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Covalent Modification of Diruthenium Alkynyl Compounds: Novel Application of *Click* Reactions in Organometallic Chemistry

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Summary: Diruthenium alkynyl compounds containing one or two 1,2,3-triazoles were prepared via the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction (click reaction). Electrochemical, magnetic, and molecular structural features of the click products indicate that peripheral modification with the 1,2,3-triazole substituent induces minimal changes in both the molecular structure and electronic properties of Ru$_2$ alkynyl compounds.

Methodologies for conjugation of biological systems with transition-metal complexes have attracted immense interest in recent years.[1,2] The majority of research efforts have focused on ferrocene modification of biomolecules, while the use of other metal centers such as Ru, Cu, and Zn is also known.[1,2] Recently, the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between an alkyne and an organic azide,[3] a *click* reaction, has gained tremendous popularity and been applied to the field of chemistry, biology, and materials science, owing to its exclusive regioselectivity, expansive substrate scope, mild reaction conditions, and very high yields.[4] While the Cu(I)-catalyzed azide alkyne reaction is most often applied to the field of organic/bioorganic chemistry, its application to inorganic/organometallic species is rare. To the best of our knowledge, there are only two examples involving inorganic/organometallic species: the synthesis of ferrocene carbohydrate conjugates by Santoyo-González[5] and the in situ ferrocene functionalization of electrode surfaces by Collman and Chidsey.[6]

Our laboratory has reported many Ru$_2$ alkynyl compounds, with an emphasis on their applications as electronic and optoelectronic materials.[7] In addition to the facile charge mobility across the conjugated backbone,[8] these metal alkynyl compounds are excellent electrophores and chromophores and, hence, are ideal as the reporter group for chemical and biochemical sensors. As the first step toward the long-term goal of Ru$_2$ alkynyl biosensors, we have begun to examine the applicability of the Cu(I)-catalyzed azide alkyne reaction to Ru$_2$ alkynyl compounds and preliminary results are reported herein.

With the recent success in postmetalation ligand modification of diruthenium alkynyl compounds, our initial attempt in the application of the *click* reaction was based on Ru$_2$(*D*mAni*F*)$_3$(DMBA-4-C$_2$H)Cl (**1a** in Scheme 1; *D*mAni*F* is *N*,*N*′-di(*m*-methoxyphenyl)formamidinate and DMBA-4-C$_2$H is *N*,*N*′-dimethyl-4-ethynylbenzamidinate), where the terminal ethyne is located on the periphery of the DMBA ligand.[9] The *click* reaction between **1a** and PhCH$_2$N$_3$ in a solution of Bu^{t}OH and H$_2$O in a 2:1 ratio (v/v) using 5 mol % CuSO$_4$ and 10 mol % sodium ascorbate afforded the anticipated Ru$_2$-containing *click* product **2a** in excellent yields (quantitative in situ; 63% purified). Purification of **2a** was achieved by simple extraction with CH$_2$Cl$_2$ from the reaction mixture, and the compound was authenticated by FAB-MS and elemental analysis. To date, attempts to crystallize **2a** have been unsuccessful.

Similar to the previously established alkynylation chemistry of diruthenium compounds,[7] the reaction between **2a** and 10 equiv of LiC$_4$SiMe$_3$ resulted in the bis(butadiynyl) compound **4a**. Compound **4a** was successfully crystallized and characterized by X-ray diffraction,[10] and its structural plot is presented in Figure 1 along with some selected geometric parameters. The overall geometry of the Ru$_2$ core in molecule **4a** is quite similar to those of Ru$_2$(*D*mAni*F*)$_3$(DMBA-4-X)(C$_4$SiMe$_3$)$_2$ type compounds (X = I, C≡CSi^{i}Pr$_3$).[9] The geometry of

