

A Rapid Convergent Approach to Organometallic Dendrimers: Sterically Controlled Dendron Synthesis

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Summary: Facile formation of organometallic dendrons utilizing steric control is demonstrated, affording rapid access to nanometer-sized π -delocalized quadrupolar and octopolar complexes.

Introduction

Dendrimers have attracted significant attention due to applications in medical diagnostics and possible applications in molecular recognition, catalysis, and photoactive device engineering.¹ While organic dendrimers have dominated the field, metal-containing dendrimers have been the focus of many recent studies, as the presence of the metals potentially affords monodisperse macromolecules with interesting electronic, optical, and/or magnetic properties.^{2–5} The great majority of organometallic dendrimers comprise an organic dendrimer with ligated metal units decorating the periphery or located at the dendritic core; efficient synthetic procedures to dendrimers containing metals at the branching units are therefore a current challenge.

Organometallic dendrimers with potentially π -delocalizable systems are of particular interest. Zero-generation examples (octopolar alkynyl complexes formally derived from 1,3,5-triethynylbenzene and metal halides) have been featured in several recent publications,^{6–14} with interest centered on, inter alia, their electrochemical and nonlinear optical properties. Extending the synthetic methodology by utilizing metal

dihalides and the same or similar alkynes potentially affords alkynylmetal dendrimers, a procedure demonstrated by Takahashi, Stang, and their co-workers using *trans*-[PtX₂(PR₃)₂] (R = Buⁿ, Et; X = Cl, I)^{15–17} and by us using *cis*-[RuCl₂(dppe)₂] as metal-containing precursors.¹¹ The divergent routes assayed by Takahashi¹⁸ and Stang¹⁶ require use of large excesses of reagents at each dendritic growth step to ensure formation of the desired product, a procedure difficult to apply to higher generation dendrimers.¹⁷ The convergent procedure to dendrimers generally results in increased ease of purification and is arguably the method of choice for dendrimer construction. The convergent routes for alkynylmetal dendrimer synthesis used by Takahashi¹⁷ and us¹⁹ involve preparation of 1,3-diethynyl-5-triisopropylethynylbenzene (3 steps from 1,3-dibromo-5-iodobenzene) or 1,3-bis(4-ethynylphenylethynyl)-5-trimethylsilylethynylbenzene (5 steps from 1,3-dibromo-5-iodobenzene), respectively, before metal complexation to form the organometallic dendrons. These lengthy syntheses discourage subsequent chemistry and physical properties investigations. To explore the potential of alkynylmetal dendrimers in materials science, a more facile synthesis is required. We report herein the use of *steric control* of extent of reaction as a new and rapid methodology for dendron synthesis, a procedure applicable to other metal-containing systems.

We,⁶ and subsequently Long and co-workers,¹⁰ demonstrated that 1,3,5-triethynylbenzene reacts with *cis*-[RuCl₂(dppm)₂] to give 1,3-{*trans*-[(dppm)₂ClRuC≡C]}₂-5-HC≡CC₆H₃; it proved impossible to form the trisproduct, even with excess ruthenium-containing reagent. A structural study confirmed steric crowding as the reaction-limiting factor.⁶ This complex is an archetypal organometallic dendron, with the “AB₂” trisubstituted benzene composition required for alkynylmetal dendrimer construction. Although it is possible to form bisacetylide complexes using the Ru(dppm)₂ unit,^{20–24} the

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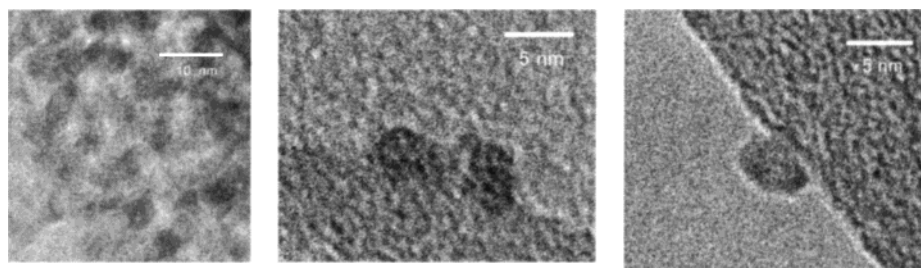


