FULL PAPER

Formation of Cyclopentadienyl and Ruthenacyclopentadienyl Derivatives through Ynenyl–Diyne and Ynenyl–Alkyne Couplings onto a Triruthenium Cluster Core**

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Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

Abstract: The compound [Ru$_3$(μ-H)(μ_3-η^2-ampy)(CO)$_9$] (**1**; Hampy = 2-amino-6-methylpyridine) reacts with diynes RC$_4$R in THF at reflux temperature to give the ynenyl derivatives [Ru$_3$(μ_3-η^2-ampy)(μ-η^3-RC≡CC=CHR)(μ-CO)$_2$(CO)$_6$] (**2**: R = CH$_2$OPh; **3**: R = Ph). These products contain a 1,4-disubstituted butynen-3-yl ligand attached to two ruthenium atoms. The compound [Ru$_3$(μ-η^2-ampy){μ_3-η^6-PhCC$_5$(C≡CPh)-HPh$_2$}(CO)$_7$] (**4**), which contains an η^5-cyclopentadienyl ring and a bridging carbene fragment, has also been obtained from the reaction of **1** with diphenylbutadiyne. This compound arises from a remarkable [3+2] cyclo-addition reaction of a preformed 1,4-diphenylbutynen-4-yl ligand with a triple bond of a second diphenylbutadiyne molecule. The reactivity of the ynenyl derivatives **2** and **3** with diynes and alkynes has been studied. In all cases, compounds of the general formula [Ru$_3$(μ-η^2-ampy){μ_3-η^5-C(=CHR)-C=CRCR^1=CR^2}(CO)$_7$] (**5–17**) have been obtained. They all contain a ruthenacyclopentadienyl fragment formed by coupling of the coordinated ynenyl ligand of **2** (R = CH$_2$OPh) or **3** (R = Ph) with a triple bond of the new reagent (the CR^1=CR^2 fragment results from the incoming diyne or alkyne reagent). While most of the products derived from **2** have the alkenyl C=CHR fragment with a *Z* configuration (R *cis* to Ru), all the compounds obtained from **3** have this fragment with an *E* configuration. Except **2** and **3**, all the cluster complexes described in this article have a five-electron donor ampy ligand attached to only two metal atoms, a coordination mode unprecedented in cluster chemistry.

Keywords: alkynes · cluster compounds · cycloaddition · diynes · ruthenium

Introduction

The reactivity of diynes toward molecular polymetallic ensembles is currently attracting attention.[1–8] This research activity has been motivated by a growing interest in polyunsaturated molecules and by the fact that diynes are expected to lead to a richer derivative chemistry than monoalkynes.

Extensive studies in our groups have shown that amidopyridine-bridged hydridotriruthenium complexes[9–12] are ideal candidates for the activation of alkynes under the form of alkenyl derivatives of the type [Ru$_3$(μ_3-η^2-apy)(μ-η^2-alkenyl)(μ-CO)$_2$(CO)$_6$] (apy = 2-amidopyridine-type ligand).[12–14] Indeed, the face-capping 2-amidopyridine ligand helps maintain the cluster integrity while still providing low activation energy reaction pathways.[15] To date, over a hundred carbonyl triruthenium clusters containing μ_3-2-amidopyridine ligands have already been reported,[9–20] including some catalyst precursors for alkyne hydrogenation,[12–14, 17, 18] dimerization,[19] polymerization,[19] and hydroformylation[20] reactions.

Unpublished results on the present collaborative project had revealed that the reactions of this type of cluster complexes with a butadiyne can lead to *two non-interconver-*

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tible insertion products (Scheme 1), namely a butyn-3-en-3-yl species (**A**) and a butyn-3-en-4-yl species (**B**).[4]
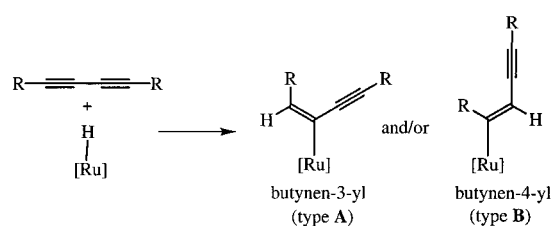
Scheme 1. The two possible isomers formed on reaction of a symmetric butadiyne with a hydridoruthenium complex.

Interestingly, only a limited number of ynenyl derivatives have so far been reported as products of reactions of carbonyl metal clusters with diynes. The ruthenium derivatives $[Ru_2(\mu\text{-}N\text{=}CPh_2)(\mu\text{-}\eta^2\text{-}CH_2\text{=}CCH_2C\text{≡}CSiMe_3)(CO)_6]$[5] and $[Ru_4(\mu\text{-}\eta^2\text{-}Me_2pz)(\mu_4\text{-}\eta^4\text{-}MeCH\text{=}CC\text{≡}CMe)(\mu\text{-}CO)(CO)_{10}]$ ($Me_2pz = 3,5$-dimethylpyrazolate)[6] arise from the insertion of diynes into a metal–hydride bond of trinuclear cluster precursors. The osmium derivatives $[Os_3(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}(E)\text{-}FcCH\text{=}CC\text{≡}CFc\}(CO)_9]$ (Fc = ferrocenyl), $[Os_3(\mu\text{-}OH)\{\mu_3\text{-}\eta^3\text{-}(Z)\text{-}FcCH\text{=}CC\text{≡}CFc\}(CO)_9]$, and $[Os_3(\mu\text{-}OH)\{\mu_3\text{-}\eta^3\text{-}(E)\text{-}FcCH\text{=}CC\text{≡}CFc\}(CO)_9]$ were recently obtained in the reaction of $[Os_3(\mu_3\text{-}\eta^2\text{-}FcC\text{≡}CC\text{≡}CFc)(CO)_{10}]$[1a] with water.[1b] Finally, an additional cluster complex bearing an ynenyl ligand attached to three metal atoms, namely $[Ru_3\{\mu\text{-}NS(O)\text{-}MePh\}(\mu_3\text{-}\eta^3\text{-}PhCH\text{=}CC\text{≡}CPh)(CO)_9]$, was obtained through a metal-mediated acetylide–vinylidene coupling.[21]

All the above-mentioned data prompted us to study, in a collaborative project between our research groups, the reactivity of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}ampy)(CO)_9]$ (**1**; Hampy = 2-amino-6-methylpyridine)[11] with diynes. We used the ampy ligand because its methyl group facilitates the monitoring of the reactions by ^1H NMR spectroscopy, making it easier to see how many products are in the reaction mixtures.

We now report that compound **1** is prone to incorporate more than one molecule of diyne. In addition to one of the expected ynenyl species effectively obtained as the primary product of diyne insertion, we have isolated an *ynenyl-diyne coupling product resulting from an unprecedented cluster-mediated [3+2] cycloaddition process*. As shown below, attempts to shed light on the mechanism of this odd coupling reaction have led to the isolation of a growing family of *novel metallacyclic derivatives*, which also arise from ynenyl-diyne or ynenyl-alkyne coupling processes. The results reported herein reveal that the nature of the primary insertion product (Scheme 1) determines the nature of the coupled product obtained with an incoming diyne or alkyne. One development of the present work is the hint that such coupling reactions may be facilitated by subtle changes in the coordination mode of the ancillary 2-amidopyridine ligand relative to the cluster core.

Results and Discussion

Reactions of complex 1 with diynes: The reaction of **1** with 1,6-diphenoxy-2,4-hexadiyne in THF at reflux temperature

gave the $\mu\text{-}\eta^3$-ynenyl derivative $[Ru_3(\mu_3\text{-}\eta^2\text{-}ampy)(\mu\text{-}\eta^3\text{-}PhOCH_2C\text{≡}CC\text{=}CHCH_2OPh)(\mu\text{-}CO)_2(CO)_6]$ (**2**) in 40% yield. A similar reaction using diphenylbutadiyne allowed the isolation of two products, namely, the $\mu\text{-}\eta^3$-ynenyl derivative $[Ru_3(\mu_3\text{-}\eta^2\text{-}ampy)(\mu\text{-}\eta^3\text{-}PhC\text{≡}CC\text{=}CHPh)(\mu\text{-}CO)_2(CO)_6]$ (**3**, 24% yield) and the cyclopentadienyl derivative $[Ru_3(\mu\text{-}\eta^2\text{-}ampy)\{\mu_3\text{-}\eta^6\text{-}PhCC_5(C\text{≡}CPh)HPh_2\}(CO)_7]$ (**4**, 9% yield) (Scheme 2). A slight excess of diyne (1.5–1.7 equivalents) proved necessary for the total consumption of the starting complex. The reactions were followed by IR spectroscopy and were worked up when the IR absorptions of compound **1** were no longer observed. Longer reaction times or the use or a larger amount of diyne did not increase the yield, but did increase the amount of intractable decomposition materials.
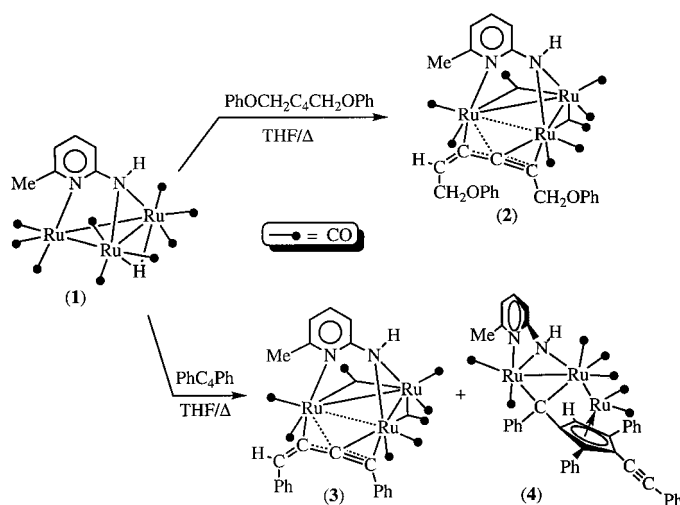
Scheme 2. Synthesis of compounds **2**–**4**.

