

Formation of a Highly Functionalized Azulene Ligand by Metal Cluster-Mediated Coupling of Three Conjugated Diynes

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Summary: The highly functionalized azulene ligand of the diruthenium complex $[Ru_2(\mu-\eta^8-C_{38}H_{26})(CO)_5]$, $C_{38}H_{26} = 1$ -(phenylethynyl)-2,4-diphenyl-5-(propyn-1-yl)-6-methyl-7,8-benzoazulene, has been synthesized by treating $[Ru_3(\mu-H)(\mu_3-\eta^2-apyr)(CO)_9]$, Hapyr = 2-aminopyrimidine, with 2 equiv of diphenylbutadiyne and 1 equiv of 2,4-hexadiyne.

Introduction

During the last 30 years, azulene and its substituted derivatives have increasingly attracted the interest of organometallic chemists.¹ In this field, ruthenium has been one of the most studied metals since, to date, mono-,^{2,3} di-,^{3–6} tri-,^{3,4e,6–8} and tetraruthenium^{3,9} azulene complexes have been reported. This research activity has shown that azulene ligands can interact with one or several metal atoms in a variety of coordination modes,^{2–9} which, in some instances, lead to interesting haptotropic rearrangements.^{4–6}

It should be noted that, without exceptions, the above-mentioned complexes have been prepared by treating the corresponding azulene ligands with the appropriate metal complex precursors.

We now report the synthesis of a diruthenium complex containing a highly substituted azulene ligand. Interestingly, such a ligand is formed by coupling of

three conjugated diyne molecules on a triruthenium cluster core. The metal-mediated synthesis of large unsaturated hydrocarbyl ligands is currently receiving increasing interest.^{10,11}

The results described herein were obtained in the course of a study on the reactivity of conjugated diynes¹² with amidopyridine-bridged hydrido-triruthenium carbonyl complexes.^{13–15} We have already reported that the complex $[Ru_3(\mu-H)(\mu_3-\eta^2-ampy)(CO)_9]$ (Hampy = 2-amino-6-methylpyridine) reacts with 2,4-hexadiyne,¹⁶ diphenylbutadiyne,¹⁷ and 1,6-diphenoxy-2,4-hexadiyne¹⁷ to give ynenyl derivatives which are prone to react with diynes to afford interesting coupling products, including diyne-dienyl,¹⁶ η^5 -cyclopentadienyl,¹⁷ and η^5 -ruthenacyclopentadienyl¹⁷ derivatives.

Results and Discussion

The thermal reaction (refluxing THF) of diphenylbutadiyne with $[Ru_3(\mu-H)(\mu_3-\eta^2-apyr)(CO)_9]$ (**1**; Hapyr = 2-aminopyrimidine), in a 2:1 mol ratio, led to a ca. 1:4 mixture of $[Ru_3(\mu-\eta^2-apyr)\{\mu_3-\eta^6-C_5(CPh)(C\equiv CPh)HPH_2\}(CO)_7]$ (**2**) and $[Ru_3(\mu_3-\eta^2-apyr)(\mu-\eta^3-PhCH=CC\equiv CPh)(\mu-CO)_2(CO)_6]$ (**3**) (Scheme 1), which were separated by chromatographic methods. The use of other diphenylbutadiyne to complex **1** ratios did not increase the final yield of complex **2**, which was never higher than 10%. Their analytical and spectroscopic data indicated that these products are structurally analogous to those