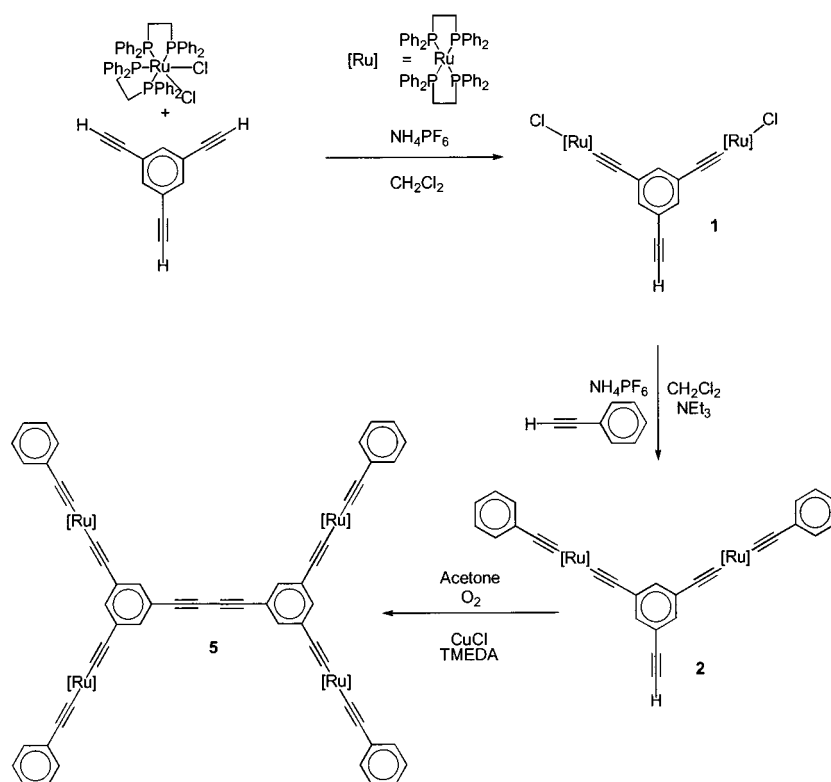
Figure 1. Transmission electron micrographs of molecules of **6** supported on alumina/holey carbon.

Table 1. Cyclic Voltammetric Data for 1–6

| complex | $E_{1/2}$ Ru ^{II/III} (V) | $[i_{pc}/i_{pa}]$ | $\Delta E_{1/2}$ (V) | K_{com} |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|-------------------|----------------------|--------------------|
| 1,3- <i>trans</i> -[(dppe) ₂ ClRuC≡C] ₂ -5-HC≡CC ₆ H ₃ (1) | 0.53, 0.72 | 1.0, 1.0 | 0.19 | 1.6×10^3 |
| 1,3- <i>trans</i> -[(dppe) ₂ (PhC≡C)RuC≡C] ₂ -5-HC≡CC ₆ H ₃ (2) | 0.47, 0.60 | 1.0, 1.0 | 0.13 | 1.57×10^2 |
| 1,3- <i>trans</i> -[(dppe) ₂ (PhC≡C)RuC≡C] ₂ -5-(Me ₃ SiC≡C-4-C ₆ H ₄ C≡C)C ₆ H ₃ (3) | 0.49, 0.61 | 1.0, 1.0 | 0.12 | 1.07×10^2 |
| 1,3- <i>trans</i> -[(dppe) ₂ (PhC≡C)RuC≡C] ₂ -5-(HC≡C-4-C ₆ H ₄ C≡C)C ₆ H ₃ (4) | 0.50, 0.62 | 1.0, 1.0 | 0.12 | 1.07×10^2 |
| (3,5- <i>trans</i> -[(dppe) ₂ (PhC≡C)RuC≡C] ₂ C ₆ H ₃ C≡C) ₂ (5) | 0.50, 0.62 | 1.0, 1.0 | 0.12 | 1.07×10^2 |
| 1,3,5-(3,5- <i>trans</i> -[(dppe) ₂ (PhC≡C)RuC≡C] ₂ C ₆ H ₃ C≡CC ₆ H ₄ -4-C≡C) ₃ C ₆ H ₃ (6) | 0.48, 0.59 | 1.0, 1.0 | 0.11 | 72 |

^a Ferrocene/ferrocenium couple 0.56 V.

