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Methylidyne–diyne coupling reactions onto a triruthenium cluster core

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Dedicated to Professor Rafael Usón, an outstanding pioneer of Spanish organometallic chemistry

Abstract

Treatment of the methoxymethylidyne-bridged triruthenium cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ (**1**) with the symmetric diynes $RC{\equiv}CC{\equiv}CR$ (R = Me, Ph, CH_2OPh) led to separable mixtures of two regioisomers, $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCCR{=}CC{\equiv}CR)(CO)_9]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(C{\equiv}CR){=}CR)(CO)_9]$. These products arise from the insertion of one of the alkyne moieties of the corresponding diyne into a Ru–C bond of the methylidyne ligand. In all cases, the second alkyne functionality remains uncoordinated. In contrast, the reactions of the trihydride cluster $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ (**2**) with diphenylbutadiyne led to a mixture of regioisomers in which one alkyne group of the original diyne has inserted into a Ru–C bond of the methylidyne ligand while the remaining triple bond has been hydrogenated to a double bond. The X-ray structures of the two regioisomers formed in the reaction of **1** with 2,4-hexadiyne are reported.

Keywords: Ruthenium; Clusters; Methylidyne ligands; Diynes; Insertion reactions

1. Introduction

Since the early 1980s, a rapid development of the synthetic chemistry of the methylidyne cluster complexes $[M_3(\mu\text{-}H)(\mu\text{-}CX)(CO)_{10}]$ and $[M_3(\mu\text{-}H)_3(\mu\text{-}CX)(CO)_9]$ (M = Ru or Os; X = a monovalent group) has provided a large number of clusters of these types [1]. Their reactivity, which has also been extensively studied, generally involves: (a) modification of the alkylidyne substituent; (b) ligand substitution or addition at the metal; (c) protonation and deprotonation reactions; (d) reductive elimination of CX groups; and (e) insertion of unsaturated molecules into the M–CX bond [1].

In this context, the reactions of the methylidyne-bridged triruthenium clusters $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ (**1**) and $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ (**2**) toward alkynes have been studied [2]. The interesting reactivity patterns observed, which involve C–C bond forming reactions along with hydrogenation processes made these complexes to be regarded as potential models for Fischer–Tropsch chain growth [2].

Recently, our group has been paying significant attention to the reactivity of diynes toward ruthenium carbonyl cluster complexes [3]. This research activity has been motivated by the fact that, to date, only a few reactions of ruthenium clusters with diynes have appeared in the literature [3–5], though these polyunsaturated molecules are expected to be more reactive than monoalkynes and, therefore, lead to a richer derivative chemistry. In the course of these studies, results of special note were found, including C–C [3] and C–N [3e] bond-forming reactions and unprece-

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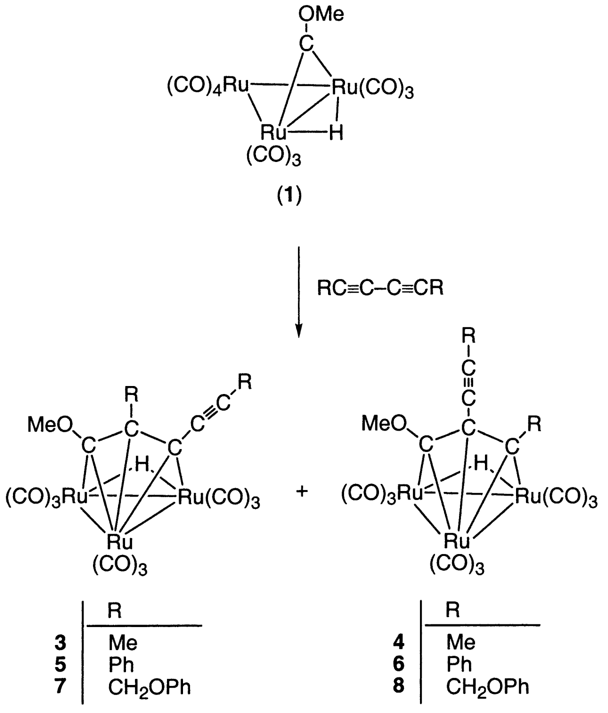
dented cluster mediated [3+2] cycloaddition processes [3c].

