

Tetrametallic clusters (Ir_2Rh_2) through an ancillary *ortho*-carborane-1,2-dichalcogenolato ligands

Guo-Xin Jin* and Jian-Qiang Wang

Received 24th August 2005, Accepted 26th October 2005

First published as an Advance Article on the web 10th November 2005

DOI: 10.1039/b512027f

The tetrametallic cluster complexes $\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ ($\text{E} = \text{S}$ (**3a**); Se (**3b**)) have been synthesized by reactions of the 16-electron half-sandwich iridium complexes $[\text{Cp}^*\text{Ir}\{\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]$ [$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{E} = \text{S}$ (**1a**), Se (**1b**)] with $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ at room temperature in toluene solution. In the solid state, this tetrametallic cluster exhibits an irregular nearly planar metal skeleton with the two carborane dichalcogenolato ligands bridging the four metal centers from both sides of the tetrametallic plane. Even though all metal atoms coordinate bridging chalcogen atoms, they show different electronic and coordination environments. The molecular structures of **3a** and **3b** have been determined by X-ray crystallography.

Introduction

The chemistry of mixed-metal clusters has been of enduring interest because of the unique chemistry resulting from having two or more metals with different chemistry properties in close proximity and also because of their potential catalytic applications.^{1,2} Many dithiolene ligands have been employed for the preparation of heterometallic clusters.³ During the past decade, considerable attention has been devoted to metal complexes containing chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands, to take advantage of their unique molecular structure.⁴ A number of mononuclear 16-electron Cp and Cp* half-sandwich complexes of Co, Rh and Ir have been described which contain a bidentate, chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand, $[(\text{B}_{10}\text{H}_{10})\text{C}_2\text{E}_2]^{2-}$ ($\text{E} = \text{S}, \text{Se}$) and a “pseudo-aromatic” metalladichalcogenolene five-membered ring.⁴ These compounds have been used as models to study the insertion of alkynes into one of the metal–sulfur bonds; this may lead to the formation of a metal-to-boron bond or substitution of the carborane cage in the positions of B(3)/B(6).^{5,6} In recently, we have developed a methodology to build up polynuclear frameworks, containing metal–metal

bonds, by using the 16-electron mononuclear complexes of metals such as $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$, $\text{Cp}^*\text{Rh}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ and $\text{Cp}^*\text{Co}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}, \text{Se}$) (see Scheme 1 for selected examples **A**, **B** and **C**).⁵

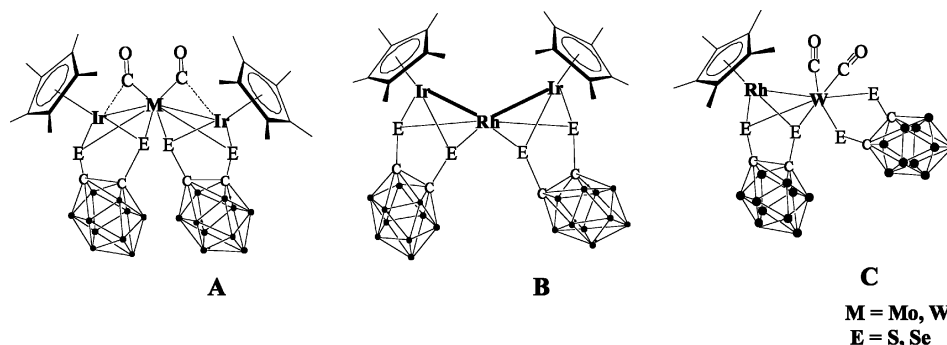
The incorporation of the 1,2-dithiolato or 1,2-diselenolato structural unit into the bulky *closo*-dicarbododecaborane ligand protects the inner coordination sphere and stabilized the metal–metal bond, which has occasionally been observed at dithiolene ligands.⁷ Such properties aid in the construction of different types of binuclear, trinuclear and other unprecedented hetero-metallic clusters.

