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Reactivity of a triruthenium alkenyl cluster complex with conjugated diynes: Coupling of two diyne molecules via a face-capping diyne intermediate

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Abstract

The cluster $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu\text{-}CO)_2(CO)_6]$, which has a face-capping 1,1-dimethylhydrazido and an edge-bridging 1,2-diphenylethenyl ligand, reacts with diphenylbutadiyne or 2,4-hexadiyne to give the isomeric triruthenium carbonyl cluster complexes $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}RCCCC(R)C(R)CCCR\}(CO)_6]$ (**3a**, R = Ph; **3b**, R = Me) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}RCCCC(R)C(CCR)CR\}(CO)_6]$ (**4a**, R = Ph; **4b**, R = Me). These compounds contain a large unsaturated hydrocarbyl ligand that arises from a metal-cluster-mediated head-to-head (**3**) or head-to-tail (**4**) coupling of two diyne molecules and maintain the original hydrazido and ethenyl ligands. Metal clusters that contain a face-capping diyne coordinated through only one alkyne fragment, such as $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu_3\text{-}\kappa^2\text{-}RCCCCR)(CO)_7]$, have also been isolated (**2a**, R = Ph; **2b**, R = Me). They are the intermediates that incorporate a second diyne reagent to give **3** and **4**. The structural parameters of intermediate **2b** have been obtained from DFT calculations.

Keywords: Ruthenium; Cluster compounds; Hydrocarbyl ligands; Alkenyl ligands; Diynes

1. Introduction

Alkenyl groups are important ligands in organometallic chemistry because they are related to many metal-mediated transformations of alkynes and alkenes. However, to date, the number of reports dealing with triruthenium carbonyl cluster complexes containing alkenyl ligands is relatively small [1–9], despite the fact that some of these clusters have been recognized as intermediates or as catalyst precursors for alkyne–alkene codimerization [8] and alkyne hydrogenation [9], dimerization [2b], polymerization [2b] and hydroformylation [2c] processes.

In the context of alkenyl triruthenium complexes, we have recently revisited the studies of Hansel and Vahrenkamp [4] on the reactivity of the Süss-Fink's hydrazido-bridged hydrido carbonyl triruthenium complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(CO)_9]$ [10] (**A**) with terminal and internal alkynes without α-hydrogen atoms, showing that the products may have alkenyl ligands in edge-bridging or face-capping positions (**B** and **C**, respectively, in Scheme 1) [5]. We have also reported that alkynes with α-hydrogen atoms react with complex **A** to give trinuclear derivatives that may contain edge-bridging allyl ligands (**D** and **E** in Scheme 1) [6]. In all cases, the nature of the substituents of the alkyne reagent strongly affects the stability of each product and the regioselectivity of the reactions [5,6].

We have shown that face-capped alkenyl clusters of type **B** react with alkynes to give unprecedented trinuclear

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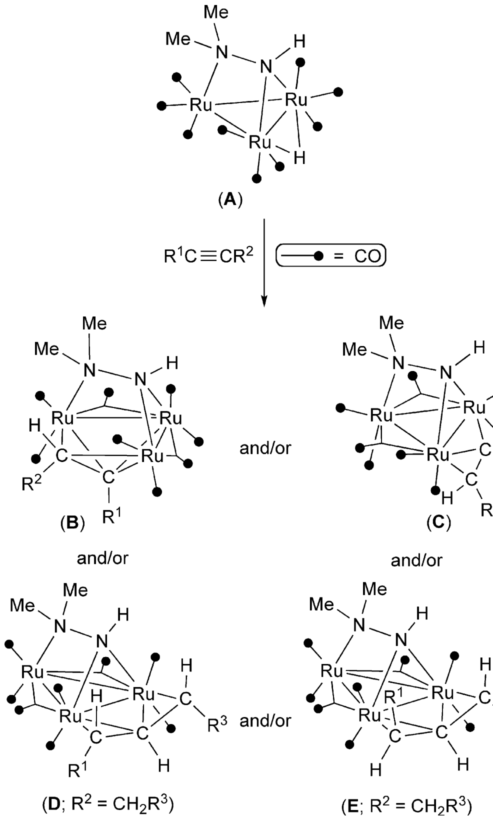


Scheme 1. Reactivity of cluster **A** with alkynes.

clusters with edge-bridging parallel alkyne or edge-bridging vinylidene ligands, in which the original alkenyl ligand remains intact [7]. Edge-bridging dienoyl derivatives that arise from a three-component coupling of alkyne, alkenyl and carbonyl ligands have also been isolated from these reactions [7]. These interesting results prompted us to continue investigating the reactivity of trinuclear alkenyl cluster complexes with alkyne reagents.