With these facts in mind, we embarked on the study of the reactivity of **1** and **2** with conjugated diynes. In the present work, we report on the synthesis of trinuclear ruthenoallyl cluster complexes formed by insertion of one of the alkyne moieties of diyne ligands into a Ru–C bond of the methylidyne ligand. Hydrogenation of the second alkyne group of the diyne ligands to the corresponding alkene is observed when the trihydride cluster **2** is used as starting material. The X-ray structures of the two regioisomers formed in the reaction of **1** with 2,4-hexadiyne are also described.

2. Results and discussion

When complex **1** was treated with a stoichiometric amount of diphenylbutadiyne, 2,4-hexadiyne or 1,6-diphenoxy-2,4-hexadiyne, 1:1 mixtures of the two possible insertion regioisomers, $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCCR{=}CC{\equiv}CR)(CO)_9]$ (R = Me, **3**; Ph, **5**; CH_2OPh, **7**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(C{\equiv}CR){=}CR)(CO)_9]$ (R = Me, **4**; Ph, **6**; CH_2OPh, **8**) were obtained (Scheme 1). In all cases, other products were also formed in lower yields. The pure regioisomers were separated by TLC.

The elemental analyses and mass spectra of compounds **3**–**8** clearly indicated their trinuclear nature, while their IR spectra displayed similar patterns in the carbonyl stretching region, suggesting analogous ligand arrangements. Their ^1H NMR spectra showed the incorporation of one molecule of diyne *per* cluster. In all cases, the signal corresponding to the hydrogen atoms of the original methylidyne ligand appeared as a singlet at $\delta \approx 4$ ppm, while a singlet resonance at high field ($\delta \approx -19.5$ ppm) indicated the presence of a hydride ligand.



Scheme 1.

Although all these data are in accordance with the structures proposed for **3**–**8** in Scheme 1, they were not enough to unambiguously determine the ligand disposition within the cluster shell. Therefore, two regioisomers, the couple **3** and **4**, were analyzed by X-ray diffraction methods. Molecular plots for these complexes are shown in Figs. 1 and 2, respectively. A selection of bond distances is listed in Table 1. For comparison purposes, a common labeling scheme has been used in both structures where possible.

The structure of **3** consists of a triruthenium core triply bridged by an allyl ligand which arises from the insertion of an alkyne group of the incoming diyne into a Ru–C bond of the original methylidyne moiety. This ligand binds Ru(2) through its three allylic carbon atoms, C(1), C(15) and C(16) in a π-fashion, being formally σ-bonded to Ru(1) and Ru(3). The bond distances Ru(1)–C(1), 2.074(4), and Ru(3)–C(15), 2.082(6) Å, are shorter than those corresponding to Ru(2)–C(1), Ru(2)–C(15) and Ru(2)–C(16), 2.403(6), 2.278(9) and 2.309(10) Å, respectively, accordingly with a stronger σ-interaction in the first two cases. These bond distances are comparable to those reported previously for analogous triruthenium allylic systems [6]. The bond distances within the allyl fragment, C(1)–C(16), 1.443(7) Å and C(16)–C(15), 1.427(6) Å, are similar, accounting for its electronic delocalization. The central atom of the allylic moiety, C(16), bears a terminal methyl group of the original 2,4-hexadiyne ligand, while C(15) supports the uncoordinated alkyne fragment. A hydride ligand symmetrically spans the Ru(1)–Ru(3) edge, positioned *trans* to two terminal carbonyl ligands. The Ru(1)–Ru(3) distance, 2.934(13) Å, is some 0.15 Å longer than those corresponding to Ru(1)–Ru(2) and Ru(2)–Ru(3), respectively, as observed previously for related systems [6]. The cluster shell is completed with nine terminal CO ligands.

