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# Dendronized Diruthenium Compounds via the Copper(I)-Catalyzed Click Reaction

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Novel $Ru_2$-containing dendritic compounds were prepared from the $Cu^I$-catalyzed 1,3-dipolar cycloaddition between $Ru_2$ compounds containing one or two ethynes, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-n}(DMBA\text{-}4\text{-}C_2H)_n$ with $n = 1$ and 2, and azidopoly(benzyl ether) dendrons. These new compounds were also characterized with X-ray diffraction and voltammetric techniques.

The study of metallodendrimers has been topical in recent years because of the rich topological features and versatile materials properties achieved upon the introduction of metal centers to dendrimers.[1,2] Metallodendrimers are currently investigated for applications such as catalysts,[3] nonlinear optical chromophores,[4] and drug delivery.[5] Metal centers may function as connectors, branching points, or terminal (surface) centers and can be located at either specific or random loci within dendritic architectures.[1] Metal-containing species incorporated are predominantly mononuclear species.[1] High-nuclearity clusters, such as $[Re_6Se_6]$,[6] $[Fe_4S_4]$,[7] and polyoxometalates,[8] have also been used as either the foci or termini of dendrimers. On the other hand, the dendritic chemistry of bimetallic species with a paddlewheel motif, one of the most common types of coordination compounds,[9] has remained largely unexplored. In fact, there is only one literature precedent, by Liwporncharoenvong and Luck,[10] where a series of $Mo^{II}Mo^{II}$ compounds supported by four Fréchet-type dendritic polyesters were prepared from $K_4Mo_2Cl_8$. The recent success in ligand modification on the periphery of $Ru_2$ compounds permits us to functionalize $Ru_2$ units with a variety of groups including terminal alkynes and olefins,[11−13] and the presence of these reactive functional groups provides venues for further covalent modifications. In particular, $Ru_2$ species bearing one or two terminal ethynes underwent the $Cu^I$-catalyzed 1,3-dipolar cycloaddition reaction (click reaction) with benzyl azide under very mild conditions.[14] Since its reintroduction by Sharpless and coworkers in 2001,[15] the click reaction has enjoyed great successes in polymer and materials syntheses.[16] Described in this contribution is the preliminary study of the attachment of poly(benzyl ether) dendrons (Fréchet type; Chart 1)[17] to $Ru_2$ compounds via the click reaction.

The initial attempt of dendritic modification was based on the reaction between D1-$N_3$ and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}4\text{-}C_2H)Cl$,[13] where $D(3,5\text{-}Cl_2Ph)F$ and DMBA-4-$C_2H$ are respectively *N*,*N*′-bis(3,5-dichlorophenyl)formamidinate and *N*,*N*′-dimethyl-4-ethynylbenzamidinate, in the presence of $CuSO_4$ and sodium ascorbate (Scheme 1). The solvent combination of $^t$BuOH/$H_2O$ in a 2:1 ratio, optimized in our early study,[14] resulted in a slow and incomplete reaction. Nonetheless, the use of tetrahydrofuran (THF)/$H_2O$ (1:1) afforded the anticipated $Ru_2$-containing click product **1** in the course of a few hours to overnight. Similar click reactions with higher generation dendrons, D2-$N_3$ and D3-

