



## New diruthenium (II,III) compounds bearing terminal olefin groups

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### ABSTRACT

The reaction between  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  (DmAniF is *N,N'*-di(*m*-methoxyphenyl)formamidinate) and  $\text{HO}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2$  ( $m = 3, 4$  and  $8$ ) under reflux afforded new diruthenium species  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$  ( $m = 3, 4$  and  $8, \mathbf{1a}, \mathbf{1b}$ ; and  $\mathbf{8, 1c}$ ). Similarly, the reaction between *cis*- $\text{Ru}_2(\text{DmAniF})_2(\text{OAc})_2\text{Cl}$  and  $\text{HO}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2$  resulted in  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$  ( $m = 3, \mathbf{2a}$ ; and  $\mathbf{8, 2c}$ ). Compounds  $\mathbf{2}$  subsequently underwent an olefin ring closing metathesis reaction catalyzed by  $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}(\text{=CHPh})$  to afford the dimerized compounds  $\text{Ru}_2(\text{DmAniF})_2(\mu\text{-O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$  ( $m = 3, \mathbf{3a}$ ; and  $\mathbf{8, 3c}$ ). All compounds reported herein were analyzed by voltammetry, high resolution mass spectrometry and Vis–NIR spectroscopy, with the structures of  $\mathbf{1c}$  and  $\mathbf{2c}$  established through X-ray single crystal diffraction.

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### 1. Introduction

Metal-catalyzed olefin metathesis has become one of the most widely used carbon–carbon bond formation reactions in organic synthesis. It has been demonstrated with a large number of successful examples that olefin cross metathesis (CM) can be utilized as an elegant synthetic tool to either link two units together or to achieve intramolecular cyclization (ring closing metathesis or RCM) [1,2]. The Gladysz group has described the RCM assembly of a series of complex structures containing diverse metallic supports as templates, including Pt, Pd, Rh, Re, and W [3–7]. Several recent reports include employment of olefin metathesis to prepare metallocenes, metallocenes (Ni, Fe) and phosphine chelate chromium complexes [8–12].

Efforts from our laboratory focus on the modular nature of bimetallic paddlewheel species, in which dimeric and oligomeric assemblies can be achieved by modifying the ligand periphery [13–18]. Among the previously reported  $\text{Ru}_2$  species are a series of compounds containing one or two terminal olefins and their olefin metathesis products [14,15]. These diruthenium species are particularly attractive as building blocks for supramolecular materials as well as active components for molecular devices due to their robust redox chemistry over a broad potential window, net molecular spin and the possibility of ligand engineering. A potential application of  $\text{Ru}_2$  species bearing a peripheral olefin is the incorporation of molecules onto Si surfaces to realize hybrid-molecule CMOS devices (Scheme 1) [19]. In order to achieve

effective and dense passivation of H–Si surface with these types of compounds, the diruthenium species needs to contain an extended hydrocarbon tether due to the bulky nature of  $\text{Ru}_2$  species (Scheme 1).

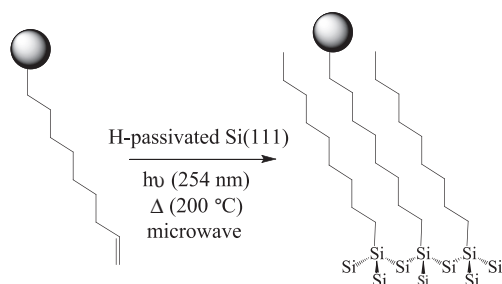
Described in this contribution are the synthesis and structural study of  $\text{Ru}_2(\text{DmAniF})_3(\mu\text{-O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$  ( $m = 3, \mathbf{1a}; 4, \mathbf{1b}; 8, \mathbf{1c}$ ; DmAniF is *N,N'*-di(*m*-methoxyphenyl)formamidinate) and *cis*- $\text{Ru}_2(\text{DmAniF})_2(\mu\text{-O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$  ( $m = 3, \mathbf{2a}; 8, \mathbf{2c}$ ), the latter of which underwent the ring closing metathesis reaction to afford *cis*- $\text{Ru}_2(\text{DmAniF})_2(\mu\text{-O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$  ( $m = 3, \mathbf{3a}; 8, \mathbf{3c}$ ).