As outlined in Section 4, the structure of **4** suffered from some crystallographic unpleasantness of uncertain nature, giving two possible independent positions for the molecule in the crystal. The major position was treated giving a 90% occupancy to their metal atoms and a 100% occupancy to the remaining atoms, whereas the minor position was treated giving a 10% occupancy to the metal atoms, maintaining unlocated its non-metallic atoms. An entirely analogous problem, the nature of which remains unknown, was found by Keister et al. in the crystals of the related compound $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}$

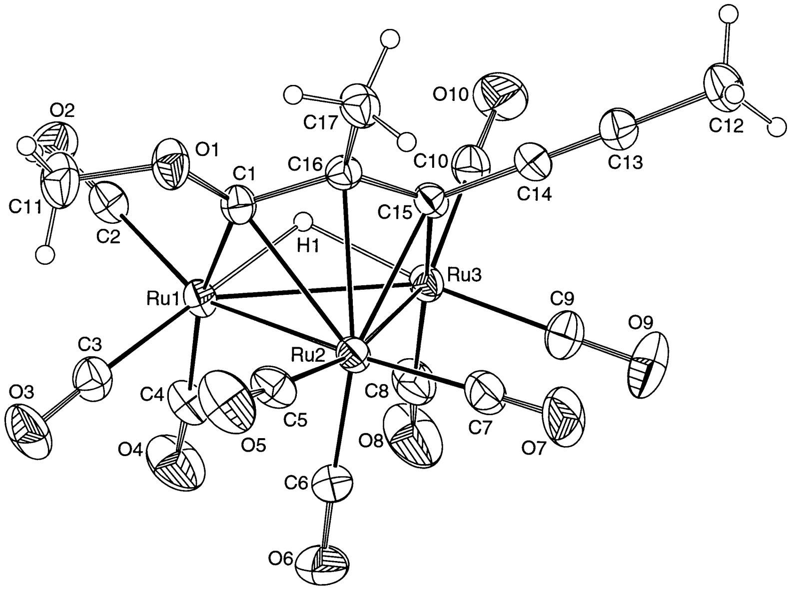


Fig. 1. Molecular structure of compound **3**. Ellipsoids are drawn at the 30% probability level.

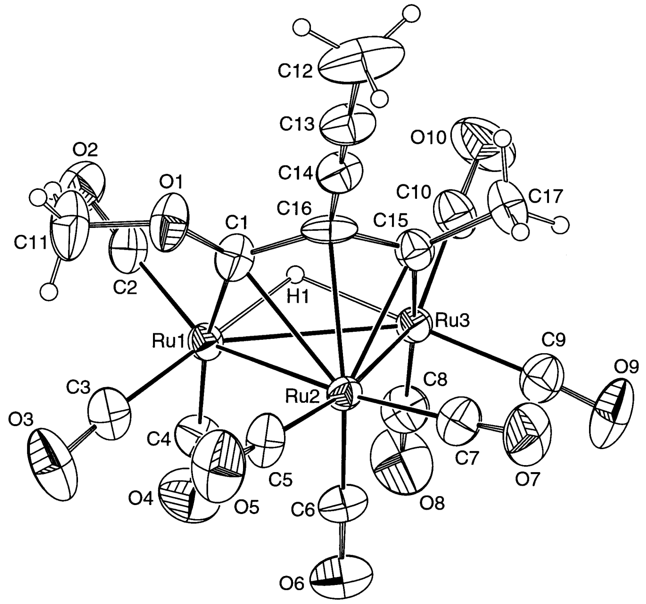


Fig. 2. Molecular structure of compound **4**. Ellipsoids are drawn at the 30% probability level.