In previous work, we have already described, treatment of $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ with $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ resulted in the formation of a trimetallic cluster with the Ir_2Rh core.⁵ For comparison, now the reactions of **1a**, **1b** with analogous complexes $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ have been investigated. Here, we present the results of these studied along with details of the synthesis and characterization of novel tetranuclear cluster complexes **3a**, **3b**.

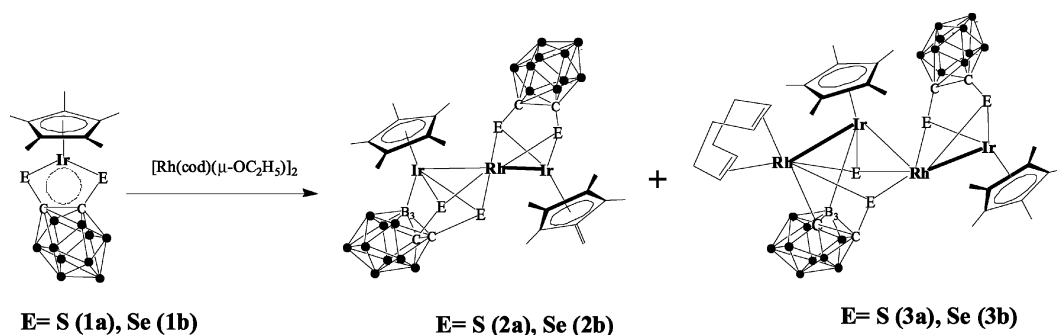
Results and discussion

In our previous report, the dimer $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ was an acceptable material to produce the Ir_2Rh trinuclear metallic clusters **2a**, **2b**.⁵ However, the work of Vinas *et al.* shows that the reaction of carborane complexes with other types of rhodium

Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, 200433, Shanghai, P. R. China. E-mail: gxinjin@fudan.edu.cn; Fax: +86-21-65641740; Tel: +86-21-65643776



Scheme 1 Examples of structurally characterized complexes.



Scheme 2 Reaction of **1a** and **1b** with $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$.

complexes, such as $[\text{Rh}(\text{cod})(\text{acac})]$, would lead to some interesting reactions.⁸ Taking into account the similarity of $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ with $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$, which has been long known to be an useful precursor to prepare a variety of rhodium complexes, we consider whether this similar reaction can give different results. The experimental procedure is similar to the reaction of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$. The 16-electron complexes **1a** and **1b** can be easily synthesized from the half-sandwich iridium dichloride complex $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2]$ with dilithium 1,2-dicarba-*closo*-dodecaborane (12)-1,2-dithiolate in THF solution (Scheme 3).⁹ **1a** and **1b** were reacted with $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ in the molar ratio 2 : 1 in toluene, and the green solution changed to red gradually. After the products were separated by column chromatography, two products: $\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}(\text{cod})$ (**2a**) and $\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ (**3a**) were obtained in 18 and 30% yield, respectively (Scheme 2). In addition, analogous products $\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}(\text{cod})$ (**2b**) and $\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ (**3b**) were also obtained by the same method in yields of 16 and 30% respectively. Complexes **3a** and **3b** can be obtained in higher yields when longer reaction times are applied.

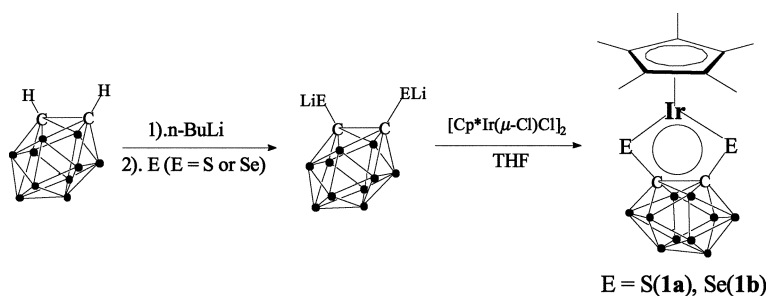
The complexes **3a** and **3b** are neutral, diamagnetic and air-sensitive in solution. The IR spectra of the products **3a** and **3b** in the solid state exhibit intense B–H of carborane stretching at about 2573 (vs) and 2588 (vs) cm^{-1} .