We now report our results on the reactivity of $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu\text{-}CO)_2(CO)_6]$ (**1**), an edge-bridged alkenyl cluster of type **C** ($R^1 = R^2 = Ph$; Scheme 1), with conjugated diynes. These reactions afforded remarkable products containing large hydrocarbyl ligands that arise from the coupling of two diyne molecules via a face-capping κ^2-diyne intermediate. Although, we have also investigated the reactivity of compound **1** with various monoalkynes, these experiments led to mixtures of many products that could not be satisfactorily separated and characterized.

2. Results and discussion

The reaction of the alkenyl cluster complex $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu\text{-}CO)_2(CO)_6]$ (**1**) with diphenylbutadiyne (1:1.1 mol ratio, toluene, reflux temperature, 30 min) gave a mixture of three products, $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu_3\text{-}\kappa^2\text{-}PhCCCCPh)(CO)_7]$ (**2a**), $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}PhCCCC(Ph)C(Ph)CCCPh\}(CO)_6]$ (**3a**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}PhCCCC(Ph)C(CCPh)CPh\}(CO)_6]$ (**4a**), which were separated by preparative TLC and isolated in 10%, 25% and 21% yields, respectively (Scheme 2). The use of a larger amount of diyne reagent (1:2.2 mol ratio) resulted in a lower yield of **2a** (4%) and higher yields of **3a** and **4a** (38% and 26%, respectively).

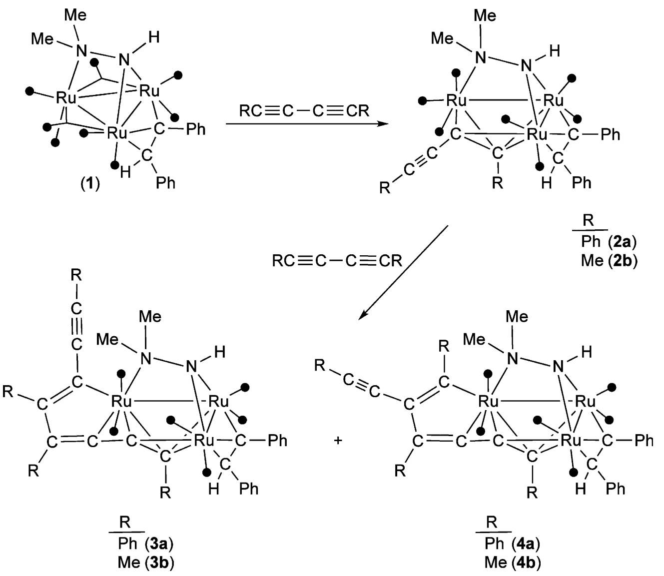
Complex **1** was also treated with 2,4-hexadiyne (toluene, reflux temperature, 30 min, 1:4.2 mol ratio). In this case, the products $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu_3\text{-}\kappa^2\text{-}MeCCCCMe)(CO)_7]$ (**2b**), $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}MeCCCC(Me)C(Me)CCCMe\}(CO)_6]$ (**3b**) and $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}MeCCCC(Me)C(CCMe)CMe\}(CO)_6]$ (**4b**) were separated by column chromatography and isolated in yields of 10%, 36% and 28%, respectively (Scheme 2).

In subsequent experiments we determined that compounds **2a** and **2b** are intermediates in the processes that lead to **3a**/**4a** and **3b**/**4b**, respectively, since treatment of **2a** with diphenylbutadiyne and **2b** with 2,4-hexadiyne, in toluene at reflux temperature, led to **3a**/**4a** and **3b**/**4b**, respectively.

All these results clearly indicate that the regioselectivity of the reactions is little influenced by the nature of the substituents of the 1,3-diyne reagent.

The positive-ion FAB mass spectra of all these products show the group of molecular ion peaks corresponding to their formulation, each group of peaks with the correct isotopomeric abundance. The product composition was also confirmed by CNH microanalysis.