Table 1
Selected interatomic distances (Å) in compounds **3** and **4**

	3	**4**
Ru(1)–Ru(2)	2.778(12)	2.784(4)
Ru(1)–Ru(3)	2.934(13)	2.925(3)
Ru(2)–Ru(3)	2.778(12)	2.760(3)
Ru(1)–C(1)	2.074(7)	2.059(12)
Ru(2)–C(1)	2.403(6)	2.423(13)
Ru(2)–C(15)	2.082(6)	2.278(12)
Ru(2)–C(16)	2.309(10)	2.279(12)
Ru(3)–C(15)	2.278(9)	2.088(12)
Ru(1)–H(1)	1.79(5)	1.85(2)
Ru(3)–H(1)	1.75(4)	1.85(2)
C(1)–C(16)	1.443(7)	1.428(18)
C(1)–O(1)	1.364(5)	1.364(14)
C(11)–O(1)	1.415(6)	1.378(16)
C(15)–C(16)	1.427(6)	1.443(18)

MeCCMeCSEt)$(CO)_9$] [6a], for which they performed an analogous structure treatment.

The structure of **4** is similar to that described above for **3**, although in this case the central atom of the allylic fragment supports the uncoordinated alkyne group, while the terminal methyl group is bonded to C(15). The hydride-bridged edge, Ru(1)–Ru(3), is again slightly longer than the other two unbridged edges. In the allylic fragment, the C(1)–Ru(1), C(1)–Ru(2) and C(16)–Ru(2) distances are similar to those found in complex **3**. In contrast, the different substituent at the C(15) atom accounts for the difference of approximately 0.2 Å observed in the C(15)–Ru(2) and C(15)–Ru(3) distances when compared to those in **3**. The remaining structural features are entirely analogous to those described above for **3**.

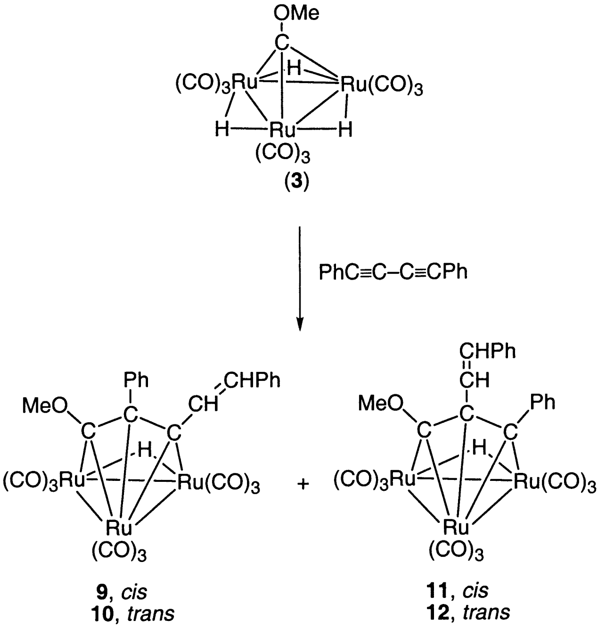
In the case of complexes **5**–**8**, their IR and NMR data strongly indicate that they are isostructural to **3** and **4**, although these data are not enough to unequivocally establish the correct diyne position in each regioisomeric couple. Therefore, the ligand arrangement was assigned by comparison of their TLC elution order. However, a different assignment cannot be completely ruled out.

The reactivity of the trihydride cluster $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ (**2**) towards simple monoalkynes has been reported previously [2]. In these reactions, the first process observed is the hydrogenation of one molecule of alkyne to afford an unsaturated monohydride intermediate that undergoes further reaction with a second molecule of alkyne to give an allylic derivative similar to those obtained when **1** is used as starting material. In our case, the use of diyne ligands instead of simple monoalkynes made possible that these processes took place at the same molecule, leading to novel organic fragments.