Characterization of compounds 2 and 3: The trinuclear nature of **2** and **3** (Scheme 2) was suggested by their microanalyses and mass spectra. Their IR spectra indicated that both contain bridging CO ligands. Their ^1H NMR spectra confirmed the absence of hydride ligands and the transfer of a hydrogen atom to the original diyne. For compound **2**, the multiplicity of this signal (doublet of doublets, $J = 8.1$ and 7.1 Hz) together with selective decoupling experiments indicated that this hydrogen is located on a carbon atom adjacent to a methylene group. This was consistent with the occurrence of a migratory insertion of the corresponding diyne into the Ru–H bond to give an ynenyl ligand. In order to gain more insight into the structural arrangement of the ligands, both compounds were studied by X-ray diffraction methods.

Figure 1 shows the molecular structure of compound **2**. Selected interatomic distances are listed in Table 1. The structure consists of an isosceles triangular arrangement of ruthenium atoms, with one long, Ru1–Ru3, and two short edges, Ru1–Ru2 and Ru2–Ru3. The ampy ligand is attached to the three metal atoms in the same way as previously found for 2-amidopyridine ligands in many other trinuclear ruthenium clusters.[9–20] A butyn-3-en-3-yl ligand is attached to the metal atoms of the longest Ru–Ru edge through three carbon atoms, C15, C16, and C17. The coordination shell of the
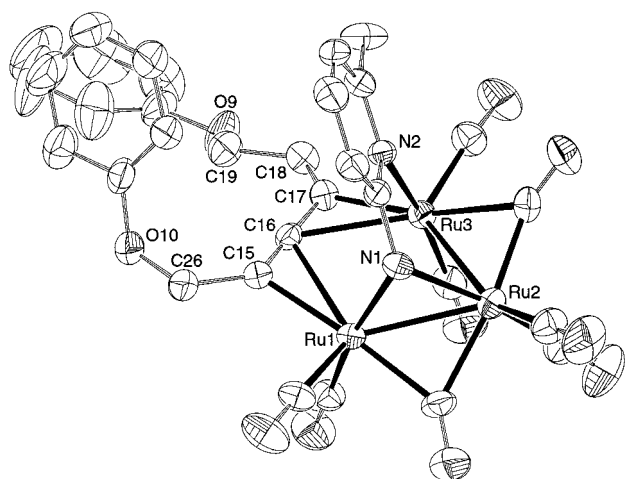
Figure 1. ORTEP representation of the molecular structure of compound **2**.

Table 1. Selected interatomic distances [Å] in compounds **2** and **3**.

	2	**3**
Ru1−Ru2	2.693(2)	2.675(1)
Ru1−Ru3	2.918(2)	2.924(2)
Ru2−Ru3	2.747(1)	2.752(2)
Ru1−N1	2.144(5)	2.140(6)
Ru1−C15	2.131(7)	2.127(7)
Ru1−C16	2.572(6)	2.572(7)
Ru2−N1	2.122(5)	2.141(6)
Ru3−N2	2.210(5)	2.203(6)
Ru3−C16	2.490(6)	2.456(7)
Ru3−C17	2.075(6)	2.086(7)
C15−C16	1.260(9)	1.283(9)
C15−C26	1.486(9)	–
C15−C27	–	1.479(9)
C16−C17	1.363(8)	1.333(9)
C17−C18	1.339(9)	1.33(1)
C18−C19	1.49(1)	–
C18−C20	–	1.45(1)

cluster is completed with eight carbonyl ligands, two of them spanning the two short Ru−Ru edges.

Regarding the ynenyl ligand, the C17−C18 bond length, 1.339 Å, and the angle C17-C18-C19, 122.2°, indicate the presence of a double bond between C17 and C18. The arrangement of the C15, C16, and C17 atoms is nearly linear, 178.7°. Although the C15−C16 bond length, 1.260 Å, is slightly longer than that found in coordinated η^2-alkynes (1.20 Å),[22] the C16−C17 bond length, 1.363 Å, is about 0.1 Å shorter than that expected for single C−C bonds. In addition, the C15−Ru1 bond length, 2.131 Å, is approximately 0.25 Å shorter than expected for coordinated η^2-alkynes,[22] and there is a clear interaction between C16 and Ru3, 2.490 Å.

These structural data indicate that compound **2** can be considered as a resonance hybrid of two cannonical forms, one with a three-electron donor 1,4-disubstituted butynen-3-yl ligand and the other with a five-electron donor 1,4-disubstituted butatrienyl ligand (Scheme 3), with the former contributing more than the latter. This proposal is also supported by the fact that the Ru1−Ru3 distance, 2.918 Å, is longer than expected for normal Ru−Ru bonds, that are in the range 2.6–2.8 Å, but short enough to be considered a metal−metal
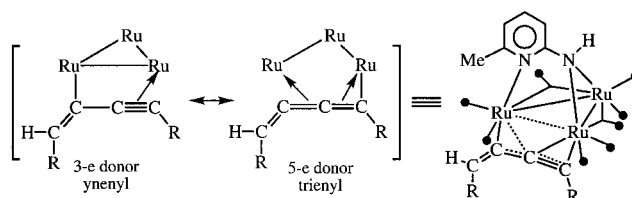
Scheme 3. Canonical forms contributing to compounds **2** and **3**.

interaction. As the electron count for each cannonical form is 48 and 50, respectively, corresponding to the existence of three and two metal−metal bonds,[23] respectively, the resonance hybrid should present an intermediate bonding situation, as observed in compound **2**.

Figure 2 shows the molecular structure of compound **3**. Selected interatomic distances are listed in Table 1. For quick comparisons, a common atomic numbering scheme was used for the structures of compounds **2** and **3**. The structure of **3** is entirely analogous to that of complex **2**, except for the R groups attached to the butynenyl fragment.
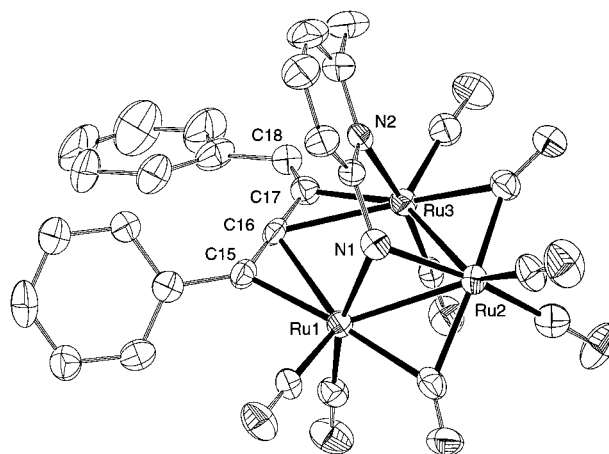

Figure 2. ORTEP representation of the molecular structure of compound **3**.

While a few mononuclear complexes containing butynenyl ligands have been reported (they all made by coupling of monoalkyne fragments),[24] the number of known polymetallic complexes containing these ligands is reduced to one binuclear complex (also made by coupling of monoalkyne fragments)[22] and to those mentioned in the introduction of this article. To the best of our knowledge, only one complex containing a butatrienyl ligand has been published, namely [Ru$_3${μ_3-NS(O)MePh}(μ_3-η^3-PhCH=C=C=CPh)(μ-CO)(CO)$_7$]. In this complex, the butatrienyl ligand also arises from the coupling of two monoalkyne fragments.[21]

Early in our investigation, it appeared that both **2** and **3** resulted from one of the two possible insertion products mentioned in the introduction (Scheme 1, type **A**), in sharp contrast with what had been observed in the reaction of diphenylbutadiyne with a slightly different precursor, [Ru$_3$(μ-H)(μ_3-η^2-pyNMe)(CO)$_9$], which led to the two isomers.[4] However, as shown below, indirect evidence for the existence

(in one case) of the "missing" isomer (type **B**) was subsequently obtained.

Structure of compound 4: Both the microanalysis and the mass spectrum of compound **4** suggested a trinuclear structure, but no relevant structural features could be obtained from its IR and NMR spectra. Its structure was determined by X-ray diffraction methods (Figure 3). A selection of interatomic distances is given in Table 2.
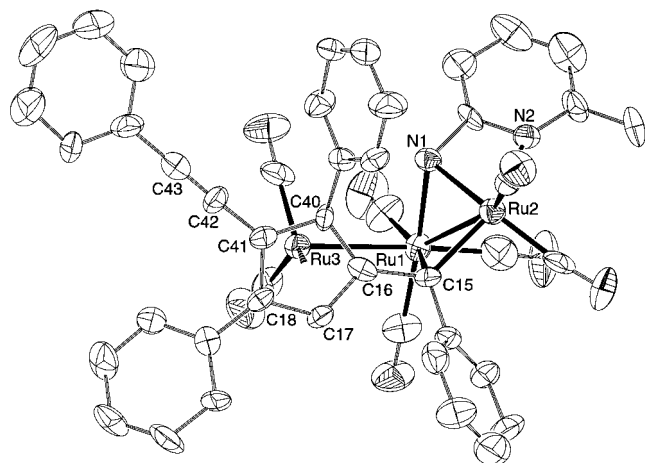

Figure 3. ORTEP representation of the molecular structure of compound **4**.

