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Organoruthenium Dendrimers Possessing Tris(4-ethynylphenyl)amine Bridges

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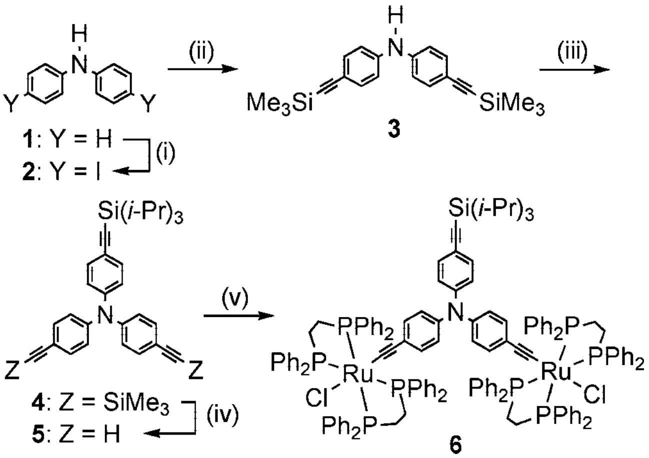
Summary: Novel ruthenium−acetylide dendrimers were synthesized by using tris(4-ethynylphenyl)amine as the bridging ligand up to the second generation by a convergent method. Multistep reversible redox behavior in the cyclic voltammogram and a bathochromic shift with an increase in the number of ruthenium species except for the second-generation dendrimer in the UV–vis spectra suggested an intramolecular interaction among ruthenium species.

Organometallic dendrimers have been attracting considerable attention, because the organometallic species may provide new functionalities based on their unique properties and reactivities to the dendritic molecule.[1] Considerable numbers of organometallic dendrimers that contain metal species at specific positions in their molecules, i.e., at the core or the periphery, have been synthesized as new catalysts.[2] Dendrimers in which metal atoms are linked by unsaturated hydrocarbons in every generation are also of interest, because they are expected to enhance electronic and optical properties by interaction among metals through π-conjugated systems.[3] However, these types of dendrimers are still limited in number and are challenging synthetic targets,[4] though multinuclear complexes that are possible component units for such types of dendrimers have been reported.[5]

Scheme 1. Synthesis of the Building Block 6[a]



[a] Reagents and conditions: (i) $BnEt_3NICl_2$, MeOH, room temperature, 98%; (ii) $HC{\equiv}CSiMe_3$, $PdCl_2(PPh_3)_2$, CuI, Et_2NH, room temperature, 89%; (iii) $4\text{-}BrC_6H_4C{\equiv}CSi(i\text{-}Pr)_3$, $Pd_2(dba)_3$, $(t\text{-}Bu)_2(2\text{-}PhC_6H_4)P$, t-BuONa, toluene, reflux, 56%; (iv) K_2CO_3, acetone−H_2O, room temperature, 97%; (v) *cis*-$RuCl_2(dppe)_2$, KPF_6, CH_2Cl_2, room temperature, and then Et_3N, room temperature, 81%.

As an extension of our studies on organometallic macromolecules composed of transition-metal−acetylide complexes, we have developed convergent and divergent routes for the synthesis of platinum−acetylide dendrimers.[6] However, no strong intramolecular interaction among metal species was observed in the dendritic molecules. Thus, we have designed new organometallic dendrimers that are expected to exhibit strong intramolecular metal−metal interactions. Recently, we synthesized trinuclear ruthenium−acetylide complexes possessing a tris(4-ethynylphenyl)amine bridge, in which intramolecular electronic coupling between ruthenium species was observed.[7] We present herein the synthesis and properties of organoruthenium dendrimers possessing the tris(4-ethynylphenyl)amine bridge.

To synthesize the target organoruthenium dendrimer, we adopted a convergent method, because the progress of the reactions could be traced and unreacted substrates and defective products could be removed by gel permeation chromatography (GPC). A synthetic route including the dinuclear ruthenium−acetylide complex **6** as a key intermediate is given in Scheme 1. The Sonogashira coupling reaction of bis(4-iodophenyl)amine (**2**), which was prepared by reacting diphenylamine (**1**) with benzyltriethylammonium dichloro-

