



## Communication

# Synthesis, crystal structure and electronic properties of [3.3]metaparacyclophane-bridged bimetallic ruthenium alkynyl complexes



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## ARTICLE INFO

## Article history:

Received 13 July 2015

Received in revised form

23 October 2015

Accepted 4 December 2015

Available online 15 December 2015

## Keywords:

Bimetallic complexes

Ruthenium

[3.3]metaparacyclophanes

Crystal structure

Synthesis

Electronic properties

## ABSTRACT

A series of [3.3]metaparacyclophanes bridged bimetallic ruthenium complexes have been designed, synthesized and characterized. <sup>1</sup>H NMR and X-ray crystal structure studies revealed that there are prominent intramolecular edge-to-face interaction in these diruthenium complexes, both in the solution and solid states. Electrochemical analyses indicated that the electron-withdrawing substituent groups (–CN, –NO<sub>2</sub>) can enhance the thermodynamic stability of corresponding mixed-valence species.

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## 1. Introduction

Ligand bridged bimetallic complexes has received a great deal of interest due to their potential application as nonlinear optical materials, molecular wires, molecular electronics and luminescent materials [1,2]. The bridging ligand, with its extended  $\pi$ -electron delocalization, and ability to interact with metal centers via  $p\pi-d\pi$  overlap, has dominant effect on the electronic properties of bimetallic complexes. Significant research effort has been devoted to bimetallic systems that contain unsaturated hydrocarbon ligands with  $\sigma$ -bonded bridging metal centers [3]. These carbon-based  $sp$ -,  $sp^2$ -,  $sp/sp^2$ -bridged systems, as well as systems with aromatic rings as bridges, usually feature a one-dimensional architecture [4]. Using 2D building blocks as bridges may provide novel electronic properties to the bimetallic complexes [5].

We noted that the transannular  $\pi-\pi$  interactions associated with a high degree of structural rigidity in dithia[3.3]paracyclophane, which two benzene rings are held together with two  $-CH_2SCH_2-$  units, was recently used to explore the optical and electronic properties of novel organic materials and  $\pi$ -conjugated oligomers [6,7]. It also has been established that weak noncovalent

$\pi-\pi$  interactions can have a significant effect on the electron transport processes in some biological and chemical systems [8,9]. Very recently, we reported the synthesis and characterization of a series dithia[3.3]cyclophane bridged bimetallic ruthenium complexes [10]. We found that the ligand redox-noninnocent behavior of dithia[3.3]paracyclophane bridged bimetallic ruthenium vinyl and alkynyl complexes [10a]. After modified the upper deck of dithia[3.3]cyclophane with naphthalenyl, anthracenyl, thiophene, furan and pyridine rings, respectively, we have also shown that the area and heteroatom effect of transannular  $\pi-\pi$  interaction has pronounced influence on electronic transitions of corresponding bimetallic ruthenium complexes [10b,c].

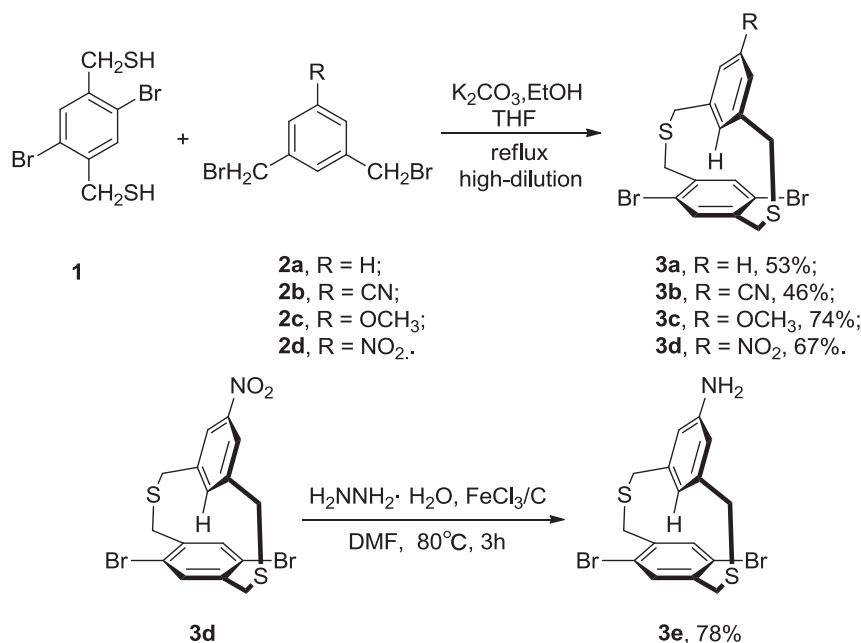
Previously, we have used the [3.3]metaparacyclophane skeleton to investigate intramolecular edge-to-face interactions [11], in which the *para*- and *meta*-substituted rings could provide the “face” and “edge” partners, respectively. The spontaneous edge-to-face interaction within [3.3]metaparacyclophane and its substituent effect, may provide a way to tune the electronic properties of bimetallic complexes. Herein, we report that the synthesis, crystal structures and characterization of a series of [3.3]metaparacyclophanes bridged bimetallic ruthenium complexes **5a–e**.