Thus, treatment of **2** with diphenylbutadiyne led to derivatives **9**–**12** (Scheme 2), in which the hydrogenation of one of the two alkyne functionalities took place, while the second alkyne group underwent insertion into a Ru–C bond of the methylidyne fragment to afford an allyl fragment similar to those described above. Hydrogenation of the alkene functionality or insertion of the alkene group into a Ru–C bond of the methylidyne were not observed in any case.

The *cis*- and *trans*-alkene isomers of the two alkyne insertion regioisomers were observed in the reaction mixture by ^{1}H NMR spectroscopy, along with small amounts of complexes **5** and **6** and decomposition products. TLC chromatography, using multiple elution with hexanes, allowed the separation of all the insertion regioisomers, but the *cis* and *trans* isomers of the alkene products **9**–**12** were not separated. We managed to obtain most of their ^{1}H NMR data from the spectra of different chromatography fractions. Again, the TLC elution order was used to distinguish between the two couples of insertion regioisomers.

Thus, the reaction pathway seems to be as follows: compound **2** reacts with the diyne to give a mixture of *cis* and *trans* enynes and an unsaturated monohydride cluster intermediate which reacts either with the enynes to give **9**–**12** or with the remaining diyne to give **5** and **6**.



Scheme 2.

3. Conclusions

The results reported herein indicate that when **1** is used as starting material, diynes behave as asymmetric alkynes, since all the isolated products contain a pendant (non-coordinated) alkyne fragment, affording allylic compounds similar to those formed in the reaction of **1** and **2** with mono-alkynes. In contrast, when the trihydride derivative **2** is treated with symmetric diynes, hydrogenation and insertion processes take place at the same diyne molecule, resulting in novel organic fragments. Unfortunately, the isolation of the pure products obtained in this latter reaction has not been accomplished yet.

4. Experimental

4.1. General data

Solvents were dried over sodium benzophenone ketyl (THF, hydrocarbons) or CaH_2 (CH_2Cl_2) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen and were monitored by solution IR and spot TLC. All reagents were obtained from commercial sources. Compounds **1** and **2** were prepared according to literature methods [7]. IR spectra were recorded in solution on a Perkin–Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on AC-200, AC-300 or DPX-300 instruments, using the residual solvent peak as reference. Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

4.2. General procedure for the reactions of 1 with diynes

In a typical reaction, a solution of **1** in THF (50 ml) was stirred at reflux temperature with the appropriate amount of diyne until complete consumption of the starting material **1** (IR monitoring), whereupon the color changed from pale orange to brown. The solvent was concentrated under reduced pressure to approximately 2 ml and the residue was applied onto silica gel preparative TLC plates. Repeated elution with hexanes afforded the products.

4.2.1. Synthesis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(Me){=}CC{\equiv}CMe)(CO)_9]$ (**3**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(C{\equiv}CMe){=}CMe)(CO)_9]$ (**4**)

Reactants: **1** (350 mg, 0.56 mmol); 2,4-hexadiyne (56.5 mg, 0.725 mmol). Reaction time: 2 h 30 min.

Data for **3**: TLC second band (yellow). Yield: 45 mg (12%). IR (CH_2Cl_2) ν_{CO}: 2093(m), 2066(s), 2041(s), 2019(m), 2005(m), 1991(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 3.92$ (s, 3H, O*Me*), 2.19 (s, 3H, *Me*), 2.06 (s, 3H, *Me*), −19.50 (s, 1H, μ-*H*) ppm. ^{13}C{^{1}H) NMR (CD_2Cl_2): $\delta = 232.9$ (*C*OMe); 198.5, 197.5, 192.9, 191.6 (2 C), 189.5 (2C), 189.4 (2 C) (9 *C*Os); 159.4 (*C*), 115.3 (*C*), 103.7 (*C*), 88.9 (*C*); 65.0 (CO*Me*), 22.4 (*Me*), 5.5 (*Me*) ppm. FAB-MS: *m*/*z*: 679 [M^+]. *Anal.* Calc. for $C_{17}H_{10}O_{10}Ru_3$ (677.5): C, 30.13; H, 1.48; Found: C, 30.55; H, 1.63%.

