



# Benzodicarbene-bridged dinuclear complexes as building blocks for metalosupramolecular architectures



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## ABSTRACT

Dinuclear benzodicarbene-bridged iridium(III) and rhodium(III) complexes  $[\text{Cp}^*(\text{Cl})_2\text{M}(\text{benzodicarbene})\text{M}(\text{Cl})_2\text{Cp}^*]$  **[3]–[5]** have been synthesized from  $N,N',N'',N'''$ -tetraalkylbenzobisimidazolium salts and  $[\text{MCp}^*(\text{Cl})_2]_2$  via the  $\text{Ag}_2\text{O}$  method. Molecular structure determinations show an *anti*-arrangement of the  $\{\text{MCp}^*\}$  moieties relative to the bridging dicarbene ligand. Complexes **[3]–[5]** have been dehalogenated once at each metal atom which led to the formation of tetranuclear rectangles **[7](BF<sub>4</sub>)<sub>4</sub>–[9](BF<sub>4</sub>)<sub>4</sub>** featuring two benzodicarbene and two dichloro bridges between the metal centers. Removal of all halogen atoms from complexes **[3]** and **[4]** with  $\text{AgBF}_4$  in acetonitrile yielded dinuclear iridium(III) and rhodium(III) complexes of type  $[\text{Cp}^*(\text{MeCN})_2\text{M}(\text{benzodicarbene})\text{M}(\text{MeCN})_2\text{Cp}^*](\text{BF}_4)_2$  **[10](BF<sub>4</sub>)<sub>4</sub>–[11](BF<sub>4</sub>)<sub>4</sub>**.

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## 1. Introduction

For the last 25 years, the field of metalosupramolecular chemistry has been studied intensively after Lehn et al. first demonstrated in 1987 the spontaneous self-assembly of dinuclear helicates from bipyridine and  $\text{Cu}^{\text{I}}$  **[1]**. This research has led to a substantial number of metalosupramolecular structures derived from different polydentate ligands. Most of these assemblies are held together by classical Werner-type interactions, *i.e.* by nitrogen or oxygen donor atoms coordinating to the metal center **[2]**. Some of these supramolecular architectures feature internal cavities where small molecules can be encapsulated **[3]**. Both the encapsulation and stabilization of reactive molecules **[3b,3f,3k]** and the acceleration of selected catalytic transformations **[3g–j]** within such cavities have been reported.

Compared to the vast number of metalosupramolecular assemblies derived from Werner-type ligands, metal-organic polyhedra built from polydentate ligands with carbon donors are quite rare. A few examples featuring bridging diisocyanide **[4]**, acyclic diaminecarbene **[5]**, remote-NHC **[6]** and  $\alpha,\omega$ -dicarbanion ligands **[7]** have been reported.

Although carbenes and especially NHC ligands have become an important class of ligands in organometallic chemistry over the last 20 years **[8]**, the usage of carbene ligands in the preparation of

supramolecular architectures is still rather poorly investigated. Recently, a few supramolecular assemblies constructed from poly-NHC ligands have been reported. Among these are the molecular square **[A]<sup>8+</sup>** **[9]** featuring bridging NR,NR- and NH,O-substituted benzodicarbenes. In addition, molecular rectangles of type **[B]<sup>4+</sup>** **[10]** featuring rigid linear dicarbenes **[11]** and 4,4'-bipyridine are known. The molecular square **[C]<sup>4+</sup>** bearing NH,O-substituted dicarbene ligands **[12]** was obtained in a template-controlled reaction from the tetranuclear complex bearing four bridging diisocyanide ligands (Fig. 1). In addition to these molecular squares and rectangles, a number of tree-dimensional cylindrical structures have been obtained from macrocyclic **[13]** and other poly-NHC ligands **[14]** and from ligands featuring a mixed carbene/thiolate donor set **[14c,d]**.

We became interested in the preparation of new organometallic molecular assemblies of types **[A]<sup>8+</sup>**, **[B]<sup>4+</sup>** and **[C]<sup>4+</sup>**. Special interest was placed on the preparation of molecular squares and rectangles with iridium or rhodium at the vertices and NR,NR-substituted benzodicarbenes as bridging ligands. Preliminary investigations demonstrated that benzodicarbene-bridged dinuclear diplatinum complexes bearing sterically demanding diphosphines are not always perfectly suitable starting materials for the generation of molecular squares and rectangles as the potential binding sites at the metal centers needed to generate the molecular assemblies are oriented in *anti*-positions relative to the bridging dicarbene ligand **[10b]**. Here we present several new dinuclear, benzodicarbene-bridged iridium(III) and rhodium(III) complexes and their use for the generation of metalosupramolecular structures.