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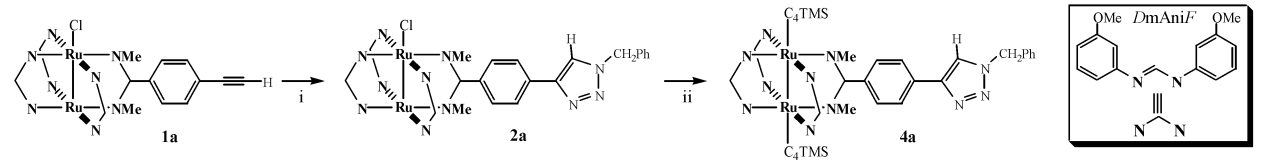
[10] X-ray diffraction data for crystals **4a** and **3c** were collected on a Bruker SMART1000 CCD diffractometer using Mo Kα radiation at 300 K. Crystal data for **4a**·2(toluene): C$_{91}$H$_{81}$N$_{11}$O$_6$Ru$_2$Si$_2$, M_r = 1682.99, triclinic, $P\bar{1}$, a = 14.3200(6) Å, b = 16.7241(7) Å, c = 18.8792(8) Å, α = 99.497(1)°, β = 98.636(1)°, γ = 93.273(1)°, V = 4393.3(3) Å^3, Z = 2, ρ = 1.272 g cm^{-3}. Least-squares refinement based on 8368 reflections with $I = 2\sigma(I)$ and 928 parameters led to convergence with final R1 = 0.050 and wR2 = 0.105. Crystal data for **3c**·(toluene)·0.5(benzene): C$_{93}$H$_{87}$N$_{14}$O$_6$Ru$_2$Si, M_r = 1727.00, monoclinic, $P2_1/c$, a = 22.9842(7) Å, b = 20.0256(6) Å, c = 19.5247(6) Å, β = 98.752(1)°, V = 8882.0(5) Å^3, Z = 4, ρ = 1.291 g cm^{-3}. Least-squares refinement based on 6848 reflections with $I = 2\sigma(I)$ and 995 parameters led to convergence with final R1 = 0.058 and wR2 = 0.092.

10.1021/om0501632 CCC: $30.25

Scheme 1. Synthetic Routes of the *Click* Product 2a and Alkynylated Product 4a[a]



[a] Legend: (i) $CuSO_4 \cdot 5H_2O$ (5 mol %), sodium ascorbate (10 mol %), $PhCH_2N_3$, Bu^tOH/H_2O (2:1, v/v); (ii) LiC_4TMS (10 equiv), THF.

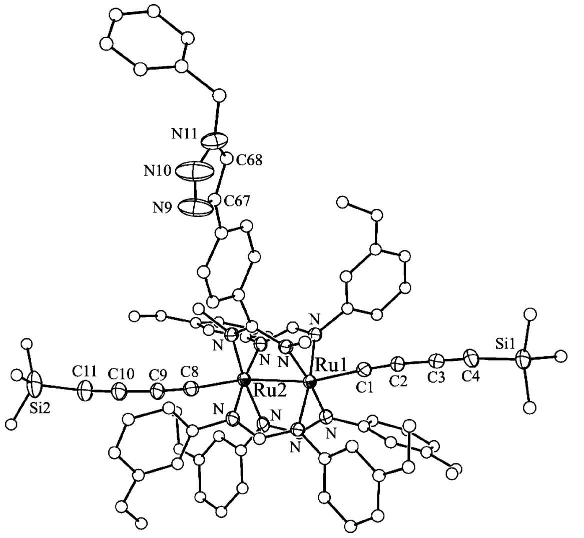


Figure 1. ORTEP representation of molecule **4a** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.5509(5); Ru1−C1, 1.962(5); Ru2−C8, 1.957(5); Ru−N(averaged), 2.047[4]; C67−C68, 1.345(7); N(9)−C(67), 1.338(7); N(11)−C(68), 1.342(7); N(9)−N(10), 1.319(7); N(10)−N(11), 1.329(7).