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

Ru1−Ru2	2.693(4)	Ru3−C40	2.24(1)
Ru1−Ru3	2.797(4)	Ru3−C41	2.25(1)
Ru2−Ru3	4.546(2)	C15−C16	1.51(2)
Ru1−N1	2.17(1)	C16−C17	1.42(1)
Ru1−C15	2.27(1)	C16−C40	1.46(1)
Ru2−N1	2.104(9)	C17−C18	1.41(1)
Ru2−N2	2.21(1)	C18−C41	1.43(1)
Ru2−C15	2.04(1)	C40−C41	1.44(2)
Ru3−C16	2.31(1)	C41−C42	1.42(2)
Ru3−C17	2.23(1)	C42−C43	1.19(2)
Ru3−C18	2.28(1)	C43−C45	1.45(2)

The compound is a trinuclear cluster with only two Ru–Ru bonds, since the metal atoms of its longest edge, Ru2–Ru3 are very far apart, 4.546 Å. The ampy ligand is only attached to the metal–metal bonded ruthenium atoms Ru1 and Ru2, with its amidic nitrogen atom N1 spanning both metal atoms and its pyridinic nitrogen N2 bonded to Ru2. This results in a very small N1-Ru2-N2 bite angle, 62.6°. The hydrocarbyl ligand can be described as a tetrasubstituted cyclopentadienyl ring attached in an η^5-manner to Ru3, with Ru3–C(Cp) distances in the range 2.23–2.31 Å, with one substituent, a CPh fragment which acts as a carbene ligand, asymmetrically spanning the other two ruthenium atoms through the carbon atom C15, Ru1–C15 2.27 Å, Ru2–C15 2.04 Å. The remaining substituents of the cyclopentadienyl ring are two phenyl groups and one phenylethynyl group. The coordination shell of the cluster is completed with seven terminal carbonyl ligands.

As far as we know, complex **4** is the first example of a trinuclear cluster in which a 2-amidopyridine ligand acts as a five-electron donor attached to only two metal atoms. In trinuclear rhenium clusters,[25] these ligands have hitherto behaved as μ_3-η^2 five-electron donor ligands. In the case of triruthenium[9–20] and triosmium clusters,[26] the μ_3-η^2 five-electron-donor coordination mode predominates (there are hundreds of examples) over the μ-η^2 three-electron-donor coordination mode, for which only two examples, one for ruthenium[9] and one for osmium,[26] have been reported.

Insights into the formation of compounds 2–4: The coordination of the diyne to complex **1** should be one of the first steps in the formation of compounds **2–4**. This may be accompanied by the release of a CO ligand. As mentioned above, the primary diyne complex would have the possibility to undergo a migratory insertion into a Ru–H bond to give either a butyn-3-en-3-yl ligand (intermediate **A** in Scheme 4) or a butyn-3-en-4-yl ligand (intermediate **B** in Scheme 5). A simple rearrangement in the coordination of the ynenyl ligand of **A** through σ–π interchange in the coordination of the C≡C fragment to both metal atoms, followed by coordination of the triple bond would lead to compounds **2** and **3** (Scheme 4).

The cyclopentadienyl ligand of compound **4** appears as the result of a remarkable [3+2] cycloaddition of a C≡C fragment of a butadiyne molecule with a preformed butyn-3-en-4-yl ligand. Thermal[27] and metal mediated[28] [3+2]-cycloaddition processes, although common when the reagents contain heteroatoms (1,3-dipolar cycloadditions give five-membered heterocycles as products), are unusual for the synthesis of C_5 rings (substituted cyclopentanes and cyclopentenes), and
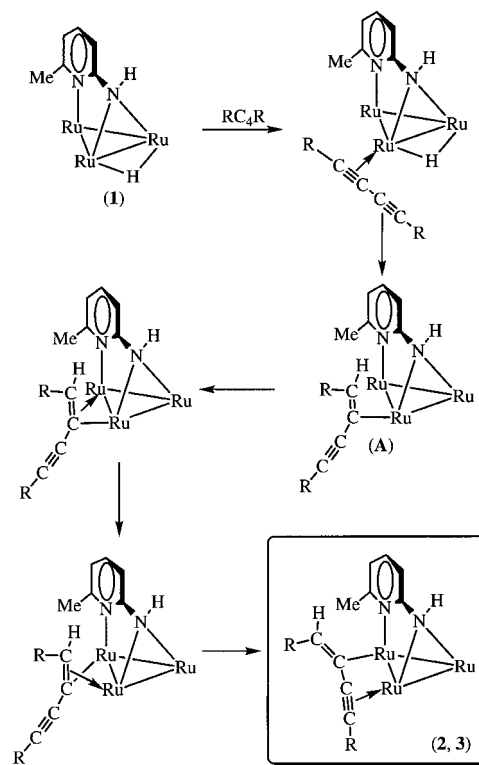
Scheme 4. Reaction pathway that leads to compounds **2** and **3** (carbonyl groups are omitted for clarity).
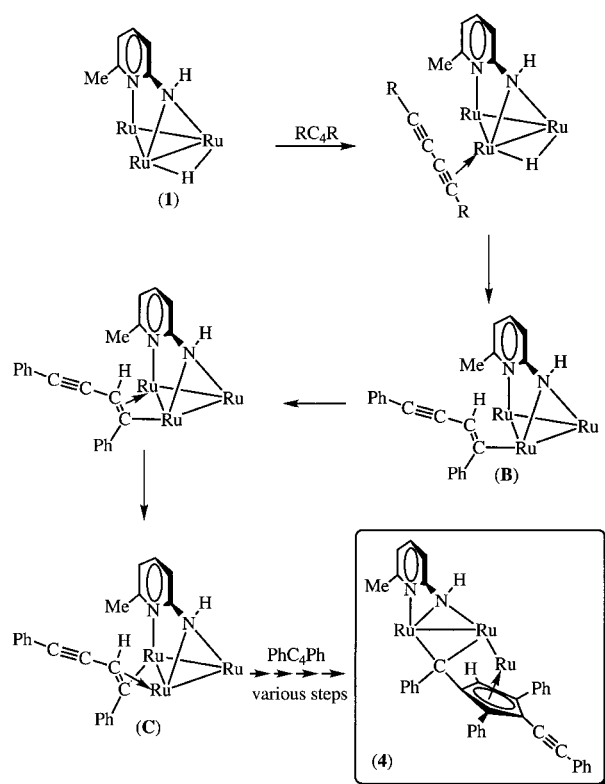
Scheme 5. Reaction pathway that leads to compound **4** (carbonyl groups are omitted for clarity).

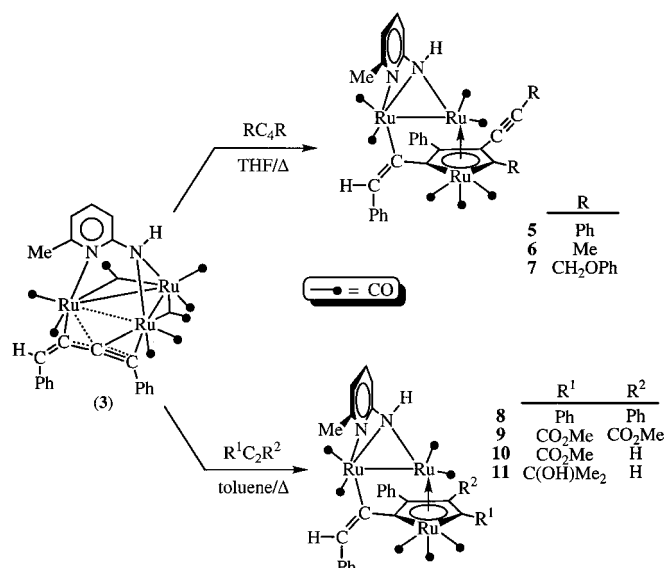Scheme 6. Synthesis of compounds **5 – 11**.

heretofore unknown for the preparation of cyclopentadiene and cyclopentadienyl rings.

The position of the hydrogen atom in the cyclopentadienyl ring of **4** indicates that the ynenyl intermediate should have the hydrogen atom on C^3 (intermediate **B** in Scheme 5). A subsequent rearrangement of this butyn-3-en-4-yl ligand on the cluster and the addition of a new molecule of diyne would lead, in several steps, to compound **4** (Scheme 5). Clearly the existence of **4** provides an indirect evidence for the existence of the elusive, unobserved, type-**B** butyn-3-en-4-yl isomer. The latter is probably too reactive to be intercepted and undergoes fast reaction with an incoming diyne to produce **4**.

All attempts (using different solvents, and varying temperature and/or reactant ratios) to isolate a cyclopentadienyl complex analogous to **4** but derived from **1** and 2,6-diphenoxy-2,4-hexadiyne were unsuccessful, thereby suggesting that this diyne is selectively inserted under the form of a butyn-3-en-3-yl intermediate (type **A**).

Reactions of complexes 2 and 3 with diynes and alkynes: With the above observations in mind, it was of interest to examine whether the butyn-3-en-3-yl complex **3** was also susceptible to undergo further reaction with an incoming diyne.

Effectively, compound **3** was found to react with excess (1.5 – 3.0-fold) of disubstituted butadiynes in THF at reflux temperature to give the ruthenacyclopentadienyl derivatives $[Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^5\text{-}(E)\text{-}C(=CHPh)C=CPhC(C\equiv CR)=CR\}(CO)_7]$ (**5**: R = Ph; **6**: R = Me; **7**: R = CH$_2$OPh) in 20 – 32 % yield (Scheme 6). The excess of diyne was necessary in order to consume all the starting material **3** in a reasonable time

(1.5 – 3.0 h), avoiding extensive decomposition. The reactions were followed by IR spectroscopy and were worked up when the IR absorptions of compound **3** were no longer observed. Higher temperatures, longer reaction times, or the use of a larger amount of diyne did not increase the product yields, but did increase the amount of intractable decomposition materials, due to the limited thermal stability of the products.

The notations *E* or *Z* in the formulas of the ruthenacyclopentadienyl derivatives described in this article refer to *trans* or *cis* arrangements of the ruthenium atom and the R group attached to the alkenyl fragment of these complexes, respectively.

