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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.

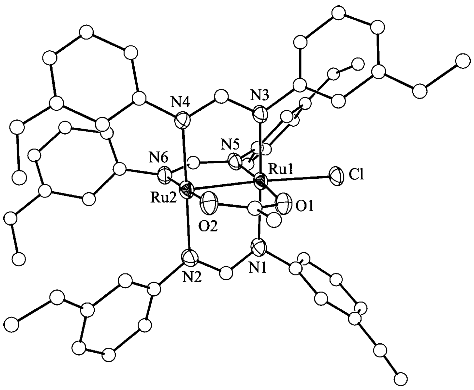

Figure 1. ORTEP representation of molecule **1** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.3220(7); Ru1−Cl, 2.405(2).

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≡CY (Y = $\mathrm{Si^iPr_3}$, 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$_4$SiMe$_3$ 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$_4$SiMe$_3$ resulted in *trans*-Ru$_2^{III,III}$(*D*mAni*F*)$_3$(I-DMBA)(C$_4$SiMe$_3$)$_2$ (**5**; 46%). However, the reaction between **5** and HC$_2$Y under Sonogashira conditions yielded a mixture of Ru$_2$ compounds

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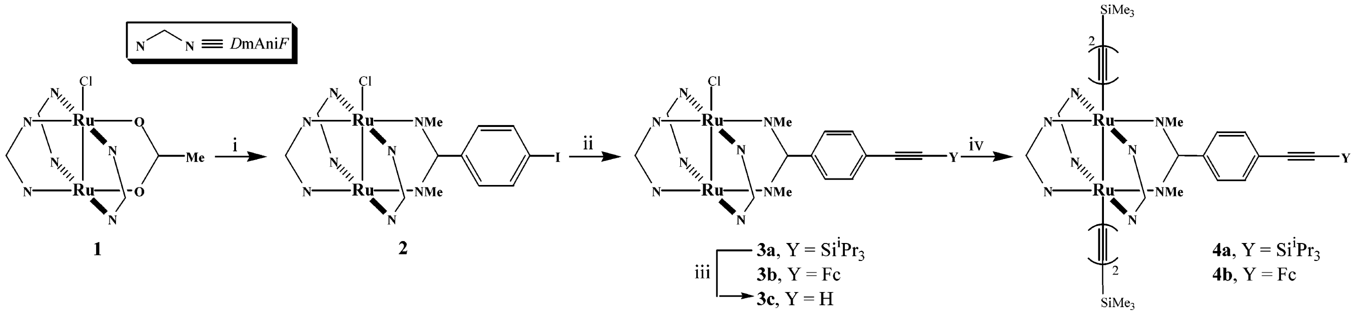
10.1021/om049702d CCC: $27.50

Scheme 1[a]



[a] Legend: (i) 2 equiv of *N,N′*-dimethyl-4-iodobenzamidine, LiCl, Et$_3$N; 79%; (ii) HC$_2$Y, *trans*-Pd(PPh$_3$)$_2$Cl$_2$, CuI, ^{i}Pr$_2$NH, THF, room temperature, yield 41% (**3a**), 49% (**3b**); (iii) Bu$_4$NF, THF; quantitative; (iv) 3 equiv of LiC$_4$TMS, THF, yield 43% (**4a**), 37% (**4b**).

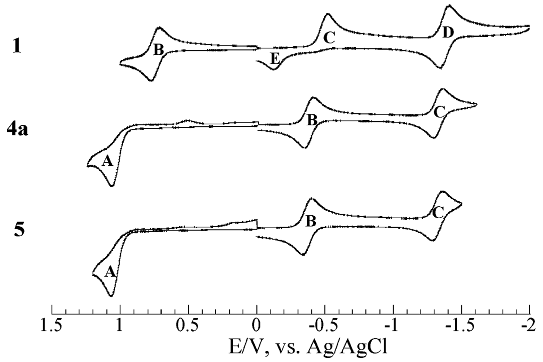


Figure 2. Cyclic voltammograms of compounds **1**, **4a**, and **5** recorded in a 0.20 M THF solution of Bu$_4$NPF$_6$ at a scan rate of 0.10 V/s.

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$_2$(*D*Ar*F*)$_4$Cl 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$_2$(*D*Ar*F*)$_4$(C$_2$R)$_2$ 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.

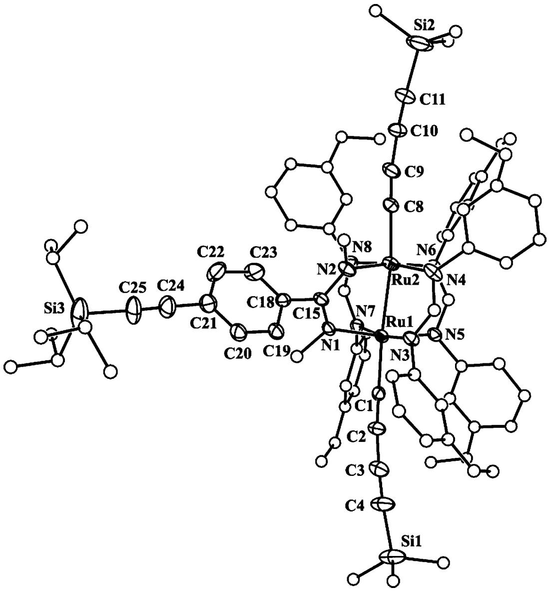


Figure 3. ORTEP representation of molecule **4a** at the 20% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.5467(7); Ru1−C1, 1.976(6); Ru2−C8, 1.988(7); Ru−N(averaged), 2.051[6].

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$_2$O: C$_{47}$H$_{48}$N$_6$O$_9$Ru$_2$Cl, fw = 1078.50, triclinic, $P\bar{1}$, a = 13.173(1) Å, b = 15.358(1) Å, c = 16.802(1) Å, α = 116.426(1)°, β = 107.284(1)°, γ = 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$_8$O$_6$Ru$_2$-Si$_3$, fw = 1537.0, triclinic, $P\bar{1}$, a = 15.375(2) Å, b = 17.521(2) Å, c = 18.281(3) Å, α = 80.35(1)°, β = 82.95(1)°, γ = 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$_8$O$_6$-Ru$_2$Si$_2$I, fw = 1483.6, monoclinic, $P2_1/n$, a = 21.260(1) Å, b = 10.406(1) Å, c = 33.170(1) Å, β = 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.

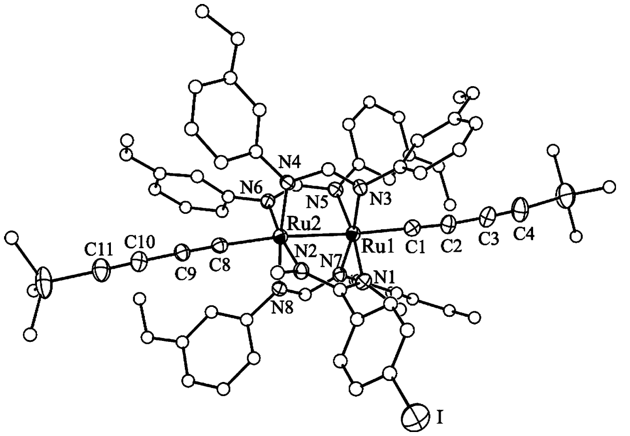

Figure 4. ORTEP representation of molecule **5** at the 30% probability level. Selected bond lengths (Å): Ru1−Ru2, 2.5581(5); Ru1−C1, 1.949(5); Ru2−C8, 1.954(5); Ru−N(averaged), 2.050[4].

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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