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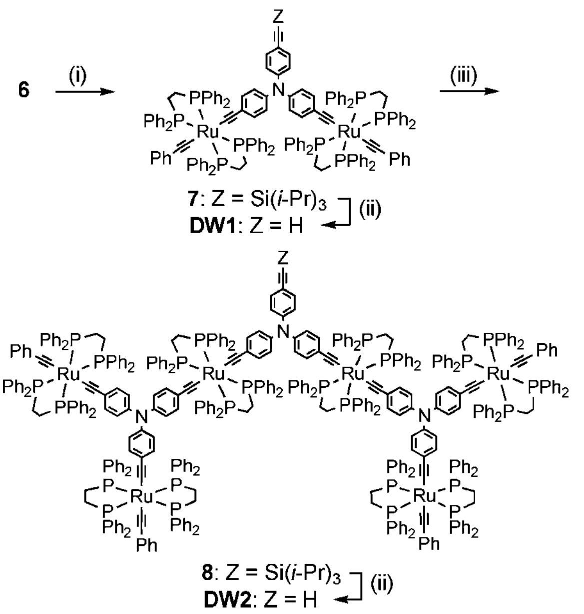
Scheme 2. Synthesis of Dendrons DW1 and DW2[a]



[a] Reagents and conditions: (i) HC≡CPh, KPF_6, Et_3N, THF, reflux, 90%; (ii) Bu_4NF, THF, −78 °C, and then room temperature, **DW1** 91%, **DW2** 91%; (iii) **6**, KPF_6, Et_3N, THF, reflux, 43%.

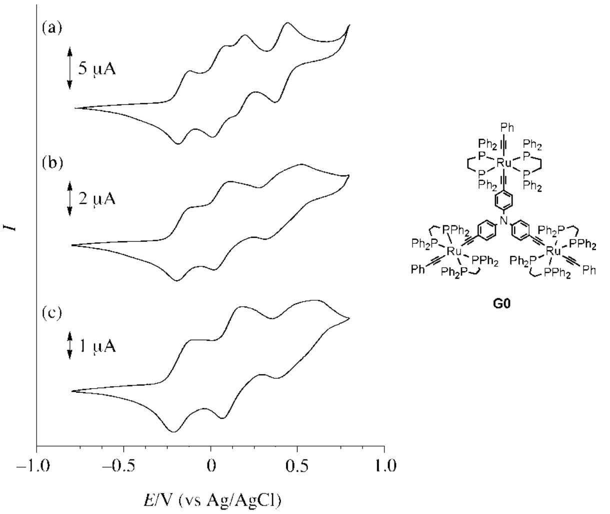


Figure 1. Cyclic voltammograms of the dendrimers (a) **G0**, (b) **G1**, and (c) **G2** in dichloromethane solution containing 0.1 M $[Bu_4N][PF_6]$ at room temperature with a scan rate of 50 mV/s.

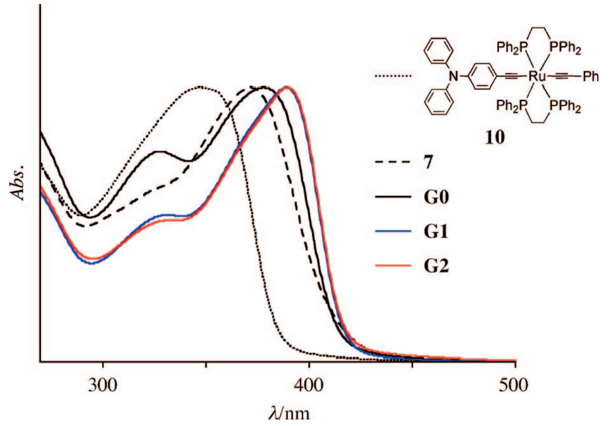


Figure 2. UV–vis spectra of dendrimers and model compounds in dichloromethane, normalized to the MLCT band.

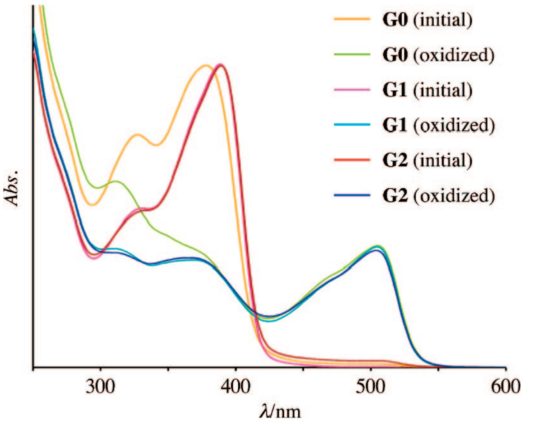


Figure 3. Electrochemical UV–vis spectra of dendrimers in dichloromethane, normalized to the MLCT band.

