

# 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  $\{\text{Cp}^*\text{IrCl}_2\}_2(\mu\text{-}2,6(7)\text{-bis(4-pyridyl)-}1,4,5,8\text{-tetrathiafulvalene})$  (**3**) and  $\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2(\mu\text{-}2,6(7)\text{-bis(4-pyridyl)-}1,4,5,8\text{-tetrathiafulvalene})$  ( $\text{E} = \text{S}$  (**5a**),  $\text{Se}$  (**5b**)) were prepared from the reaction of  $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2]$  or the “pseudo-aromatic” half-sandwich iridium complex  $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$  ( $\text{E} = \text{S}$  (**4a**),  $\text{Se}$  (**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**.

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**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,  $\{\text{Cp}^*\text{M}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{E} = \text{S}, \text{Se}$ ) [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 *tetrathiafulvalene* (TTF) moieties has attracted attention due to the potential applications of these novel organic-inorganic hybrid building blocks. Association of

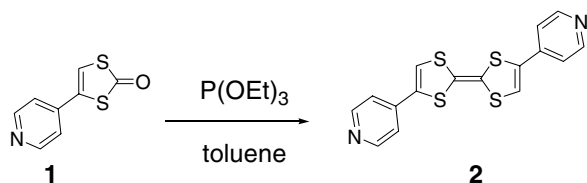
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the TTFs to the metal can be realized through an intervening coordination function such as pyridyl substituents well-known for their chelating ability toward various transition metal derivatives [9].

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  $\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2$ ( $\mu$ -2,6(7)-bis(4-pyridyl)-1,4,5,8-tetra-thiafulvalene) ( $\text{E} = \text{S}$ (**5a**),  $\text{Se}$ (**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-pyr-

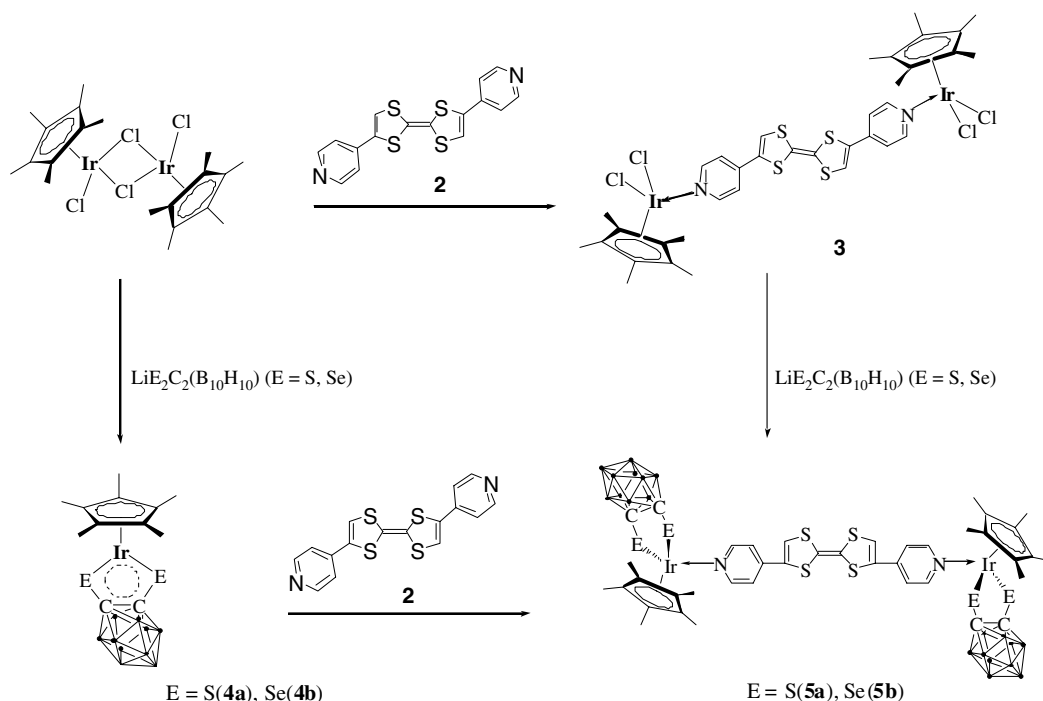


Scheme 1. Synthesis of ligand **2**.

