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Postmetalation Ligand Modification on the Periphery of a Diruthenium Compound: Toward Novel Metallayne Scaffoldings

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Summary: A diruthenium compound bearing a peripheral iodo substituent cross-couples with acetylenes under Sonogashira conditions to yield a novel family of diruthenium compounds bearing a peripheral alkyne functionality, which can be further functionalized at the axial positions via a reaction with lithiated butadiynyl.

Boosted by the immense interest in carbon-rich materials such as fullerenes and carbon nanotubes, there have been growing efforts in recent years in both the synthesis of new metallaynes[1] and their material applications as nonlinear optical chromophores[2] and active species in molecular electronic devices.[3] Equally exciting is the possibility of using metallaynes as scaffoldings for 2-D and 3-D carbon-rich networks that may rival fullerene in both the beauty and diversity of material properties.[4] Our laboratory has reported a host of diruthenium compounds bearing axial σ-ethynyl/polyynyl ligands[5] and demonstrated the facile electron delocalization along the conjugated backbone.[6] Ru_2 metallaynes are both intense visible−near-infrared chromophores and excellent electrophores with multiple reversible redox couples over a broad potential window.[5] Clearly of great interest is whether Ru_2 metallaynes can be (i) incorporated in 2- and 3-D supramolecular assemblies and (ii) used as the reporter group in chemical and biochemical sensors. To achieve these objectives, Ru_2 metallaynes need to be functionalized in the direction(s) orthogonal to the Ru_2−σ-alkynyl vector, and our initial exploratory efforts are described in this contribution.

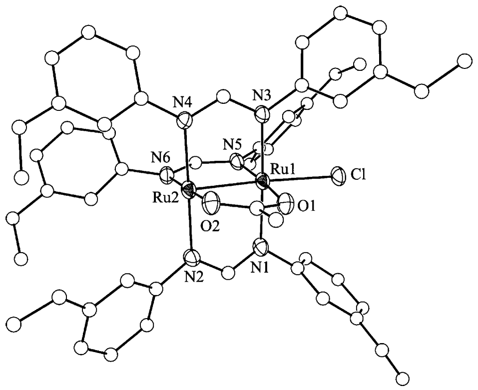

Figure 1. ORTEP representation of molecule **1** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.3220(7); Ru1−Cl, 2.405(2).

Critical to the orthogonal functionalization of Ru_2-metallayne is the accessibility of the $Ru_2^{II,III}(LL)_3(OAc)Cl$ type compounds (LL = *N*,*N*′-diarylformamidinate). Ru_2(*D*mAni*F*)$_3$(OAc)Cl (**1**; *D*mAni*F* is *N*,*N*′-bis(*m*-methoxyphenyl)formamidinate) was obtained in 87% yield using a modification of the recently published procedures,[7] and its molecular structure is provided in Figure 1. As shown in Scheme 1, the acetate in compound **1** can be readily displaced with *N*,*N*′-dimethyl-4-iodobenzamidinate (I-DMBA) to yield $Ru_2^{II,III}$(*D*mAni*F*)$_3$(I-DMBA)Cl (**2**). The presence of the iodo substituent gives access to a variety of Pd-catalyzed cross-coupling reactions.[8] Hence, treating **2** with the terminal alkynes $HC{\equiv}CY$ (Y = Si^iPr_3, Fc) under Sonogashira conditions furnished compounds **3a**,**b**. To our knowledge, the conversion of **2** to **3** is the first example of postmetalation modification of a bridging ligand in a paddle-wheel species *by design*. Compounds **3a**,**b** reacted with 3 equiv of LiC_4SiMe_3 to yield *trans*-bis(butadiynyl) derivatives **4a**,**b** analogous to the established alkynylation chemistry of diruthenium compounds.[5] We also sought an alternative route to **4**: treating **2** with 3 equiv of LiC_4SiMe_3 resulted in *trans*-$Ru_2^{III,III}$(*D*mAni*F*)$_3$(I-DMBA)$(C_4SiMe_3)_2$ (**5**; 46%). However, the reaction between **5** and HC_2Y under Sonogashira conditions yielded a mixture of Ru_2 compounds

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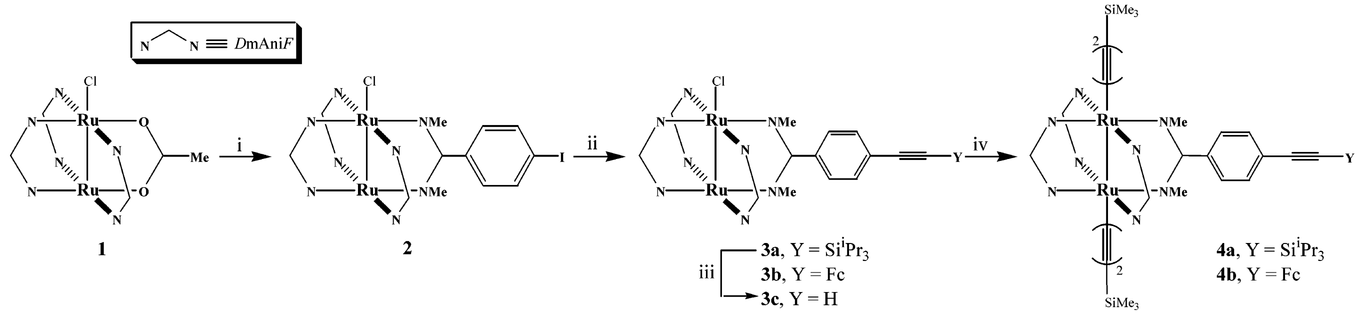
Scheme 1[a]