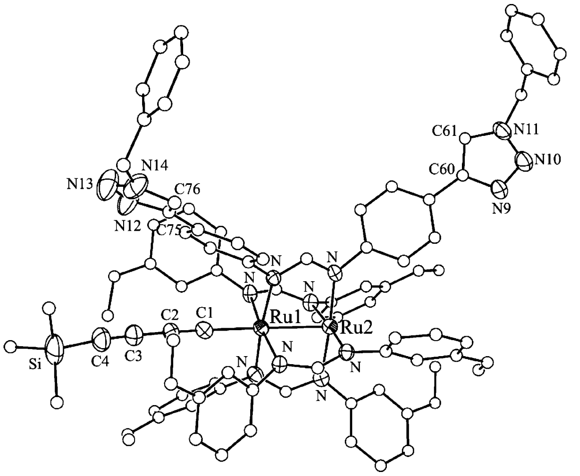


Figure 2. ORTEP representation of molecule **3c** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.4795(7); Ru1−C1, 2.028(7); Ru−N(averaged), 2.035[5]; C(60)−C(61), 1.349(8); N(9)−C(60), 1.360(8); N(9)−N(10), 1.322(8); N(10)−N(11), 1.315(8); N(11)−C(61), 1.339(8); C(75)−C(76), 1.355(8); N(12)−C(75), 1.357(7); N(12)−N(13), 1.332(6); N(13)−N(14), 1.332(7); N(14)−C(76), 1.327(7).

the 1,2,3-triazole group (C67−C68−N11−N10−N9) in **4a** verifies the regiospecificity of the Cu(I)-catalyzed azide alkyne reaction: trans [2 + 3] cycloaddition between the terminal acetylene group (−C≡CH) and azide group (−N=N≡N).[3]

The success of the Cu(I)-catalyzed azide alkyne reaction on the periphery of the DMBA ligand encouraged the extension of the approach to diruthenium species supported by other N,N′-bidentate ligands containing peripheral ethyne(s). Specifically, Ru_2(*D*mAni*F*)$_3$(OAc)Cl reacts with either *N*-phenyl-*N*′-(4-iodophenyl)formamidine (H*D*Ph*F*1) or *N*,*N*′-di(4-iodophenyl)formamidine (H*D*Ph*F*2) to yield either Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*1)Cl or Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*2)Cl, respectively (Supporting Information). Subsequently, Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*1)Cl and Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*2)Cl react with trimethylsilylacetylene under Sonogashira conditions, followed by desilylation with K_2CO_3 in THF/CH_3OH, to yield Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*3)Cl (**1b**; *D*Ph*F*3 = *N*-phenyl-*N*′-(4-ethynylphenyl)formamidinate) and Ru_2(*D*mAni*F*)$_3$(*D*Ph*F*4)Cl (**1c**; *D*Ph*F*4 = *N*,*N*′-di(4-ethynylphenyl)formamidinate), respectively (Supporting Information). As shown in Table 1, both the mono(ethyne) compound **1b** and bis(ethyne) compound **1c** undergo *click* reactions with $PhCH_2N_3$ to furnish compounds **2b**,**c**, respectively. Further alkynylation of compounds **2b** with 10 equiv of LiC_4TMS resulted in a mixture of mono(butadiynyl) (**3b**) and bis(butadiynyl) axial adducts (**4b**) that were separated via column chromatography. Compounds **3c** and **4c** were prepared from **2c** under similar conditions.

The molecular structure of **3c** was established through a single-crystal X-ray diffraction study, and the formation of two 1,2,3-triazoles is obvious from its ORTEP plot (Figure 2). The Ru−Ru bond length in **3c** is slightly shorter than that of Ru_2(*D*mAni*F*)$_4$(C_4SiMe_3) (2.506 Å),[11] while the Ru−C_α and averaged Ru−N bond lengths are identical. The similarities between the new compounds reported herein and those based on unfunctionalized *D*Ar*F* are apparent in physical properties such as magnetism and optical properties as well. Compounds of either single chloro or butadiynyl axial ligands, namely **1a**−**c**, **2a**−**c**, and **3b**,**c**, are paramagnetic with room-temperature magnetic moments ranging from 3.52 to 3.96 μ_B, indicating an $S = {}^3/_2$ ground state typical of Ru_2L_4X (X as halide or alkynyl) type compounds.[7] Compounds bearing two axial butadiynyl ligands (**4a**−**c**) are diamagnetic with well-resolved NMR spectra, as is common to other bis(alkynyl) Ru_2(III,III) compounds.

Similar to the diruthenium paddlewheel compounds previously reported,[7,9] all compounds reported herein are rich in redox activity, and their cyclic voltammograms (CV) are provided in the Suppoting Information. As an example, the CVs of both compound **4c** and the previously reported Ru_2(*D*mAni*F*)$_4$(C_4SiMe_3)$_2$[11] are shown in Figure 3. Both compounds exhibit an irreversible oxidation (**A**) and two (quasi)reversible reductions (**B** and **C**) with little differences in electrode potentials. Clearly, the modification of Ru_2 alkynyl compounds through these peripheral *click* reactions resulted in a very minimal electronic perturbation.