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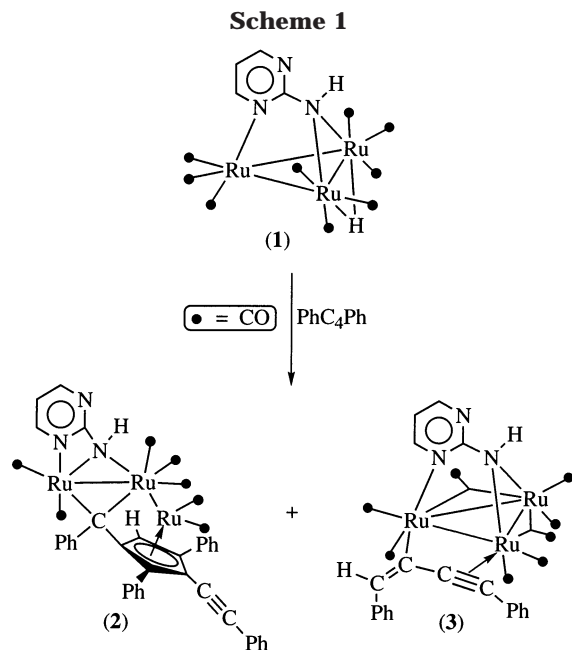
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obtained from the reaction of diphenylbutadiyne with $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-ampy})(\text{CO})_9]$ (Hampy = 2-amino-6-methylpyridine).¹⁷ We have previously discussed the mechanism of this reaction,¹⁷ so, for the sake of brevity, no mechanistic aspects are discussed here.

As we are interested in reactions that could lead to carbon-rich organometallics, we treated compounds **2** and **3** (and their ampy analogues) with alkynes and diynes, looking for possible insertion products of the incoming reagents into C–Ru bonds of the organometallic precursors.

When complex **2** was treated with 2,4-hexadiyne in refluxing THF, a yellow product, subsequently identified as $[\text{Ru}_2(\mu\text{-}\eta^8\text{-C}_{38}\text{H}_{26})(\text{CO})_5]$ (**4**), was isolated in 48% yield after TLC separation (Scheme 2). Its microanalysis, FAB mass spectrum, and NMR spectroscopic data indicated its binuclear nature, the absence of the ampy ligand, and the presence of a large hydrocarbyl ligand ($\text{C}_{38}\text{H}_{26}$).

An X-ray diffraction study (Figure 1) revealed that complex **4** consists of a metal–metal bonded $\text{Ru}_2(\text{CO})_5$ fragment attached to the azulene fragment of a 1-(phenylethynyl)-2,4-diphenyl-5-(propyn-1-yl)-6-methyl-7,8-benzoazulene ligand in the same manner as that found in $[\text{Ru}_2(\mu\text{-}\eta^8\text{-azulene})(\text{CO})_5]$,⁶ i.e., to three carbon atoms of the seven-membered ring and to all carbon atoms of the cyclopentadienyl ring. The most striking feature of this complex is that the azulene skeleton has only one C–H bond; therefore, this ligand is an unprecedented highly functionalized azulene with substituents as reactive as alkynyl fragments.

The reaction described above is the first example of a metal-mediated synthesis of an azulene ligand. Although a complete reaction pathway of the process that leads to the azulene derivative **4** from complex **2** cannot be easily envisaged, it is reasonable to propose that the azulene ligand arises from the coupling of an unsaturated carbon atom of 2,4-hexadiyne with the carbon atom of the bridging carbene fragment of complex **2** (probably via insertion of a triple bond into a C–Ru bond) and subsequent cyclization with an *ortho* carbon atom of the

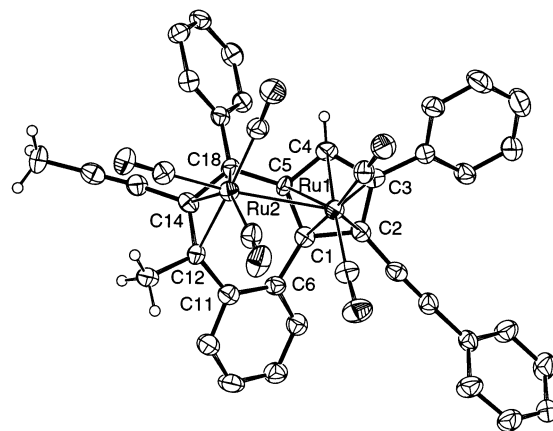
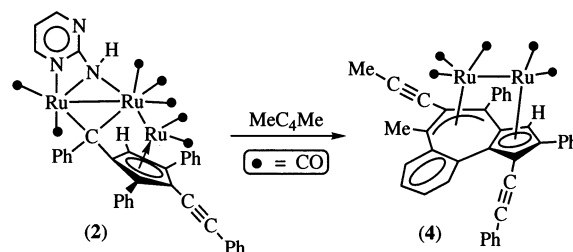


