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Diruthenium-DMBA compounds bearing extended cross-conjugated ligands

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Dedicated to John Gladysz, a good friend and pioneer of metal-polyne chemistry, on the occasion of his 65th birthday.

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ABSTRACT

A series of bis(alkynyl) $\text{Ru}_2(\text{DMBA})_4$ (DMBA = *N,N'*-dimethylbenzamidinate) compounds bearing extended, acyclic, cross-conjugated frameworks (number of acetylene units ≥ 3), namely $\text{Ru}_2(\text{DMBA})_4(\text{L1Si}^t\text{Pr}_3)_2$ (**1a**, see Scheme 1 for the definition of **L1** and **L2**) and $\text{Ru}_2(\text{DMBA})_4(\text{L2Si}^t\text{Pr}_3)_2$ (**2a**), were prepared under aerobic, weak base conditions in good yields. Compounds **1a** and **2a** showed moderate stability and underwent protiodesilylation aided with the addition of (n-Bu)₄NF to the free ethynyl compounds $\text{Ru}_2(\text{DMBA})_4(\text{L1H})_2$ (**1b**) and $\text{Ru}_2(\text{DMBA})_4(\text{L2H})_2$ (**2b**), respectively. An X-ray structural study of **1a** revealed a significant deviation from the idealized D_{4h} geometry in the coordination sphere of the Ru_2 core, accompanied by one of the shortest Ru-C_α bonds reported thus far. Electronic absorption spectral measurements imply that compounds **1a** and **1b** possess a smaller HOMO-LUMO gap (ca. 1.38 eV), while the gap of **2a** and **2b** (ca. 1.40 eV) is closer to the range of typical $\text{Ru}_2(\text{DMBA})_4(\text{C}_2\text{R})_2$ -type compounds (ca. 1.42 eV). Cyclic voltammetry measurements indicate a subtle interplay between structural and electronic properties, dependent only on the placement of the intervening olefin across the conjugation pathway.

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1. Introduction

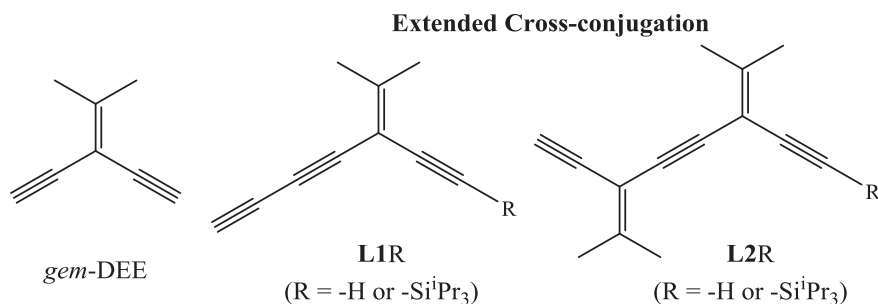
The rich electrochemical and optical properties of organometallic compounds possessing conjugated carbon rich backbones have fascinated synthetic and material chemists for decades [1,2], leading to the investigations of these compounds as prospective molecular wires [3–7], active species within memory devices [8,9], and nonlinear optical (NLO) chromophores [10–12]. Progress in the field has focused primarily on linearly conjugated σ -polyenyl (–C=C–) [13–15], and σ -polyynyl (–C≡C–) bridges [16,17], due to their proficiency at facilitating charge transfer. While the majority of reported work focuses on short polyyn-diyl frameworks (number of acetylene units ≤ 2) [18–22], there has always been a strong desire in both pushing the synthetic limit of such conjugated backbones (number of acetylene units ≥ 3) and uncovering unique topologies [23]. Recently, extended carbon frameworks have been realized for compounds based on Re [24–26], Ru [27–30], Fe [31,32] and Co [33]. Especially noteworthy are the efforts from the laboratory of Gladysz that resulted in both the longest metal-

capped polyyn-diyl (C_{28}) [34,35] and diplatinum polyynes surrounded by sp^3 carbon double helices [36–38].

Though far less developed compared to linear conjugated carbon rich compounds, compounds containing nonlinear (branched) carbon-rich linkers are interesting targets for achieving large dynamic range in attenuating charge transfer [39] and as scaffolds from which to build intricate topologies [40,41]. Recent synthetic advances from the laboratories of Diederich [42] and Tykwinski [43–45] have made it possible to explore acyclic cross-conjugated eneyne and enediene scaffolds as building blocks, such as σ -geminal-diethynylethene (*gem*-DEE, Scheme 1), for metal-alkynyl chemistry [46]. It is important to note that cross-conjugation is defined as the conjugation between two unsaturated π -segments that, although not conjugated to each other, are conjugated to an intervening unsaturated segment [47]. While such systems are intriguing, there are only a handful of organometallic compounds bearing cross-conjugated ligands, likely due to the limited lifetime of ligand precursor and their instability toward lithio-alkynyl techniques [44,45,48]. Early examples of metal compounds bearing cross-conjugation were reported by Tykwinski and co-workers, where a $\text{Pt}(\text{PPh}_3)_2$ fragment was coordinated by two σ -*gem*-DEE in the *trans*-positions [49]. More recently, a ferrocenyl capped 3-(dibromomethylidene)penta-1,4-diene complex was

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Scheme 1. Acyclic cross-conjugated ligands.

reported, for which the degree of Fc-Fc interaction was assessed by voltammetry methods [50]. The laboratories of Bruce [51] and Ren [52] have also reported synthetic strategies in reaching bridged cross-conjugated ruthenium compounds. Earth abundant transition metal complexes of Co(III) [53,54], Cr(III) [55], and Fe(III) [56] of the type *trans*-[M(cyclam)(*gem*-DEE)₂]⁺ have also been prepared and interrogated.

