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Synthesis and characterization of half-sandwich iridium complexes containing 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene and ancillary ortho-carborane-1,2-dichalcogenolato ligands

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Dedicated to Herr Professor Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

The binuclear half-sandwich iridium complexes $\{Cp^*IrCl_2\}_2$(μ-2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene) (**3**) and $\{Cp^*Ir[E_2C_2(B_{10}H_{10})]\}_2$(μ-2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene) (E = S(**5a**), Se(**5b**)) were prepared from the reaction of $[Cp^*IrCl(\mu\text{-}Cl)]_2$ or the "*pseudo*-aromatic" half-sandwich iridium complex $Cp^*Ir[E_2C_2(B_{10}H_{10})]$ (E = S(**4a**), Se(**4b**)) with a tetrathiafulvalene (TTF) derivative 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) at room temperature. The complexes (**3**, **5a** and **5b**) have been fully characterized by IR and NMR spectroscopy, as well as elemental analysis. And the molecular structures of **2** and **5a** were established through X-ray crystallography. It is interesting that infinite tunnels are created by repeating 'buckled bowl' molecules of **5a**.

Keywords: Iridium; Half-sandwich complexes; Carborane; Tetrathiafulvalene; Molecular structures

1. Introduction

Derivatives of the 1,2-dicarba-*closo*-dodecaborane (12) have attracted interests in recent years because their fundamental properties and their wide-ranging potential applications [1]. The efforts to build supramolecular structures are expected to offer many fascinating research problems with potentially significant ramifications [2]. In particular, carboranes are obvious candidates for such application because of their synthetic versatility and well-developed derivative chemistry. On the other hand, poly-pyridyl metal complexes have demonstrated their multifunctional properties in many aspects, for example molecular sensing [3], molecular-level wires [4], as well as non-linear optical (NLO) properties [5]. We were interested in supramolecular complexes based on ancillary *ortho*-carborane-1,2-dichalcogenolato ligands and their derivatives and have already reported on the synthesis of the 16-electron "*pseudo*-aromatic" half-sandwich carborane species, such as, $\{Cp^*M[E_2C_2(B_{10}H_{10})]\}$ (M = Co, Rh, Ir; E = S, Se) [6], and suggested that this species may be electron deficiency at the metal center which can be used to build *hetero*-metallic clusters [7]. Recently, we have explored the stepwise assembly of several multinuclear cluster complexes that contains two, three or four identical carborane ligands with the bi-, tri- or tetra-pyridyl-type ligands as the key functional groups in a variety of bridging ligands [8]. Such a strategy has led to a variety of diverse architectures.

Coordination of metals ions by electro-active ligands containing *tetra*thiafulvalene (TTF) moieties has attracted attention due to the potential applications of these novel organic-inorganic hybrid building blocks. Association of

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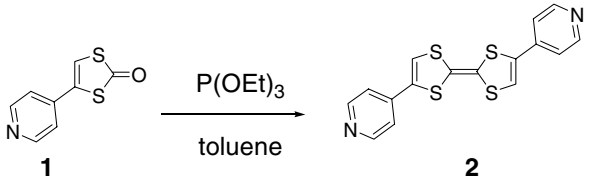
the TTFs to the metal can be realized through an intervening coordination function such as pyridyl substituents well-known for their chelating ability toward various transition metal derivatives [9].

To understand the factors that govern the crystal growth via metal-coordination-driven self-assembly processes better, we have prepared TTF derivatives as ligands. Their employment in preparing coordination polymers may provide a chance of creating novel open framework structures. Herein we report the preparation and structure of 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene ligand (**2**) and the stepwise assembly of the binuclear complexes $\{Cp^*Ir[E_2C_2(B_{10}H_{10})]\}_2$(μ-2,6(7)-bis(4-pyridyl)-1,4,5,8-tetra-thiafulvalene) (E = S(**5a**), Se(**5b**)). A remarkable feature of the new binuclear complex in **5a** is the packing pattern, the packing in the crystals is to create infinite tunnels which consist of repeating 'buckled bowl' molecules.