Figure 1. Molecular structure of compound **4** (thermal ellipsoids are drawn at the 40% probability level). Selected interatomic distances (Å): Ru(1)–Ru(2) 2.8451(6), Ru(1)–C(1) 2.242(5), Ru(1)–C(2) 2.244(5), Ru(1)–C(3) 2.273(5), Ru(1)–C(4) 2.236(5), Ru(1)–C(5) 2.260(5), Ru(2)–C(12) 2.288(6), Ru(2)–C(14) 2.231(5), Ru(2)–C(18) 2.291(6), C(1)–C(2) 1.463(7), C(1)–C(5) 1.445(7), C(1)–C(6) 1.481(8), C(2)–C(3) 1.433(7), C(3)–C(4) 1.429(7), C(4)–C(5) 1.420(7), C(5)–C(18) 1.474(7), C(6)–C(11) 1.407(9), C(11)–C(12) 1.515(7), C(12)–C(14) 1.471(8), C(14)–C(18) 1.426(7).

Scheme 2



phenyl substituent which is next to the bridging carbene on the C₅ ring (probably after an orthometalation of this phenyl ring). In the process, a hydrogen atom, a Ru(CO)_x fragment, and the ampy ring are released, but their fate remains unknown (a dark residue was observed on the TLC plates which could not be identified).

Considering the asymmetry of each triple bond of 2,4-hexadiyne, it is noteworthy that the reaction is regioselective, since complex **4** is one of two possible regioisomers (the methyl and propyn-1-yl substituents of the alternative product would be in exchanged positions). It seems that the use of 2,4-hexadiyne is a “must” for the reaction, since no azulene derivatives were obtained from the reactions of complex **2** with alkynes and other diynes, such as phenylacetylene, 3-hexyne, 1,6-diphenoxy-2,4-hexadiyne, or diphenylbutadiyne.

In addition, the presence of the ampy ligand in complex **2** seems to be important for its transformation into complex **4**, since the ampy analogue of **2** did not give an azulene derivative when it was treated with 2,4-hexadiyne (most probably, the methyl substituent on the pyridine ring of the ampy ligand hampers an appropriate approach of the incoming diyne to the trinuclear complex). The ynenyl derivative **3** showed the same reactivity¹⁸ as its ampy analogue¹⁷ when it was treated with alkynes and diynes, and therefore, these reactions do not merit further comments.

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In conclusion, this paper describes the first metal-mediated synthesis of an azulene ligand. Such a ligand arises from the assembling of two diphenylbutadiyne and one 2,4-hexadiyne molecule on a triruthenium cluster core. The great number of functional groups on the azulene skeleton is also unprecedented. It is a pity that other cluster compounds related to **2** and/or other alkynes fail to react in the same way as that described here for **2**, since this means that the creation of this highly unsaturated azulene will remain a curiosity rather than being the springboard for further syntheses.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH₂ (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). Compound **1** was prepared as described previously.¹⁵ Diphenylbutadiyne and 2,4-hexadiyne were obtained from Aldrich. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run at room temperature on a Bruker DPX-300 instrument, using SiMe₄ as internal standard ($\delta = 0$). 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.

