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Study of small oligomers based on $Ru_2(DMBA)_4$ and *meta*-phenylene diethynylene

Jie-Wen Ying, Carl W. Liskey, Sean N. Natoli, Stella K. Betancourt, Li Liu, Phillip E. Fanwick, Tong Ren*

Departments of Chemistry, Purdue University, West Lafayette, IN 47907, USA

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Dedicated to Rick Adams, a dear friend and connoisseur of carbon rich organometallics, on the occasion of his 70th birthday.

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ABSTRACT

The reactions between Ru_2 $(DMBA)_4(NO_3)_2$ (DMBA = *N,N'*-dimethylbenzamidinate) and *meta*-phenylene diethynylenes bearing 5-ester substituents ($-CO_2^iPr$, L1; $-CO_2Bn$, L2) in the presence of Et_2NH afforded a series of oligomeric compounds with *meta*-phenylene diethynylene bridge, namely L-$[Ru_2$ $(DMBA)_4L]_m$ with m as integers. With L1, the compounds with $m = 1-3$ (**1a**, **2a** and **3a**) were separated and fully characterized. With L2, only the compound with $m = 1$ (**1b**) was successfully isolated. In addition to routine spectroscopic characterizations, the structures of both compounds **1b** and **2a** were determined using single crystal X-ray diffraction. For the series of **1a**, **2a** and **3a**, both the voltammetric and absorption spectroscopic characteristics bear close resemblance to those of simple Ru_2 $(DMBA)_4(C_2R)_2$ compounds, indicating the absence of significant inter-unit electronic couplings in the oligomers.

1. Introduction

Preparation of metal-σ-alkynyl compounds has been an active area of research since the 1950s [1,2]. Extensive efforts in the recent years revealed many intriguing and useful attributes of metal-alkynyl species, which include interesting electronic structures and novel topologies [3], their applications as nonlinear optical materials [4–6], OLED and photovoltaic materials [7–9], and active species for molecular electronics [10–13]. The possibility of forming $[M-C{\equiv}C-Y-C{\equiv}C-]_n$ type oligomers/polymers was recognized from the beginning of metal-alkynyl chemistry [1,14], where M is one of either coinage metals or platinum group metals and Y is an aromatic group. During the ensuing decades, the Osaka group led by Hagihara and Takahashi reported many Pd/Pt based polymers based on the original $[M-C{\equiv}C-Y-C{\equiv}C-]_n$ motif [14], while the Cambridge group led by Lewis produced similar polymers based on mono-nuclear Pt and Ru species [15,16]. More recently, Wong and coworkers have developed many Pt-based metal-alkynyl polymers with an emphasis on optoelectronic applications [17–21]. Though much of the aforementioned successes on metal-σ-alkynyls are based on 4*d* and 5*d* metals, chemistry of σ-alkynyls based on 3*d* metal complexes of polyaza-macrocycles has received considerable interest [22–27]. Besides σ-alkynyl species, another interesting avenue of metal-alkynyl chemistry is the formation of the Pauson-Khand type adducts (η^2-C≡C) between oligoynes and mono-/oligo-metallic species [28–32].

A major focus area of our laboratory is the diruthenium alkynyl chemistry, where the charge mobility along the Ru_2-σ-alkynyl backbone has been demonstrated in both bulk solution [33–38] and nano-scale devices [39–43]. It is worth noting that the development of diruthenium and triruthenium alkynyl chemistry has also benefited from key contributions from the laboratories of Cotton [44], Bear and Kadish [45–47], Lehn [48] and Peng [49]. Among several families of diruthenium alkynyl compounds developed in our laboratory, those based on the DMBA (DMBA is *N,N'*-dimethylbenzamidinate) supporting ligand are unique in the formation of Ru_2-alkynyl bond under weak base conditions (Scheme 1) [36,50–52]. In addition to affording symmetric bisalkynyl species under mild conditions such as ambient atmosphere and room temperature, the weak base protocol enables the one-pot synthesis of novel unsymmetric bisalkynyl species exhibiting voltammetric characteristic consistent with a molecular diode [53]. In

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* Corresponding author.
E-mail address: tren@purdue.edu (T. Ren).

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$$\mathrm{Ru_2(DMBA)_4(NO_3)_2 + 2\ HC_2R \xrightarrow[THF]{R_3N} Ru_2(DMBA)_4(C_2R)_2}$$

Scheme 1. Ru_2-alkylnylation under Weak Base Conditions.

the aforementioned studies, ligation of mono-ethynes was the focus. We became intrigued by the *meta*-phenylene diethynylene type ligands, based on which hexagon and helical supramolecules were realized in the laboratories of Moore and others [54–56]. Reported herein are the reactions between Ru_2 $(DMBA)_4(NO_3)_2$ and *meta*-phenylene diethynylene ligands under aerobic weak base conditions, and the identification of resultant oligomers.

2. Results and discussion

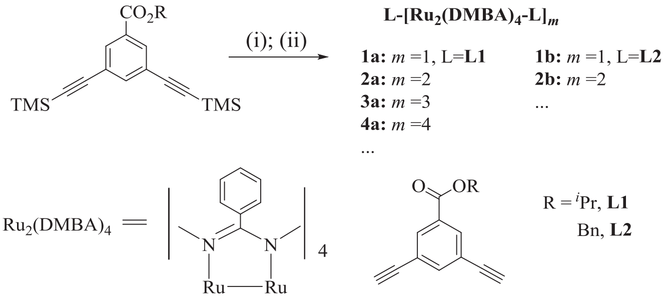
2.1. Syntheses

Syntheses of *meta*-arylene diethynylene ligands were based on the Sonogashira type cross coupling reactions as outlined in Scheme 2 [57,58], and the experimental details are provided in the supplementary content. Trimethylsilyl (TMS) was retained as the protecting group of terminal ethyne owing to its chemical stability over the free ethyne. In order to optimize the solubility of the resultant L-[Ru_2 $(DMBA)_4$-L]$_m$ type compounds, two side chains, isopropyl (^{i}Pr) and benzyl (Bn), on the aromatic ring of the organic spacer were introduced through esterification, as shown in Scheme 2. Typical desilylation of L1TMS$_2$ and L2 TMS$_2$ using K_2CO_3 in MeOH would lead to transesterification of the ester group [59]. Hence, the desilylation of L1TMS$_2$ and L2 TMS$_2$ was achieved in excellent yield with TBAF (containing 5% of water) in THF.

