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New Route to Dehydroannulenes by Coupling Linear Polyynes Using Ruthenium Carbonyl

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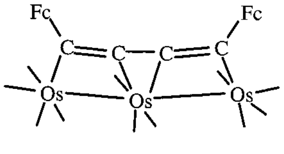
Introduction

Recently, there has been great interest and advances in the synthesis of conjugated polyyne macromolecules.[1] These molecules may serve as precursors for the synthesis of new carbon-rich materials[2] and as media for the transmission of electrons in futuristic nanoscale electronic devices.[3] We have recently shown that the placement of metal atoms along the diyne chain of 1,4-bis(ferrocenyl)butadiyne ligand in the complex $Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-FcCCCCFc})$, Fc = $C_5H_4FeC_5H_5$, leads to an increase in the electronic communication between the ferrocenyl groups of the 1,4-bis(ferrocenyl)-1,3-butadiyne ligand.[4]



$Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-FcC}_4\text{Fc})$

In further studies, we have now investigated the reaction of 1,8-bis(ferrocenyl)-1,3,5,7-octatetrayne[5] (**1**) with $Ru_3(CO)_{12}$. This reaction has yielded the new dehydroannulene complex $[Ru_2(CO)_6\{\mu\text{-(Fc)}C_4\text{(Fc)}C{\equiv}C{-}C{\equiv}C\}]_2$ (**2**), Fc = $(C_5H_5)Fe(C_5H_4)$, formed by metal-induced coupling of two molecules of **1** at each end. The synthesis and characterization of **2** are reported herein.

Results and Discussion

The novel dehydroannulene complex **2** was obtained in low yield (4% overall) from the reaction of **1** with $Ru_3(CO)_{12}$ in hexane solvent at reflux. Compound **2** was characterized by IR, ^{1}H NMR, single-crystal X-ray diffraction analysis, UV−vis spectroscopy, and differential pulse voltammetry. An ORTEP diagram of its molecular structure is shown in Figure 1. The molecule contains two $Ru_2(CO)_6$ groups composed of RuC(Fc)-CCCFc metallacycles formed by the coupling of the alkyne groups at both of the polyyne termini of two molecules of **1**. Both groups exhibit the ferrole-type structure that was first recognized many years ago by the coupling of alkynes at diiron centers.[6] The double coupling observed here results in the formation of a large [12]dehydroannulene that contains four C−C triple bonds.[7,8] The ring is nearly planar as shown in Figure 2, and all four ferrocenyl groups lie on the same side of the ring. The ferrocenyl groups are equivalent, and the molecule exhibits only one C_5H_5 resonance in the ^{1}H NMR spectrum. The C−C bond lengths within the tetrayne ring show normal single bond and triple bond alternation. Compound **2** is structurally similar to the families of tetradehyroannulenes **3**[7] (R = H, Bu^n, Bu^t, Hex^n, decyl, dodecyl, dodecoxy) and **4**[9] (R = $C{\equiv}CSiPr^i{}_3$) that have recently been prepared by other alkyne coupling methods.

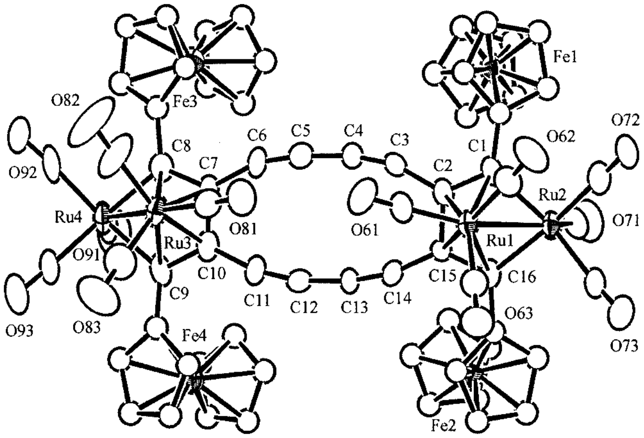


Figure 1. ORTEP diagram of the molecular structure of **2** showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are Ru(1)−Ru(2) = 2.7310(13), Ru(3)−Ru(4) = 2.7209(15), C(1)−C(2) = 1.41(1), C(2)−C(3) = 1.46(1), C(2)−C(15) = 1.48(1), C(3)−C(4) = 1.19(1), C(4)−C(5) = 1.37(1), C(5)−C(6) = 1.22(1), C(6)−C(7) = 1.46(1), C(7)−C(8) = 1.43(1), C(7)−C(10) = 1.46(1), C(9)−C(10) = 1.41(1), C(10)−C(11) = 1.45(1), C(11)−C(12) = 1.20(1), C(12)−C(13) = 1.35(1), C(13)−C(14) = 1.18(1), C(14)−C(15) = 1.42(1), C(15)−C(16) = 1.42(1).

