012 (s), 1980 (s), 1955 (w), 1876 (w), 1815 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.92 (dd, *J* = 4.3, 2.1 Hz, 1 H), 7.73 (dd, *J* = 5.5, 2.1 Hz, 1 H), 6.36 (dd, *J* = 5.5, 4.3 Hz, 1 H), 6.09 (q, *J* = 7.6 Hz, 1 H), 4.22 (br. s, 1 H), 3.12 (s, 3 H), 2.84 (s, 3 H), 2.15 (s, 3 H), 2.11 (d, *J* = 7.6 Hz, 3 H) ppm.

[Ru$_3$(μ_3-η^2-apyr){μ_3-η^7-PhC≡CC=CPhCMe=CC(=CHMe)-C(C≡CPh)=CPh}(μ-CO)(CO)$_6$] (4): A solution of complex **2** (45 mg, 0.064 mmol) and diphenylbutadiyne (29 mg, 0.143 mmol) in THF (30 mL) was stirred at reflux temperature for 150 min. The colour changed from yellow to brown. After concentration under reduced pressure to approximately 2 mL, the solution was applied to preparative silica gel TLC plates. Multiple elution with hexane/dichloromethane (2:1) allowed the isolation of compound **4** (10 mg, 15%) from the major band, orange, upon extraction with dichloromethane. C$_{49}$H$_{31}$N$_3$O$_7$Ru$_3$ (1077.05): calcd. C 54.64, H 2.90, N 3.90; found C 54.34, H 2.80, N 3.77. FAB-MS: *m/z* = 1023 [M$^+$ − 2CO]. IR (CH$_2$Cl$_2$): ν(CO) = 2092 (s), 2029 (vs), 2013 (m), 1963 (m), 1809 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.05 (d, *J* = 7.4 Hz, 1 H), 7.95 (dd, *J* = 4.4, 2.5 Hz, 1 H), 7.82 (dd, *J* = 5.4, 2.5 Hz, 1

Table 3. Relevant Crystal and Refinement Data for Compounds **3** and **4**

Compound	**3**	**4**
Formula	$C_{23}H_{17}N_3O_7Ru_3$	$C_{49}H_{31}N_3O_7Ru_3$
Molecular weight	750.61	1076.98
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	11.019(3)	9.7568(7)
b [Å]	13.125(5)	14.7937(6)
c [Å]	18.308(5)	16.0347(7)
α [°]	90	106.385(2)
β [°]	104.67(4)	101.442(4)
γ [°]	90	101.120(4)
V [Å^3]	2561.5(14)	2098.7(2)
Z	4	2
F(000)	1456	1068
$D_{calcd.}$ [g cm^{-3}]	1.946	1.704
λ (radiation) [Å]	0.71073 (Mo-K_α)	1.54184 (Cu-K_α)
Crystal size [mm^3]	0.45 × 0.36 × 0.23	0.15 × 0.10 × 0.05
T [K]	293(2)	200(2)
μ [mm^{-1}]	1.793	9.108
Min./max. h, k, l	0/13, 0/16, −22/21	−11/11, −17/17, −18/19
Measured reflns	5287	11222
Unique reflns	5020	7858
Reflns with [$I > 2\sigma(I)$]	4385	6826
Parameters	393	563
GoF on F^2	1.147	1.158
R_1 [on F, $I > 2\sigma(I)$]	0.0253	0.0394
wR_2 (on F^2, all data)	0.0716	0.1276
Min., max. Δρ, [e Å^{-3}]	−0.651, 0.528	−0.862, 0.983

H), 7.6−7.1 (m, 19 H), 6.48 (q, J = 7.4 Hz, 1 H), 6.28 (dd, J = 5.4, 4.4 Hz, 1 H), 4.01 (br. s, 1 H), 2.29 (s, 3 H), 2.18 (d, J = 7.4 Hz, 3 H) ppm.

X-ray Crystallographic Studies: Selected crystal and refinement data are given in Table 3. Crystals of compound **3** were obtained by slow diffusion of pentane into a solution of the complex in dichloromethane. Crystals of **4** were obtained by slow diffusion of pentane vapor into a solution of the complex in 1,2-dichloroethane. Diffraction data were obtained on Nonius CAD4 (**3**) and KappaCCD (**4**) diffractometers. Absorption corrections were applied using DIFABS[16] (for **3**) or XABS2[17] (for **4**). Maximum and minimum transmission factors 0.631 and 0.480 (for **3**) and 0.131 and 0.062 (for **4**). The structures were solved by Patterson interpretation using DIRDIF-96.[18] Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL-97.[19] All non H-atoms were refined anisotropically. All the hydrogen atoms of **3** were found and refined. For **4**, the NH hydrogen atom was located and its position was refined, while the remaining hydrogen atom positions were calculated and refined riding in their parent atoms. The molecular plots were made with the EUCLID program package.[20] The WINGX program system[21] was used throughout the structure determinations.

CCDC-185400 (**3**) and CCDC-185401 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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