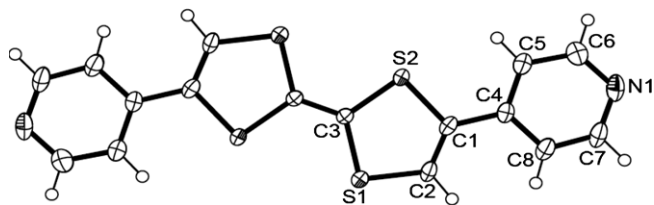
idyl)-1,4,5,8-tetrathiafulvalene can be obtained in 51% yields upon treatment 4-(4'-Pyridyl)-1,3-dithiol-2-one (**1**) with  $\text{P}(\text{OEt})_3$  in toluene solution, and then recrystallized through  $\text{CH}_2\text{Cl}_2$ /hexane to give 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) preferentially (Scheme 1). Compound **2** was characterized by IR,  $^1\text{H}$  NMR spectroscopy, elemental analysis and X-ray diffraction. The absorption band at  $1592\text{ cm}^{-1}$  in the IR spectrum of ligand **2** can be assigned to the pyridyl band. The appearance to the  $^1\text{H}$  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.

According to our previous work, the 16-electron complexes **4a** and **4b** can be easily synthesized from the half-sandwich iridium dichloride complexes  $[\text{Cp}^*\text{IrCl}_2]_2$  [11] with dilithium 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolates  $\text{Li}_2\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$  ( $\text{E} = \text{S}, \text{Se}$ ) in THF solution. The synthesis of the binuclear complexes **3** take advantage of the linear pyridyl based ligand (Scheme 2). Stirring a mixture of  $[\text{Cp}^*\text{IrCl}_2]_2$  and 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 18 h produced red solution of **3** in a yield of 86%, which has been characterized by  $^1\text{H}$  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  $\text{Li}_2\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$  ( $\text{E} = \text{S}, \text{Se}$ ) in THF at room temperature. The complexes **5a** and **5b** can be also directly obtained from the reaction of  $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$  ( $\text{E} = \text{S}$ (**4a**),  $\text{Se}$ (**4b**)) with **2** in  $\text{CH}_2\text{Cl}_2$ . Recrystallization of **5(a, b)** from  $\text{CH}_2\text{Cl}_2$ /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**.

Fig. 1. Molecular structure of **2**.Table 1  
Selected Bond Distances (Å) and Angles (°) for **2** and **5**