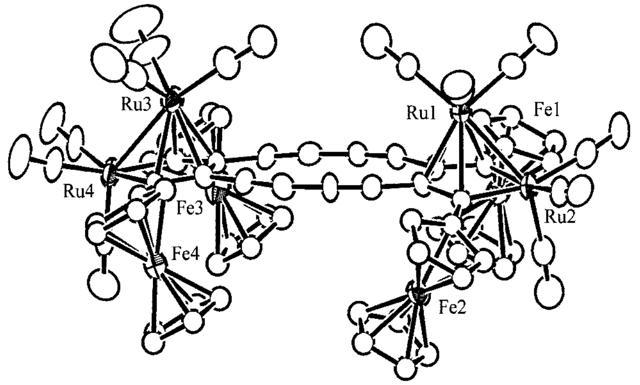


Figure 2. Side view of the molecular structure of **2** showing 40% probability thermal ellipsoids.

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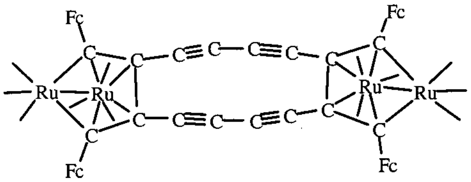

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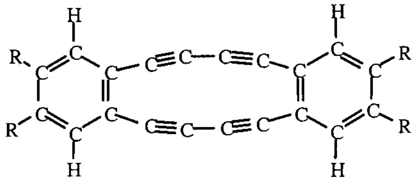

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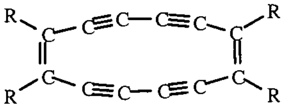

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Although all ferrocenyl groups are equivalent, a differential pulse voltammogram measurement shows the presence of two closely spaced two-electron ferrocenyl oxidations at $E° = +0.490$ and $+0.537$ V vs the Ag/AgCl electrode. The difference ($\Delta E = 47$ mV) is slightly larger than would be expected on the basis of simple charging effects[10] and suggests that there may be a weak intramolecular electronic coupling between the ferrocenyl groups.[11] For comparison, compound **1** shows only a single oxidation wave at $E° = +0.576$ V under the same conditions. Coupling observed in **2** may proceed through the metallacycle, which is a much shorter linkage than the long tetrayne chain between the ferrocenyl groups in **1**.

The UV−vis spectrum exhibits a broad absorption at $\lambda_{max} = 482$ nm and $\epsilon = 13\,630$ M^{-1} cm^{-1} and a shoulder at $\lambda_{max} = 338$ nm and $\epsilon = 51\,930$ M^{-1} cm^{-1} that lies on the side of a strong UV charge-transfer absorption.

It seems like a bistriynyl Ru_2 metallacyclic complex formed by a coupling at one end of two molecules of **1** should be formed prior to the cyclization to yield **2**, but we have not observed this species yet, so the mechanism of the formation of **2** is not yet established.

The coupling of alkynes by transition metal complexes is a well-documented reaction.[12] Therefore, we expect that the polyyne coupling reported here for **1** will also be observed for a variety of other metals and should easily be extended to a range of other linear polyynes. In addition, one can readily imagine the synthesis of larger polyyne cycles formed by the coupling of three, four, or more polyyne molecules.[8,13]

Experimental Section

General Data. Although the reagents and products are air-stable, the reactions were performed under 1 atm of nitrogen. Reagent-grade solvents were freshly distilled prior to use. $Ru_3(CO)_{12}$ was purchased from Strem and was used without further purification. **1** was prepared according to a literature procedure.[5] Product separation was performed by TLC in air on Analtech 0.25-mm silica gel, 60 Å, F_{254} glass plates. The infrared spectrum was recorded on a Nicolet 5 DXBO FT-IR spectrophotometer. The ^1H NMR spectrum was recorded on a Varian Mercury spectrometer operating at 399.94 MHz. The electronic absorption spectrum was recorded in methylene chloride solvent using a Perkin-Elmer Lambda 14 UV−visible spectrophotometer. Elemental analysis was performed by Desert Analytics, Tucson, AZ.