Compound **3a** was characterized by X-ray diffraction (Fig. 1). A selection of interatomic distances is given in Table 1. The metallic skeleton can be described as an open triangle of ruthenium atoms, in which the Ru(2)–Ru(3) edge is more than 1 Å longer than the other two. A 1,1-dimethylhydrazido ligand caps one side of the metallic triangle while a 1,2-diphenylethenyl ligand spans the same



Scheme 2. Reactivity of compound **1** with diynes.

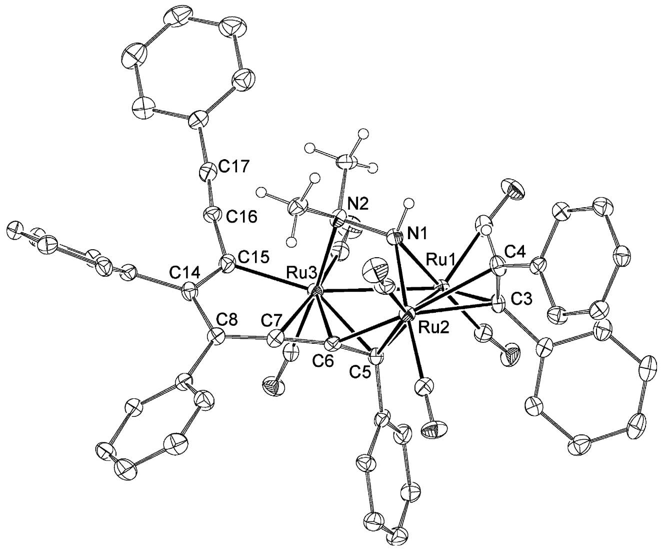


Fig. 1. Molecular structure of compound **3a**. Ellipsoids are drawn at the 30% probability level.

Table 1
Selected interatomic distances (Å) in compound **3a**

Ru(1)–Ru(2)	2.6993(6)	Ru(1)–Ru(3)	2.9228(6)
Ru(2)–Ru(3)	3.9945(6)	N(1)–Ru(1)	2.112(5)
N(1)–Ru(2)	2.104(5)	N(2)–Ru(3)	2.184(5)
N(1)–N(2)	1.463(7)	C(3)–Ru(1)	2.081(6)
C(3)–Ru(2)	2.284(5)	C(3)–C(4)	1.399(9)
C(4)–Ru(2)	2.370(6)	C(5)–Ru(1)	2.230(5)
C(5)–Ru(2)	2.332(6)	C(5)–Ru(3)	2.247(6)
C(5)–C(6)	1.410(8)	C(6)–Ru(2)	2.101(5)
C(6)–Ru(3)	2.301(5)	C(6)–C(7)	1.335(8)
C(7)–Ru(3)	2.235(5)	C(7)–C(8)	1.361(8)
C(8)–C(14)	1.481(8)	C(14)–C(15)	1.382(8)
C(15)–Ru(3)	2.117(6)	C(15)–C(16)	1.424(9)
C(16)–C(17)	1.200(9)		

edge as the amido fragment of the hydrazido ligand. A new ligand, which consists of an 8-carbon chain containing four phenyl groups on the carbon atoms C(5), C(8), C(14) and C(17), caps the remaining face of the metal triangle in such a way that it is attached to Ru(1)–C(5), to Ru(2)–C(5) and C(6) and to Ru(3)–C(5), C(6), C(7) and C(15). A detailed analysis of the C–C bond distances of this hydrocarbyl ligand suggests that it can be formally described as a resonance hybrid of two idealized canonical forms, namely, a 1,4,5,8-tetraphenylocta-3,5-dien-1-yn-6-yl and a 1,4,5,8-tetraphenylocta-1,2,3,5-tetraen-1,6-diyl. The cluster shell is completed by six terminal CO ligands, two on each metal atom. If the hydrocarbyl ligand contributes six electrons, this cluster obeys the EAN rule, since it is a 50-electron trinuclear species with two metal–metal bonds.

Compound **4a** could not be crystallized, but the similarity of the carbonyl region of its IR spectrum with that of **3a** undoubtly indicates that both clusters have the same arrangement of CO ligands. They also have the same molecular weight (FAB MS) and very similar ^{1}H NMR spectra. With these data, we propose that **3a** and **4a** differ in the nature of their hydrocarbyl ligand (Scheme 2). If the ligand of **3a** arises from a head-to-head coupling of two diphenylbutadiyne molecules, that of **4a** should arise from a head-to-tail coupling.