Since the structure of products **5 – 7** revealed that one of the C≡C bonds of the diyne reagents was not involved in the cyclization (vide infra), we wondered whether closely related products could be prepared upon reaction of **3** with monoalkynes. This effectively proved to be the case. Typically, the reaction of complex **3** with alkynes produced the ruthenacyclopentadienyl derivatives $[Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^5\text{-}(E)\text{-}C(=CHPh)C=CPhCR^2=CR^1\}(CO)_7]$ (**8**: R^1 = R^2 = Ph; **9**: R^1 = R^2 = CO$_2$Me; **10**: R^1 = CO$_2$Me, R^2 = H; **11**: R^1 = C(OH)Me$_2$, R^2 = H) (Scheme 6). In this case, the best yields, though low (5 – 15 %), were obtained carrying out the reactions in refluxing toluene.
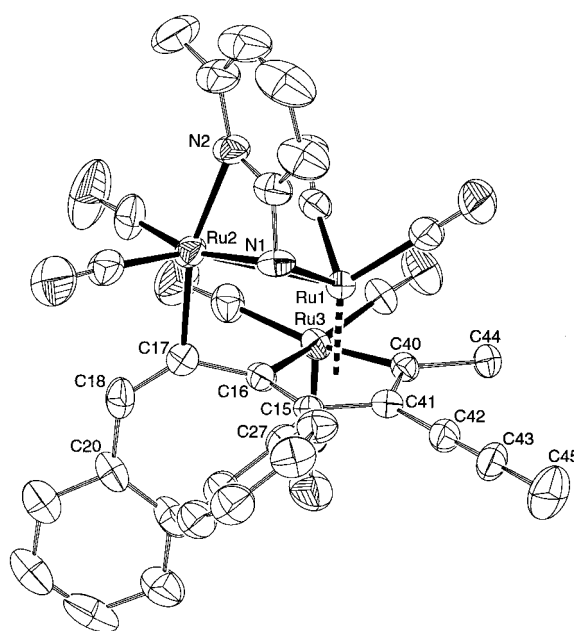
Related results, but not analogous as far as structure is concerned, were obtained by treatment of compound **2** with disubstituted butadiynes and alkynes. These reactions led to the ruthenacyclopentadienyl derivatives $[Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^5\text{-}(Z)\text{-}C(=CHCH_2OPh)C=C(CH_2OPh)C(C\equiv CR)=CR\}(CO)_7]$ (**12**: R = Ph; **13**: R = CH$_2$OPh), $[Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^5\text{-}(Z)\text{-}C(=CHCH_2OPh)C=C(CH_2OPh)CR^2=CR^1\}(CO)_7]$ (**14**: R^1 = R^2 = Ph; **15**: R^1 = C(OH)Ph$_2$, R^2 = H; **16a**: R^1 = CO$_2$Me, R^2 = H; **17a**: R^1 = C(OH)Me$_2$, R^2 = H), and $[Ru_3(\mu\text{-}\eta^2\text{-ampy})\{\mu_3\text{-}\eta^5\text{-}(E)\text{-}C(=CHCH_2OPh)C=C(CH_2OPh)CR^2=CR^1\}(CO)_7]$ (**16b**: R^1 = CO$_2$Me, R^2 = H; **17b**: R^1 = C(OH)Me$_2$, R^2 = H) (Scheme 7). It should be noted that, in contrast to the products derived from compound **3**, which are *E* isomers (**5 – 11**), most of the ruthenacyclopentadienyl complexes
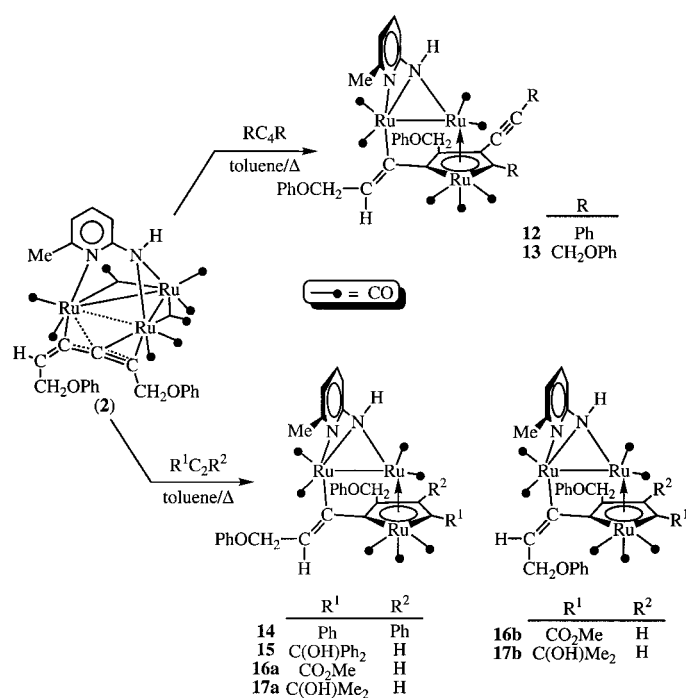
Scheme 7. Synthesis of compounds 12–17.

Figure 4. ORTEP representation of the molecular structure of compound 6.

Table 3. Selected interatomic distances [Å] in compounds 6 and 11.

	6	11
Ru1–Ru2	2.786(1)	2.792(2)
Ru1–Ru3	2.716(1)	2.741(2)
Ru1–N1	2.177(6)	2.21(1)
Ru1–C15	2.290(6)	2.28(1)
Ru1–C16	2.271(6)	2.30(2)
Ru1–C40	2.216(6)	2.26(2)
Ru1–C41	2.266(6)	2.29(1)
Ru2–N1	2.118(6)	2.09(2)
Ru2–N2	2.223(6)	2.22(1)
Ru2–C17	2.072(7)	2.02(2)
Ru3–C16	2.123(6)	2.12(2)
Ru3–C40	2.059(6)	2.06(2)
C15–C16	1.425(8)	1.44(2)
C15–C27	1.492(9)	1.51(2)
C15–C41	1.435(8)	1.43(2)
C16–C17	1.463(8)	1.53(2)
C17–C18	1.347(9)	1.32(2)
C18–C20	1.47(1)	1.43(3)
C40–C41	1.445(9)	1.45(2)
C40–C44	1.522(9)	1.55(2)
C41–C42	1.442(9)	–
C42–C43	1.162(9)	–
C43–C45	1.46(1)	

derived from 2 are *Z* isomers, and in the cases where *E* isomers are observed (compounds 16b and 17b), these are formed together with their corresponding *Z* isomers (compounds 16a and 17a).

Characterization of compounds 5–17: All these compounds show the same pattern of carbonyl absorptions in their IR spectra, indicating that the complexes have similar structural skeletons that differ only in the nature of their substituents. Crystals of compounds 6 and 11 were studied by X-ray diffraction methods.

Figure 4 shows the molecular structure of compound 6. Selected interatomic distances are listed in Table 3. The compound is a trinuclear cluster with two metal–metal bonds, Ru1–Ru2 and Ru1–Ru3. The ampy ligand is only attached to Ru1 and Ru2, with its amidic nitrogen atom N1 spanning both metal atoms and its pyridinic nitrogen N2 bonded to Ru2, in the same way as in complex 4. The metal atom Ru3 is integrated within a ruthenacyclopentadienyl ring which is η^5-coordinated to Ru1. An alkenyl fragment connects Ru2 to one of the carbon atoms of the ruthenacyclopentadienyl ring, C16, through one of its carbon atoms, C17. The substituents of the other carbon atom of the alkenyl fragment, C18, are a hydrogen atom and a phenyl group, the latter being *trans* to the metal atom Ru2. The remaining substituents of the ruthenacyclopentadienyl ring are a phenyl (attached to C15), a methylethynyl (attached to C41), and a methyl group (attached to C40). It seems clear that the two phenyl groups and the carbon atoms C15–C18 arise from the original ynenyl ligand of compound 3, whereas the methylethynyl and methyl groups as well as the carbon atoms C40 and C41 arise from the 2,4-hexadiyne reagent. The coordination shell of the cluster is completed with seven terminal carbonyl ligands.

Figure 5 shows the molecular structure of compound 11. Selected interatomic distances are listed in Table 3. For quick comparisons and as far as possible, a common atomic numbering scheme has been used for the structures of compounds 6 and 11. The structure of 11 is entirely analogous to that of complex 6, except for the groups attached to the carbon atoms C40 and C41 of the ruthenacyclopentadienyl ring, a CMe$_2$OH group and a hydrogen atom, respectively, which now arise from the dimethylpropargyl alcohol reagent.

In both compounds the substituent on C40 is bulkier than that on C41. This incited us to propose that R^1 the bulkier substituent of the diyne or alkyne reagents, which leads to the
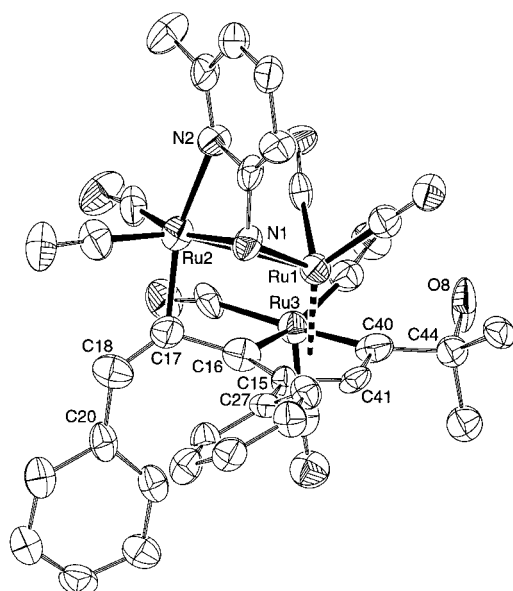
Figure 5. ORTEP representation of the molecular structure of compound **11**.

products depicted in Scheme 6 and Scheme 7, ends on the carbon atom adjacent to the metal atom of the ruthenacyclopentadienyl ring.

