Formation of a Diynedienyl Ligand by Coupling of Hexa-2,4-diyne and Hex-2-yn-4-en-4-yl Ligands onto a Triruthenium Cluster Core

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*Summary: The reaction of the cluster complex [Ru₃(μ-H)(μ₃-η²-ampy)(CO)₉] (Hampy = 2-amino-6-methylpyridine) with an excess of hexa-2,4-diyne gives the trinuclear derivative [Ru₃(μ₃-η²-ampy){μ-η⁵-MeC≡CC(=CHMe)-CMe=CC≡CMe}(μ-CO)₂(CO)₅] as the final product. This compound contains an unprecedented diynedienyl ligand that arises from the coupling of hexa-2,4-diyne with the hex-2-yn-4-en-4-yl ligand of the intermediate [Ru₃(μ₃-η²-ampy)(μ-η³-MeCH=CC≡CMe)(μ-CO)₂(CO)₆], which is the first compound observed in the reaction of **1** with hexa-2,4-diyne.*

Introduction

Diynes have recently started to attract the attention of organometallic cluster chemists[1−10] because they are more reactive and generally lead to a richer, though more complicated, derivative chemistry than mono-alkynes.

Previous studies have shown that amidopyridine-bridged hydrido-triruthenium carbonyl complexes[11,12] are ideal candidates for the activation of alkynes, affording alkenyl derivatives of the type [Ru₃(μ₃-η²-apy)-(μ-η²-alkenyl)(μ-CO)₂(CO)₆] (apy = 2-amidopyridine-type ligand).[12,13] The face-capping apy ligands help maintain the cluster integrity while still providing reaction pathways of low activation energy.[14]

The natural evolution of these investigations led us to study the reactivity of apy-bridged hydrido-triruthenium complexes with diynes. In this field, we have already reported that the complex [Ru₃(μ-H)(μ₃-η²-ampy)(CO)₉] (**1**) (Hampy = 2-amino-6-methylpyridine) reacts with diphenylbutadiyne and 1,6-diphenoxyhexa-2,4-diyne to give ynenyl derivatives, which are prone to react with alkynes and diynes to give interesting coupling products, including η⁵-cyclopentadienyl and η⁵-ruthenacyclopentadienyl derivatives.[10]

Apart from the compounds mentioned above, only a few ynenyl derivatives have so far been reported as products of reactions of carbonylmetal clusters with diynes. They arise from the insertion of diynes into a metal−hydride bond of cluster precursors and include the ruthenium compounds [Ru₂(μ-N=CPh₂)(μ-η²-CH₂=CCH₂C≡CSiMe₃)(CO)₆],[6] [Ru₃(μ₃-η²-pyNMe)(μ-η³-PhCH=CC≡CPh)(μ-CO)₂(CO)₆],[7] and [Ru₄(μ-η²-dmpz)(μ₄-η⁴-MeCH=CC≡CMe)(μ-CO)(CO)₁₀] (Hdmpz = 3,5-dimethylpyrazole).[8] An additional ruthenium cluster complex

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containing an ynenyl ligand has been reported, [Ru₃{μ-NS(O)MePh}(μ-η³-PhCH=CC≡CPh)(CO)₉], but in this case the ynenyl ligand arises from an alkynyl−vinylidene coupling.[15] The osmium derivatives [Os₃(μ-H)(μ₃-η³-E-FcCH=CC≡CFc)(CO)₉] (Fc = ferrocenyl), [Os₃(μ-OH)(μ₃-η³-Z-FcCH=CC≡CFc)(CO)₉], and [Os₃(μ-OH)-(μ₃-η³-E-FcCH=CC≡CFc)(CO)₉] are formed in the reaction of [Os₃(μ₃-η²-FcC≡CC≡CFc)(CO)₁₀]²ᵃ with water.²ᵇ The tetraosmium ynenyl derivative [Os₄(μ-H)₃(μ-η²-E-FcC=CHC≡CFc)(CO)₁₁] has been recently obtained from [Os₄(μ-H)₄(CO)₁₂] and bis(ferrocenyl)butadiyne.²ᶜ The reaction of [Os₃(μ-H)₂(CO)₁₀] with bis(trimethylsilyl)butadiyne also gives a trinuclear ynenyl derivative.⁴ᵃ It is noteworthy that no reactivity studies on these ynenyl complexes have been published.