[a] Legend: (i) 2 equiv of *N*,*N*′-dimethyl-4-iodobenzamidine, LiCl, Et_3N; 79%; (ii) HC_2Y, *trans*-$Pd(PPh_3)_2Cl_2$, CuI, $^iPr_2NH$, THF, room temperature, yield 41% (**3a**), 49% (**3b**); (iii) Bu_4NF, THF; quantitative; (iv) 3 equiv of LiC_4TMS, THF, yield 43% (**4a**), 37% (**4b**).

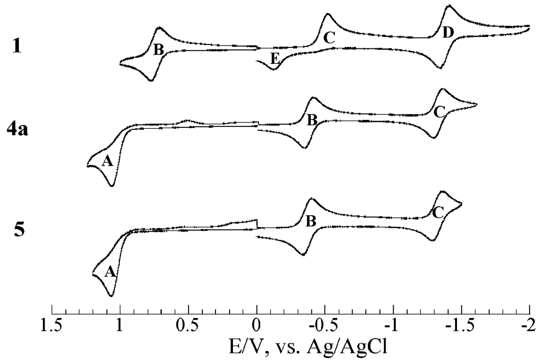


Figure 2. Cyclic voltammograms of compounds **1**, **4a**, and **5** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

free of axial alkynyl ligands instead of **4**. Clearly, the axial Ru−butadiynyl bonds are unstable under Sonogashira conditions.

Similar to other $Ru_2(LL)_3(OAc)Cl$ type compounds,[7] compound **1** is purple. Compounds **2** and **3a**,**b** are green, which is typical for $Ru_2(DArF)_4Cl$ type compounds.[9] Compounds **1**−**3** are paramagnetic, with effective magnetic moments corresponding to an $S = {}^3/_2$ ground state. On the other hand, compounds **4a**,**b** and **5** are diamagnetic and deep red, both being characteristics of *trans*-$Ru_2(DArF)_4(C_2R)_2$ species (*D*Ar*F* is diarylformamidinate).[10] All compounds display at least three redox couples (cyclic voltammograms of compounds **1**−**5** are provided in the Supporting Information). As typified by the CV of **1** in Figure 2, compounds of $Ru_2^{II,III}(LL)_3(LL')$-Cl type (**1**−**3**; LL′ is either OAc or I-DMBA) exhibit a one-electron oxidation (**B**) and two one-electron reductions (**C** and **D**). The first reduction of **1** is irreversible, due to the fast dissociation of the axial Cl^- ligand, and the resultant $Ru_2(LL)_3(LL')$ species is reoxidized at a more positive potential (**E**).[9b] Similar to the previously studied bis(alkynyl) $Ru_2^{III,III}$ compounds,[10] compounds **4** and **5** exhibit one irreversible oxidation (**A**) and two reversible one-electron reductions (**B** and **C**), and the latter reflect the robustness of Ru−C bonds upon reduction.

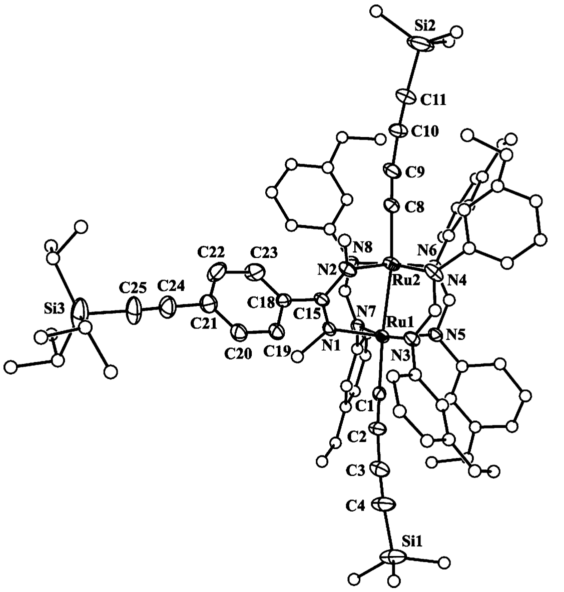


Figure 3. ORTEP representation of molecule **4a** at the 20% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.5467(7); Ru1−C1, 1.976(6); Ru2−C8, 1.988(7); Ru−N(averaged), 2.051[6].

