Summary: The highly functionalized azulene ligand of the diruthenium complex \([\text{Ru}_2(\mu_3\eta^3-\text{CO})_3\text{C}_8\text{H}_8 = 1-(\text{phenyldienyl})-2,4-\text{diphenyl}-5-(\text{propynyl}-1\text{-yl})-6\text{-methyl}-7,8-\text{benzoazulene}],\) has been synthesized by treating \([\text{Ru}_3(\mu_3\eta^3-\text{apyr})(\text{CO})_9],\) Hampy = 2-aminoypyrimidine, with 2 equiv of diphenylbutadiyne and 1 equiv of 2,4-hexadiyne. 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.

The results described herein were obtained in the course of a study on the reactivity of conjugated diynes with amidopyridine-bridged hydridotriruthenium carbonyl complexes. We have already reported that the complex \([\text{Ru}_3(\mu_3\eta^3-\text{ampy})(\text{CO})_9],\) (Hampy = 2-amino-6-methylpyridine) reacts with 2,4-hexadiyne, diphenylbutadiyne, and 1,6-diphenoxy-2,4-hexadiyne to give yenyl derivatives which are prone to react with diynes to afford interesting coupling products, including diyne-\(\eta^3,\eta^5\)-cyclopentadienyl, and \(\eta^5\)-ruthenacyclopentadienyl derivatives.

Results and Discussion

The thermal reaction (refluxing THF) of diphenylbutadiyne with \([\text{Ru}_3(\mu_3\eta^3-\text{apyr})(\text{CO})_9],\) (Hampy = 2-aminoypyrimidine), in a 2:1 mol ratio, led to a ca. 1:4 mixture of \([\text{Ru}_3(\mu_3\eta^3-\text{apyr})(\text{CO})_9],\) (Hampy = 2-amino-6-methylpyridine) reacts with 2,4-hexadiyne, diphenylbutadiyne, and 1,6-diphenoxy-2,4-hexadiyne to give yenyl derivatives which are prone to react with diynes to afford interesting coupling products, including diyne-\(\eta^3,\eta^5\)-cyclopentadienyl, and \(\eta^5\)-ruthenacyclopentadienyl derivatives.

obtained from the reaction of diphenylbutadiyne with \([\text{Ru}_2(\mu-H)(\mu-\eta^2-\text{ampy})(\text{CO})_5]\) (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 \([\text{Ru}_2(\mu-\eta^8-\text{C}_{38}H_{26})(\text{CO})_5]\) (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 apyr ligand, and the presence of a large hydrocarbyl ligand \((\text{C}_{38}H_{26})\).

An X-ray diffraction study (Figure 1) revealed that complex 4 consists of a metal–metal bonded \([\text{Ru}_2(\mu-\eta^8-\text{azulene})(\text{CO})_5]\) 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 \([\text{Ru}_2(\mu-\eta^8-\text{azulene})(\text{CO})_5]\),\(^6\) 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 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 apyr ligand 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 apyr 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 reactivity\(^{18}\) as its ampy analogue\(^{17}\) when it was treated with alkynes and diynes, and therefore, these reactions do not merit further comments.

\(^{(17)}\) Cabeza, J. A.; Moreno, M. Unpublished results.
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.

Diphenylbutadiyne and 2,4-hexadiyne were obtained from Aldrich. IR spectra were recorded in solution on a Bruker DPX-300 instrument, using SiMe₄ as internal standard (δ = 0). Microanalyses were obtained from the University of Valencia 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 and solvent removal.

23% from the second band) after extraction with dichloromethane (4:1) as eluant. The two major bands (both orange) afforded compound 4 after extraction with dichloromethane and solvent removal (12 mg, 48%). Calcd for C₇₄H₆₁O₈Ru₃: C, 51.63; H, 2.61; N, 4.15. MS (m), 1949 (w), 1928 (m) cm⁻¹. IR (CH₂Cl₂): vco 2055 (vs), 1999 (vs), 1929 (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.

Found: C, 40.94; H, 1.86; N, 4.57. MS (m), 1949 (w), 1928 (m) cm⁻¹. IR (CH₂Cl₂): vco 2055 (vs), 1999 (vs), 1929 (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).

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: C₇₄H₆₁O₈Ru₃; fw = 824.78; crystal size = 0.27 × 0.12 × 0.07 mm; crystal system = monoclinic; space group = P2₁/a; a = 17.6274(3) Å; b = 12.0685(3) Å; c = 16.1909(3) Å; β = 93.702(1)°; V = 3437.21(2) Å³; Z = 4; dcalc = 1.594 g/cm³; λ = 1.54184 Å; μ = 7.495 mm⁻¹; F(000) = 1648; index range −20 ≤ h ≤ 19, −13 ≤ k ≤ 7, −16 ≤ l ≤ 17; ρcalc = 2.51–66.53°; T = 2002 K; collected reflns = 14999; unique reflns = 5182; Rint = 0.0813; refns with I < 2σ(I) = 4428; no. of variables = 451; weighting scheme w⁻¹ = σ²F² + (0.105σ²); P = (F² + 2F₂)/3; GoF = 1.043; final R₁ = 0.0514; final wR₂ = 0.1535; largest diff peak and hole = 1.112 and −1.963 eÅ⁻³.


(22) Sheldon, G. M.; SHELXL97, version 97-2; University of Göttingen: Germany, 1997.