In this short note, we report that complex **1** reacts with hexa-2,4-diyne to give an ynenyl species as the first observed compound. A subsequent reaction of this ynenyl intermediate with more hexa-2,4-diyne leads to a product containing an unprecedented diynedienyl ligand that arises from the coupling of a diyne with an ynenyl ligand.

Results

The thermal reaction (refluxing THF) of hexa-2,4-diyne with compound **1**, in 1.5:1 mol ratio, led to a mixture of [Ru₃(μ₃-η²-ampy)(μ-η³-MeCH=CC≡CMe)(μ-CO)₂(CO)₆] (**2**) and [Ru₃(μ₃-η²-ampy){μ-η⁵-MeC≡CC-(=CHMe)CMe=CC≡CMe}(μ-CO)₂(CO)₅] (**3**), which could not be satisfactorily separated due to the instability of compound **2** on chromatographic supports (silica gel and alumina). The use of smaller hexa-2,4-diyne to **1** ratios led to mixtures of compounds **1**, **2**, and **3**, while ratios greater than 2 led to compound **3**.

Although compound **2** could not be prepared free of compound **3**, we managed to obtain its IR and NMR spectroscopic data by comparing the spectra of mixtures with different **2**:**3** ratios. The IR spectrum of **2** shows the presence of two bridging CO ligands. This is validated by its ¹³C NMR spectrum, which also indicates the presence of six terminal CO ligands, the ampy ligand, and an ynenyl ligand (the *C*H carbon atom resonance, at 126.8 ppm, was assigned with the help of DEPT techniques). The ¹H NMR spectrum also confirms the transfer of a hydrogen atom (the hydride ligand of **1**) to the original diyne to give an ynenyl ligand. The multiplicity of the signal of this hydrogen atom (quartet, *J* = 6.0 Hz) indicates that it is adjacent to a methyl group. The structure depicted for compound **2** in Scheme 1, which shows a bridging three-electron donor hex-2-yn-4-en-4-yl ligand, is also supported by the similarity of its spectroscopic data with those of the compounds [Ru₃(μ₃-η²-ampy)(μ-η³-RCH=CC≡CR)(μ-CO)₂(CO)₆] (R = Ph, CH₂OPh), the structures of which have been determined by X-ray diffraction. These latter complexes have been isolated from the reactions of **1** with diphenylbutadiyne and 1,6-diphenoxy-2,4-hexadiyne.[10]