All the spectroscopic (IR, ^{1}H NMR) and analytical (FAB MS, microanalysis) data of the 2,4-hexadiyne-derived compounds **3b** and **4b** are very similar, indicating that both compounds are isomers. The band pattern of the carbonyl region of their IR spectra is also related to that of **3a** and **4a**. Therefore, they should also be structurally related to these complexes. These data are not enough to unambiguously establish the structures of **3b** and **4b**. However, the order of elution of each product in the corresponding chromatographic separation supports the structural assignment shown in Scheme 2. As **4a** is eluted faster than **3a** and both are eluted faster than **2a**, it is reasonable to propose that the elution order of the products of the reaction of compound **1** with 2,4-hexadiyne should be **4b**, **3b** and **2b**, since the components of each of the pairs **4a/4b**, **3a/3b** and **2a/2b** should be structurally related.

The analytical and spectroscopic data of compounds **2a** and **2b** indicate that they contain one equivalent of the corresponding diyne in addition to one 1,1-dimethylhydrazido, one 1,2-diphenylethenyl and seven CO ligands. Their IR spectra confirm that they have a common ligand arrangement. Considering that **2a** and **2b** react with more diyne to give **3a/4a** and **3b/4b**, respectively, and knowing the structure of **3a**, we propose that the diynes of **2a** and **2b** cap the metal triangles through only one of the alkyne moieties, in the same way as the face-capping alkyne fragment of compound **3a**.

Two isomeric structures, which differ in the placement of the R and RCC groups on the coordinated alkyne moiety but maintain the positions of the remaining ligands, are possible for compounds **2a** and **2b**. However, only that depicted in Scheme 2, that has the uncoordinated alkynyl group close to the open Ru–Ru edge, would be able to react with more diyne to give products such as **3a** and **3b** or **4a** and **4b**.

In order to know the geometrical parameters of such a structure, we carried out DFT calculations on compound **2b**, which has terminal methyl groups on the diyne moiety. The optimized structure is shown in Fig. 2. A selection of calculated interatomic distances is given in Table 2. The structure of this molecule is related to that of compound **3a**, the major differences being that (a) **2b** has an additional CO ligand on Ru(3), in the equatorial position occupied by the hydrocarbyl ligand in **3a**, (b) the hydrocarbyl ligand of **2b** is a face-capping perpendicular alkyne with a pendant alkynyl moiety, and (c) the metal atoms of the open edge of **2b** are 0.27 Å closer to each other than those of **3a**.

Trinuclear clusters containing a face-capping alkyne ligand with the alkyne moiety perpendicular to one of the metal–metal edges are rare [11] and, as far as we are aware, none of them is an open cluster. Trinuclear clusters capped by alkyne ligands that have the alkyne moiety parallel to a metal–metal edge are much more common [11a,11b,12].

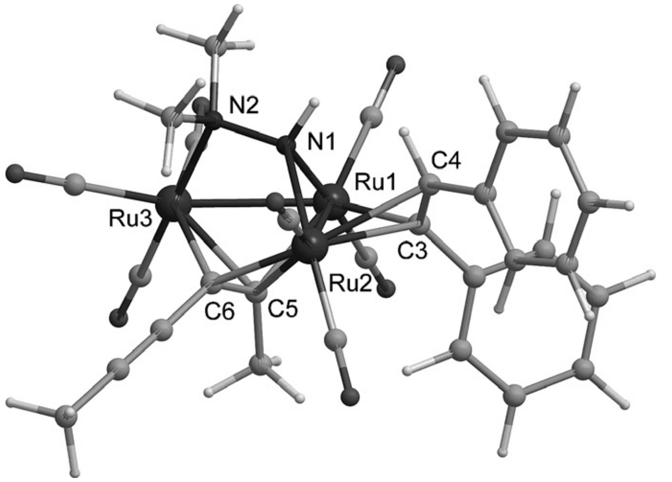


Fig. 2. DFT-Optimized molecular structure of compound **2b** (B3LYP/6-31G/LanL2DZ).