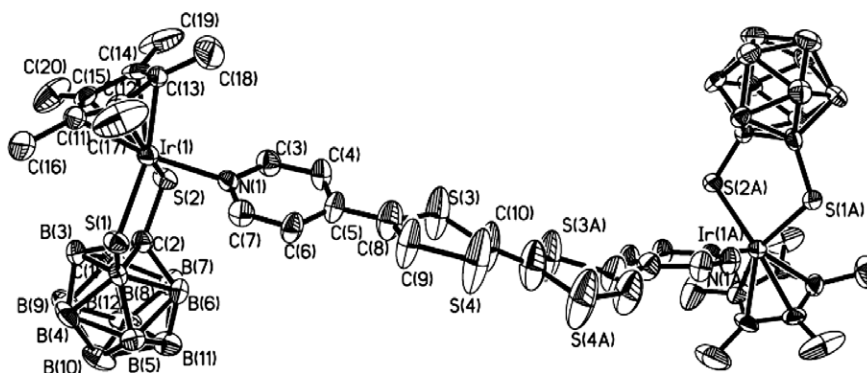
Bond distance (Å) in <b>2</b>			
S(1)–C(2)	1.731(4)	S(1)–C(3)	1.751(3)
S(2)–C(1)	1.768(3)	S(2)–C(3)	1.758(4)
N(1)–C(6)	1.336(5)	N(1)–C(7)	1.339(6)
C(1)–C(2)	1.329(5)	C(1)–C(4)	1.475(5)
C(4)–C(5)	1.382(6)	C(4)–C(8)	1.400(5)
C(5)–C(6)	1.392(6)	C(7)–C(8)	1.378(6)
Bond angle (°) in <b>2</b>			
C(2)–S(1)–C(3)	95.2(2)	C(1)–S(2)–C(3)	95.1(2)
C(6)–N(1)–C(7)	115.6(4)	C(2)–C(1)–C(4)	126.1(3)
C(2)–C(1)–S(2)	116.2(3)	C(4)–C(1)–S(2)	117.7(3)
S(1)–C(2)–C(1)	119.0(3)	S(1)–C(3)–S(2)	114.5(2)
C(5)–C(4)–C(8)	117.2(3)	C(5)–C(4)–C(1)	121.9(3)
C(8)–C(4)–C(1)	120.9(3)	C(6)–C(5)–C(4)	119.4(4)
N(1)–C(6)–C(5)	124.1(4)	C(8)–C(7)–n(1)	124.9(4)
C(4)–C(8)–C(7)	118.8(4)		
Bond distance (Å) in <b>5</b>			
Ir(1)–N(1)	2.135(7)	Ir(1)–C(12)	2.156(9)
Ir(1)–S(1)	2.355(3)	Ir(1)–S(2)	2.364(2)
N(1)–C(3)	1.360(10)	N(1)–C(7)	1.361(10)
C(5)–C(8)	1.430(14)	S(3)–C(10)	1.744(11)
S(3)–C(8)	1.748(11)	S(4)–C(9)	1.716(11)
S(4)–C(10)	1.748(12)	C(10)–C(10) <sup>#1</sup>	1.35(2)
Bond angle (°) in <b>5</b>			
N(1)–Ir(1)–C(12)	107.0(4)	N(1)–Ir(1)–C(14)	116.4(4)
C(12)–Ir(1)–C(14)	62.9(4)	N(1)–Ir(1)–C(15)	154.8(4)
C(12)–Ir(1)–C(15)	62.5(4)	C(14)–Ir(1)–C(15)	38.6(4)
N(1)–Ir(1)–C(11)	142.3(4)	N(1)–Ir(1)–C(13)	93.9(3)
N(1)–Ir(1)–S(1)	89.0(2)	N(1)–Ir(1)–S(2)	88.0(2)
S(1)–Ir(1)–S(2)	90.92(8)	C(10)–S(3)–C(8)	95.4(6)
C(9)–S(4)–C(10)	93.7(6)	C(10) <sup>#1</sup> –C(10)–S(3)	125.9(4)
C(10) <sup>#1</sup> –C(10)–S(4)	119.4(4)	S(3)–C(10)–S(4)	114.6(6)

solvents is better than **2** and **3**. In the solid state, the complexes **5a** and **5b** are stable in air. The IR spectra of complexes **5a** and **5b** in the solid state exhibit intense B–H of carborane stretching at about 2583 cm<sup>-1</sup> and 2575 cm<sup>-1</sup>, respectively. In <sup>1</sup>H NMR spectrum of complexes **5a** and **5b**, the Cp\* methyl protons appear as a singlet at  $\delta = 1.86$  ppm and 1.81 ppm, respectively.

Crystals of **2** and **5a** suitable for X-ray diffraction study were obtained by slow diffusion of hexane into a concentrated solution of the complexes in dichloromethane at –18 °C. Selected bond distances and angles of **2** and **5a** are listed in Table 1.

The molecular structure of **2** with the atom-numbering scheme is depicted in Fig. 1. The molecular structure indicates that two pyridyl rings are linked by a tetrathiafulvalene moiety and the molecular is *E* configuration. Consequently, the two pyridyl groups are oriented in a *trans* manner. In addition, the two pyridyl rings and tetrathiafulvalene moiety are coplanar.

The molecular structure of **5a** with the atom-numbering scheme is depicted in Fig. 2, which is in the form of red prisms in tetragonal crystal system. Linked by the bidentate organic linker **2**, 7-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene ligand, the *di* nuclear complex adopts a *trans* conformation, with the two functional carboranyl clusters pointing to different directions. The iridium atoms are surrounded by two sulfur atoms and one nitrogen atom. The coordination sphere of the iridium metal can be described as a distorted octahedron, if the coordination number of the Cp\* ligand is taken to be three, and the two iridium atoms are separated by 18 Å. The Ir–N bond length is 2.135(7) Å and Ir–S bond length range from 2.355(3) to 2.364(2) Å (see Table 1), respectively. Due to the coordination to the half-sandwich iridium units, the 2,7-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene ligand is no longer coplanar. The five-member ring C(10)–S(3)–S(4)–C(8)–C(9) is folded along the S–S vector, forming a dihedral angle of 167°. At the meantime, the pyridyl group is slightly twisted from the S(3)–S(4)–C(8)–C(9) plane, and the torsion angle is 16.7°. It is interesting that the ligand's unit in complex **5a** was converted from *E* to *Z* configuration.