That all the products derived from compound **3** (Scheme 6) have the same arrangement of the alkenyl substituents (Ph *trans* to Ru) is also supported by their ^{1}H NMR spectra, which show the alkenyl proton resonances in a very narrow range of chemical shifts (ca. $\delta = 6.0$, structure **I** in Table 4). In addition, most of the products derived from compound **2** (Scheme 7) also have their alkenyl proton resonances in a narrow range of chemical shifts, but shifted to lower frequencies (ca. $\delta = 5.4$) from those of the products derived from compound **3**. Curiously, the reactions of compound **2** with methyl propynate and dimethylpropargyl alcohol led to two isomers, compounds **16a,b** and **17a,b**, respectively. The compounds

Table 4. ^{1}H NMR chemical shifts for the alkenyl protons of compounds **5–17**.

R^1	R^2	Structure **I**		Structure **II**		Structure **III**	
		δ	comp.	δ	comp.	δ	comp.
Ph	C≡CPh	5.99	**5**	5.47	**12**		
Me	C≡CMe	5.92	**6**				
CH$_2$OPh	C≡CCH$_2$OPh	5.94	**7**	5.42	**13**		
Ph	Ph	6.02	**8**	5.44	**14**		
C(OH)Ph$_2$	H			5.41	**15**		
CO$_2$Me	CO$_2$Me	6.05	**9**				
CO$_2$Me	H	5.99	**10**	5.42	**16a**	6.16	**16b**
C(OH)Me$_2$	H	6.00	**11**	5.43	**17a**	6.14	**17b**

16a and **17a** have their alkenyl proton resonances at $\delta = 5.4$, whereas those of **16b** and **17b** are observed at ca. $\delta = 6.1$ (Table 4). The chemical shifts of the ruthenacyclopentadienyl substituents are nearly the same for each pair of isomers; for example, the ^{1}H chemical shifts of the hydrogen atoms attached to the RuC$_4$ rings of compounds **16a,b** and **17a,b** (R^2 = H) differ by less than 0.1 ppm for each pair of isomers. Consequently, we are inclined to propose that the compounds differ in the arrangement of the alkenyl substituents, rather than in the arrangement of the RuC$_4$ ring substituents. Accordingly, we have assigned a *cis* structure to compounds **12–15**, **16a**, and **17a** (structure **II** in Table 4) and a *trans* structure to compounds **16b** and **17b** (structure **III** in Table 4). Other isomeric structures in which both isomers have a *trans* arrangement of the alkenyl substituents, but differing in the attachment of the ruthenacyclopentadienyl fragment to one of the remaining ruthenium atoms (vide infra), cannot be completely ruled out with the available data.
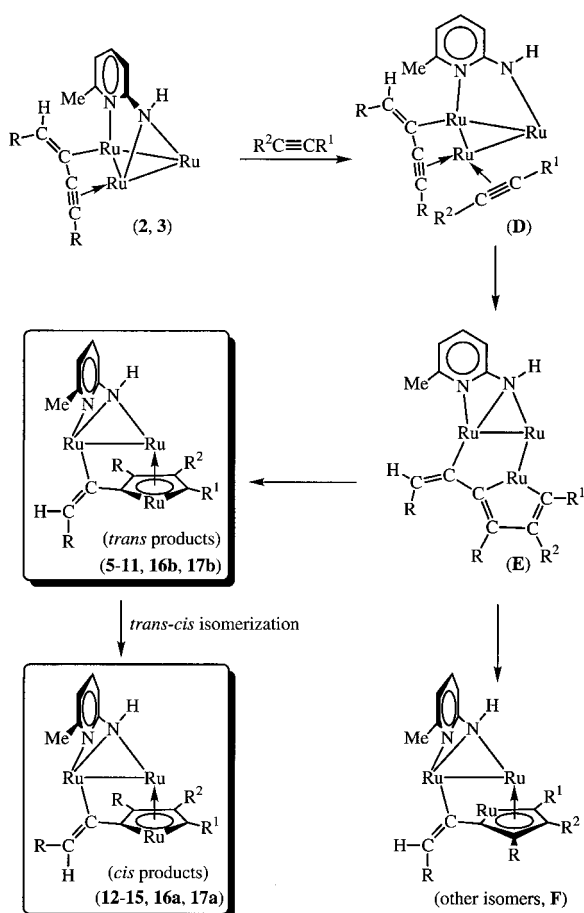
As mentioned previously for compound **4**, the coordination showed by the ampy ligand in all these complexes has no precedent in cluster chemistry, although the derivative chemistry of 2-amidopyridine-bridged trinuclear clusters has been extensively studied.[9–20, 25, 26] It is curious that such a hitherto elusive coordination mode has not appeared in an isolated example. This article describes 16 trinuclear compounds with the ampy ligand acting as a five-electron donor μ-η^2-ligand. The coupling reactions described in this article may be facilitated by subtle changes in the coordination mode of the ancillary 2-amidopyridine ligand relative to the cluster core.

Comments on the formation of compounds 5–17: The formation of a metallacyclopentadienyl ring requires the coordination of two alkyne fragments to the same metal atom. In the ynenyl complexes **2** and **3**, the vacant site necessary for coordination of the alkyne or diyne reagent may be created by rupture of one of the N–Ru bonds (intermediate **D** in Scheme 8). Kinetic studies have previously shown that such a cluster activation pathway does occur for triruthenium clusters with μ_3-2-amidopyridine ligands.[15] As the R group of the ynenyl ligand and one of the substituents of the alkyne reagent should be close to each other in intermediate **D** (Scheme 8), for steric reasons, this substituent should be the smallest one. In other words, if R^1 is bulkier than R^2, it is the carbon atom that bears R^2 that couples to the ynenyl fragment during the subsequent cyclization step. After cyclization (intermediate **E** in Scheme 8), the coordination of the carbon atoms of the cycle to the central ruthenium atom, in addition to the release of a CO molecule, would lead to the products with R^2 adjacent to R in the RuC$_4$ cycle and the alkenyl R group *trans* to ruthenium (**5–11**, **16b** and **17b**).

The remaining ruthenacyclic compounds (**12–15**, **16a** and **17a**) have spectroscopic data (IR, ^{1}H NMR) very similar to those of **5–11**, **16b** and **17b**, except for the ^{1}H chemical shifts of their alkenyl hydrogen atoms. Excluding the possibility that compounds **12–15**, **16a** and **17a** differ from **5–11**, **16b** and **17b** in the positions of the R^1 and R^2 groups on the ruthenacyclopentadienyl ring (the isomeric structures would arise from the two alternative orientations of the alkyne

Scheme 8. Reaction pathway that leads to compounds **5–17** (carbonyl groups are omitted for clarity).

reagent in intermediate **D** of Scheme 7), two other types of isomers of the *trans* products may be considered; a) those labeled as "other isomers **F**" in Scheme 8, which would arise from the attachment of the central ruthenium atom to the opposite face of the ruthenacyclopentadienyl ring from that which leads to compounds **5–11**, **16b** and **17b**; and b) those arising from a *cis-trans* isomerization of the alkenyl double bond of the *trans* products (or of any of their synthetic intermediates).

We propose that compounds **12–15**, **16a** and **17a** have a *cis* arrangement of the alkenyl substituents, while maintaining the remaining atoms in the same positions as those of the *trans* products **5–11**, **16b** and **17b**. The following supports this proposal: a) isomers of type **F** would also have a *trans* arrangement of the alkenyl substituents and the same atom connectivity as the *trans* products **5–11**, **16b** and **17b**. These characteristics would not lead to the marked differences observed in the ^{1}H chemical shifts of the alkenyl hydrogen atoms (Table 4). b) Metal-mediated *cis–trans* isomerization of alkenes has often been observed under mild conditions by using metal clusters[17, 18, 29] or mononuclear complexes as catalysts,[30] particularly when the C=C double bond is attached to a CH_2 group, as happens with the compounds derived from complex **2** (R = CH_2OPh).

Some examples of addition of two diyne molecules to ruthenium carbonyl clusters and their subsequent

coupling to give larger unsaturated hydrocarbyl ligands,[2b–e, 2g, 3, 7a, 8] which sometimes form ruthenacyclopentadienyl rings,[2b, 2c, 2e, 2g, 3, 7a, 8a] have been reported. However, this article reports the first coupling reactions of ynenyl ligands with diynes.

Experimental Section

General: Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or calcium hydride (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, by using Schlenk-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, except compound **1**, which was prepared as published.[11] IR spectra were recorded on a Perkin–Elmer FT 1720-X spectrometer. NMR spectra were measured at room temperature by using a Bruker AC200 and AC300 NMR spectrometer with TMS as an internal standard. Microanalyses were performed on a Perkin–Elmer 2400 instrument. Mass spectra were recorded on a VG Autospec double-focussing 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; data given refer to the most abundant molecular ion isotopomer.

[Ru$_3$(μ_3-η^2-ampy)(μ-η^3-PhOCH$_2$C≡CC=CHCH$_2$OPh)(μ-CO)$_2$(CO)$_6$] (2): A solution of **1** (150 mg, 0.226 mmol) and 1,6-diphenoxy-2,4-hexadiyne (89 mg, 0.339 mmol) in THF (20 mL) was stirred at reflux temperature for 10 min. The color changed from yellow to orange. The solvent was removed under reduced pressure, and the residue dissolved in dichloromethane (2 mL). This solution was separated by column chromatography (20 × 2 cm) on neutral alumina (activity I). Elution with hexane/dichloromethane (1:1) afforded two bands. The first band (pale green) contained the excess of the diyne. The second band (yellow) afforded compound **2** (81 mg, 40%). A dark residue remained at the top of the column. ^{1}H NMR (CDCl$_3$): δ = 7.2–6.9 (m, 10H), 6.88 (dd, J = 8.1, 2.6 Hz, 1H; CH$_2$), 6.80 (t, J = 7.9 Hz, 1H; ampy), 6.52 (dd, J = 8.1, 7.1 Hz, 1H; CH), 6.36 (d, J = 7.9 Hz, 1H; ampy), 5.88 (d, J = 7.9 Hz, 1H; ampy), 5.77 (d, J = 16.0 Hz, 1H; CH$_2$), 4.91 (dd, J = 7.1, 2.6 Hz, 1H; CH$_2$), 2.64 (br s, 1H; NH), 2.58 (s, 3H; ampy); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 245.5, 241.2, 198.8, 197.4, 195.7, 194.1, 193.9, 193.6, 167.1, 159.7, 158.3, 157.5, 138.2–112.1 (m), 102.5, 72.4, 69.7, 67.9, 57.8, 14.0; IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2065 (vs), 2030 (vs), 2021 (vs), 1994 (s), 1968 (w), 1878 (w), 1828 cm^{-1} (m) (C=O); FAB-MS: m/z: 899 [M]$^+$; elemental analysis calcd (%) for C$_{32}$H$_{22}$N$_2$O$_{10}$Ru$_3$ (897.78): C 42.81, H 2.47, N 3.12; found C 43.20, H 2.56, N 2.81.