Table 2
Selected interatomic distances (Å) in compound **2b** (DFT calculations)

Ru(1)–Ru(2)	2.75	C(3)–C(4)	1.39
Ru(1)–Ru(3)	2.93	C(4)–Ru(2)	2.50
Ru(2)–Ru(3)	3.72	C(5)–Ru(1)	2.26
N(1)–Ru(1)	2.15	C(5)–Ru(2)	2.39
N(1)–Ru(2)	2.13	C(5)–Ru(3)	2.33
N(2)–Ru(3)	2.25	C(6)–Ru(2)	2.15
N(1)–N(2)	1.45	C(6)–Ru(3)	2.37
C(3)–Ru(1)	2.13	C(5)–C(6)	1.38
C(3)–Ru(2)	2.44		

Therefore, the large hydrocarbyl ligands of **3a**/**3b** and **4a**/**4b** are formed by coupling of one alkyne moiety of an entering diyne reagent with the Ru(3) atom and the pendant alkyne fragment of **2a**/**2b**. A carbonyl ligand is released in these processes. Although the hydrocarbyl ligands of compounds **3a**/**3b** and **4a**/**4b** are unprecedented, the coupling of two diyne molecules onto trinuclear cluster complexes have been previously reported in a few occasions [13].

The alkenyl ligand of compound **1** does not get involved in coupling reactions with the diynes. This is curious. In fact, it has been reported that some clusters having enynyl ligands react with diynes to give large hydrocarbyl ligands [14] and that some enynes can be prepared by coupling of alkenyl ligands with alkynes on triruthenium clusters [2b].

The hydrazido ligand of the cluster complexes described herein is not a simple spectator. On the contrary, although it is not directly involved in the cluster transformations, it efficiently anchors the metal atoms, preventing cluster fragmentation processes [15], and favors the selective substitution of CO ligands [16].

3. Experimental

3.1. General synthetic and characterization data

Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. Complex **1** was prepared by published method [5]. The remaining reagents were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin–Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument, at 293 K, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; the *m*/*z* value given for a molecular ion corresponds to that of the most abundant isotopomer.

*3.2. Reaction of complex **1** with diphenylbutadiyne*

A toluene solution (20 mL) of compound **1** (50 mg, 0.065 mmol) and diphenylbutadiyne (15 mg, 0.072 mmol) was stirred at reflux temperature for 30 min. The color changed from red-orange to black. The solvent was removed under reduced pressure, the residue was dissolved into dichloromethane (1 mL) and the resulting solution was applied onto preparative TLC plates. Hexane-dichloromethane (1:1) eluted several bands. They all were worked-up extracting them into dichloromethane. The products were precipitated with hexane. The first band, black, gave $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}PhCCCC(Ph)C(CCPh)CPh\}(CO)_6]$ (**4a**) (15 mg, 21%). The second band, red-orange, contained some starting material **1**. The third band, black, gave $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)\{\mu_3\text{-}\kappa^4\text{-}PhCCCC(Ph)C(Ph)\text{-}CCCPh\}(CO)_6]$ (**3a**) (18 mg, 25%). The fourth band, orange, gave $[Ru_3(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}\kappa^2\text{-}PhCHCPh)(\mu_3\text{-}\kappa^2\text{-}PhCCCCPh)(CO)_7]$ (**2a**) (6 mg, 10%). A similar reaction compound **1** (50 mg, 0.065 mmol) with a larger amount of diphenylbutadiyne (30 mg, 0.142 mmol) afforded the same products, **4a** (26%), **3a** (38%) and **2a** (4%). *Data for **2a***: Calc. for $C_{39}H_{28}N_2O_7Ru_3$ (939.86): C, 49.84; H, 3.00; N, 2.98. Found: C, 49.90; H, 3.08; N, 2.90%. FAB MS: *m*/*z* 941 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2059 (w), 2023 (m), 2008 (s), 1991 (m, sh), 1965 (m, br), 1944 (w, sh). ^1H NMR ($CDCl_3$): δ 8.17 (m, 2H, Ph), 7.20 (m, 16H, Ph), 8.61 (m, 2H, Ph), 4.40 (s, 1H, C*H*), 2.78 (s, 6H, 2 Me), 1.41 (s, 1H, N*H*). *Data for **3a***: Calc. for $C_{54}H_{38}N_2O_6Ru_3$ (1114.12): C, 58.22; H, 3.44; N, 2.51. Found: C, 58.25; H, 3.48; N, 2.47%. FAB MS: *m*/*z* 1115 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2043 (w), 2026 (s), 2004 (s), 1973 (m, br), 1941 (w, br). ^1H NMR ($CDCl_3$): δ 7.28 (m, 30H, 6 Ph), 4.59 (s, 1H, C*H*), 2.91 (s, 3H, Me), 2.20 (s, 3H, Me), 1.76 (s, 1H, N*H*). *Data for **4a***: Calc. for $C_{54}H_{38}N_2O_6Ru_3$ (1114.12): C, 58.22; H, 3.44; N, 2.51. Found: C, 58.34; H, 3.51; N, 2.43%. FAB MS: *m*/*z* 1115 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2047 (w), 2026 (s), 2002 (s), 1974 (m, br), 1940 (w, br). ^1H NMR ($CDCl_3$): δ 7.24 (m, 30H, 6 Ph), 6.49 (s, 1H, C*H*), 2.27 (s, 3H, Me), 1.69 (s, 3H, Me), 1.07 (s, 1H, N*H*).