The molecule **2a** is unsymmetrical, as confirmed by the ^1H NMR spectrum with two singlets of Cp^* rings at δ 2.11 and 2.19 ppm.⁵ The ^1H NMR data for complexes **3a** display two intense methyl singlets of pentamethylcyclopentadienyl ligands (2.07, 2.19 ppm) and a number of multiplets in the ranges 4.02–4.29 ppm (olefinic

and 1.58–1.83 ppm (aliphatic) which can be ascribed to the 1,5-cyclooctadiene ligand. Both molecules **2a** and **3a** contain an Ir–B bond, as indicated by the appearance of Ir–B resonances in the ^{11}B NMR spectrum at about -20 ppm.¹⁰ Excellent elemental analyses were obtained for all complexes and consistent with the proposed structures.

Crystals of **2a**, **3a**, **2b** and **3b** suitable for X-ray diffraction study were obtained by slow diffusion of hexane into a concentrated solution of the complexes in dichloromethane at low temperature. The molecular structures of **2a** and **2b** have been described in our previous papers,⁵ so they were only used to compare with **3a** and **3b** here. Selected bond distances and angles of **3a** and **3b** are listed in Table 1.

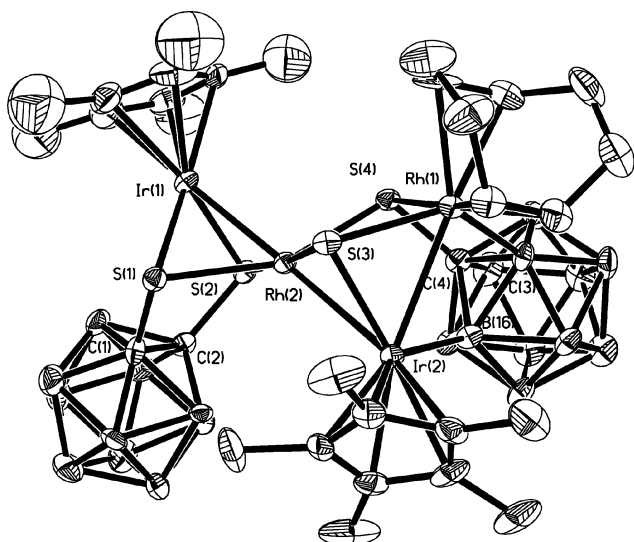
The molecular structure of **3a** is shown in Fig. 1. The metal atoms of the core adopt a quite irregular nearly planar Ir_2Rh_2 arrangement (Ir(1), Ir(2), Rh(1) and Rh(2) metals are coplanar with maximum deviation at 0.177 Å). To our knowledge, this type of Ir_2Rh_2 core cluster is rare, only some pyramidal shape metal carbonyl clusters of $\text{Ir}_2\text{Rh}_2(\text{CO})_{12}$ and its derivatives were reported previously.¹¹ The two dithiolato ligands of carboranes are situated at the both sides of the tetrametallic plane with three of the sulfur atoms acting as μ_2 -bridging ligands and the other sulfide simultaneously connecting three metals. The Ir(2), Rh(1) and Rh(2) metals exhibit six-coordinate environments and Ir(1) is five coordinate if considering the metal–metal bonds, and their coordination spheres are clearly different (Fig. 2). Ir(2) coordinates a different set of ligands bonding to Ir(1), boron and two metal bonds with Rh(1) and Rh(2), except for the similar Cp^* bridging thiolates ligands. By use of the thiolate ligands, Rh(2) connects the Ir(1) and Ir(2) atoms.



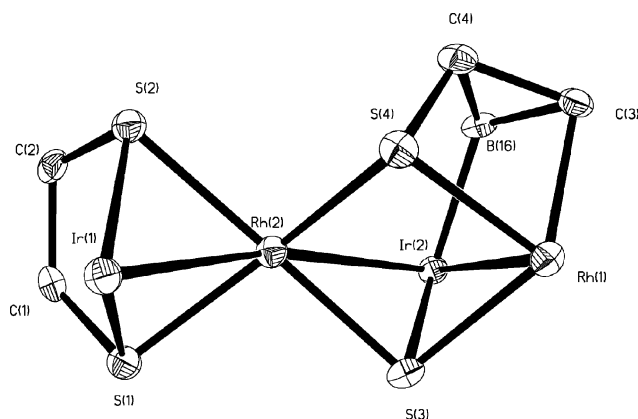
Scheme 3 Synthesis of complexes **1a** and **1b**.