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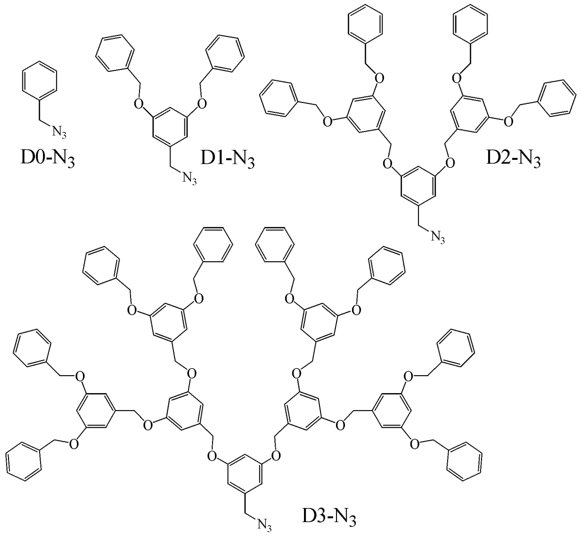
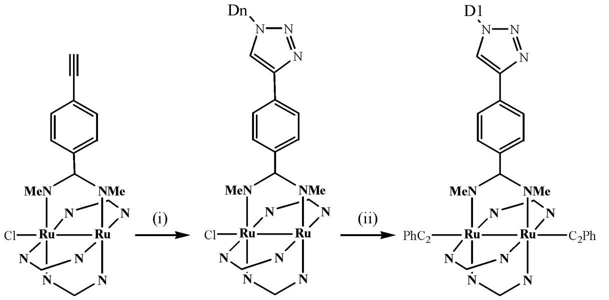
**Chart 1.** Azido-Containing Poly(benzyl ether) Dendrons



**Scheme 1.** Dendritic Modification of $Ru_2Cl(D(Cl_2Ph)F)_3(DMBA\text{-}C_2H)$[a]



*n* = 1 (**1**), 2 (**2**), and 3 (**3**)

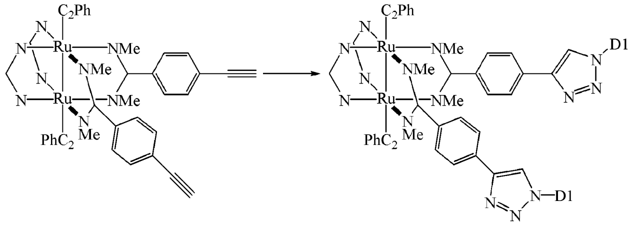
**4**

[a] Conditions: (i) $CuSO_4{\cdot}5H_2O$ (5 mol %), sodium ascorbate (10 mol %), D*n*-$N_3$ ($n = 1-3$), THF/$H_2O$ (1:1, v/v). (ii) $LiC_2Ph$ (10 equiv), THF; $n = 1$ only. N^N ≡ bis(3,5-dichlorophenyl)formamidinate.

$N_3$, proceeded under the same conditions with good yields. The purification of compounds **1**−**3** was achieved by a simple extraction with $CH_2Cl_2$ from the reaction mixture and subsequent flash silica column chromatography. Compound **1** reacted with 5 equiv of LiCCPh to yield its bis(phenylacetylide) derivative **4** under conditions previously established for similar $Ru_2$ compounds.[11] While the high-spin ($S = {}^3/_2$) nature of compounds **1**−**3** hinders their characterization by NMR spectroscopy, they were satisfactorily analyzed by mass spectrometry and combustion analysis. The structure of compound **1** was established through X-ray crystallography studies. The bis(phenylacetylide) adduct **4** is diamagnetic, which enables its characterization via $^1H$ NMR spectroscopy.

Dendritic modification of $Ru_2$ compounds containing two terminal ethynes via the click reaction was also investigated. A $Ru^{II}Ru^{III}$ compound, *cis*-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2Cl$,[13] was used in the initial trial, but the reaction only led to a mixture of unidentified products. A plausible explanation of the failed reaction is that the axial chloro ligand in $Ru_2(DArF)_2(DMBA)_2$-type compounds is quite labile and that the starting material undergoes several different reactions under the click conditions. On the other hand, the click reaction between a $Ru^{III}Ru^{III}$ compound bearing two axial phenylacetylides, *cis*-$(C_2Ph)_2$-$Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}4\text{-}C_2H)_2$,[13] and D1-$N_3$ proceeded smoothly to furnish compound **5** (Scheme 2). Compound **5** was characterized with electrospray ionization mass spectrometry and $^1H$ NMR spectroscopy.