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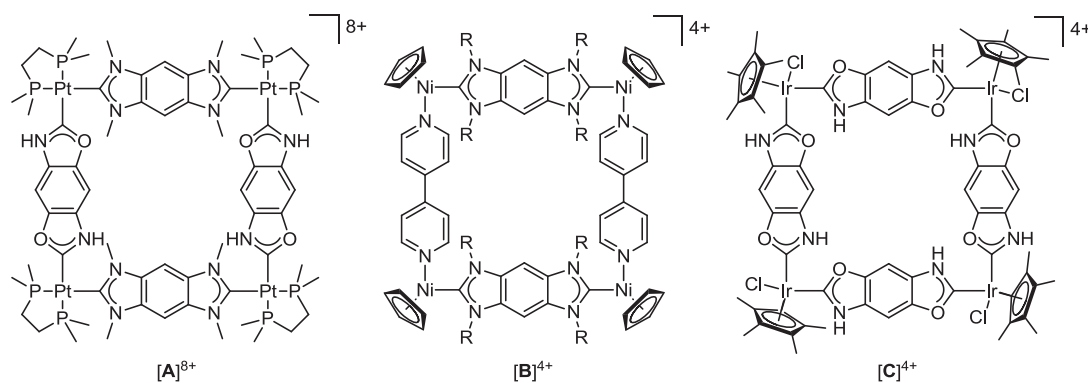


Fig. 1. Molecular square  $[A]^{8+}$ , rectangle  $[B]^{4+}$  and square  $[C]^{4+}$  obtained from dicarbene ligands.

## 2. Results and discussion

The benzobisimidazolium salts **1-Br<sub>2</sub>** and **2-I<sub>2</sub>** were prepared according to the procedure described by Bielawski and coworkers [15]. Reaction of benzobisimidazolium salt **1-Br<sub>2</sub>** with Ag<sub>2</sub>O in dichloromethane at 40 °C and subsequent treatment of the *in situ* formed silver carbene complex with [IrCp\*Cl<sub>2</sub>]<sub>2</sub> or [RhCp\*Cl<sub>2</sub>]<sub>2</sub> gave the dicarbene-bridged dinuclear complexes **[3]** and **[4]** in nearly quantitative yield (Scheme 1). Contrary to this, the reaction of ligand precursor **2-I<sub>2</sub>** with silver oxide followed by treatment with [RhCp\*Cl<sub>2</sub>]<sub>2</sub> did not yield the desired dinuclear Rh<sup>III</sup> complex while the use of [IrCp\*Cl<sub>2</sub>]<sub>2</sub> led to a mixture of the dicarbene complex **[5]** and the monocarbene complex **[6]** in low yields of 16% and 35%, respectively. The iridium complexes **[5]** and **[6]** could be separated by crystallization from dichloromethane.

The new complexes **[3]**–**[6]** were fully characterized by NMR spectroscopy, high resolution mass spectrometry and X-ray crystallography. Equivalent spectroscopic parameters for complexes **[3]** and **[4]** do not differ significantly. Complex **[3]** was identified via <sup>13</sup>C {<sup>1</sup>H} NMR spectroscopy by the characteristic singlet for the carbene carbon atom at  $\delta = 173.0$  ppm. The equivalent resonance for **[4]** was found due to Rh–C coupling as a doublet at  $\delta = 188.0$  ppm (<sup>1</sup>J<sub>Rh,C</sub> = 56.1 Hz). Rotation about the N–C bonds of the N-substituents appears to be hindered in both complexes as the methylene protons become diastereotopic. Only one set of NMR resonances was observed for **[3]**–**[5]**. Together with the observation of diastereotopic N–CH<sub>2</sub> protons in **[3]** and **[4]**, we take this as an indication for the preferred formation of only one, namely the

subsequently crystallographically characterized *anti*-isomers (*vide infra*) in solution. Rotation about the M–C bonds must, at least after removal of a chloro ligand from each metal center, be possible as demonstrated by the formation of the tetranuclear species **[7]**–**[9]** (Scheme 2, *vide infra*). High resolution mass spectrometry (ESI, positive ions) showed the molecular mass of the cationic complex ions  $[[3]-Cl]^+$  and  $[[4]-Cl]^+$  as peaks of high intensity.