Compound **3** is the final product of the reaction of **1** with an excess of hexa-2,4-diyne in refluxing THF. IR monitoring of the reaction clearly revealed the intermediacy of compound **2**, which was initially formed but
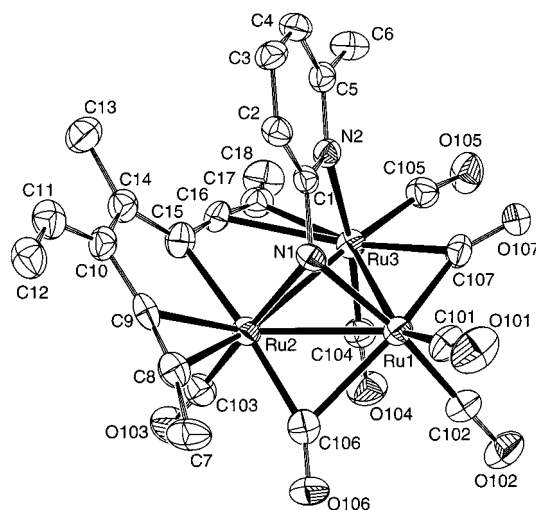
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Figure 1. Molecular structure of compound **3**. Selected interatomic distances (Å): Ru(1)−Ru(2) 2.6905(9), Ru(1)−Ru(3) 2.7713(8), Ru(2)−Ru(3) 2.8586(9), C(7)−C(8) 1.48-(1), C(8)−C(9) 1.23(1), C(8)−Ru(2) 2.351(9), C(9)−C(10) 1.44(1), C(9)−Ru(2) 2.260(8), C(10)−C(11) 1.34(1), C(10)−C(14) 1.44(1), C(11)−C(12) 1.50(1), C(13)−C(14) 1.48(1), C(14)−C(15) 1.35(1), C(15)−C(16) 1.39(1), C(15)−Ru(2) 2.127(8), C(16)−C(17) 1.26(1), C(16)−Ru(3) 2.403(8), C(17)−C(18) 1.46(1), C(17)−Ru(3) 2.263(8), av Ru−C₍terminal CO₎ 1.877(9), C(106)−Ru(2) 2.02(1), C(106)−Ru(1) 2.34(1), C(107)−Ru(1) 1.982(9), C(107)−Ru(3) 2.240(9), av C−O₍terminal CO₎ 1.14(1), C(106)−O(106) 1.14(1), C(107)−O(107) 1.14(1).

Scheme 1
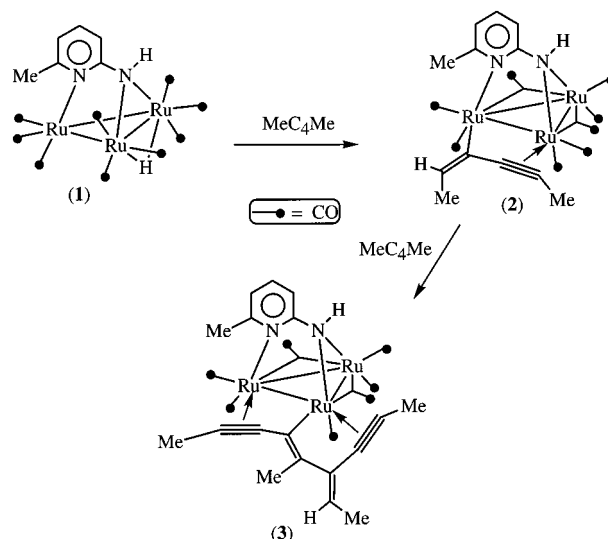
progressively converted into **3**. Its analytical and spectroscopic data, although indicating the absence of hydride ligands, the presence of the ampy ligand and two bridging and five terminal CO ligands, and the incorporation of two diyne molecules, do not reveal its molecular structure, which was determined by X-ray diffraction.

Figure 1 shows a view of compound **3**. A selection of bond distances is given in the figure caption. The new hydrocarbyl ligand, a diynedienyl which can be described as a 5-methyl-6-(ethyliden)nona-2,7-diyn-4-en-4-yl ligand, behaves as a five-electron donor and spans the Ru(2)−Ru(3) edge of the metal triangle, being attached to the Ru(3) atom through a C≡C triple bond

(two-electron π-type interaction) and to the Ru(2) atom through the remaining C≡C triple bond (two-electron π-type interaction) and the C^4 (C(15) in Figure 1) carbon atom (one-electron σ-type interaction). Each remaining edge of the metallic triangle is asymmetrically spanned by a CO ligand. The ampy ligand caps the Ru_3 triangle in its usual form.[10,11b,13b] The cluster shell is completed with five terminal CO ligands. The compound is a closed-shell 48-electron cluster.