Table 1 Selected bond distances (Å) and angles (°) for **3a** and **3b**

3a			
Ir(1)–S(1)	2.332(3)	Ir(1)–S(2)	2.347(3)
Ir(1)–Rh(2)	2.5990(10)	C(1)–C(2)	1.610(14)
Ir(2)–Rh(2)	2.9814(10)	Rh(2)–S(3)	2.304(3)
Rh(2)–S(4)	2.295(3)	Ir(2)–Rh(1)	2.7862(11)
Ir(2)–S(3)	2.315(3)	Ir(2)–B(16)	2.139(11)
Rh(1)–S(3)	2.332(3)	Rh(1)–S(4)	2.365(3)
Rh(1)–C(3)	2.132(10)	C(3)–C(4)	1.627(14)
S(1)–Ir(1)–S(2)	57.69(7)	C(1)–S(1)–Ir(1)	104.1(4)
C(1)–S(1)–Rh(2)	103.3(3)	S(1)–Rh(2)–S(2)	79.25(9)
Ir(1)–S(1)–Rh(2)	66.76(7)	Ir(1)–S(2)–Rh(2)	66.48(7)
Ir(1)–Rh(2)–Ir(2)	168.99(3)	S(4)–Rh(2)–S(3)	83.43(10)
S(3)–Rh(2)–Ir(2)	49.95(7)	S(3)–Ir(2)–Rh(2)	49.64(6)
S(3)–Ir(2)–Rh(1)	53.45(7)	Rh(2)–S(4)–Rh(1)	95.40(9)
Rh(1)–Ir(2)–Rh(2)	73.32(3)	S(3)–Rh(1)–S(4)	81.31(9)
C(3)–Rh(1)–S(4)	75.0(3)	C(3)–Rh(1)–Ir(2)	83.8(3)
C(4)–S(4)–Rh(1)	81.6(3)	B(16)–Ir(2)–Rh(1)	66.6(3)
3b			
Ir(1)–Se(1)	2.4316(16)	Ir(1)–Se(2)	2.4433(16)
Ir(1)–Rh(2)	2.6281(12)	C(1)–C(2)	1.614(19)
Ir(2)–Rh(2)	3.0085(13)	Rh(2)–Se(3)	2.4038(18)
Rh(2)–Se(4)	2.3975(18)	Ir(2)–Rh(1)	2.8258(13)
Ir(2)–Se(3)	2.4435(16)	Ir(2)–B(16)	2.151(15)
Rh(1)–Se(3)	2.4578(18)	Rh(1)–Se(4)	2.4777(18)
Rh(1)–C(3)	2.138(15)	C(3)–C(4)	1.648(19)
Se(1)–Ir(1)–Se(2)	83.41(5)	C(1)–Se(1)–Ir(1)	102.6(4)
C(1)–Se(1)–Rh(2)	101.8(4)	Se(1)–Rh(2)–Se(2)	81.42(6)
Ir(1)–Se(1)–Rh(2)	64.63(4)	Ir(1)–Se(2)–Rh(2)	64.39(4)
Ir(1)–Rh(2)–Ir(2)	169.63(5)	Se(4)–Rh(2)–Se(3)	83.96(6)
Se(3)–Rh(2)–Ir(2)	52.23(4)	Se(3)–Ir(2)–Rh(2)	51.04(4)
Se(3)–Ir(2)–Rh(1)	55.03(4)	Rh(2)–Se(4)–Rh(1)	94.15(6)
Rh(1)–Ir(2)–Rh(2)	75.39(4)	Se(3)–Rh(1)–Se(4)	81.18(6)
C(3)–Rh(1)–Se(4)	76.2(4)	C(3)–Rh(1)–Ir(2)	83.5(4)
C(4)–Se(4)–Rh(1)	78.5(4)	B(16)–Ir(2)–Rh(1)	66.2(4)