Fig. 2. Molecular structure of **5a**.

Compared with reported literature [7i], 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (**2**) has distinctly different symmetry and orientation of its pyridyl arms and tetrathiafulvalene moiety may serve as template for architectures with novel topology that are not achievable by other types of rigid *N,N*-bipyridyl ligands. Viewed along the *b* axis, the complex **5a** showing a linear chain structure and the S···S are shown as lines linking the molecules (Fig. 3). The distances of S3···S3' is about 3.6 Å.

Another remarkable feature of **5a** is the packing pattern along *c*-axis. These 'buckled bowls' stack along the *c*-axis to form an interesting stacking structure which only be found when tpt (2,4,6-tris(4-pyridyl)-1,3,5-triazine) as ligand [8e]. As shown in Fig. 4, each of the 16 molecules **5** is paired up to form two types of infinite channels. In other words, each molecule of **5** is locked into position by pairing up with neighboring molecules in the crystal lattice. It is interesting that such channels consisted of repeating 'buckled bowl' molecule with the approximate dimensions  $8.5 \times 8.5 \text{ \AA}$ .

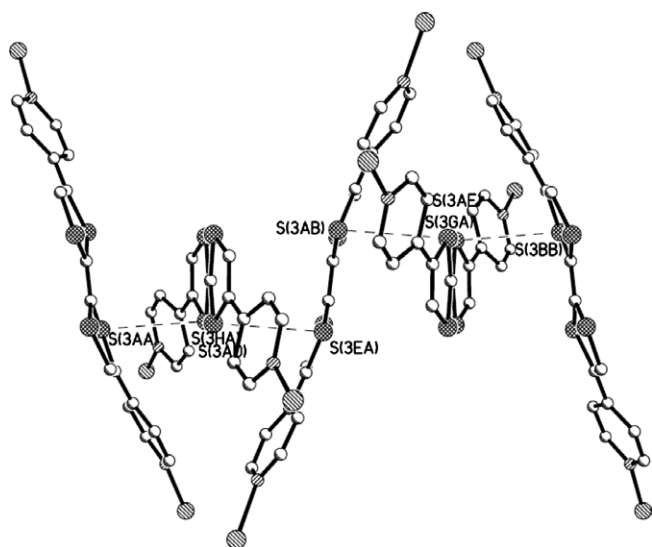


Fig. 3. Crystal structure of **5a**, viewed along the *b* axis.

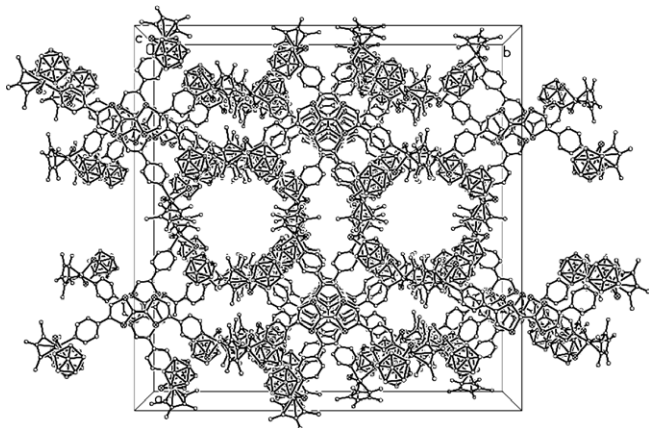


Fig. 4. Crystal structure of **5a**, viewed down the *c* axis.

### 3. Conclusion

In this context, the new coordination binuclear complexes **5a** and **5b** were synthesized and characterized by introducing carborane dichalcogenolates into pyridyl functionalized organic building blocks. The synthetic approach, based upon stepwise buildup of metal clusters with organic fragments, offers the potential for exquisite control over the detailed architecture of the materials, and we also anticipate this is a noteworthy approach for the design of a variety of more complexes coordination motifs with novel patterns.

### 4. Experimental

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System (4464) and collected just before use.  $[\text{Cp}^*\text{IrCl}_2]_2$  [11],  $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$  ( $\text{E} = \text{S}$  (**4a**),  $\text{Se}$  (**4b**)) [6b] and 4-(4'-pyridyl)-1,3-dithiol-2-one (**1**) [10] were prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, Elemental analyses were carried out by Elementar III Vario EI Analyzer.  $^1\text{H}$  NMR (500 MHz) and  $^{11}\text{B}$  NMR (160 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in  $\text{CDCl}_3$  solution.