**Scheme 2.** Dendritic Modification of $(PhC_2)_2Ru_2(D(Cl_2Ph)F)_2(DMBA\text{-}C_2H)_2$[a]



[a] Conditions: $CuSO_4{\cdot}5H_2O$ (10 mol %), sodium ascorbate (20 mol %), D1-$N_3$, THF/$H_2O$ (1:1, v/v).

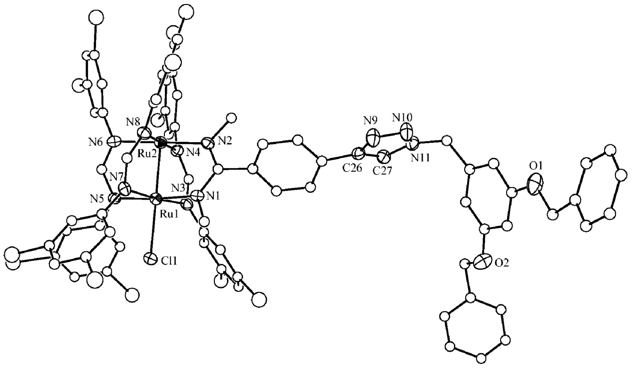


**Figure 1.** ORTEP representation of molecule **1** at 30% probability. All H atoms were omitted for clarity. Selected bond lengths (Å): Ru1−Ru2, 2.2968(7); Ru1−Cl1, 2.421(2); Ru−N(averaged), 2.073[5]; C26−C27, 1.383(9); N9−C26, 1.352(8); N9−N10, 1.317(7); N10−N11, 1.343(7); N11−C27, 1.458(8).

The molecular structure of **1** was established through a single-crystal X-ray diffraction study, and its structural plot is presented in Figure 1 along with some selected bond distances. The overall geometry of the $Ru_2$ core in molecule **1** is very similar to that of the parent compound, $Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_3(DMBA\text{-}C_2H)Cl$.[13] The Ru−Ru bond distance in **1** [2.2968(7) Å] is about 0.04 Å shorter than that of $Ru_2(D(3,5\text{-}Cl_2Ph)_2F)_3(DMBA\text{-}C_2H)Cl$ [2.3386(6) Å]. The averaged bond length of Ru−N (DMBA) is $2.036^5$ Å, about 0.05 Å shorter than that of Ru−N (formamidinate), which reflects the strong donor nature of the DMBA ligand. The geometry of the 1,2,3-triazole group (C26−C27−N11−N10−N9) in **1** confirms the regiospecificity of the $Cu^I$-catalyzed 1,3-dipolar cycloaddition reaction that was noted in prior studies.[14,15]

The overall topology of compound **1** is somewhat eye-catching because of the extended paddle formed by the D1 dendron. Although an inspection of the packing diagrams of **1** did not reveal any peculiar intermolecular interaction, it did show that molecules of **1** form a loose head-to-tail pair, as noted from a space-filling plot (see the Supporting Information). Specifically, three 3,5-dichlorophenyls linked to N6, N7, and N8 centers are twisted to form a shallow cleft that is covered by the D1 dendron from the other molecule.