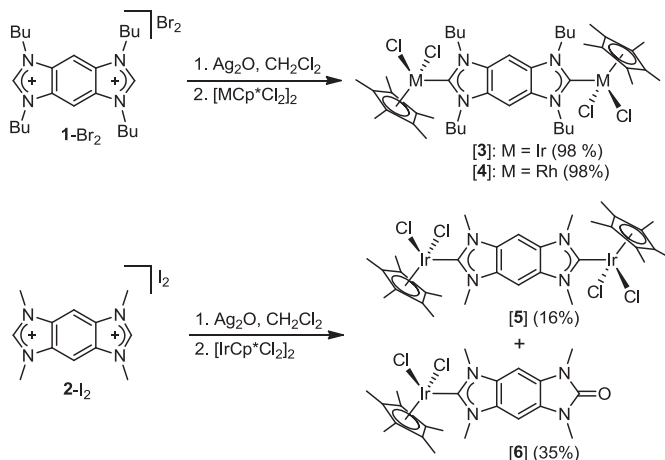
Single crystals, suitable for X-ray diffraction studies, of **[3]**·4CH<sub>2</sub>Cl<sub>2</sub> and **[4]**·4CH<sub>2</sub>Cl<sub>2</sub> were obtained by slow evaporation of the solvent from solutions of the complexes in dichloromethane. The molecular structures of **[3]** and **[4]** are depicted in Fig. 2.

Both **[3]** and **[4]** crystallize in the triclinic space group  $P\bar{1}$  with  $Z = 2$ . The {Cp\*M} complex fragments adopt the *anti*-arrangement in the solid state which would, without rotation about the M–C<sub>carbene</sub> bond, prevent the subsequent formation of a molecular square or rectangle. Metric parameters in **[3]** and **[4]** fall in the range previously described for related Ir<sup>III</sup> [16] and Rh<sup>III</sup> NHC [17] complexes. It should be noted that the M–C and M–Cl bond lengths in both complexes are identical within experimental error in spite of the different transition metals present.

Starting from the benzobisimidazolium diiodide **2-I<sub>2</sub>** we could not prepare the dinuclear Rh<sup>III</sup> complex. It can be speculated that the poor solubility of **2-I<sub>2</sub>** in dichloromethane together with the ability of the sterically less demanding substituted dicarbene obtained from **2-I<sub>2</sub>** to form oligomeric silver complexes hinders the carbene transfer to rhodium and iridium. The influence of the halide counter ion in benzimidazolium salts on the formation of gold NHC complexes has been discussed [18] and similar processes are very likely to be operative during the formation of the even more labile silver NHC complexes.

We obtained, however, the iridium(III) complex **[5]** together with the mononuclear complex **[6]**, where one imidazolium group has been converted into the cyclic urea derivative in low yield (Scheme 1). We assume that the formation of **[6]** is caused by reaction with the water released from the reaction of **2-I<sub>2</sub>** with silver oxide. We have previously demonstrated the monoplating of benzobisimidazolium salts [10b] leading to the mononuclear complex with one remaining imidazolium group. The oxidation of NHCs to yield urea derivatives has also previously been reported [19].

Complexes **[5]** and **[6]** were also fully characterized by NMR spectroscopy and mass spectrometry. The <sup>1</sup>H NMR data for **[5]** are very similar to those of iridium complex **[3]**. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **[5]** did not reveal the resonance for the C<sub>carbene</sub> atom due to the low solubility of the compound in dichloromethane. For complex **[6]** two characteristic resonances, one for the carbene carbon atom ( $\delta = 167.4$  ppm) and one for the urea carbon atom ( $\delta = 155.2$  ppm) were observed. The molecular structures of **[5]** in **[5]**·2CH<sub>2</sub>Cl<sub>2</sub> (top) and **[6]** in **[6]**·0.5CH<sub>2</sub>Cl<sub>2</sub> (bottom) are depicted in Fig. 3.



Scheme 1. Synthesis of the Ir<sup>III</sup>- and Rh<sup>III</sup>- NHC complexes **[3]**–**[6]**.

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