Synthesis of $[Ru_2(CO)_6\{\mu\text{-}(Fc)C_4(Fc)C{\equiv}C{-}C{\equiv}C\}]_2$, 2. A 20.0-mg amount of $Ru_3(CO)_{12}$ (0.0313 mmol) was dissolved in 30 mL of hexane in a 100-mL three-necked round-bottom flask. A 22-mg amount of **1** (0.0470 mmol) was added, and the solution was then heated to reflux for 3 h. The solvent was then removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was separated by TLC on silica gel with a hexane/CH_2Cl_2 (3:1) solvent mixture. Three bands were eluted. The first two (yellow and orange) were unreacted $Ru_3(CO)_{12}$ (7.2 mg) and **1** (6.5 mg). The third band (orange) yielded 1 mg of product **2** in a 4% yield (6% based on the amount of $Ru_3(CO)_{12}$ consumed). Analytical and spectral data for **2**: IR (cm^{-1}, hexane) ν_{CO}: 2084 (m), 2079 (s), 2053 (vs), 2020 (vs), 1998 (w), 1979 (m). ^1H NMR ($CDCl_3$, δ): 5.25 (m, 4H, C_5H_4); 4.53 (m, 8H, C_5H_4); 4.38 (m, 4H, C_5H_4); 4.27 (s, 20H, 4Cp). UV−vis λ_{max}, nm (ϵ): 482 (13 630) and a shoulder at 338 (51 930). Anal. Calcd: C, 48.84; H, 2.15. Found: C, 48.67; H, 2.07.

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Crystallographic Analysis. Red crystals of **2** were grown by slow evaporation of the solvent from a hexane/CH_2Cl_2 (5:1) solution of the complex at 25 °C. A red rod-shaped crystal of dimensions 0.28 × 0.05 × 0.05 mm was used for the diffraction analysis. The X-ray intensity data were measured on a Bruker SMART APEX 4K CCD-based diffractometer equipped with a Mo-target X-ray tube. The raw frame data were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The cell constants are based on the refinement of the XYZ centroids of 4365 reflections above 10 s(I). The structure was solved (direct methods) and refined using the Bruker SHELXTL Version 5.1 suite of programs. Neutral-atom scattering factors were calculated by the standard procedures. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function: $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/(\sum(w(F_o^2)^2))]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + 0.0230(1/3F_o^2 + 2/3F_c^2)]$. All calculations were performed on a Gateway E4200 800 MHz computer by using the SHELXTL Version 5.1 suite of programs. Lorentz/polarization and absorption corrections (SADABS) were applied. Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified on the basis of the systematic absences observed in the intensity data. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included without refinement in calculated positions with C−H distances of 0.96 Å. A total of 1 equiv of CH_2Cl_2/formula of complex from the crystallization solvent was found in the crystal. The chlorine atoms were disordered over three sites, but the molecule was refined satisfactorily with anisotropic thermal parameters. Crystallographic data are listed in Table 1.

Table 1. Crystallographic Data for Compound **2**

formula	$C_{68}H_{36}Fe_4O_{12}Ru_4 \cdot CH_2Cl_2$
fw	1757.57
a (Å)	21.222(4)
b (Å)	10.121(2)
c (Å)	31.938(7)
β (deg)	107.262(4)
V (Å^3)	6551(2)
space group	$P2_1/c$ (No. 14)
Z	4
T (°C)	23
λ(Mo) (Å)	0.71073
ρ_{calc} (g/cm^3)	1.78
μ(Mo Kα) (mm^{-1})	1.90
R (F^2)[a]	0.052
R_w (F^2)[a]	0.100

[a] $R = \sum_{hkl}(||F_o| - |F_c||/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o^2| - |F_c^2|^2)/\sum_{hkl}(wF_o^2)^2]^{1/2}$.

Electrochemical Measurements. Differential pulse voltammetric (DPV) measurements were performed by using a three-electrode system consisting of a glassy carbon working electrode, a platinum counter, and a Ag/AgCl reference electrode on a CV-50W voltammetric analyzer purchased from Bioanalytical Systems, West Lafayette, IN. Samples were prepared in 1.0 mM solutions by using a CH_3CN/CH_2Cl_2 (1:1) solvent mixture containing 0.1 M tetrabutylammonium hexafluorophosphate. The DPV of **2** shows two very closely spaced two-electron oxidations for the ferrocenyl groups at $E° = +0.490$ and $+0.537$ V, $\Delta E = 0.047$ V. The DPV of **1** shows only a single two-electron oxidation at $E° = +0.576$ V.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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