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Note

Stepwise formation of metallo-prisms of iridium and rhodium complexes bearing pentamethylcyclopentadienyl ligands

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Abstract

Reactions of $[M(Cp^*)Cl(\mu\text{-}Cl)]_2$ (M = Ir(**1a**); M = Rh(**1b**)) with tridentate ligands tpt (tpt = 2,4,6-tripyridyl-1,3,5-triazine) gave the corresponding trinuclear complexes $[M_3(Cp^*)_3(\mu_3\text{-}4\text{-tpt-}\kappa N)Cl_6]$ (M = Ir(**2a**); M = Rh(**2b**)), which can be converted into hexanuclear complexes $[M_6(Cp^*)_6(\mu_3\text{-}4\text{-tpt-}\kappa N)_2(\mu\text{-}Cl)_6](O_3SCF_3)_6$ (M = Ir(**3a**); M = Rh(**3b**)) by treatment with AgO_3SCF_3, respectively. X-ray of **3b** revealed that each of six pentamethylcyclopentadienyl metal moieties was connected by two μ-Cl-bridged atoms and a tridentate ligand to construct a cation triangular metallo-prism cavity with the volume of about 273 $Å^3$ based on the distance of the two triazine moieties is 3.62 Å.

Keywords: Iridium; Rhodium; Half-sandwich complexes; Metallo-prisms; Molecular structure

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1. Introduction

Organometallic half-sandwich complexes have become very interesting building blocks for supramolecular chemistry. Many half-sandwich complexes of iridium, rhodium and ruthenium occupy the corner positions are of the most promising building blocks for two- and three-dimensional supramolecular constructions [1]. In particular, metallo-prisms complexes of platinum and palladium bearing diphosphine and diamine derivatives have been used extensively by many groups [2]. Hupp and co-workers have employed two hexa-rhenium molecular prisms [3]. Recently, some (Arene)ruthenium metallo-prisms have been reported by Therrien et al. [4]. In contrast, to our knowledge, organo-iridium and organo-rhodium complexes containing chloro ligands have not been extensively studied [5].

In previous work, we [6] and others [7] have designed and synthesized tetranuclear rhodium and iridium supramolecules bearing cyclopentadienyl derivatives and two different types of ligands. Using the similar approach, we report the stepwise formation of iridium and rhodium metallo-prisms bearing pentamethylcyclopentadienyl and bridging chloro ligands, connected by two 2,4,6-tripyridyl-1,3,5-triazine (tpt) subunits (Scheme 1).

2. Results and discussion

In our previous report [8], the trinuclear complex **2a** can be obtained in high yield by stirring a mixture of $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1a**) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) in CH_2Cl_2 at room temperature for 18 h. The molecular consists of three (Cp^*Ir) fragments linked by one tpt ligand in a star-shape trimer.

Similarly, the red solids of trinuclear complex **2b** can be prepared in 92% yield through stirring a CH_2Cl_2 solution of a mixture of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (**1b**) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) at room temperature for 18 h. In the ^1H NMR spectra, the Cp^* methyl protons appear at 1.63 ppm as a singlet and the resonances for the pyridyl are around 8.93 and 8.63 ppm.

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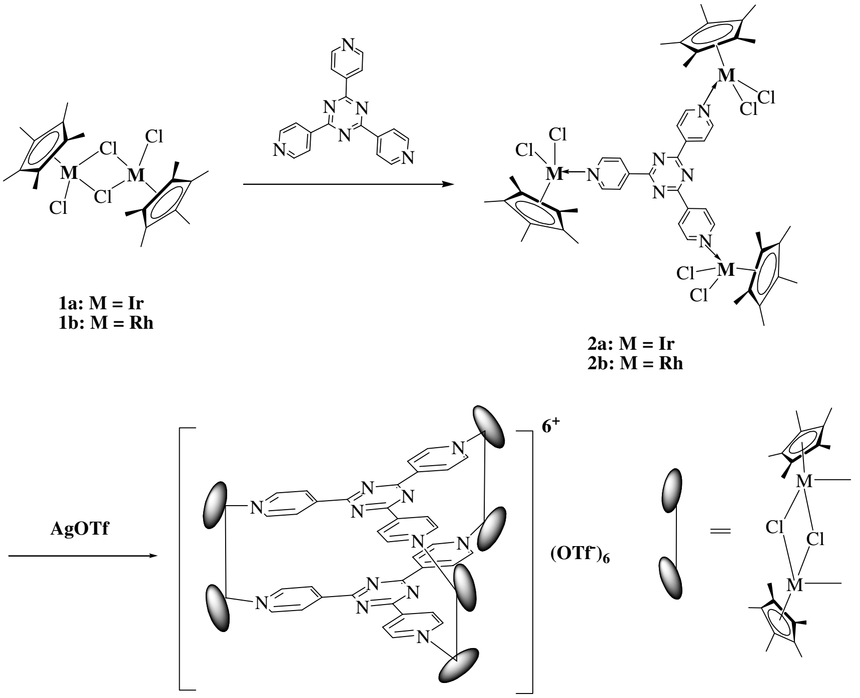

1a: M = Ir
1b: M = Rh

2a: M = Ir
2b: M = Rh

3a: M = Ir
3b: M = Rh

Scheme 1. Synthesis of complexes **3a** and **3b**.