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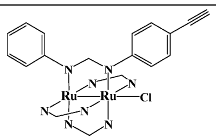
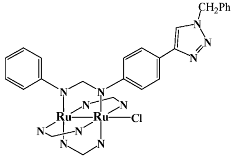
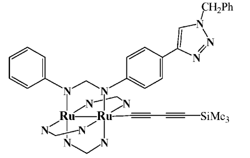
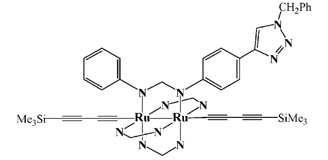
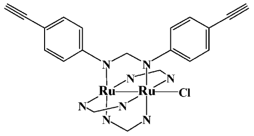
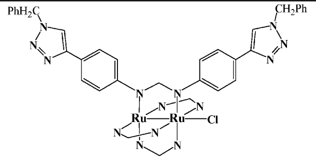
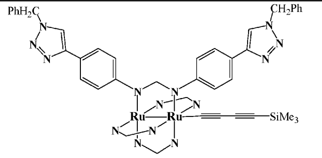
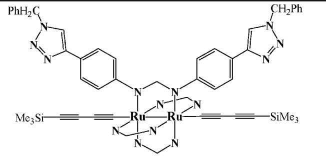
Table 1. Ru_2-Containing Ethynes and Their *Click* Products

{Ru_2}-ethyne **1**	*Click* product **2**[a]	Axial butadiynyl adducts **3/4**[b]	
 **1b**	 **2b**	 **3b**	 **4b**
 **1c**	 **2c**	 **3c**	 **4c**

[a] Conditions for **2**: $CuSO_4 \cdot 5H_2O$ (5 mol %), sodium ascorbate (10 mol %), $PhCH_2N_3$, Bu^tOH/H_2O (2:1, v/v). Yields: 86% for **2b** and 77% for **2c**. [b] Conditions for **3** and **4**: LiC_4TMS (10 equiv), THF; Yields: 52% for **3b** and 34% for **4b**. Yields: 43% for **3c** and 28% for **4c**.

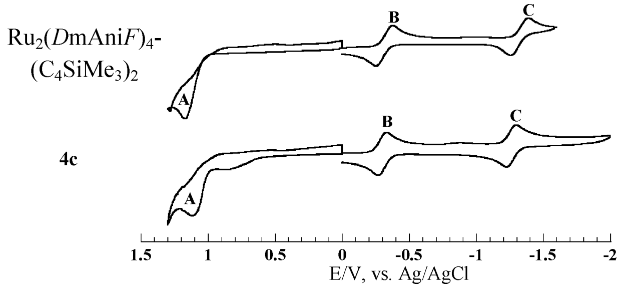


Figure 3. Cyclic voltammograms of compound **4c** and $Ru_2(DmAniF)_4(C_4SiMe_3)_2$ recorded in 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

We have demonstrated that the Cu(I)-catalyzed azide alkyne reaction can be applied to inorganic and organometallic species through the use of ligands bearing peripheral ethyne groups. This *click* reaction occurs quantitatively in situ, which is essential for the formation of bioconjugates, and yields of purified *click* products were satisfactory as well (63−86%). Most significantly, the formation of 1,2,3-triazole on the periphery of Ru_2 metallaynes has almost no effect on both the coordination geometry around the Ru_2 core and electronic properties of Ru_2 metallaynes. Extension of the *click* methodology reported herein to both the synthesis of Ru_2-containing bioconjugates and surface modification is currently under way. It is noteworthy that the *D*Ar*F* type ligands have played a critical role in both the supramolecular assemblies and DNA-binding agents based on metal−metal-bonded dinuclear compounds.[12] Hence, the Cu(I)-catalyzed azide alkyne reaction based on both *D*Ph*F*3 and *D*Ph*F*4 ligands may add a new dimension to the research of metal−metal bonded dinuclear compounds.

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Supporting Information Available: Text, figures, and a table giving details of synthesis and characterizations of compounds **1**−**4** and X-ray crystallographic data as CIF files for compounds **4a** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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