Discussion

Considering the asymmetry of each triple bond of hexa-2,4-diyne, the insertion of one of its triple bonds into a Ru–H bond of **1** could lead to two different products. Interestingly, the reaction is selective and only one of such products (**2**), that containing a hex-2-yn-4-en-4-yl ligand, is observed (the alternative product would contain a hex-2-yn-4-en-5-yl ligand). This selectivity was also observed previously for the reaction of compound **1** with 1,6-diphenoxy-2,4-hexadiyne,[10] but contrasts with the previous observation of both isomeric insertion products in the reactions of apy-capped triruthenium hydrido complexes with diphenylbutadiyne.[7,10] A mechanistic proposal accounting for the formation of compounds similar to **2** from conjugated diynes and hydrido trinuclear clusters has been published.[10]

Apart from the cluster complexes mentioned in the Introduction, only some binuclear[1e,16] and a few mononuclear[17] complexes containing ynenyl ligands have been reported. Curiously, most ynenyl ligands of these low-nuclearity derivatives arise from monoalkyne fragments (metal-mediated acetylide–vinylidene coupling).[16a,17]

A reaction pathway that would account for the formation of compound **3** from **2** is given in Scheme 2. An exchange in the coordination of the double and triple bonds of the ynenyl ligand of **2** would lead to intermediate **A**, which can be considered to contain a bridging alkenyl ligand having a pendant alkyne substituent. The flyover of the alkenyl fragment over the two bridged metal atoms[18] would lead to an intermediate in which

Scheme 2
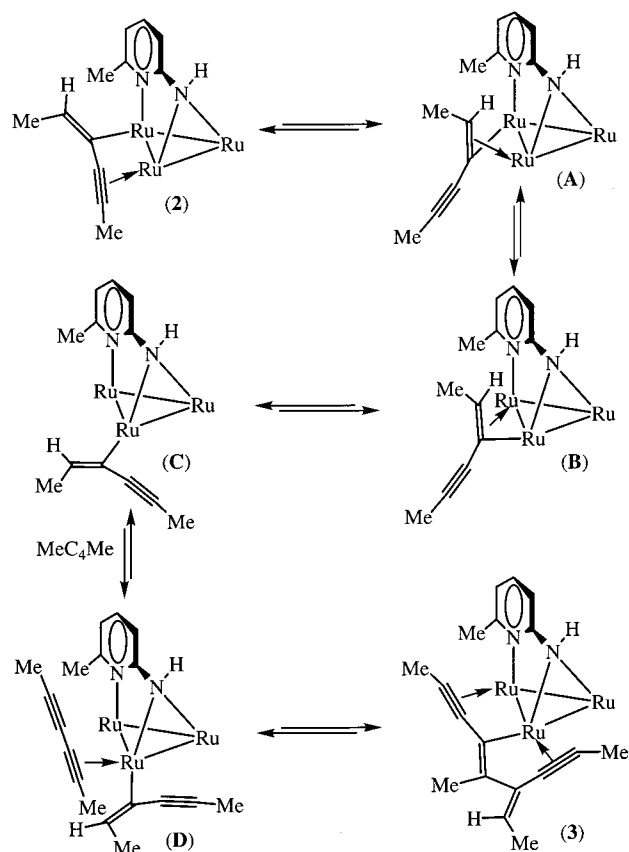
this ligand is σ-bonded to one of the Ru atoms spanned by the NH fragment (**B**). Coordination of a C≡C triple bond of the incoming diyne molecule to the Ru atom σ-bonded to the alkenyl fragment (intermediate **D**) is required for a subsequent insertion step that would lead, upon coordination of the pendant alkyne moieties, to complex **3**. A CO ligand is to be released, probably in the final step, although the coordination of one or both pendant alkyne moieties prior to the insertion step cannot be ruled out.