Our laboratory has previously explored the role of *gem*-DEE as a ligand bound to a versatile Ru₂(DMBA)₄ (DMBA = *N,N*-dimethylbenzamidinate) unit which served as a spectroscopic and/or electrochemical handle for assessing the conjugate nature of ligands [57]. The synthetic advantage of Ru₂(DMBA)₄-based compounds lies in the aerobic preparation of bis-alkynyl Ru₂(DMBA)₄(C₂R)₂-type species under weak base conditions [29,58]. Encouraged by previous results, we sought to expand upon the current understanding of acyclic cross-conjugated systems by assessing the effects of extending the cross-conjugated framework beyond that of *gem*-DEE. Described herein are the preparation and characterization of a series of diruthenium compounds with extended cross conjugated frameworks containing three acetylenic units, where the placement of the intervening olefin varies (Scheme 1).

2. Results and discussion

2.1. Synthesis

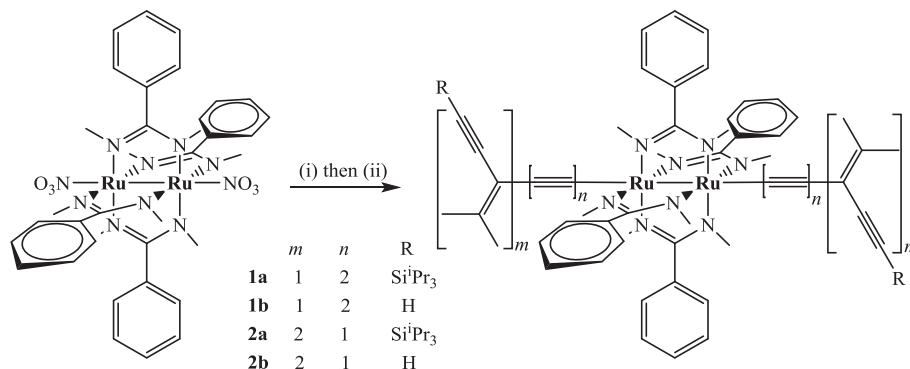
The limited stability of H-capped *gem*-DEE is well documented in the literature [45,48,52,54], and the H-capped extended *gem*-DEEs such as 2-methyl-3-ethynyl-hepta-2-ene-4,6-diyne (L1H) and 3,6-diethynyl-2,7-dimethyl-2,6-octadiene-4-yne (L2H) (Scheme 1) are even more prone to degradation than *gem*-DEE [44]. In an effort to reduce degradation, the trimethylsilyl end-capped cross-

conjugated ligand precursors Me₃SiL1SiⁱPr₃ and Me₃SiL2SiⁱPr₃ were synthesized according to literature procedures [44,45]. These ligand precursors were found to be stable for several days under refrigeration. Protio-desilylation to the ethynyl ligands L1SiⁱPr₃ or L2SiⁱPr₃ was performed just prior to metalation using a methanolic Cs₂CO₃ solution.

As shown in Scheme 2, the use of Ru₂(DMBA)₄(NO₃)₂ allows for the facile synthesis of a variety of extended *gem*-DEE compounds under weak-base conditions. The reaction between Ru₂(DMBA)₄(NO₃)₂ and L1SiⁱPr₃ in the presence of Et₂NH yielded a wine-red solution characteristic of *trans*-Ru₂(DMBA)₄(C₂R)₂-type compounds [59,60]. Thin layer chromatography (TLC) [R_f = 0.77, 1:3 (v/v) EtOAc/hexanes] analysis revealed that the reaction was complete within 3 h. Subsequent purification using a silica gel pad followed by recrystallization yielded a red crystalline material as the sole product (isolated yield 73%). The red product was unambiguously identified as *trans*-Ru₂(DMBA)₄(L1SiⁱPr₃)₂ (**1a**) by ESI-MS, ¹H NMR, elemental analysis and a single crystal X-ray diffraction study. Unlike the metal free ligands L1H, L1SiⁱPr₃, or the silyl capped precursor Me₃SiL1SiⁱPr₃, compound **1a** appears to be indefinitely stable as a solid under ambient conditions.

In a manner similar to **1a**, compound **2a** was prepared from the reaction of Ru₂(DMBA)₄(NO₃)₂ and freshly desilylated L2SiⁱPr₃. Contrary to the quick formation of **1a**, **2a** was significantly slower, with a gradual change in solution color from green to red observed over a 24 h period (via TLC analysis). The resulting red solution was purified by silica gel chromatography followed by recrystallization to yield a sticky, dark-red material identified as *trans*-Ru₂(DMBA)₄(L2SiⁱPr₃)₂ (**2a**). The reaction of **2a** occurred with a puzzling low yield (46%) considering the effective metalation for both **1a** and Ru₂(DMBA)₄(*gem*-DEE-SiⁱPr₃)₂ (77%) [57], which is likely attributed to slow degradation of desilylated L2SiⁱPr₃.

The desilylation derivatives of **1a** and **2a**, Ru₂(DMBA)₄(L1H)₂



^aConditions: (i) L1-SiⁱPr₃ or L2-SiⁱPr₃, Et₂NH, THF, rt; (ii) cat. (*n*-Bu)₄NF, THF, 0°C 2h.

Scheme 2. Synthesis of compounds **1a-b** and **2a-b**^a.

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