Data for **4**: Yield: 37 mg (10%). TLC band: fourth, yellow. IR (CH_2Cl_2) ν_{CO}: 2092(m), 2065(s), 2040(s), 2022(m), 2006(m), 1992(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 4.04$ (s, 3H, O*Me*), 3.00 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), −19.55 (s, 1H, μ-H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 232.3$ (*C*OMe); 205.6, 197.3, 196.2, 192.5, 191.9, 191.5, 190.3, 190.0, 189.8 (9 *C*Os); 187.6 (*C*), 102.4 (*C*), 90.2 (*C*), 76.6 (*C*); 64.6 (CO*Me*), 39.6 (*Me*), 4.0 (*Me*) ppm. FAB-MS: *m*/*z*: 679 [M^+]. *Anal.* Calc. for $C_{17}H_{10}O_{10}Ru_3$ (677.5): C, 30.13; H, 1.48; Found: C, 30.46; H, 1.59%.

4.2.2. Synthesis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(Ph){=}CC{\equiv}CPh)(CO)_9]$ (**5**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(C{\equiv}CPh){=}CPh)(CO)_9]$ (**6**)

Reactants: **1** (100 mg, 0.16 mmol); diphenylbutadiyne (38.7 mg, 0.20 mmol). Reaction time: 40 min.

Data for **5**: Yield: 20 mg (16%). TLC band: first, yellow. IR (CH_2Cl_2) ν_{CO}: 2096(m), 2071(s), 2042(s), 2027(m), 2013(m), 1990(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 7.22$–6.99 (m, 10 H, *Ph*), 4.12 (s, 3H, O*Me*), −19.56 (s, 1H, μ-H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 226.3$ (*C*OMe); 196.3, 196.0, 191.9, 191.5, 191.4, 190.3, 189.4, 188.6, 188.5 (9 *C*Os); 152.1 (*C*), 105.1 (*C*), 92.5 (*C*), 88.0 (*C*); 130.6, 130.5, 128.7, 128.2, 127.7, 127.6, 127.5, 127.1, 126.0, 125.9, 121.5, 121.3 (2 *Ph*); 64.5 (CO*Me*) ppm. FAB-MS: *m*/*z*: 803 [M^+]. *Anal.* Calc. for $C_{27}H_{10}O_{10}Ru_3$ (801.6): C, 40.45; H, 1.76; Found: C, 40.63; H, 1.61%.

Data for **6**: Yield: 24 mg (18%). TLC band: second, yellow. IR (CH_2Cl_2) ν_{CO}: 2095(m), 2070(s), 2044(s), 2024(m), 2009(m), 1990(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 7.53$–7.10 (m, 10 H, 2 *Ph*), 3.83 (s, 3H, O*Me*), −19.30 (s, 1H, μ-H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 231.8$ (COMe); 205.2, 197.5, 196.2, 191.8, 191.5, 190.7, 190.4, 188.5, 188.3 (9 *C*Os); 154.5 (*C*), 139.9 (*C*), 103.0 (*C*), 98.2 (*C*); 131.2, 130.4, 129.5, 128.0, 127.6, 127.3, 127.0, 126.8, 126.4, 124.0, 123.9, 122.0 (2 *Ph*); 64.7 (CO*Me*) ppm. FAB-MS: *m*/*z*: 803 [M^+]. *Anal.* Calc. for $C_{27}H_{14}O_{10}Ru_3$ (801.6): C, 40.45; H, 1.76; Found: C, 40.72; H, 1.90%.

4.2.3. Synthesis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(CH_2OPh){=}CC{\equiv}CCH_2OPh)(CO)_9]$ (**7**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(C{\equiv}CCH_2OPh){=}CCH_2OPh)(CO)_9]$ (**8**)

Reactants: **1** (100 mg, 0.16 mmol); 1,6-diphenoxy-2,4-hexadiyne (50 mg, 0.20 mmol). Reaction time: 60 min.