iodate,[8] with (trimethylsilyl)acetylene resulted in the formation of bis[4-((trimethylsilyl)ethynyl)phenyl]amine (**3**).[9] Treatment of **3** with 4-[(triisopropylsilyl)ethynyl]bromobenzene in the presence of a Pd catalyst gave the tris(4-ethynylphenyl)amine derivative **4**,[10] which had two trimethylsilyl-protected acetylenes and one triisopropylsilyl-protected acetylene. Selective removal of the trimethylsilyl group of **4** was performed by treatment with K_2CO_3 to give the monoprotected tris(4-ethynylphenyl)amine derivative **5**. Ruthenium moieties were introduced by reaction with *cis*-$RuCl_2(dppe)_2$ and KPF_6, followed by treatment with triethylamine to give **6**.[11]

As shown in Scheme 2, building block **6** was easily converted into the first-generation dendron **DW1** via the end-capped dinuclear ruthenium complex **7** by reaction with phenylacetylene and Bu_4NF. Then, the reaction of **DW1** with **6** in a 2:1 ratio produced the end-capped hexanuclear ruthenium complex **8**, which was converted into the second-generation dendron **DW2** by desilylation.

Treatment of **DW1** and **DW2** with the trinuclear ruthenium−acetylide core **9**[7] in a 3:1 ratio gave the first- and second-generation dendrimers **G1** and **G2**) in 25% and 19% yields, respectively (Scheme 3). Although defective dendrimers consisting of one or two molecules of **DW1** and **DW2** with one molecule of **9** were also generated in these reactions, **G1** and **G2** were isolated by GPC. Characterization of **G1** and **G2** was performed by spectral analyses. For example, the ^{31}P NMR spectrum of **G2** showed two singlets at δ 68.5 and 68.4 that were assignable to $Ru(C{\equiv}CR)_2(dppe)_2$ species, while no signal at approximately δ 64, which could be assignable to $RuCl(C{\equiv}CR)(dppe)_2$ species characteristic of defective dendrimers, was observed.

The cyclic voltammograms (CVs) of **G1**, **G2,** and the model triruthenium complex **G0** are given in Figure 1. In comparison with the CV of an analogous triruthenium complex,[7] the two waves at lower potential ($E_{1/2}$ = –0.16 and 0.12) for **G1** and **G2** revealed stepwise $Ru^{II}-Ru^{III}$ redox, whereas the highest broad wave was assignable to the redox of triphenylamine moieties of the bridging ligand. These properties were in sharp

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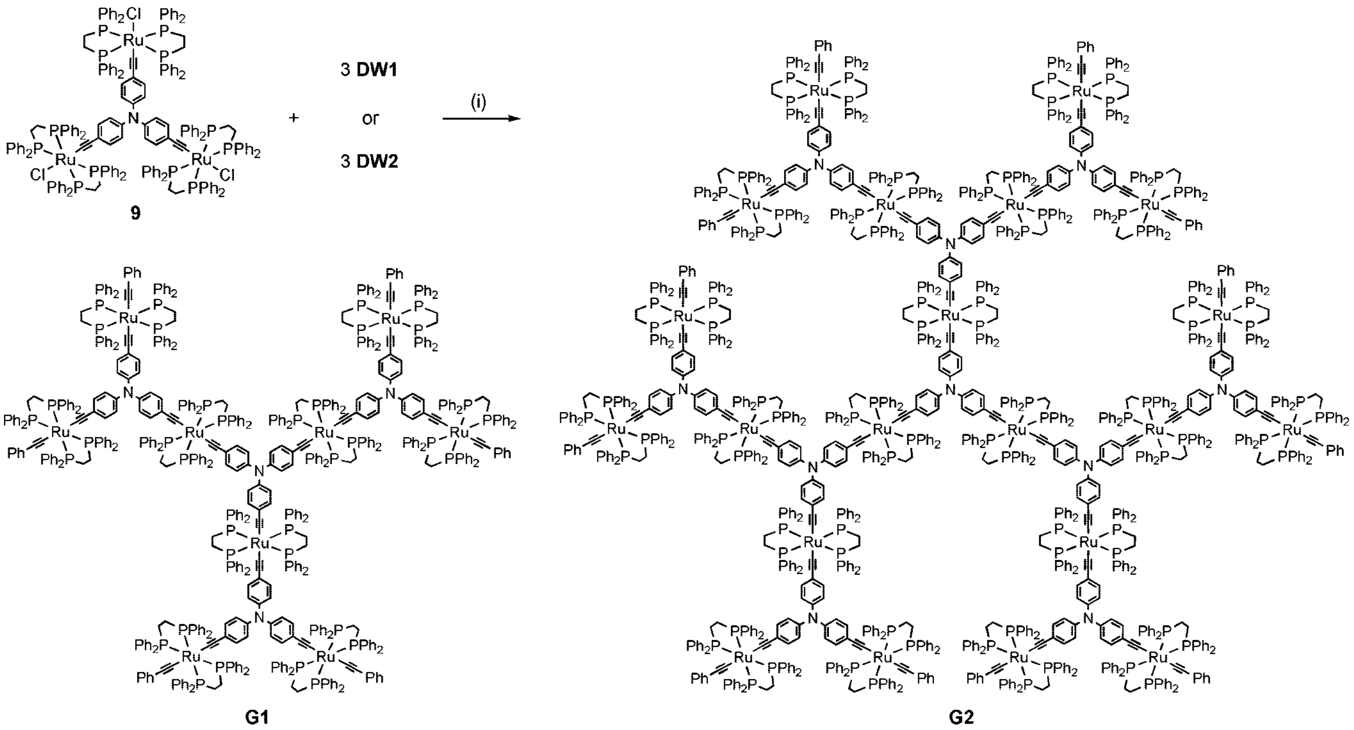
Scheme 3. Synthesis of Dendrimers G1 and G2[a]