[Ru$_3$(μ_3-η^2-ampy)(μ-η^3-PhC≡CC=CHPh)(μ-CO)$_2$(CO)$_6$] (3) and [Ru$_3$(μ-η^2-ampy){μ_3-η^6-PhCC$_5$(C≡CPh)HPh$_2$}(CO)$_7$] (4): A solution of **1** (650 mg, 0.980 mmol) and diphenylbutadiyne (337 mg, 1.666 mmol) in THF (70 mL) was stirred at reflux temperature for 15 min. The color changed from yellow to brown-yellow. The solution was concentrated under reduced pressure to about 3 mL and was applied onto silica gel preparative TLC plates. Repeated elution with hexane/dichloromethane (2:1) allowed the isolation of compound **3** (197 mg, 24%) from the fourth band (yellow), and **4** (88 mg, 9%) from the first band (orange). A dark residue remained on the base line.

*Data for **3***: ^{1}H NMR (CDCl$_3$): δ = 7.8–7.1 (m, 10H), 7.43 (s, 1H; CH), 7.02 (t, J = 7.8 Hz, 1H; ampy), 6.47 (d, J = 7.8 Hz, 1H; ampy), 6.09 (d, J = 7.8 Hz, 1H; ampy), 2.82 (s, 3H; Me); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 244.0, 239.6, 200.5, 199.0, 197.0, 195.9 (2 C), 194.4, 168.1, 160.2, 139.7–113.3 (m), 106.9, 68.8, 62.6, 39.5, 28.9; IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2063 (vs), 2031 (s), 2017 (s), 1994 (m), 1968 (w), 1880 (w), 1826 cm^{-1} (m) (C=O); FAB-MS: m/z: 839 [M]$^+$; elemental analysis calcd (%) for C$_{30}$H$_{18}$N$_2$O$_8$Ru$_3$ (837.73): C 43.01, H 2.16, N 3.34; found C 42.85, H 2.17, N 3.11.

*Data for **4***: ^{1}H NMR (CDCl$_3$): δ = 8.0–6.8 (m, 21H), 6.73 (d, J = 8.0, 1H; ampy), 5.84 (d, J = 8.0, 1H; ampy), 5.34 (s, 1H; NH), 3.54 (s, 1H; H of Cp), 2.30 (s, 3H; Me); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 209.1, 207.0, 206.7, 201.6, 197.2, 196.5, 195.5, 172.8, 162.1, 158.5, 140.9–109.9 (m), 107.2, 105.9, 99.3, 93.6, 89.0, 83.9, 75.7, 23.3; IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2056 (s), 2014 (vs), 1973 (m), 1960 (m), 1946 (m), 1923 cm^{-1} (m) (C=O); FAB-MS: m/z: 1013 [M]$^+$; elemental analysis calcd (%) for C$_{45}$H$_{28}$N$_2$O$_7$Ru$_3$ (1011.97): C 53.41, H 2.79, N 2.77; found C 53.41, H 2.98, N 2.72.

[Ru$_3$(μ-η^2-ampy){μ_3-η^5-C(=CHPh)C=CPhC(C≡CR) =CR}(CO)$_7$] (5: R = Ph; 6: R = Me; 7: R = CH$_2$OPh): A solution of compound **3** and the corresponding diyne in THF (20 mL) was stirred at reflux temperature. The color changed from yellow to brown. The solution was concentrated under reduced pressure to approximately 1 mL and was applied onto silica gel preparative TLC plates. Repeated elution with hexane/dichloromethane (4:1) allowed the isolation of the corresponding compound from the major band. A brown residue remained on the base line.

Data for 5: Reagents: **3** (15 mg, 0.018 mmol), diphenylbutadiyne (10 mg, 0.050 mmol); reaction time: 80 min; TLC band: first (yellow); yield: 6 mg, 32 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.9 - 6.7$ (m, 22H), 6.11 (d, $J = 7.9$ Hz, 1H; ampy), 5.99 (s, 1H; CH), 5.14 (s, 1H; NH), 2.45 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2069$ (vs), 2025 (vs), 2011 (s), 1984 (m), 1958 (m), 1923 cm^{-1} (w) (C=O); FAB-MS: m/z: 1013 [M]$^+$; elemental analysis calcd (%) for C$_{45}$H$_{28}$N$_2$O$_7$Ru$_3$ (1011.97): C 53.41, H 2.79, N 2.77; found C 53.62, H 2.94, N 2.67.

Data for 6: Reagents: **3** (50 mg, 0.057 mmol), 2,4-hexadiyne (10 mg, 0.128 mmol); reaction time: 3 h; TLC band: first (yellow); yield: 10 mg, 20 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.8 - 7.1$ (m, 11H), 6.73 (d, $J = 7.3$ Hz, 1H; ampy), 6.08 (d, $J = 7.3$, 1H; ampy), 5.92 (s, 1H; CH), 3.72 (s, 1H; NH), 2,59 (s, 3H; Me), 2.40 (s, 3H; Me), 2.05 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2067$ (vs), 2025 (vs), 2005 (s), 1978 (m), 1957 (m), 1926 cm^{-1} (w) (C=O); FAB-MS: m/z: 889 [M]$^+$; elemental analysis calcd (%) for C$_{35}$H$_{24}$N$_2$O$_7$Ru$_3$ (887.83): C 47.35, H 2.72, N 3.16; found C 47.55, H 2.93, N 2.88.

Data for 7: Reagents: **3** (25 mg, 0.029 mmol), 1,6-diphenoxy-2,4-hexadiyne (15 mg, 0.057 mmol); reaction time: 4 h; TLC band: second (yellow); yield: 8 mg, 24 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.6 - 6.7$ (m, 22H), 6.05 (d, $J = 8.0$, 1H; ampy), 5.94 (s, 1H; CH), 4.82 (s, 2H; CH$_2$), 4.80 (d, $J = 10.8$ Hz, 1H; CH$_2$), 4.65 (d, $J = 10.8$ Hz, 1H; CH$_2$), 2.43 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2072$ (vs), 2028 (vs), 2011 (s), 1986 (m), 1960 (m), 1936 cm^{-1} (w) (C=O); FAB-MS: m/z: 1073 [M]$^+$; elemental analysis calcd (%) for C$_{47}$H$_{32}$N$_2$O$_9$Ru$_3$ (1072.03): C 52.66, H 3.01, N 2.61; found C 52.72, H 3.12, N 2.55.

[Ru$_3$(μ-η^2-ampy){μ_3-η^5-C(=CHPh)C=CPhCR^2=CR^1}(CO)$_7$] (8: R^1 = R^2 = Ph; 9: R^1 = R^2 = CO$_2$Me; 10: R^1 = CO$_2$Me, R^2 = H; 11: R^1 = C(OH)Me$_2$, R^2 = H): A solution of compound **3** and the corresponding alkyne in toluene (20 mL) was stirred at reflux temperature. The color changed from yellow to brown. The solution was concentrated under reduced pressure to about 1 mL and was applied onto silica gel preparative TLC plates. Repeated elution with the appropriate eluant allowed the isolation of the corresponding compound from the major band. A brown residue remained on the base line.

Data for 8: Reagents: **3** (102 mg, 0.122 mmol), diphenylacetylene (45 mg, 0.247 mmol); reaction time: 30 min; eluant: hexane/dichloromethane (3:1); TLC band: fourth (yellow-orange); yield: 18 mg, 15 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.57$ (t, $J = 7.6$ Hz, 1H; ampy), 7.4 - 6.7 (m, 21H), 6.07 (d, $J = 7.6$ Hz, 1H; ampy), 6.02 (s, 1H; CH), 2.48 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ (= 2068 (s), 2026 (s), 2002 (s), 1983 (m), 1958 (m), 1915 cm^{-1} (w) (C=O); FAB-MS: m/z: 989 [M]$^+$; elemental analysis calcd (%) for C$_{43}$H$_{28}$N$_2$O$_7$Ru$_3$ (987.95): C 52.28, H 2.86, N 2.83; found C 52.43, H 2.99, N 2.62.

Data for 9: Reagents: **3** (100 mg, 0.119 mmol), dimethyl acetylenedicarboxylate (35 μL, 0.285 mmol); reaction time: 50 min; eluant: hexane/dichloromethane (1:2); TLC band: second (yellow); yield: 15 mg, 13 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.68$ (t, $J = 7.8$ Hz, 1H; ampy), 7.2 - 6.7 (m, 11H), 6.69 (d, $J = 7.8$ Hz, 1H; ampy), 6.29 (s, 1H; NH), 6.05 (s, 1H; CH), 3.89 (s, 3H; OMe), 3.78 (s, 3H; OMe), 2.48 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2067$ (s), 2035 (vs), 2009 (s), 1999 (m), 1965 (m), 1931 cm^{-1} (w) (C=O); FAB-MS: m/z: 953 [M]$^+$; elemental analysis calcd (%) for C$_{35}$H$_{24}$N$_2$O$_{11}$Ru$_3$ (951.83): C 44.17, H 2.54, N 2.94; found C 44.33, H 2.77, N 2.83.