Data for **7**: Yield: 28 mg (21%). TLC band: second, yellow. IR (CH_2Cl_2) ν_{CO}: 2096(m), 2068(s), 2040(s), 2020(m), 2007(m), 1988(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 7.50$–7.02 (m, 10H, Ph), 4.78 (s, 2H, C*H*$_2$), 4.77 (d, $J = 13.8$, 1H, C*H*$_2$), 4.69 (d, $J = 13.8$, 1H, C*H*$_2$), 3.97 (s, 3H, O*Me*), −19.43 (s, 1H, μ-H) ppm. FAB-MS: *m*/*z*: 863 [M^+]. *Anal.* Calc. for $C_{29}H_{18}O_{12}Ru_3$ (861.3): C, 40.42; H, 2.10; Found: C, 40.13; H, 2.02%.

Data for **8**: Yield: 20 mg (16%). TLC band: third, yellow. IR (CH_2Cl_2) ν_{CO}: 2096(m), 2071(s), 2042(s), 2027(m), 2013(m), 1990(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 7.50$–7.00 (m, 10H, 2 *Ph*), 5.13 (d, $J = 13.9$, 1H, CH_2), 4.92 (s, 2H, C*H*$_2$), 4.84 (d, $J = 13.9$, 1H, CH_2), 4.02 (s, 3H, O*Me*), −19.70 (s, 1H, μ-H) ppm. FAB-MS: *m*/*z*: 861.9 [M^+]. *Anal.* Calc. for $C_{29}H_{18}O_{12}Ru_3$ (861.3): C, 40.42; H, 2.10; Found: C, 40.74; H, 2.21%.

4.3. Reaction of **2** with diphenylbutadiyne

A solution of **2** (100 mg, 0.166 mmol) in THF (50 ml) was stirred for 3 h at room temperature with 37 mg (0.182 mmol) of diphenylbutadiyne. The color changed to red–brown. The solvent was concentrated under vacuum to approximately 2 ml and the residue was applied onto silica gel preparative TLC plates. Repeated elution with hexanes afforded three yellow bands. The first band contained approximately 5 mg of complex **5**. The second band (12 mg) was a mixture of complexes **6**, **9** and **10** in a 3:10:5 ratio, respectively (^{1}H NMR integration). The third band contained approximately 10 mg of complexes **11** and **12** in a 1:1 ratio.

Selected ^{1}H NMR data for *cis*-$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3MeOCC(Ph){=}CCH{=}CHPh)(CO)_9]$ (**9**): δ (CD_2Cl_2): 6.35 (d, $J = 7.9$, 1H, C*H*), 4.01 (d, $J = 7.9$, 1H, C*H*), 3.96 (s, 3H, O*Me*), −18.00 (s, 1H, μ-H) ppm.

Selected ^{1}H NMR data for *trans*-$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(Ph){=}CCH{=}CHPh)(CO)_9]$ (**10**): δ (CD_2Cl_2): 6.65 (d, $J = 12.8$, 1H, C*H*), 5.61 (d, $J = 12.8$, 1H, C*H*), 3.84 (s, 3H, O*Me*), −19.02 (s, 1H, μ-H) ppm.

Selected ^{1}H NMR data for *cis*-$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3MeOCC(CH{=}CHPh){=}CPh)(CO)_9]$ (**11**): δ (CD_2Cl_2): 3.75 (s, 3H, O*Me*), −19.51 (s, 1H, μ-H) ppm.

Selected ^{1}H NMR data for *trans*-$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeOCC(CH{=}CHPh){=}CPh)(CO)_9]$ (**12**): δ (CD_2Cl_2): 6.17 (d, $J = 11.8$, 1H, C*H*), 6.05 (d, $J = 11.8$, 1H, C*H*), 3.70 (s, 3H, O*Me*), −19.67 (s, 1H, μ-H) ppm.