[a] Reagents and conditions: (i) KPF_6, Et_3N, THF, reflux, **G1** 25%, **G2** 19%.

contrast with those of ruthenium−acetylide dendrimers bridged by 1,3,5-triethynylbenzene derivatives, which exhibited only one wave for Ru^{II}−Ru^{III} redox,[3b] suggesting electron coupling between ruthenium species in **G1** and **G2**.

The UV–vis spectra of **G0**, **G1**, **G2**, the dinuclear ruthenium−acetylide complex **7**, and the mononuclear ruthenium−acetylide complex **10** were measured. In all spectra, absorptions assignable to the metal–ligand charge transfer (MLCT) band characteristic of the ruthenium−acetylide complex were observed, and their molar absorptivities were nearly proportional to the number of ruthenium−acetylide species in the molecules.[12] Figure 2 shows the spectra normalized to the MLCT band. It should be noted that the λ_{max} value of the MLCT band increased with an increasing number of ruthenium species in the order **10**, **7**, **G0**, and **G1**, whereas the λ_{max} value of the MLCT band of **G2** was essentially the same as that of **G1**. These data suggest that the π-conjugated system expanded through the ruthenium−acetylides and tris(4-ethynylphenyl)amine in the dendrimers. Neither the known ruthenium−acetylide dendrimers nor platinum−acetylide dendrimers showed similar phenomena.[3b,6] Although the reason for the saturation of the λ_{max} value of the MLCT band of **G2** is unclear at present, it is surmised that a difference in conformation of the outermost ruthenium moieties in **G2** from those in the other molecules, which is due to intramolecular steric repulsion, may be a contributing factor.

Because we have experimental evidence that the first mixed valence state is stable in the trinuclear ruthenium complexes of **G0**,[7] we performed electrochemical UV–vis measurements of **G1** and **G2** at 0 V (Figure 3), which is between the first and second redox waves in Figure 1. Upon oxidation, the absorption of the MLCT band was decreased and a new absorption band appeared at λ_{max} 505 nm together with a shoulder at λ_{max} 450 nm for both **G1** and **G2**. As was observed for **G0**,[7] these spectral changes were completely reversible. When these spectra were normalized to the intensity of the MLCT band in the initial state, the spectra in the mixed valence state almost overlapped with each other in the region >350 nm. These results indicated that one ruthenium species in each triruthenium unit was oxidized in the mixed valence state, and they were supported by the redox titration of **G0**−**G2** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone while the absorption was monitored at λ_{max} 505 nm. The electron numbers of the first redox waves were estimated to be 1e for **G0**, 3e for **G1**, and 7e for **G2**, which were one-third of the number of ruthenium species in the dendritic molecules. The contribution of the allenylidene structure in the oxidized ruthenium−acetylide species likely enhances the stability of the triruthenium units in the mixed valence state even for the dendrimers.[7]

In summary, we have prepared a new multiredox type of ruthenium−acetylide dendrimer using tris(4-ethynylphenyl)-amine as the bridging ligand. Intramolecular interaction among ruthenium species was elucidated by electrochemical and spectral analyses. Further studies focusing on the properties of these dendrimers are in progress.

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Supporting Information Available: Text giving experimental procedures and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The λ_{max} value (nm) and the molar absorptivity ($\times 10^5$ M^{-1} cm^{-1}) are as follows: **10**, 349, 0.520;[7] **7**, 372, 1.06; **G0**, 381, 1.11;[7] **G1**, 389, 4.33; **G2**, 390, 8.98.