When the trinuclear complexes **2a** or **2b** were treated with AgOTf in a 1:3 molar ratio in CH_2Cl_2 solution at room temperature, yellow crystals, formulated as $[M_6(Cp^*)_6(\mu_3\text{-}4\text{-tpt-}\kappa N)_2(\mu\text{-Cl})_6](O_3SCF_3)_6$ (M = Ir(**3a**); M = Rh(**3b**)) were formed in high yields followed by separation of AgCl, respectively, which bridged by chloro ligands, and connected by two 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) subunits. In IR spectra, the absorptions of the coordinated 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine ligand of **3a** and **3b** appear at about 1520, 1380, 810 cm^{-1} and the strong absorptions at about 1261, 1030, 639 cm^{-1} which can be assigned to the triflate anions stretching. The ^1H NMR spectra of **3a** and **3b** displayed similar signal patterns for the pyridyl protons with two singlets at $\delta = 8.95$ and 8.65 for **3a** and at $\delta = 9.00$ and 8.66 for **3b**. In addition, the structure of $[Rh_6(Cp^*)_6(\mu_3\text{-}4\text{-tpt-}\kappa N)_2(\mu\text{-Cl})_6](O_3SCF_3)_6$ (**3b**) was determined by single crystal X-ray analysis (Fig. 1).

The molecular structure of **3b** contains six octahedral rhodium centers, which are bridged by six chloro ligands and two tpt units with an average Rh···Rh separation of 3.66 Å, these Rh···Rh distances are comparable to those found in the chloro-bridged tetranuclear complexes [6a]. All of the rhodium clips are nearly 90° and the triazine moieties are paralleled from each other. Interestingly, the pyridines are slight twisted from the normal to the corresponding triazine moieties range of 7.8–11.7°, respectively. The centroid···centroid distance between the two triazine moieties is 3.62 Å, which show strong parallel π-stacking

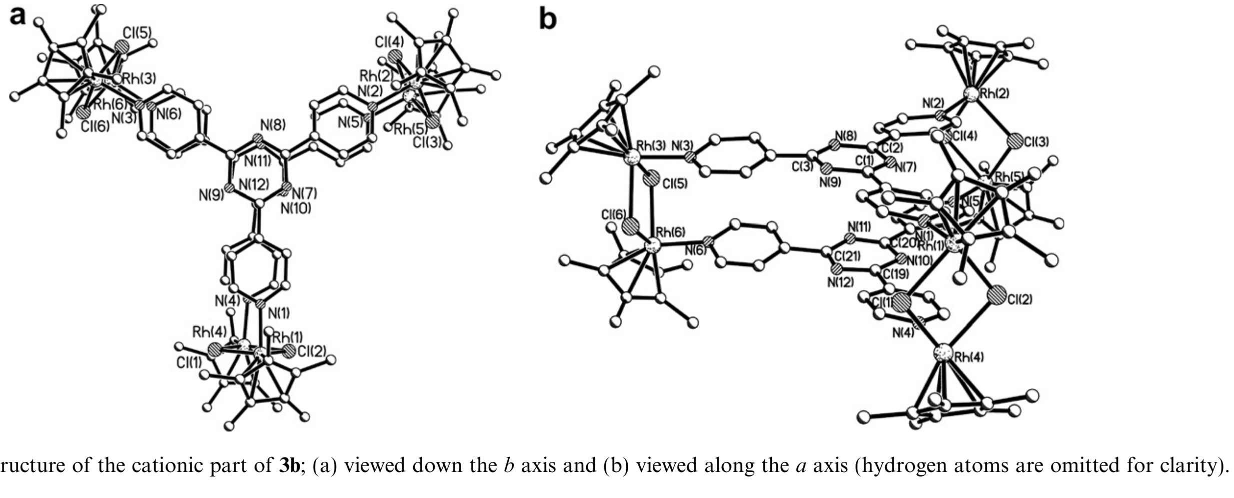

Fig. 1. Crystal structure of the cationic part of **3b**; (a) viewed down the *b* axis and (b) viewed along the *a* axis (hydrogen atoms are omitted for clarity).