Compounds **1**−**5** are generally crystalline, and the molecular structures of **1**, **4a**, and **5** have been determined through X-ray diffraction studies.[11] The structural plots of **4a** and **5** are presented in Figures 3 and 4, respectively, along with some selected geometric parameters. While the Ru−Ru bond is short in the parent compound **1** (2.3220(7) Å), bis(butadiynyl) derivatives **4a** and **5** have significantly elongated Ru−Ru

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(11) X-ray single-crystal data for crystals of **1**, **4a**, and **5** were collected on a Bruker SMART1000 CCD diffractometer using Mo Kα radiation at 300 K. Crystal data for **1**·H_2O: $C_{47}H_{48}N_6O_9Ru_2Cl$, fw = 1078.50, triclinic, $P\bar{1}$, $a = 13.173(1)$ Å, $b = 15.358(1)$ Å, $c = 16.802(1)$ Å, $\alpha = 116.426(1)°$, $\beta = 107.284(1)°$, $\gamma = 96.207(1)°$, $V = 2789.2(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.284$ g cm^{-3}. Of 14 739 reflections measured, 9687 were unique ($R_{int} = 0.040$). Least-squares refinement based on 5913 reflections with $I \geq 2\sigma(I)$ and 586 parameters led to convergence with final R1 = 0.065 and wR2 = 0.189. Crystal Data for **4a**: $C_{79}H_{93}N_8O_6Ru_2Si_3$, fw = 1537.0, triclinic, $P\bar{1}$, $a = 15.375(2)$ Å, $b = 17.521(2)$ Å, $c = 18.281(3)$ Å, $\alpha = 80.35(1)°$, $\beta = 82.95(1)°$, $\gamma = 66.348(9)°$, $V = 4439(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.150$ g cm^{-3}. Of 28 565 reflections measured, 19 986 were unique ($R_{int} = 0.062$). Least-squares refinement based on 7921 reflections with $I \geq 2\sigma(I)$ and 876 parameters led to convergence with final R1 = 0.067 and wR2 = 0.182. Crystal Data for **5**: $C_{68}H_{73}N_8O_6Ru_2Si_2I$, fw = 1483.6, monoclinic, $P2_1/n$, $a = 21.260(1)$ Å, $b = 10.406(1)$ Å, $c = 33.170(1)$ Å, $\beta = 107.811(1)°$, $V = 6986.2(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.411$ g cm^{-3}. Of 44 520 reflections measured, 16 601 were unique ($R_{int} = 0.071$). Least-squares refinement based on 8316 reflections with $I \geq 2\sigma(I)$ and 784 parameters led to convergence with final R1 = 0.053 and wR2 = 0.078.

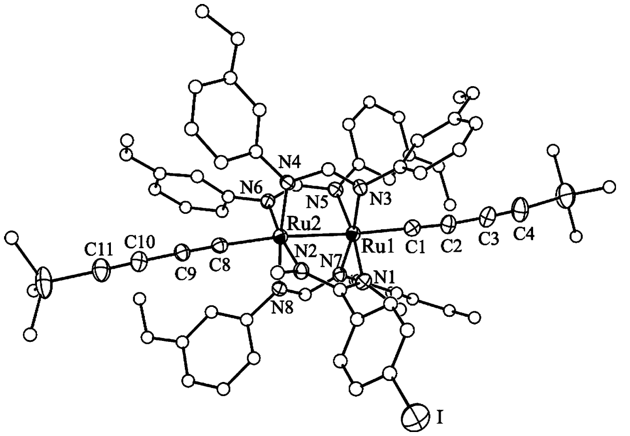

Figure 4. ORTEP representation of molecule **5** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.5581(5); Ru1−C1, 1.949(5); Ru2−C8, 1.954(5); Ru−N(averaged), 2.050[4].

bonds, reflecting the loss of σ(Ru−Ru) upon the formation of two σ(Ru−C) bonds (Ru1−C1 and Ru2−C8). The coordination geometries around the diruthenium core in compounds **4a** and **5** are very similar to those previously reported for the $Ru_2(DArF)_4(C_2R)_2$ type compounds,[10] which indicates a minimal impact on the electronic properties of Ru_2 metallaynes upon the covalent modification of the *N,N′*-bidentate bridging ligand.

Recent years have witnessed significant progress in supramolecular chemistry based on linking dimetallic units at the equatorial positions,[12] where the ditopic linkers are typically *preformed*. Our preliminary studies outlined in Scheme 1 demonstrated the facile synthesis of a series of novel Ru_2 compounds **3**−**5**, which may provide a viable alternative in constructing supramolecules. One can easily envision the formation of a linked dimer through either the homocoupling of **3c** under Glaser conditions or cross-coupling between **2** and **3c** under Sonogashira conditions. Furthermore, the presence of the peripheral iodo substituent in compound **2** should enable both the functionalization of biological macromolecules such as proteins and nucleic acids with the diruthenium unit and incorporation of the diruthenium unit into a dendrimer. These interesting aspects are being vigorously pursued in our laboratory.

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Supporting Information Available: Text giving details of syntheses and characterizations of compounds **1**−**5** and X-ray crystallographic files in CIF format for compounds **1**, **4a,** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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