The compounds $[Ru_3(\mu_3\text{-}\eta^2\text{-ampy})(\mu\text{-}\eta^3\text{-RCH=CC≡}\allowbreak CR)(\mu\text{-CO})_2(CO)_6]$ (R = Ph, CH_2OPh), structurally analogous to **2**, are the only ynenyl derivatives for which their reactivity with alkynes and diynes has been studied. They systematically give trinuclear products containing η^5-ruthenacyclopentadienyl fragments which arise from the coupling of the coordinated ynenyl ligands with a C≡C triple bond of the new reagent (alkyne or diyne).[10] It is very interesting that the reaction of **2** with hexa-2,4-diyne does not give a related trinuclear product, but compound **3**, which contains a novel diynedienyl ligand that arises from an unprecedented coupling of a diyne with an ynenyl ligand.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) 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). Compound **1** was prepared as described previously.[11b] Hexa-2,4-diyne was obtained from Aldrich. IR spectra were recorded in

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solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run at room temperature on a Bruker DPX-300 instrument, using SiMe$_4$ as internal standard (δ = 0 ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

[Ru$_3$(μ_3-η^2-ampy)(μ-η^3-MeCH=CC≡CMe)(μ-CO)$_2$(CO)$_6$] (2). Hexa-2,4-diyne (45 mg, 0.567 mmol) was added to a solution of compound **1** (250 mg, 0.377 mmol) in THF (60 mL). The solution was heated at reflux temperature until the complete disappearance of the starting complex (ca. 40 min). The solvent was removed under reduced pressure, and the resulting solid residue was washed with hexane (3 × 3 mL) and dried in vacuo to give 220 mg of a yellow solid. A proton NMR spectrum indicated a 3:1 mixture of compounds **2** and **3**. All attempts to separate this mixture by chromatographic methods (TLC and column chromatography on silica and alumina) led to decomposition of compound **2**. The use of a smaller hexa-2,4-diyne to **1** ratio led to mixtures of compounds **1**, **2**, and **3**. By comparing the spectra of many mixtures, the IR and NMR spectroscopic data of compound **2** could be obtained. IR (THF): ν_{CO} 2056 (s), 2023 (vs), 2010 (vs), 1984 (s), 1957 (m), 1857 (w), 1820 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.38 (t, J = 7.8 Hz, 1 H, H$_{ampy}$), 6.81 (d, J = 7.8 Hz, 1 H, H$_{ampy}$), 6.64 (q, J = 6.0 Hz, 1 H, CHMe), 6.32 (d, J = 7.8 Hz, 1 H, H$_{ampy}$), 4.01 (s, 1 H, NH$_{ampy}$), 3.25 (s, 3 H, Me), 3.21 (s, 3 H, Me), 2.79 (d, J = 6.0 Hz, 3 H, CHMe) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 244.8 (CO), 243.9 (CO), 200.7 (CO), 199.8 (CO), 197.7 (CO), 196.6 (CO), 195.9 (CO), 194.7 (CO), 168.1 (C$_{ampy}$), 160.2 (C$_{ampy}$), 138.8 (CH$_{ampy}$), 132.2 (C), 126.8 (CHMe), 118.9 (CH$_{ampy}$), 113.0 (CH$_{ampy}$), 90.7 (C), 49.8 (C), 28.7 (Me), 26.8 (Me), 18.9 (Me) ppm.