### 2. Results and discussion

The syntheses of compounds  $\mathbf{1-3}$  are based on the  $\text{Ru}_2(\text{DArF})_{4-n}(\text{OAc})_n$  type synthons developed in the laboratories of Cotton [20–24], Jiménez-Aparicio [25–30] and Ren [14,15,18,31–33]. As shown in Scheme 2, the species containing one or two  $\omega$ -alkene- $\alpha$ -carboxylate ligands can be prepared from carboxylate exchange reactions by following a procedure that has been reported in literature [14,15]. Gentle reflux of  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  in the presence of excess carboxylic acid such as 5-hexenoic, 6-heptenoic or 10-undecylenic affords the new compounds  $\text{Ru}_2(\text{DmAniF})_3(\mu\text{-O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$  ( $m = 3, \mathbf{1a}; 4, \mathbf{1b}; 8, \mathbf{1c}$ ) in good yields. In contrast to the preparation of compound  $\mathbf{1}$ , the carboxylate exchange reaction between *cis*- $\text{Ru}_2(\text{DmAniF})_2(\text{OAc})_2\text{Cl}$  and either 10-undecylenic or 5-hexenoic acids required more rigorous conditions. The synthesis of  $\mathbf{2}$  was achieved by refluxing in toluene aided by an acetic acid scrubbing apparatus as described previously [34]. The two  $\omega$ -alkene- $\alpha$ -carboxylates in the coordination sphere of compounds  $\mathbf{2}$  underwent ring closing metathesis (RCM) in the

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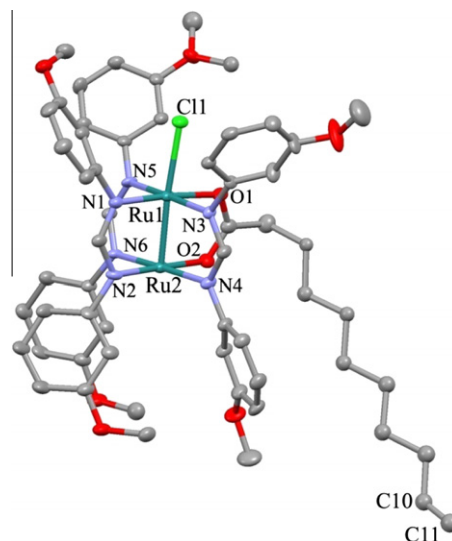


**Scheme 1.** Functionalization of Si surface with olefin-capped molecule, sphere represents diruthenium coordination sphere.

presence of the first generation Grubbs catalyst to give compounds **3**. Compounds **3** were identified as the ring RCM product based on the ESI-MS data. Interestingly, refluxing compound **2a** under the same conditions resulted in the formation of two new compounds that are distinct on TLC ( $R_f = 0.45$  and  $0.35$ , THF/Hex 1:1) but yield the same 940 ( $[3a-Cl]^+$ ) peak in ESI-MS. These compounds are likely the *Z/E* isomers of  $Ru_2(DmAniF)_2(\mu-O_2C(CH_2)_3CH=)Cl$ . Similar to their precursors, compounds **1–3** have effective magnetic moments at room temperature in a narrow range of  $3.93$ – $3.96 \mu_B$  (Bohr magneton), which is consistent with a  $S = 3/2$  ground state [35].

Compound **1c** crystallizes in the space group  $P\bar{1}$ , and compound **2c** in  $C2/c$ . The asymmetric unit of **1c** contains two complete molecules, while that of **2c** contains one. The structural plot of **1c** (Fig. 1) shows three DmAniF ligands and one 10-undecylenate around the diruthenium core, with a chloro ligand in the axial position. It is clear from the structural plot of **2c** (Fig. 2) that the coordination sphere of the  $Ru_2$  unit consists of two DmAniF and two 10-undecylenate bidentate ligands in a *cis*-arrangement, with chloro and water ligands occupying opposite axial positions.