#### 4.1. Synthesis of the ligand (**2**)

2,6(7)-Bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene was synthesized by slightly modified literature procedure [10].  $\text{P}(\text{OEt})_3$  (10 mL) in toluene (10 mL) was added 4-(pyridyl)-1,3-dithiol-2-one (**1**) (1.23 g, 6.3 mmol), the mixture was heated  $105^\circ\text{C}$  for 4 h and then filtered. The resulting red crystalline solid was washed with methanol ( $3 \times 5 \text{ mL}$ ) and dried in air. The ligand **2** was obtained through recrystallization from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ . Elemental Anal. Calc. for  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}_4$  (%): C, 53.64; H, 2.82; N, 7.82. Found: C, 53.76; H, 2.97; N, 7.63%; IR (KBr):  $\nu = 1592, 1556 \text{ cm}^{-1}$  ( $\nu_{\text{py}}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 8.67$  (d, 2H), 8.62 (d, 2H), 7.31 (d, 2H), 7.16 (d, 2H), 6.86 (s, 2H).

#### 4.2. Synthesis of $\{\text{Cp}^*\text{IrCl}_2\}_2(\mu\text{-}2,6(7)\text{-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene})$ (**3**)

A solution of  $\text{Cp}^*\text{IrCl}_2$  (**1**) (80.0 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene **2** (35.8 mg, 0.1 mmol) at room temperature. After stirring for 24 h, the solvent was evaporated under reduced pressure and the dark red residue was washed by diethyl ether. The dark red solids (93.2 mg, 80.5%) were gained through recrystallization from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  at  $-18^\circ\text{C}$ . Elemental Anal. Calc. for  $\text{C}_{36}\text{H}_{40}\text{Cl}_4\text{Ir}_2\text{N}_2\text{S}_4$  (%): C, 37.43; H, 3.49; N, 2.42. Found: C, 37.42; H, 3.56; N, 2.50%. IR (KBr):  $\nu = 1603, 1552 \text{ cm}^{-1}$  ( $\nu_{\text{py}}$ ).  $^1\text{H}$  NMR

(500 MHz,  $d^6$ -DMSO, ppm):  $\delta = 8.72$  (d, 2 H), 8.65 (d, 2H), 7.28 (d, 2H), 7.16 (d, 2H), 6.80 (s, 2H), 1.86 (s, 30H, Cp\*).

#### 4.3. Synthesis of $\{Cp^*Ir[S_2C_2(B_{10}H_{10})]\}_2(\mu-2,6(7)$ -bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene) (**5a**)

A solution of  $Li_2S_2B_{10}H_{10}$  (0.1 mmol 19.8 mg) in diethyl ether was added to the solution of **3** (54.2 mg, 0.05 mmol) in  $CH_2Cl_2$  at room temperature. After stirring for 24 h, the solvent was evaporated under reduced pressure and the dark red residue was extracted with  $CH_2Cl_2$  to give red crystals **5a** (60.9 mg, 83.6%).

A mixture of **4a** (53.4 mg, 0.1 mmol) and 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene **2** (17.9 mg, 0.05 mmol) were dissolved in  $CH_2Cl_2$  (30 ml). The solution changed gradually from dark blue to dark red after stirred for 24 h. The solvent was evaporated under reduced pressure and the residue was washed by toluene. Red crystals **5a** (50.1 mg, 70.3%) were gained through recrystallization from  $CH_2Cl_2$ /hexane at  $-18^\circ C$ . Elemental Anal. Calc. for  $C_{40}H_{60}B_{20}Ir_2N_2S_8$ : C, 33.69; H, 4.24; N, 1.96. Found: C, 33.52; H, 4.18; N, 1.98%. IR (KBr):  $\nu = 2583\text{ cm}^{-1}$  ( $\nu_{B-H}$ ), 1606,  $1550\text{ cm}^{-1}$  ( $\nu_{py}$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta = 8.63$  (d, 2 H), 8.62 (d, 2H), 7.29 (d, 2H), 7.28 (d, 2H), 6.90 (s, 2H), 1.87 (s, 15H, Cp\*).  $^{11}B$  NMR (160 MHz,  $CDCl_3$ , ppm):  $\delta = -6.4, -7.7, -8.5, -9.4, -10.1, -11.0$ .