Reaction of Compound 1 with Diphenylbutadiyne. A solution of diphenylbutadiyne (81 mg, 0.40 mmol) and compound **1** (130 mg, 0.20 mmol) in THF (50 mL) was heated at reflux temperature for 40 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 two major bands (both orange) afforded compounds **2** (20 mg, 10%, from the first band) and **3** (38 mg, 23%, from the second band) after extraction with dichloromethane and solvent removal. *Data for 2:* Calcd for C₄₃H₂₅N₃O₇Ru₃ ($M = 998.93$): C, 51.70; H, 2.52; N, 4.20. Found: C, 51.63; H, 2.61; N, 4.15. MS (m/z): 1000 [M⁺]. IR (CH₂Cl₂): ν_{CO} 2059 (s), 2019 (vs), 2003 (m), 1977 (m), 1963 (m), 1949 (w), 1928 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 8.3–6.7 (m, 23 H), 3.55 (s, 1 H), 1.96 (s, br, 1 H, NH). *Data for 3:* Calcd for C₂₈H₁₅N₃O₈Ru₃ ($M = 824.69$): C, 40.78; H, 1.83; N, 5.09. Found: C, 40.94; H, 1.86; N, 4.57. MS (m/z): 826 [M⁺]. IR (CH₂Cl₂): ν_{CO} 2068 (vs), 2035 (s), 2027 (s), 1999 (s), 1974 (w), 1879 (w), 1825 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 8.9–6.5 (m, 13 H), 6.43 (s, 1 H), 3.11 (s, br, 1 H, NH).

[Ru₂(μ - η^8 -C₃₈H₂₆)(CO)₅] (4). A THF solution (10 mL) of compound **2** (30 mg, 0.03 mmol) and 2,4-hexadiyne (12 mg, 0.15 mmol) was heated at reflux temperature for 4 h. 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 (3:1) as eluant. The first and major

band (yellow) afforded compound **4** after extraction with dichloromethane and solvent removal (12 mg, 48%). Calcd for C₄₃H₂₆O₅Ru₂ ($M = 824.84$): C, 62.62; H, 3.18. Found: C, 62.81; H, 3.22. MS (m/z): 826 [M⁺]. IR (CH₂Cl₂): ν_{CO} 2055 (vs), 1999 (vs), 1992 (sh), 1975 (sh), 1933 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 8.43 (dd, $J = 7.6, 2.0$ Hz, 1 H), 7.76 (dd, $J = 5.2, 2.5$ Hz, 1 H), 7.7–7.1 (m, 17 H), 3.98 (s, 1 H), 2.45 (s, 3 H), 1.80 (s, 3 H).

X-ray Structure of Compound 4. The crystal was selected from a batch obtained by slow evaporation of a pentane solution of the complex. 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 K α radiation. Data were reduced to F_o^2 values. Empirical absorption correction was applied using XABS2,²⁰ with transmission factors in the range 0.6708–0.0782. 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 anisotropically refined. All hydrogen atom positions were geometrically calculated and isotropically refined riding on their parent atoms. The molecular plot was made with the EUCLID program package.²³ The WINGX program system²⁴ was used throughout the structure determination. Relevant molecular parameters are given in the caption of Figure 1.

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Supporting Information Available: Tables of bond distances and angles, atomic coordinates, anisotropic thermal parameters, and a plot of compound **4** with the complete atomic numbering scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Crystal and selected refinement data for **4**: C₄₃H₂₆O₅Ru₂; fw = 824.78; cryst size = 0.27 × 0.12 × 0.07 mm; cryst system = monoclinic; space group = $P2_1/c$; $a = 17.6274(3)$ Å; $b = 12.0685(3)$ Å; $c = 16.1909(3)$ Å; $\beta = 93.702(1)^\circ$; $V = 3437.2(1)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.594$ g/cm³; $\lambda = 1.54184$ Å; $\mu = 7.495$ mm⁻¹; $F(000) = 1648$; index range $-20 \leq h \leq 19$, $-13 \leq k \leq 7$, $-16 \leq l \leq 17$; θ range = 2.51–66.53°; $T = 200(2)$ K; collected reflns = 14 959; unique reflns = 5182; $R_{\text{int}} = 0.0813$; reflns with $I < 2\sigma(I) = 4428$; no. of variables = 451; weighting scheme $w^{-1} = \sigma^2 F_o^2 + (0.1005P)^2$, $P = (F_o^2 + 2F_c^2)/3$; GoF = 1.043; final $R_{2\sigma(I)} = 0.0514$; final $wR_{2\text{all data}} = 0.1535$; largest diff peak and hole = 1.112 and -1.563 e/Å³.

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