Data for 10: Reagents: **3** (100 mg, 0.119 mmol), methyl propynate (44 μL, 0.495 mmol); reaction time: 5 min; eluant: hexane/dichloromethane (1:1); TLC band: third (yellow); yield: 5 mg, 5 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.94$ (t, 1H; CH of ruthenacycle), 7.8 - 7.1 (m, 11H), 6.78 (d, $J = 7.9$ Hz, 1H; ampy), 6.01 (d, $J = 7.9$ Hz, 1H; ampy), 5.99 (s, 1H; CH), 3.72 (s, 3H; OMe), 2.45 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2077$ (s), 2029 (vs), 2018 (vs), 1989 (m), 1961 (m), 1936 cm^{-1} (w) (C=O); FAB-MS: m/z: 895 [M]$^+$; elemental analysis calcd (%) for C$_{33}$H$_{22}$N$_2$O$_9$Ru$_3$ (893.79): C 44.35, H 2.48, N 3.13; found C 44.62, H 2.64, N 2.98.

Data for 11: Reagents: **3** (100 mg, 0.119 mmol), 2-methyl-3-butyn-2-ol (24 μL, 0.246 mmol); reaction time: 30 min; eluant: hexane/dichloromethane (3:1); TLC band: third (yellow); yield: 12 mg, 11 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.78$ (t, $J = 8.0$ Hz, 1H; ampy), 7.64 (s, 1H; CH of ruthena-

cycle), 7.7 - 7.1 (m, 10H), 6.73 (d, $J = 8.0$ Hz, 1H; ampy), 6.00 (s, 1H; CH), 5.96 (d, $J = 8.0$ Hz, 1H; ampy), 2.43 (s, 3H; Me), 1.62 (s, 3H; Me), 1.48 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2067$ (s), 2026 (vs), 1996 (s), 1982 (m), 1959 (m), 1923 cm^{-1} (w) (C=O); FAB-MS: m/z: 895 [M]$^+$; elemental analysis calcd (%) for C$_{34}$H$_{26}$N$_2$O$_8$Ru$_3$ (893.83): C 45.69, H 2.93, N 3.13; found C 45.88, H 3.02, N 2.88.

[Ru$_3$(μ-η^2-ampy){μ_3-η^5-C(=CHCH$_2$OPh)C=C(CH$_2$OPh)C(C≡CR)=CR}-(CO)$_7$] (12: R = Ph; 13: R = CH$_2$OPh): A solution of compound **2** and the corresponding diyne in toluene (20 mL) was stirred at reflux temperature. The color changed from yellow to brown. The solution was concentrated under reduced pressure to about 1 mL and was applied onto silica gel preparative TLC plates. Repeated elution with the appropriate eluant allowed the isolation of the corresponding compound from the major band. A brown residue remained on the base line.

Data for 12: Reagents: **2** (150 mg, 0.167 mmol), diphenylbutadiyne (68 mg, 0.336 mmol); reaction time: 15 min; eluant: hexane/dichloromethane (4:1); TLC band: last (yellow); yield: 50 mg, 28 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.41$ (t, $J = 8.0$ Hz, 1H; ampy), 7.4 - 6.7 (m, 21H), 6.08 (d, $J = 8.0$ Hz, 1H; ampy), 5.47 (t, $J = 6.5$ Hz, 1H; CH), 4.82 - 4.56 (m, 4H; 2CH$_2$), 4.23 (s, 1H; NH), 2.49 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2070$ (s), 2029 (vs), 2014 (s), 1983 (m), 1960 (m), 1933 cm^{-1} (w) (C=O); FAB-MS: m/z: 1073 [M]$^+$; elemental analysis calcd (%) for C$_{47}$H$_{32}$N$_2$O$_9$Ru$_3$ (1072.03): C 52.66, H 3.01, N 2.61; found C 52.58, H 3.21, N 2.44.

Data for 13: Reagents: **2** (103 mg, 0.115 mmol), 1,6-diphenoxy-2,4-hexadiyne (60 mg, 0.229 mmol); reaction time: 10 min; eluant: hexane/dichloromethane (3:2); TLC band: second (yellow); Yield: 9 mg, 7 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.39$ (t, $J = 7.8$ Hz, 1H; ampy), 7.4 - 6.7 (m, 21H), 6.05 (d, $J = 7.8$ Hz, 1H; ampy), 5.42 (t, $J = 6.6$ Hz, 1H; CH), 4.65 - 4.51 (m, 8H; 4CH$_2$), 4.01 (s, 1H; NH), 2.45 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2073$ (s), 2030 (vs), 2012 (s), 1985 (m), 1961 (m), 1928 cm^{-1} (w) (C=O); FAB-MS: m/z: 1133 [M]$^+$; elemental analysis calcd (%) for C$_{49}$H$_{36}$N$_2$O$_{11}$Ru$_3$ (1132.08): C 51.99, H 3.21, N 2.47; found C 52.31, H 3.46, N 2.15.

[Ru$_3$(μ-η^2-ampy){μ_3-η^5-C(=CHCH$_2$OPh)C=C(CH$_2$OPh)CR^2=CR^1}(CO)$_7$] (14: R^1 = R^2 = Ph; 15: R^1 = C(OH)Ph$_2$, R^2 = H; 16a (Z) and 16b (E): R^1 = CO$_2$Me, R^2 = H; 17a (Z) and 17b (E): R^1 = C(OH)Me$_2$, R^2 = H): A solution of compound **2** and the corresponding alkyne in toluene (20 mL) was stirred at reflux temperature. The color changed from yellow to brown. The solution was concentrated under reduced pressure to approximately 1 mL and was applied onto silica gel preparative TLC plates. Repeated elution with the appropriate eluant allowed the isolation of the corresponding compound(s) from the major band(s). A brown residue remained on the base line.

Data for 14: Reagents: **2** (100 mg, 0.111 mmol), diphenylacetylene (40 mg, 0.224 mmol); reaction time: 55 min; eluant: hexane/dichloromethane (5:2); TLC band: third (yellow); Yield: 16 mg, 14 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.4 - 6.6$ (m, 21H), 6.42 (d, $J = 7.8$ Hz, 1H; ampy), 6.04 (d, $J = 7.8$ Hz, 1H; ampy), 5.44 (t, $J = 6.4$ Hz, 1H; CH), 4.83 - 462 (m, 2H; CH$_2$), 4.36 (d, $J = 11.8$ Hz, 1H; CH$_2$), 4.27 (d, $J = 11.8$ Hz, 1H; H$_2$), 3.61 (s, 1H; NH), 2.50 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2068$ (s), 2029 (vs), 2003 (s), 1983 (m), 1960 (m), 1932 cm^{-1} (w) (C=O); FAB-MS: m/z: 1049 [M]$^+$; elemental analysis calcd (%) for C$_{45}$H$_{32}$N$_2$O$_9$Ru$_3$ (1048.00): C 51.57, H 3.08, N 2.67; found C 51.62, H 3.15, N 2.60.

Data for 15: Reagents: **2** (175 mg, 0.195 mmol), 1,1-diphenyl-2-propyn-1-ol (81 μL, 0.390 mmol); reaction time: 15 min; eluant: hexane/dichloromethane (1:1); TLC band: second (yellow); yield: 11 mg, 5 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.8 - 6.7$ (m, 23H; 4Ph, 2H of ampy, and CH of ruthenacycle), 5.89 (d, $J = 7.6$ Hz, 1H; ampy), 5.41 (dd, $J = 7.6$, 6.0 Hz, 1H; CH), 4.77 (d, $J = 14.3$ Hz, 1H; CH$_2$), 4.73 (m, 1H; CH$_2$), 4.56 (m, 1H; CH$_2$), 3.87 (d, $J = 14.3$ Hz, 1H; CH$_2$), 2.51 (s, 1H; NH), 2.46 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2072$ (s), 2032 (vs), 2010 (s), 1985 (m), 1963 (m), 1932 cm^{-1} (w) (C=O); FAB-MS: m/z: 1079 [M]$^+$; elemental analysis calcd (%) for C$_{46}$H$_{34}$N$_2$O$_{10}$Ru$_3$ (1078.03): C 51.25, H 3.18, N 2.60; found C 51.38, H 3.35, N 2.44.

Data for 16a: Reagents: **2** (100 mg, 0.111 mmol), methyl propynate (21 μL, 0.236 mmol); reaction time: 20 min; eluant: hexane/dichloromethane (1:2); TLC band: first (yellow); yield: 9 mg, 8 %; ^{1}H NMR (CDCl$_3$): $\delta = 7.57$ (s, 1H, CH of ruthenacycle), 7.4 - 7.2 (m, 6H), 7.05 (t, $J = 7.7$ Hz, 1H; ampy), 7.01 - 6.87 (m, 4H), 6.78 (d, $J = 7.7$, 1H; ampy), 5.98 (d, $J = 7.7$, 1H; ampy), 5.42 (t, $J = 7.1$ Hz, 1H; CH), 4.65 (d, $J = 13.6$ Hz, 1H; CH$_2$), 4.71 - 4.50 (m, 2H; CH$_2$), 3.84 (d, $J = 13.6$ Hz, 1H; CH$_2$), 3.68 (s, 3H; OMe), 2.83 (s, 1H;

NH), 2.46 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2077 (s), 2032 (s), 2020 (vs), 1988 (m), 1963 (m), 1938 cm^{-1} (w) (C=O); FAB-MS: m/z: 955 $[M]^+$; elemental analysis calcd (%) for C$_{35}$H$_{26}$N$_2$O$_{11}$Ru$_3$ (953.84): C 44.07, H 2.75, N 2.94; found C 44.28, H 2.90, N 2.74.