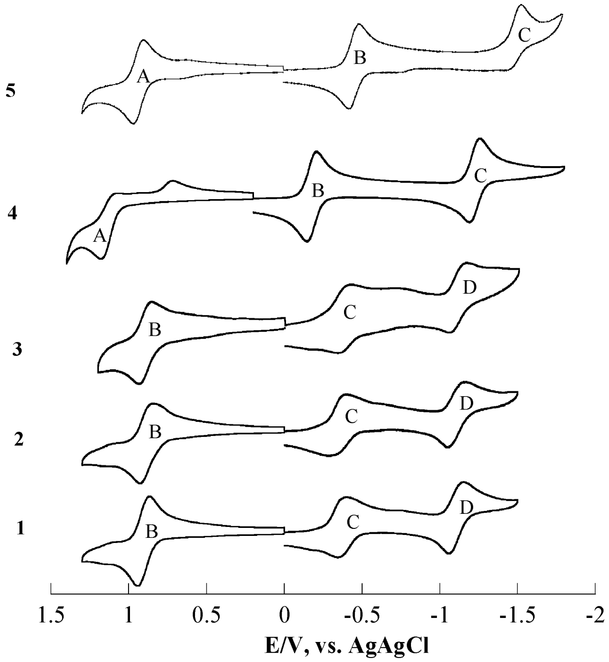


**Figure 2.** CVs of **1**−**5** recorded in a 0.20 M THF solution of $Bu_4NPF_6$ at a scan rate of 0.10 V/s.

**Scheme 3.** Designation of Redox Couples Observed in **1**−**5**

$$\mathrm{Ru_2(III,IV)} \xrightleftharpoons[\mathrm{A}]{+\,e^-} \mathrm{Ru_2(III,III)} \xrightleftharpoons[\mathrm{B}]{+\,e^-} \mathrm{Ru_2(III,II)} \xrightleftharpoons[\mathrm{C}]{+\,e^-} \mathrm{Ru_2(II,II)} \xrightleftharpoons[\mathrm{D}]{+\,e^-} \mathrm{Ru_2(I,II)}$$

Similar to $Ru_2$ paddlewheel species previously studied,[18] all compounds reported herein display multiple reversible or quasi-reversible redox couples, as exemplified by the cyclic voltammograms (CVs) of compounds **1**−**5** in Figure 2. The $Ru^{II}Ru^{III}$ species, compounds **1**−**3**, exhibit a reversible oxidation (B) and two quasi-reversible reductions (C and D) with minimal variations in the electrode potentials. All observed redox couples are $Ru_2$-based, and their assignment is given in Scheme 3. Electrode potentials ($E_{1/2}$) remain invariant as the attached dendron expands from **1** to **3**, which clearly indicates that the peripheral dendron does not perturb the electronic structure of the $Ru_2$ core. It is interesting to note that while the reversibility of the oxidation couple (B) is not affected by the dendritic modification, both reduction couples (C and D) become less reversible as the dendron expands. It is possible that the reduction processes become kinetically hindered by the increase in dendron generation as documented in prior literature examples.[7]

The CV of compound **4**, a $Ru^{II}Ru^{III}$ species, consists of an irreversible oxidation (A), a reversible reduction (B), and a quasi-reversible reduction (C). Compound **5** displays a CV quite different from that of **4**: one reversible oxidation (A), one reversible reduction (B), and one irreversible reduction (C). The electrode potentials of redox couples in **5** were cathodically shifted by at least 120 mV from those of the corresponding couples in **4**, reflecting the stronger electron-donating ability of the DMBA ligand compared to the D(3,5-$Cl_2$Ph)F ligand.

Supramolecular chemistry based on bimetallic building blocks has been a bustling area during the past decade with significant contributions from the laboratories of Cotton[19] and others,[10,20] where the majority of work is based on ligand-exchange reactions at the metal site. Most of dendritic inorganic compounds of a mononuclear focal point were also prepared from ligands that were already dendronized.[21] On the other hand, recent work from several laboratories including ours demonstrated the feasibility of hierarchical assemblies of inorganic compounds through ligand peripheral modification.[11,22] The uniqueness of this work lies in the demonstration of facile postligation dendritic modification through the peripheral click reaction, and this approach represents a new vista of inorganic supramolecular chemistry. It is hoped that analogous $Ru_2$ dendrimers with other conjugated dendrons can be prepared similarly and used as photonic antennae for solar-energy harvesting.

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**Supporting Information Available:** Detailed syntheses and characterization of compounds **1**−**5** and X-ray crystallographic details (CIF) of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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