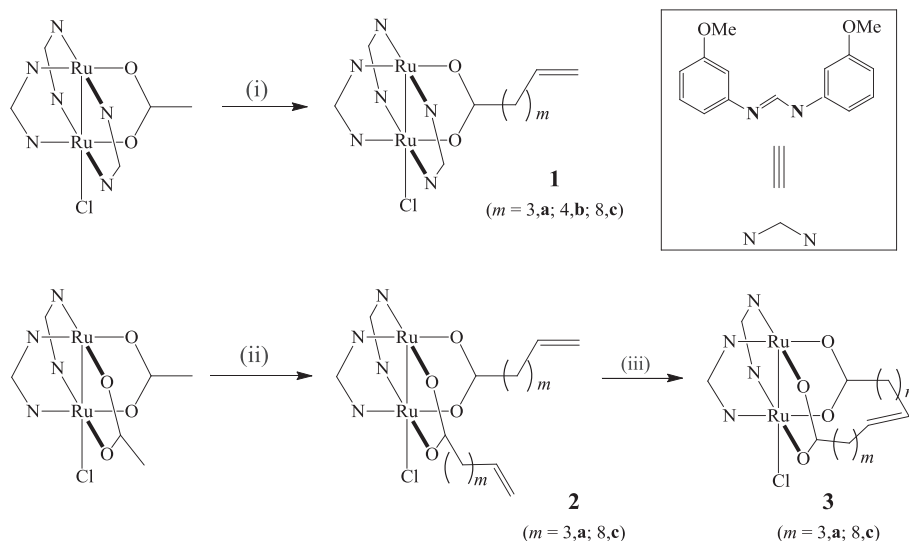
Listed in Table 1 are the selected bond lengths and angles for compounds **1c** and **2c**. Specifically, the Ru–Ru bond length of **1c** ( $2.3202(4)$  Å) is nearly identical to that of the parent compound  $Ru_2(DmAniF)_3(O_2CMe)Cl$  ( $2.3220(7)$  Å) [33]. The Ru–Ru bond length in **2c** is  $2.3194(6)$  Å, which is similar to that of  $Ru_2(DmAniF)_2(O_2CMe)_2Cl$  ( $2.3219(4)$  Å) [33]. The averaged equatorial Ru–O and Ru–N bond lengths in both **1c** and **2c** are comparable to those reported for  $Ru_2$  compounds containing  $\omega$ -alkene- $\alpha$ -



**Fig. 1.** Structural plot of **1c**. Hydrogen atoms were omitted for clarity.

carboxylate ligand [15,33,36,37]. The Ru–N bond lengths on Ru1 in **1c** are slightly elongated compared to those on Ru2, which is attributed to the attachment of an axial chloro ligand to Ru1. Less variation is noticed in the Ru–N bond lengths of **2c**, since a water molecule is coordinated to the axial site of the second Ru center.

Similar to other  $Ru_2$  paddlewheel species previously reported from our laboratory, compounds **1–3** exhibit multiple reversible or quasi-reversible one-electron redox couples as shown in Fig. 3 and the electrode potentials in Table 2. The reversible  $1e^-$  oxidation, **A**, is a  $Ru_2(III,III)/Ru_2(III,II)$  couple. As discussed in details previously [15], the first reduction couple, **B**, is irreversible due to a fast dissociation of the axial  $Cl^-$  ligand upon reduction, yielding an axial-ligand-free  $Ru_2(II,II)$  species (Scheme 3). The further reduction of the axial-ligand-free  $Ru_2(II,II)$  species results in the reversible couple, **D**. Oxidation of the axial-ligand-free  $Ru_2(II,II)$  species on the return sweep yielded wave **C** at a potential far more positive than  $E_{pc}(B)$ . The cyclic voltammograms measured for compounds **2** (Fig. 3) reveal three  $Ru_2$ -based couples similar to those recorded for related  $Ru_2(DmAniF)_2(OAc)_2Cl$  type compounds [14,15,33]. In general, the redox couples in the type **2** compounds



**Scheme 2.** Preparation of diruthenium- $\omega$ -olefin- $\alpha$ -carboxylate compounds.

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