Data for 16b: Reagents: As for compound 16a, except for the TLC band which was the second (yellow) band. Yield: 15 mg, 14%; ^{1}H NMR (CDCl$_3$): δ = 7.60 (s, 1H, ruthenacycle), 7.5–7.2 (m, 6H), 7.07 (t, J = 7.8 Hz, 1H; ampy), 7.04–6.95 (m, 4H), 6.81 (d, J = 7.8, 1H; ampy), 6.16 (t, J = 6.3 Hz, 1H; CH), 6.01 (d, J = 7.8, 1H; ampy), 4.71 (d, J = 11.4 Hz, 1H; CH$_2$), 4.76–4.63 (m, 2H; CH$_2$), 3.85 (d, J = 11.4 Hz, 1H; CH$_2$), 3.69 (s, 3H; OMe), 2.82 (s, 1H; NH), 2.48 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2077 (s), 2030 (s), 2020 (vs), 1988 (m), 1962 (m), 1938 cm^{-1} (w) (C=O); FAB-MS: m/z: 955 $[M]^+$; elemental analysis calcd (%) for C$_{35}$H$_{26}$N$_2$O$_{11}$Ru$_3$ (953.84): C 44.07, H 2.75, N 2.94; found C 44.25, H 2.91, N 2.83.

Data for 17a: Reagents: 2 (100 mg, 0.111 mmol), 2-methyl-3-butyn-2-ol (22 μL, 0.225 mmol); reaction time: 15 min; eluant: hexane/dichloromethane (1:2); TLC band: first (yellow); yield: 9 mg, 8%; ^{1}H NMR (CDCl$_3$): δ = 7.45–7.25 (m, 6H; Ph), 7.23 (s, 1H; CH of ruthenacycle), 7.05 (t, J = 7.6 Hz, 1H; ampy), 6.98–6.91 (m, 4H; Ph), 6.77 (d, J = 7.6, 1H; ampy), 5.97 (d, J = 7.6, 1H; ampy), 5.43 (dd, J = 7.3, 5.9 Hz, 1H; CH), 4.68 (m, 1H; CH$_2$), 4.66 (d, J = 13.6 Hz, 1H; CH$_2$), 4.52 (m, 1H; CH$_2$), 3.88 (d, J = 13.6 Hz, 1H; CH$_2$), 2.83 (s, 1H; NH), 2.45 (s, 3H; Me), 1.41 (s, 3H; Me), 1.26 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2068 (s), 2029 (s), 2002 (vs), 1979 (m), 1961 (m), 1923 cm^{-1} (w) (C=O); FAB-MS: m/z: 955 $[M]^+$; elemental analysis calcd (%) for C$_{36}$H$_{30}$N$_2$O$_{10}$Ru$_3$ (953.89): C 45.33, H 3.17, N 2.94; found C 45.61, H 3.36, N 2.79.

Data for 17b: Reagents: As for compound 17a, except for the TLC band which was the second (yellow) band. Yield: 10 mg, 9%; ^{1}H NMR (CDCl$_3$): δ = 7.43–7.30 (m, 6H; Ph), 7.29 (s, 1H, CH of ruthenacycle), 7.06 (t, J = 7.6 Hz, 1H; ampy), 7.03–6.91 (m, 4H; Ph), 6.78 (d, J = 7.7, 1H; ampy), 6.14 (t, J = 6.4 Hz, 1H; CH), 5.97 (d, J = 7.7, 1H; ampy), 4.76–4.63 (m, 2H; CH$_2$), 4.67 (d, J = 13.6 Hz, 1H; H of CH$_2$), 3.85 (d, J = 13.6 Hz, 1H; CH$_2$), 2.84 (s, 1H; NH), 2.47 (s, 3H; Me), 1.42 (s, 3H; Me), 1.26 (s, 3H; Me); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2069 (s), 2029 (s), 2002 (vs), 1980 (m), 1960 (m), 1923 cm^{-1} (w) (C=O); FAB-MS: m/z: 955 $[M^+]$; elemental analysis calcd (%) for C$_{36}$H$_{30}$N$_2$O$_{10}$Ru$_3$ (953.89): C 45.33, H 3.17, N 2.94; found C 45.41, H 3.25, N 2.83.

X-ray crystallographic studies: Crystal data and refinement details are summarized in Table 5. Single crystals of compounds 2·acetone, 3·pentane, 4·pentane, and 6 were measured on a Nonius CAD4 diffractometer, equipped with a graphite crystal monochromator, by using the ω-Θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. Compound 11 was measured on a Nonius Kappa-CCD area detector diffractometer. In all cases, Lorentz and polarization corrections were applied and data reduced to $|F_o|^2$ values. The structures were solved by Patterson interpretation using the program DIRDIF-96.[31] Isotropic and full matrix anisotropic least squares refinements were carried out using SHELXL-97.[32] Molecular plots were made with the EUCLID program package.[33] Further geometrical calculations were made with PARST.[34] Particular data for each compound are given below.

Data for 2·acetone: An empirical absorption correction was applied by using XABS2,[35] with maximum and minimum correction factors of 1.309 and 0.792, respectively. Non H-atoms were refined anisotropically. All hydrogen atoms were refined isotropically, by using a common thermal parameter. The rather disordered acetone solvent molecule was refined by using constraints and restraints as described elsewhere.[36]

Data for 3·pentane: A semiempirical absorption correction was applied by using ψ scans,[37] correction factors in the range 0.998 to 0.806. Non H-atoms were refined anisotropically. Both coordinates and isotropic displacement factors of the hydrogen atoms located near the Ru atoms (H1, H18, H19A, H19B, H26A, H26B) were refined. The remaining hydrogen atoms were geometrically fixed to their parent atoms and refined riding with variable common temperature factors, one for the aromatic atoms and other for the methyl hydrogen atoms of the main molecule. Coordinates for the hydrogens of the solvent molecule were fixed and their displacement parameters calculated as 1.2 U_{eq}(C).

Data for 4·pentane: A semiempirical absorption correction was applied by using ψ scans,[37] with correction factors in the range between 0.820 and 0.760. Non H-atoms were refined anisotropically. The coordinates of the hydrogen atoms were fixed riding on their parent atoms and the rest of the parameters were allowed to refine free.

Data for 6: A semiempirical absorption correction was applied by using ψ scans,[37] with correction factors in the range 0.820 to 0.760. Non H-atoms

Table 5. Summary of crystal and refinement data.

	2·acetone	3·pentane	4·pentane	6	11
formula	C$_{32}$H$_{22}$N$_2$O$_{10}$Ru$_3$·C$_3$H$_6$O	C$_{30}$H$_{18}$N$_2$O$_8$Ru$_3$·C$_5$H$_{12}$	C$_{45}$H$_{28}$N$_2$O$_7$Ru$_3$·C$_5$H$_{12}$	C$_{35}$H$_{24}$N$_2$O$_7$Ru$_3$	C$_{34}$H$_{26}$N$_2$O$_8$Ru$_3$
M_r	955.80	909.82	1084.05	887.77	893.78
T [K]	293(2)	200(2)	293(2)	293(2)	200(2)
radiation (λ [Å])	Mo$_{K\alpha}$ (0.71073)	Mo$_{K\alpha}$ (0.71073)	Mo$_{K\alpha}$ (0.71073)	Mo$_{K\alpha}$ (0.71073)	Cu$_{K\alpha}$ (1.54184)
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	P2$_1$/a	P2$_1$/c	P$\bar{1}$	P2$_1$/c	P2$_1$/n
a [Å]	14.29(1)	13.835(9)	11.672(4)	11.283(3)	13.124(1)
b [Å]	9.471(5)	15.927(7)	11.96(2)	17.642(7)	16.897(1)
c [Å]	27.62(1)	16.578(9)	16.43(2)	17.773(4)	14.792(1)
α [°]	90	90	108.43(9)	90	90
β [°]	99.64(8)	105.52(6)	97.52(7)	104.12(3)	91.37(1)
γ [°]	90	90	90.26(5)	90	90
V [Å^3]	3685(4)	3520(3)	2155(6)	3431.0(19)	3279.1(4)
Z	4	4	2	4	4
ρ_{calcd} [g cm^{-3}]	1.723	1.717	1.670	1.719	1.810
μ [mm^{-1}]	1.274	1.323	1.094	1.353	11.509
$F(000)$	1888	1800	1084	1744	1760
crystal size [mm]	0.40 × 0.33 × 0.20	0.30 × 0.17 × 0.13	0.25 × 0.07 × 0.07	0.20 × 0.20 × 0.13	0.15 × 0.10 × 0.05
θ limits [°]	1.50, 24.98	1.81, 24.98	1.32, 25.98	1.65, 25.97	3.97, 65.19
h,k,l min/max	0/16, 0/11, −32/32	−16/15, 1/18, 0/19	−14/14, −14/13, 0/20	−13/13, 0/21, 0/21	−15/14, −19/17, −17/17
reflections collected	6755	6155	8454	6938	8904
unique reflections	6459	5930	8454	6712	5208
reflections [$I > 2\sigma(I)$]	4735	3353	2725	3280	2164
parameters/restraints	485/0	488/10	579/0	520/0	412/1
GOF on F^2	1.057	1.015	0.928	0.995	0.919
R_1 (on F, $I > 2\sigma(I)$)	0.0382	0.0393	0.0546	0.0380	0.0910
wR_2 (on F^2, all data)	0.1564	0.0949	0.1574	0.0883	0.2730
max/min res. [e Å^{-3}]	1.523/ −1.125	0.624/ −0.756	0.805/ −1.262	0.620/ −0.877	0.655/ −0.943

were refined anisotropically. All hydrogen atoms were isotropically refined.

*Data for **11***: An empirical absorption correction was applied by using XABS 2,[35] with maximum and minimum transmission factors of 0.562 and 0.150, respectively. Non H-atoms were refined anisotropically, except C1, C43, and C44, which were treated isotropically. Hydrogen atom positions were geometrically placed and refined riding on their parent atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-153545 (**2** · acetone), CCDC-153546 (**3** · pentane), CCDC-153547 (**4** · pentane), CCDC-153548 (**6**), and CCDC-153549 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: (+44)1223-336–033; e-mail: deposit@ccdc.cam.ac.uk).

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