2. Results and discussion

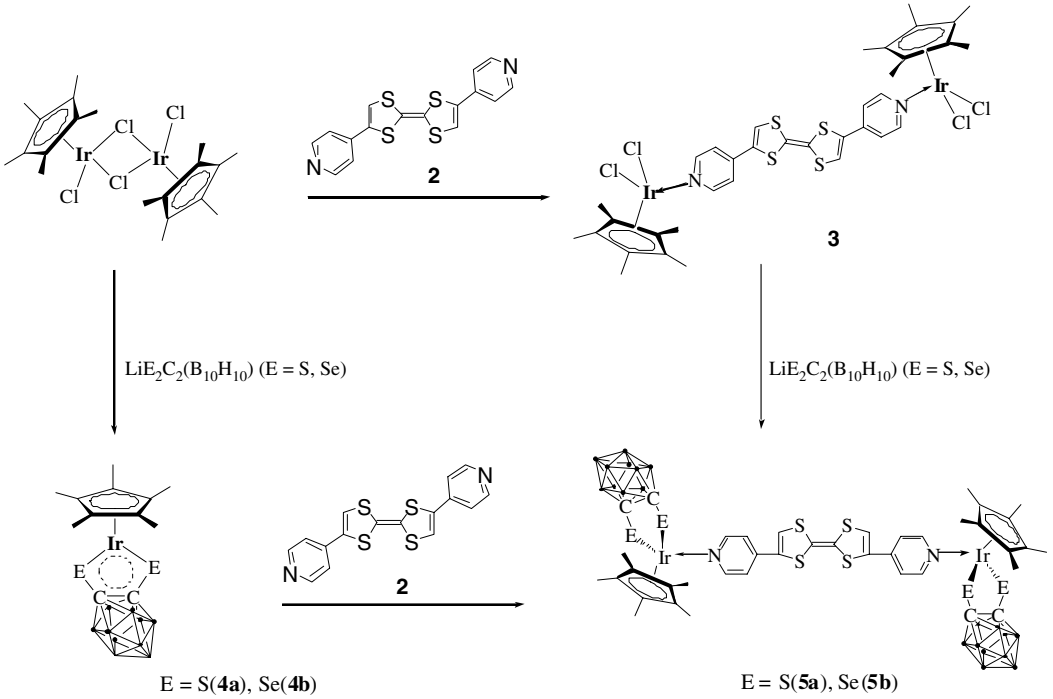
4-(4′-Pyridyl)-1,3-dithiol-2-one (**1**) was synthesized by slightly modified literature procedure [10]. 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene can be obtained in 51% yields upon treatment 4-(4′-Pyridyl)-1,3-dithiol-2-one (**1**) with $P(OEt)_3$ in toluene solution, and then recrystallized through CH_2Cl_2/hexane to give 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) preferentially (Scheme 1). Compound **2** was characterized by IR, ^1H NMR spectroscopy, elemental analysis and X-ray diffraction. The absorption band at 1592 cm^{-1} in the IR spectrum of ligand **2** can be assigned to the pyridyl band. The appearance to the ^1H NMR signals at 8.7, 8.6, 8.4, 7.3, 7.2 and 6.9 ppm are ascribed to the pyridyl ligands and dithiole rings.



Scheme 1. Synthesis of ligand **2**.

According to our previous work, the 16-electron complexes **4a** and **4b** can be easily synthesized from the half-sandwich iridium dichloride complexes $[Cp^*IrCl_2]_2$ [11] with dilithium 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolates $Li_2E_2C_2(B_{10}H_{10})$ (E = S, Se) in THF solution. The synthesis of the binuclear complexes **3** take advantage of the linear pyridyl based ligand (Scheme 2). Stirring a mixture of $[Cp^*IrCl_2]_2$ and 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) in CH_2Cl_2 at room temperature for 18 h produced red solution of **3** in a yield of 86%, which has been characterized by ^1H NMR, IR spectroscopy, and elemental analysis.

The complexes **5a** and **5b** can be obtained in ca. 70% yields by treatments of **3** with dilithium 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolates $Li_2E_2C_2(B_{10}H_{10})$ (E = S, Se) in THF at room temperature. The complexes **5a** and **5b** can be also directly obtained from the reaction of $Cp^*Ir[E_2C_2(B_{10}H_{10})]$ (E = S(**4a**), Se(**4b**)) with **2** in CH_2Cl_2. Recrystallization of **5**(**a**,**b**) from CH_2Cl_2/hexane affords the desired products as red crystalline solids in ca. 83% yields. The solubility of **5a** and **5b** in common organic



Scheme 2. Synthesis of complexes **3** and **5**.