3.3. Reaction of complex **1** with 2,4-hexadiyne

A toluene solution (20 mL) of compound **1** (50 mg, 0.065 mmol) and 2,4-hexadiyne (21 mg, 0.274 mmol) was stirred at reflux temperature for 30 min. The color changed from red-orange to black. The solution was concentrated under reduced pressure to ca. 5 mL and the resulting solution was supported on silica gel (4 g). The solid was placed onto a silica gel chromatography column (15 × 3 cm) packed in hexane. Hexane-diethyl ether (20:1) eluted the first band, black, which gave $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-}\kappa^2\text{-PhCHCPh})\{\mu_3\text{-}\kappa^4\text{-MeCCCC(Me)C(CCMe)CMe}\}(CO)_6]$ (**4b**) (16 mg, 28%). Hexane-diethyl ether (5:1) eluted two bands. The first band, very dark green, afforded $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-}\kappa^2\text{-PhCHCPh})\{\mu_3\text{-}\kappa^4\text{-MeCCCC-(Me)- C(Me)CCCMe}\}(CO)_7]$ (**3b**) (20 mg, 36%). The following band, orange, gave $[Ru_3(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-}\kappa^2\text{-PhCHCPh})\ (\mu_3\text{-}\kappa^2\text{-MeCCCCMe})(CO)_6]$ (**2b**) (6 mg, 10%). *Data for **2b***: Calc. for $C_{29}H_{24}N_2O_7Ru_3$ (815.72): C, 42.70; H, 2.97; N, 3.43. Found: C, 42.75; H, 3.05; N, 3.38%. FAB MS: *m/z* 817 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2051 (w), 2010 (m), 2002 (s), 1958 (m, br), 1940 (w, sh). ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 10H, 2 Ph), 4.39 (s, 1H, C*H*), 2.79 (s, 9H, 3 Me), 1.52 (s, 3H, Me), 1.37 (s, 1H, N*H*). *Data for **3b***: Calc. for $C_{34}H_{30}N_2O_6Ru_3$ (865.82): C, 47.17; H, 3.49; N, 3.24. Found: C, 47.10; H, 3.42; N, 3.30%. FAB MS: *m/z* 867 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2036 (w), 2020 (vs), 1996 (s), 1968 (m, br), 1935 (m, br). ^{1}H NMR ($CDCl_3$): δ 7.04 (m, 10H, 2 Ph), 4.44 (s, 1H, C*H*), 2.83 (s, 3H, Me), 2.70 (s, 3H, Me), 2.27 (s, 6H, 2 Me), 2.09 (s, 3H, Me), 1.88 (s, 3H, Me), 1.43 (s, 1H, N*H*). *Data for **4b***: Calc. for $C_{34}H_{30}N_2O_6Ru_3$ (865.82): C, 47.17; H, 3.49; N, 3.24. Found: C, 47.23; H, 3.35; N, 3.30%. FAB MS: *m/z* 867 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2036 (w), 2019 (vs), 1993 (s), 1969 (m, br), 1931 (m, br). ^{1}H NMR ($CDCl_3$): δ 7.31 (m, 10H, 2 Ph), 6.32 (s, 1H, C*H*), 2.97 (s, 3H, Me), 2.55 (s, 3H, Me), 2.21 (s, 3H, Me), 2.04 (s, 3H, Me), 2.01 (s, 3H, Me), 1.39 (s, 3H, Me), 0.80 (s, 1H, N*H*).