#### 4.4. Synthesis of $\{Cp^*Ir[Se_2C_2(B_{10}H_{10})]\}_2(\mu-2,6(7)$ -bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene) (**5b**)

A solution of  $Li_2Se_2B_{10}H_{10}$  (29.0 mg, 0.1 mmol) in diethyl ether was added to the solution of **3** (54.2 mg, 0.05 mmol) in  $CH_2Cl_2$  at room temperature. After stirring for 24 h, the solvent was evaporated under reduced pressure and the dark red residue was extracted with  $CH_2Cl_2$  to give red crystals **5b** (74.6 mg, 82.9%).

A mixture of **4b** (62.8 mg, 0.1 mmol) and 2,6-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene **2** (17.9 mg, 0.05 mmol) were dissolved in  $CH_2Cl_2$  (30 ml). The solution changed gradually from dark blue to dark red after stirred for 24 h. The solvent was evaporated under reduced pressure and the residue was washed by toluene. Red crystals **5b** (63.3 mg, 70.3%) were gained through recrystallization from  $CH_2Cl_2$ /hexane at  $-18^\circ C$ . Elemental Anal. Calc. for  $C_{40}H_{60}B_{20}Ir_2N_2Se_8$  (%): C, 26.67; H, 3.36; N, 1.56. Found: C, 26.73; H, 3.27; N%, 1.60. IR (KBr):  $\nu = 2576\text{ cm}^{-1}$  ( $\nu_{B-H}$ ), 1601,  $1553\text{ cm}^{-1}$  ( $\nu_{py}$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta = 8.66$  (d, 2H), 8.65 (d, 2H), 7.27 (d, 2H), 7.25 (d, 2H), 6.89 (s, 2H), 1.81 (s, 30H, Cp\*).  $^{11}B$  NMR (160 MHz,  $CDCl_3$ , ppm):  $\delta = -6.8, -7.5, -8.3, -9.3$ .

#### 4.5. X-ray crystallography

A red block crystal of **2** was mounted on a glass fiber. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo  $K\alpha$  radi-

Table 2

Crystallographic data for complexes **2** and **5a**

	<b>2</b>	<b>5a</b>
Formula	$C_{16}H_{10}N_2S_4$	$C_{40}H_{60}B_{20}Ir_2N_2S_8$
<i>M</i>	358.51	1425.98
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$ (#14)	$I4(1)/acd$
<i>a</i> (Å)	3.8413(2)	40.274(8)
<i>b</i> (Å)	11.646(4)	40.274(8)
<i>c</i> (Å)	21.232(7)	16.329(5)
$\alpha$ (°)	90	90
$\beta$ (°)	98.944(7)	90
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> ),	938.3(5)	26486(11)
<i>Z</i>	2	16
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.269	1.430
<i>F</i> (000)	368	11136
Crystal size (mm)	$0.07 \times 0.37 \times 0.18$	$0.15 \times 0.12 \times 0.10$
Collected reflections	21086	53586
Unique	2226	5854
Parameters	105	340
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.010	0.828
<i>R</i> <sub>1</sub>	0.048 <sup>a</sup>	0.0480 <sup>b</sup>
<i>wR</i> <sub>2</sub>	0.111 <sup>a</sup>	0.0906 <sup>b</sup>
Largest difference in peak/hole (e/Å <sup>3</sup> )	0.59, -0.46	0.971, -0.483

<sup>a</sup> [ $I > 3\sigma(I)$ ].

<sup>b</sup> [ $I > 2\sigma(I)$ ].

$$R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|};$$

$$wR_2 = \frac{[\sum w(|F_o|^2 - F_c^2)|^2]}{[\sum w|F_o|^2]}^{1/2}.$$

tion ( $\lambda = 0.71070\text{ \AA}$ ). The data were collected at a temperature of  $-80 \pm 1^\circ C$  to a maximum  $2\theta$  value of  $55.0^\circ$ . The structure was solved by direct methods and expanded using Fourier techniques [12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure [13] crystallographic software package.

Diffraction data of **5a** was collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on *F*<sup>2</sup> by using full-matrix least-squares techniques (SHELXL) [12a], SADABS [14] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. Crystal data, data collection parameters, and the results of the analyses of compounds **2** and **5a** are listed in Table 2.

#### 5. Supplementary material

CCDC 640228 and 640229 contain the supplementary crystallographic data for **2** and **5a**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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