4.4. *Crystallographic studies*

Diffraction data were collected on a Nonius CAD-4 diffractometer, with the $\omega-2\theta$ scan technique and a variable scan rate, using graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied, and data were reduced to F_o^2 values. Empirical absorption corrections were applied using XABS2 [8]. The structures were solved by Patterson interpretation using the program DIRDIF-96 [9]. Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL-97 [10]. All non-H atoms were refined anisotropically. The molecular plots were made with the EUCLID program package [11]. The WINGX program system [12] was used throughout the structure determinations. Revelant crystal and refinement data are given in Table 2.

4.4.1. *X-ray structure of* **3**

Suitable crystals were obtained by slow diffusion of pentane into an acetone solution of complex **3**. Maximum and minimum transmission factors 0.807 and 0.645, respectively. The position of the hydride atom H(1) was located by Fourier difference maps and its coordinates and thermal parameters were refined. All the other hydrogen atom positions were geometrically calculated and refined riding on their parent atoms.

Table 2
Relevant crystal and refinement data for compounds **3** and **4**

Compound	**3**	**4**
Formula	$C_{17}H_{10}O_{10}Ru_3$	$C_{17}H_{10}O_{10}Ru_3$
M	677.46	677.46
Temperature (K)	293(2)	293(2)
λ(Mo Kα) (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	13.839(10)	18.422(15)
b (Å)	12.5811(16)	7.033(3)
c (Å)	24.59(11)	18.44(3)
α (°)	90	90
β (°)	90	116.68(7)
γ (°)	90	90
V (Å^3)	4281(19)	2135(4)
Z	8	4
D_{calc} (g cm^{-3})	2.102	2.108
μ (mm^{-1})	2.138	2.145
F(000)	2592	1296
Crystyal size (mm)	0.27 × 0.20 × 0.10	0.33 × 0.23 × 0.17
θ max (°)	25.97	25.99
h, k, l ranges	$-17 \leq h \leq 0$, $-15 \leq k \leq 0$, $-30 \leq l \leq 0$	$-22 \leq h \leq 0$, $0 \leq k \leq 8$, $-20 \leq l \leq 22$
Measured reflections	4166	4338
Unique reflections	4166	4204
Reflections with [$I > 2\sigma(I)$]	2950	3065
Parameters	275	299
R_1 (on F^2, $I > 2\sigma(I)$)	0.0281	0.0667
wR_2 (on F^2, all data)	0.0709	0.2004
Goodness-of-fit on F^2	1.030	1.103
Min, max $\Delta\rho$ (e Å^{-3})	−0.463, 0.455	−1.131, 1.047

4.4.2. *X-ray structure of* **4**

Suitable crystals were obtained by slow diffusion of pentane into a benzene solution of complex **4**. Maximum and minimum transmission factors 0.694 and 0.485, respectively. The position of the hydride atom H(1) was calculated using the program XHYDEX [13], its coordinates were fixed and its thermal parameters were refined. All the remaining hydrogen atom positions were geometrically calculated and refined riding on their parent atoms. Refinement of this model converged with a high discrepancy index ($R_1 = 12.6\%$). A difference-Fourier synthesis showed three prominent peaks superimposed to the triangle of Ru atoms. Six different data sets, using different crystals, were collected either in this diffractometer or in a Kappa-CCD, but they all gave analogous results. We included these three peaks in the model, as atoms Ru(1b), Ru(2b) and Ru(3b), with their site occupancy factors coupled to those of Ru(1), Ru(2) and Ru(3), respectively. This gave occupancy factors of approximately 0.10 for these new atoms and 0.90 for Ru(1), Ru(2) and Ru(3). Full-matrix least-squares refinement of this model led to a significant reduction in the discrepancy index ($R_1 = 6.67\%$), with a Goodness-of-fit = 1.103. A final difference-Fourier map showed density in the range 1.047 to −1.131 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 184062–184063 for compounds **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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