3.4. X-ray diffraction data

Suitable dark red crystals of **3a** were obtained by slow diffusion of hexanes into a dichloromethane solution of the complex. Diffraction data were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera on a κ-goniostat, using graphite-monochromated Cu Kα radiation. Relevant crystal, measurement and refinement data are given in Table 3. An empirical absorption correction was applied using XABS2 [17], with max and min transmission factors of 0.655 and 0.499, respectively. The structure was solved by Patterson interpretation using the program 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. The NH and alkenyl CH hydrogen atoms were located in the corresponding Fourier maps, their thermal parameters were fixed and their remaining parameters were refined. The remaining hydrogen atom positions were geometrically calculated and refined riding on their parent atoms. Molecular plots were made with PLATON [20]. The WINGX program system [21] was used throughout the structure determination.

Table 3
Selected crystal, measurement and refinement data for **3a**

Formula	$C_{54}H_{38}N_2O_6Ru_3$
Formula weight	1114.07
Colour, habit	Dark red, prism
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.3636(5)
b (Å)	12.3403(7)
c (Å)	18.5588(9)
α (°)	86.489(4)
β (°)	78.722(3)
γ (°)	81.311(3)
V (Å^3)	2299.7(2)
Z	2
F(000)	1112
D_{calc} (g cm^{-3})	1.609
Radiation	Cu Kα
μ (mm^{-1})	8.310
Crystal size (mm)	0.18 × 0.08 × 0.05
Temperature (K)	150(2)
θ limits (°)	2.43–68.47
Min/max h,k,l	−12/11, −14/14, −22/22
Collected reflections	31356
Unique reflections	8416
Reflections with $I > 2\sigma(I)$	6710
Parameters/restraints	592/0
Goodness-of-fit on F^2	1.072
R_1 (on F, $I > 2\sigma(I)$)	0.0493
wR_2 (on F^2, all data)	0.1628
Max/min $\Delta\rho$ (e Å^{-3})	1.851/−1.027

3.5. Computational details

The optimization of the structure of compound **2b** was performed by hybrid DFT, within the GAUSSIAN-03 program suite [22], using the Becke's three-parameter hybrid exchange-correlation functional [23] and the B3LYP nonlocal gradient correction [24]. The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms [25]. The basis set used for the remaining atoms was the standard 6-31G, with addition of (d, p)-polarization for all atoms. The structure shown in Fig. 2 was confirmed as an energy minimum by calculation of analytical frequencies. The input model molecule was based on the X-ray structure of compound **3a**, conveniently modified by manually adding or removing the appropriate atoms.

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Appendix A. Supplementary material

CCDC 648829 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.024.

References

[1] (a) J.A. Cabeza, S. García-Granda, A. Llamazares, V. Riera, J.F. Van der Maelen, Organometallics 12 (1993) 157;
(b) J.A. Cabeza, S. García-Granda, A. Llamazares, V. Riera, J.F. Van der Maelen, Organometallics 12 (1993) 2973;
(c) P. Briard, J.A. Cabeza, A. Llamazares, L. Ouahab, V. Riera, Organometallics 12 (1993) 1006;
(d) S. Álvarez, P. Briard, J.A. Cabeza, I. del Río, J.M. Fernández-Colinas, F. Mulla, L. Ouahab, V. Riera, Organometallics 13 (1994) 4360;
(e) J.A. Cabeza, A. Llamazares, V. Riera, P. Briard, L. Ouahab, J. Organomet. Chem. 480 (1994) 205;
(f) J.A. Cabeza, J.M. Fernández-Colinas, A. Llamazares, V. Riera, S. García-Granda, J.F. Van der Maelen, Organometallics 13 (1994) 4352.

[2] (a) N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Liimatta, J.J. Bonnet, Organometallics 11 (1992) 1351;
(b) P. Nombel, N. Lugan, F. Mulla, G. Lavigne, Organometallics 13 (1994) 4673;
(c) P. Nombel, N. Lugan, B. Donnadieu, G. Lavigne, Organometallics 18 (1999) 187.

[3] (a) V. Ferrand, K. Merzweiler, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, J. Organomet. Chem. 549 (1997) 263;
(b) V. Ferrand, C. Gambs, N. Derrien, C. Bolm, H. Stoeckli-Evans, G. Süss-Fink, J. Organomet. Chem. 549 (1997) 275;
(c) V. Ferrand, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, Inorg. Chem. Commun. 2 (1999) 561.

[4] B. Hansert, H. Vahrenkamp, Chem. Ber. 126 (1993) 2017.

[5] J.A. Cabeza, I. del Río, J.M. Fernández-Colinas, S. García-Granda, L. Martínez-Méndez, E. Pérez-Carreño, Chem. Eur. J. 10 (2004) 6265.