[Ru$_3$(μ_3-η^2-ampy){μ-η^5-MeC≡CC(=CHMe)CMe=CC≡CMe}(μ-CO)$_2$(CO)$_5$] (3). Hexa-2,4-diyne (60 mg, 0.768 mmol) was added to a solution of compound **1** (200 mg, 0.301 mmol) in THF (60 mL). The solution was heated at reflux temperature for 90 min. The solvent was removed under reduced pressure, and the resulting residue was dissolved in a minimal amount of dichloromethane. The solution was separated by TLC (silica gel) using hexane/dichloromethane (4:1) as eluant. The major band afforded compound **3** after extraction with dichloromethane and solvent removal (75 mg, 35%). Calcd for C$_{25}$H$_{20}$N$_2$O$_7$Ru$_3$ (M = 763.69): C, 39.32; H, 2.64; N, 3.67. Found: C, 39.56; H, 2.75; N, 3.48. IR (CH$_2$Cl$_2$): ν_{CO} 2040 (vs), 2003 (m), 1974 (s), 1946 (m, sh), 1881 (w, br), 1809 (w, br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.89 (t, J = 7.6 Hz, 1 H, H$_{ampy}$), 6.31 (d, J = 7.6 Hz, 1 H, H$_{ampy}$), 5.93 (q, J = 7.2 Hz, 1 H, CHMe), 5.78 (d, J = 6.8 Hz, 1 H, H$_{ampy}$), 3.72 (s, 1 H, NH$_{ampy}$), 3.05 (s, 3 H, Me), 2.81 (s, 3 H, Me), 2.41 (s, 3 H, Me), 2.09 (d, J = 7.2 Hz, 3 H, CHMe), 1.93 (s, 3 H, Me). ^{13}C NMR (CD$_2$Cl$_2$): δ 254.2 (CO), 232.1 (CO), 199.7 (CO), 198.1 (CO), 197.6 (CO), 196.0 (CO), 192.6 (CO), 169.2 (C$_{ampy}$), 158.9 (C$_{ampy}$), 140.6 (C), 138.6 (CH$_{ampy}$), 133.3 (CH$_{ampy}$), 129.5 (C), 120.2 (C), 120.0 (C),

118.7 (CH$_{ampy}$), 117.6 (CHMe), 109.7 (C), 93.2 (C), 46.4 (C), 29.3 (Me), 23.1 (Me), 22.7 (Me), 17.3 (Me), 14.6 (Me) ppm.

X-ray Structure of 3·(CH$_2$ClCH$_2$Cl)$_{0.5}$. The crystal was selected from a batch obtained by slow diffusion of pentane vapor into a solution of **3** in 1,2-dichloroethane. Details of crystal and refinement data are given as a footnote.[19] X-ray diffraction data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Cu Kα radiation. Lorentz and polarization corrections were applied, and data were reduced to $|F_o|^2$ values. An empirical absorption correction was applied using XABS2,[20] with transmission factors in the range 0.353−0.091. The structure was solved by Patterson interpretation using the program DIRDIF-96.[21] Isotropic and full matrix anisotropic least squares refinements were carried out using SHELXL-97.[22] All non H atoms were refined anisotropically. Hydrogen atom positions were geometrically calculated and refined riding on their parent atoms, except the N-H hydrogen atom, which was located by Fourier difference and its coordinates refined. The molecular plot was made with the EUCLID program package.[23]

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for **3**·(CH$_2$ClCH$_2$Cl)$_{0.5}$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010478R

(19) Crystal and selected refinement data for **3**·(CH$_2$ClCH$_2$Cl)$_{0.5}$: C$_{26}$H$_{22}$ClN$_2$O$_7$Ru$_3$; fw = 813.12; cryst size = 0.15 × 0.13 × 0.08 mm; cryst system = monoclinic; space group = $C2/c$; a = 35.087(2) Å; b = 10.3301(6) Å; c = 16.6929(9) Å; β = 108.310(3)°; V = 5744.0(6) Å^3; Z = 8; ρ_{calcd} = 1.881 g/cm^3; λ = 1.54184 Å; μ = 13.869 mm^{-1}; F(000) = 3176; index range −42 < h < 41, −12 < k < 10, −20 < l < 20; θ range = 2.65−69.95°; temp = 200(2) K; collected reflns = 16 417; unique reflns = 5104; R_{Int} = 0.0677; reflns with I < 2σ(I) = 3817; no. of variables = 356; weighting scheme w^{-1} = $\sigma^2 F_o^2$ + (0.0827P)^2, P = (F_o^2 + 2F_c^2)/3; GoF = 0.989; final $R_{2\sigma(I)}$ = 0.0568; final wR2$_{all\ data}$ = 0.1631; largest diff peak and hole = 0.919 and −1.140 e/Å^3.

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