## 2. Results and discussion

Compounds with the 2,11-dithia[3.3]metaparacyclophane

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**Scheme 1.** Synthetic route to substituted 2,11-dithia [3,3]metaparacyclophanes **3a–e**.

scaffold were constructed by coupling of the appropriate dithiol and dibromide under high-dilution conditions [12], as illustrated in Scheme 1. The NH<sub>2</sub>-substituted cyclophane **3e** was obtained by catalytic hydrogenation of its NO<sub>2</sub> counterpart **3d** in the presence of FeCl<sub>3</sub>/C utilizing hydrazine hydrate as a hydrogen source. The building blocks of trimethylsilyl derivatives **4a–e** were synthesized by Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI-catalyzed Sonogashira cross-coupling reactions between **3a–e** and trimethylsilylacetylene (Scheme 2). Bimetallic ruthenium complexes **5a–e** were conveniently prepared by *in situ* desilylation/metalation [13] of trimethylsilyl-protected bis(ethynyl) ligand precursors (Scheme 3).

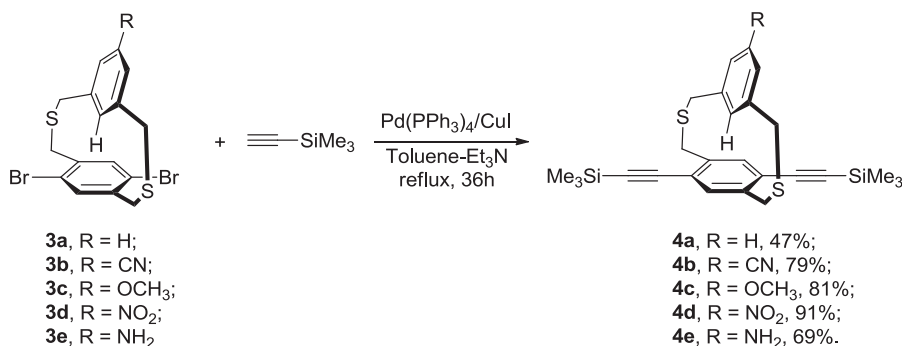
All of the synthesized compounds were thoroughly characterized by the usual spectroscopic methods. The <sup>1</sup>H NMR spectra showed unexpected upfield shifts of the signals of the aryl protons on the *meta*-substituted ring that were directed towards the face of the *para*-substituted ring. Specifically, for the diruthenium complexes **5a–e**, these signals were observed at  $\delta = 5.80, 5.92, 5.52, 6.00,$  and  $5.36$  ppm, respectively, which indicated the presence of significant edge-to-face interaction in solution [14]. The <sup>31</sup>P NMR spectrum of unsubstituted cyclophane bridged complex **5a** exhibits one broad peak at 80.97 ppm, while complexes **5b–5d** show two distinct peaks at around 80 and 83 ppm, respectively. This

observation indicates that **5a** readily underwent topomerization by flipping of the *meta*-substituted ring over the *para*-substituted one [11].

**X-ray Crystallographic Studies:** The ruthenium complexes **5a–e** were also structurally characterized by single-crystal X-ray diffraction. Plots of the structures of single molecules of **5a–e** (the independent dichloromethane solvent molecules were neglected for **5b, 5c,** and **5e**) are shown in Fig. 1. Selected bond lengths and angles are reported in Tables S1–S5, whilst Tables S6 and S7 summarize details of the data collection and refinement (Supporting Information).

Comparison of the complexes **5a–e** shows that there is significant consistency among the constituent segments, i.e., L<sub>n</sub>Ru(C≡C-Ar-C≡C)RuL<sub>n</sub>, and that the form is similar to that of the 1,4-diethynyltetrafluorobenzene-bridged diruthenium complex recently reported by Paul et al. [13]. The distance between the Ru centers in each of the complexes is close to 12 Å (Table 1).

In order to further understand the edge-to-face interaction in the solid, the perpendicular H-to-centroid distances and the inter-ring angles were taken as indicators, as illustrated in Fig. 2 and Table 1. The perpendicular H–ring plane distances (*D*<sub>H-cent.</sub>) range from 2.598 to 2.941 Å, and the inter-plane angles ( $\theta$ ) between the



**Scheme 2.** Synthesis of trimethylsilyl derivatives **4a–e**.

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