[6] J.A. Cabeza, I. del Río, S. García-Granda, L. Martínez-Méndez, E. Pérez-Carreño, Chem. Eur. J. 11 (2005) 6040.

[7] J.A. Cabeza, I. del Río, L. Martínez-Méndez, E. Pérez-Carreño, Chem. Eur. J. 12 (2006) 7694.

[8] N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Liimatta, J.J. Bonnet, J. Am. Chem. Soc. 112 (1990) 8607.

[9] Latest review on alkyne hydrogenation mediated by triruthenium carbonyl cluster complexes J.A. Cabeza, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley–VCH, Weinheim, Germany, 1999, p. 715.

[10] T. Jenke, H. Stoeckli-Evans, G. Süss-Fink, J. Organomet. Chem. 391 (1990) 395.

[11] See, for example (a) E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203;
(b) M.J. Mays, P.R. Raithby, K. Sarveswaran, G.A. Solan, J. Chem. Soc., Dalton Trans. (2002) 1671;
(c) J.F. Blount, L.F. Dahl, C. Hoogzand, W. Hübel, J. Am. Chem. Soc. 88 (1966) 292;
(d) V. Busetti, G. Granozzi, S. Aime, R. Gobetto, P.A. Dolby, M.M. Harding, A.K. Smith, J. Chem. Soc., Chem. Commun. (1987) 1829;
(e) S. Rivomanana, C. Mongin, G. Lavigne, Organometallics 15 (1996) 1195.

[12] See, for example (a) L. Busetto, M. Green, B. Hessner, J.A.K. Howard, J.C. Jeffrey, M.R. Mills, F.G.A. Stone, P. Woodward, J. Chem. Soc., Chem. Commun. (1981) 1101;
(b) J.R. Shapley, T.J. Parks, M.R. Churchill, C. Bueno, H.J. Wasserman, J. Am. Chem. Soc. 103 (1981) 7385;
(c) D. Lentz, M. Reuter, Chem. Ber. 124 (1991) 773;
(d) D. Nuel, F. Dahan, R. Mathieu, Organometallics 4 (1985) 1436.

[13] (a) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Inorg. Chim. Acta 250 (1996) 129;
(b) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Aust. J. Chem. 51 (1998) 165;
(c) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Russ. Chem. Bull. 47 (1998) 983;
(d) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Organomet. Chem. 558 (1998) 197;
(e) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, J. Organomet. Chem. 536–537 (1997) 93;
(f) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Organomet. Chem. 650 (2002) 188;
(g) S.P. Tunik, E.V. Grachova, V.R. Denisov, G.L. Starova, A.B. Nikol'skii, F.M. Dolgushin, A.I. Yanovsky, Y.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 339;
(h) C.S.W. Lau, W.T. Wong, J. Chem. Soc., Dalton Trans. (1999) 2511.

[14] (a) J.A. Cabeza, I. del Río, M. Moreno, S. García-Granda, M. Pérez-Priede, V. Riera, Eur. J. Inorg. Chem. (2002) 3204;
(b) J.A. Cabeza, I. del Río, S. García-Granda, L. Martínez-Méndez, M. Moreno, V. Riera, Organometallics 22 (2003) 1164;
(c) J.A. Cabeza, I. del Río, S. García-Granda, G. Lavigne, N. Lugan, M. Moreno, P. Nombel, M. Pérez-Priede, V. Riera, A. Rodríguez, J.F. van der Maelen, Chem. Eur. J. 7 (2001) 2370.

[15] J.A. Cabeza, Eur. J. Inorg. Chem. (2002) 1159.

[16] J.A. Cabeza, I. del Río, S. García-Granda, L. Martínez-Méndez, V. Riera, J. Organomet. Chem. 663 (2002) 227.

[17] S. Parkin, B. Moezzi, H. Hope, J. Appl. Cryst. 28 (1995) 53.

[18] P.T. Beurskens, G. Beurskens, W.P. Bosman, R. de Gelder, S. García-Granda, R.O. Gould, J.M.M. Smits, The DIRDIF-96 Program System, Crystallography Laboratory of the University of Nijmegen, Nijmegen, The Netherlands, 1996.

[19] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.

[20] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, University of Utrecht, Utrecht, The Netherlands, 2003.

[21] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN-03 (Revision C2), Gaussian Inc., Wallingford, CT, USA, 2004.

[23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[24] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[25] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.