Scheme 1. Syntheses of complexes **1**, **2**, and **5**

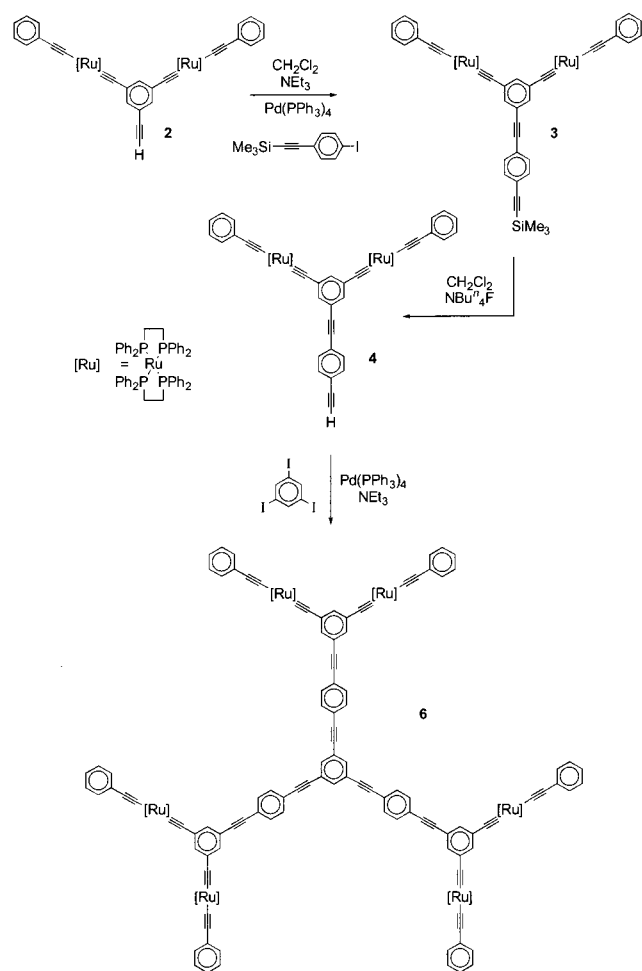


Ru(dppe)₂ building block provides a more convenient group to afford bis-acetylides,^{11,24–30} and hence facilitate dendrimer construction. Thus, reacting 1,3,5-triethy-

nylbenzene with *cis*-[RuCl₂(dppe)₂] affords the mono-acetylide dendron 1,3-*trans*-[(dppe)₂ClRuC≡C]₂-5-HC≡CC₆H₃ (**1**) (Scheme 1) under steric control. Reaction of **1** with alkynes proceeds cleanly, again with steric control, to form bis-acetylide dendrons; for example, reaction with PhC≡CH affords 1,3-*trans*-[(dppe)₂(PhC≡C)RuC≡C]₂-5-HC≡CC₆H₃ (**2**). The ethynyl group in complex **1** is sterically protected from homopolymerization, but this group and that in **2** are accessible to metal reagents. For example, the ethynyl group in complex **2** can be coupled under Hay conditions to form the butadiynyl complex **5** (Scheme 1) and can be coupled

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Scheme 2. Synthesis of complexes **3**, **4**, and **6**

with 1-iodo-4-trimethylsilylethynylbenzene under palladium-catalyzed conditions to give the dendron **3**, which can in turn be deprotected with NBu_4F to afford the dendron **4** (Scheme 2). The utility of **4** in dendrimer synthesis is currently being explored; the ethynyl unit is accessible for metal σ -alkynyl formation, homocoupling, and palladium-catalyzed coupling with 1,3,5-triiodobenzene (the last-mentioned affording the octopolar complex **6**; Scheme 2). Overall, this methodology affords rapid access to nanometer-sized π -delocalized organometallic complexes.

Complexes **1–6** were characterized by various spectroscopic data and elemental analyses.³¹ UV-vis spectra of **1–6** contain bands in the range 330–339 nm due to

the intense metal–ligand charge transfer (MLCT) band. The IR spectra show characteristic $\nu(\text{C}\equiv\text{C})$ bands around 2056 cm^{-1} accompanied, in the case of **3**, by a $\nu(\text{C}\equiv\text{C})$ band at 2157 cm^{-1} corresponding to the trimethylsilyl-protected acetylene. ^{31}P NMR spectra of complexes **1–6** contain one singlet resonance, consistent with *trans* geometry at the ruthenium centers. The mass spectrum of **6** reveals fragment ions only; it was consequently further characterized by transmission electron microscopy (TEM) (Figure 1), with the dimensions of individual molecules imaged by TEM consistent with those calculated by molecular modeling using SPARTAN (ca. 50 \AA).³² The octopolar complex **6** is remarkably stable under the 300 keV electron beam, persisting unchanged over a period of hours. Cyclic voltammetry data for complexes **1–6** are listed in Table 1; all complexes have two reversible oxidations assigned to $\text{Ru}^{\text{II/III}}$ processes at ruthenium atoms separated by 1,3-diethynylbenzene units, with comproportionation constants indicative of weakly interacting Robin and Day Class II behavior.

In summary, we have demonstrated rapid access to several nanometer-sized π -delocalized organometallic complexes, in a procedure that should have more general utility. The sterically controlled synthetic methodology employed for the facile preparation of alkynyl-ruthenium dendrons **1–4**, and thereby the quadrupolar homocoupled product **5** and octopolar product **6**, should be applicable to the synthesis of other organometallic dendrimers, judicious modification of the ligand sphere providing a ready means to modify the steric environment and thereby control the extent of reaction.

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Supporting Information Available: Text giving details of the preparation and procedures and spectroscopic and analytical data for complexes **1–6**. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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(31) See the Supporting Information for complete experimental procedures and compound classification data.

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