While the preparation of the symmetric Ru_2 $(DMBA)_4(C_2R)_2$ type compounds using LiC_2R was successful and expedient [50], the presence of an ester group in both L1 and L2 prevents the use of lithiation method. Hence, the weak base assisted reaction is the ideal alternative for the Ru_2 $(DMBA)_4$ compounds based on L1 and L2, as shown in Scheme 3. Generally, the reactions between Ru_2 $(DMBA)_4(NO_3)_2$ and excess L1/L2 in the presence of diethylamine (Et_2NH) afforded a mixture of L*n*-[Ru_2 $(DMBA)_4$-L*n*]$_m$ as monitored by TLC. Typically, overnight reaction gave the Ru_2 based monomer ($m = 1$) as the major product when three equiv of L*n* was used. Reducing the equivalents of L*n* to two, the reaction under similar conditions resulted in significant amounts of dimer, trimer and higher oligomers in addition to the monomer. These oligomers were readily identified on TLC as their R_f values decrease with the increasing degree of oligomerization. Using flash column chromatography, we were able to obtain usable quantities of compounds **1a**-**3a** and **1b**, which were characterized by ESI-MS (Figs. S2– S5), ^{1}H NMR and elemental analysis. All compounds in solid state are indefinitely stable under ambient conditions.

2.2. Molecular structures

Single crystals of X-ray quality were successfully grown for compounds **1b** and **2a** from THF/hexanes solution (**1b**) and THF/ether solution (**2a**). The structural plots of **1b** and **2a** are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles listed in the captions. The asymmetric unit of the crystal of **1b** contains only one half of the diruthenium molecule, which is related to the other half via a crystallographic 2-fold axis passing through the midpoint of Ru1- Ru1′ bond. The Ru1- Ru1′ bond length in **1b** (2.4675 (7) Å) is comparable to those previously determined for the Ru_2 $(DMBA)_4(C_2Ar)_2$ type compounds (2.45–2.46 Å) [51–53] and consistent with the existence of a Ru-Ru single bond and a ground state configuration of $\pi^4\delta^2\pi^{*4}$. The Ru1-C1 bond is short (1.998 (6) Å), reflecting the formation of a strong σ(Ru-C) bond at the expense of σ(Ru-Ru) bond [50]. It is clear from the structural parameters that there is a significant deviation from an idealized lantern structure in the first coordination sphere of the



Conditions: (i) Bu_4NF, THF; (ii) $Ru_2(DMBA)_4(NO_3)_2$, Et_2NH, THF

Scheme 3. Reaction between Ru_2-$(DMDA)_4(NO_3)_2$ and *m*-phenylene diethynylene.

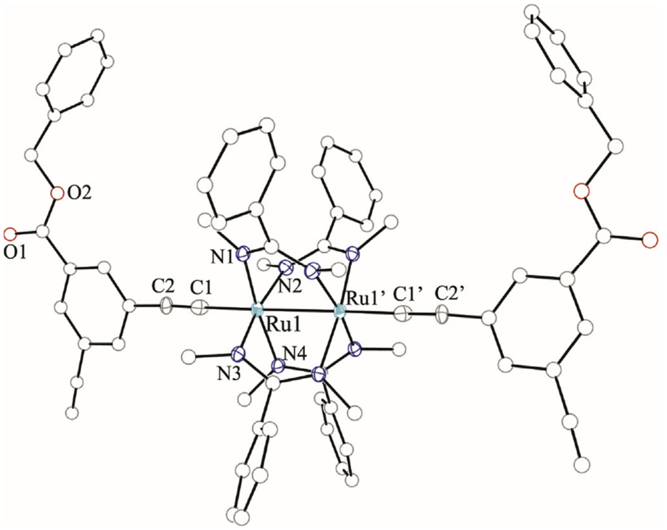
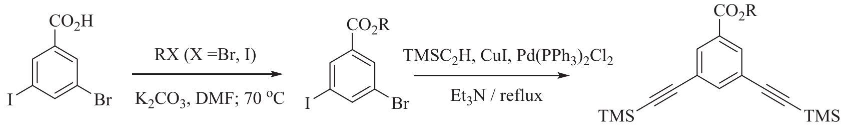


Fig. 1. Molecular structure of **1b**. The half of the molecule is related to the other half by a crystallographic axis passing through the Ru1-Ru1′ bond. Selected bond lengths (Å) and angles (deg): Ru1-Ru1′, 2.4675 (7); Ru1-C1, 1.998 (6); Ru1-N1, 2.001 (4); Ru1-N2, 2.119 (4); Ru1-N3, 1.995 (4); Ru1-N4, 2.073 (4); Ru1′-Ru1-C1, 166.0 (2).



L1TMS$_2$, R= isopropyl (^{i}Pr)
L2TMS$_2$, R= benzyl (Bn)

Scheme 2. Preparation of *m*-diethylnylbenzene ligands.

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