**Fig. 1** Molecular structure of the tetranuclear complex **3a**.

Compared with structures of **2a** and **3a**, the difference lies in the [(cod)Rh] fragment in **3a**. We can presume that in the whole reaction the [(cod)Rh] fragment exists in some reactive form and

**Fig. 2** Central skeleton of **3a** showing the different metal coordination spheres.

inserts into the original S(3)–C(3) bond, accompanying the cleavage of S(3)–C(3) bond, and **3a** is formed. The detailed mechanism of the insertion reaction of [(cod)Rh] into S–C bonds is still not clear, and further investigations of these aspects are in progress.

The structure of **3a** shows three short intermetallic separations: Ir(1)–Rh(2) 2.5990(10), Rh(2)–Ir(2) 2.9814(10), Ir(2)–Rh(1) 2.7862(11) Å. All these lie in the expected range for a metal–metal bond. Compared with the analogous fragment in **2a** (2.685(3) Å), the Ir(1)–Rh(2) metal bond become much shorter. Slightly longer Rh–Ir separations were found in many cases, such as [Cp^zZr(μ-S)₂Ir(CO)₂Rh(cod)₂] (2.8205(10) Å)¹² (with a μ-S supported metal–metal bond), and the heterodinuclear cations RhIr(CO)₂(μ-dppm)₂⁺ (2.7722(7) Å)¹³ and [RhIr(CH₃)(CO)₃(μ-dppm)₂]⁺ (2.743(1) Å).¹⁴ Much longer metal–metal distances were observed in the cluster [(Cp*Ir)₂(μ₃-S)₂Rh(cod)][RhCl₂(cod)] (2.906(1) and 2.913(9) Å).¹⁵ The presence of a shorter d⁸–d⁸ Ir(1)–Rh(2) interaction in **3a** is also supported by the Ir(1)–S–Rh(2) angles (66.76(7) and 66.48(7)°), which are smaller than the analogous Rh–S–Ir angles in **2a** (69.59(18) and 69.8(2)°). The Ir–S distances (2.332(3)–2.347(3) Å) and Rh–S distances (2.295(3)–2.365(3) Å) in **3a** are in the normal range of Ir–S and Rh–S single bonds, but the Ir–S distances are significantly longer than those in the “pseudo-aromatic” iridadithiolene ring in Cp*Ir[S₂C₂(B₁₀H₁₀)] (**1a**) (2.252(5) and 2.251(6) Å).⁴ Due to the coordination of the S atoms of carborane to Rh, the pseudo-aromatic iridadithiolene heterocyclic system (Ir(1)–S(1)–C(1)–C(2)–S(2)) is destroyed and bent with a dihedral angle of 135.3° along the S(1)⋯S(2) vector.

The complex **3b** crystallizes in the form of dark-red block in the monoclinic space group *P*2₁/*n* with four molecular in the unit cell. Its molecular structure is similar to **3a**. Fig. 3 depicts the molecular structure of **3b**. Complex **3b** also contain four metal atoms, which form an irregular nearly planar Ir₂Rh₂ core (The Ir(1), Ir(2), Rh(1) and Rh(2) metals are coplanar with maximum deviation at 0.167 Å) similarly with **3a**. There are three metal bonds: Ir(1)–Rh(2) 2.6281(12), Rh(2)–Ir(2) 3.0085(13), Ir(2)–Rh(1) 2.8258(13) Å. The Ir(1)–Se–Rh(2) angles (64.63(4) and 64.39(4)°) are smaller than the analogous Ir(1)–S–Rh(2) angles in **3a** (66.76(7) and 66.48(7)°). The planar pseudo-aromatic system of the iridadiseleno heterocycle **1b** is also no longer present in **3b**, the dihedral angle at the Se⋯Se vector in the IrSe₂C₂ ring is 135.8°. The Ir–Se bond distances (2.4316(16)–2.4435(16) Å) are similar to those in normal selenolate complexes, but are significantly longer than those in the

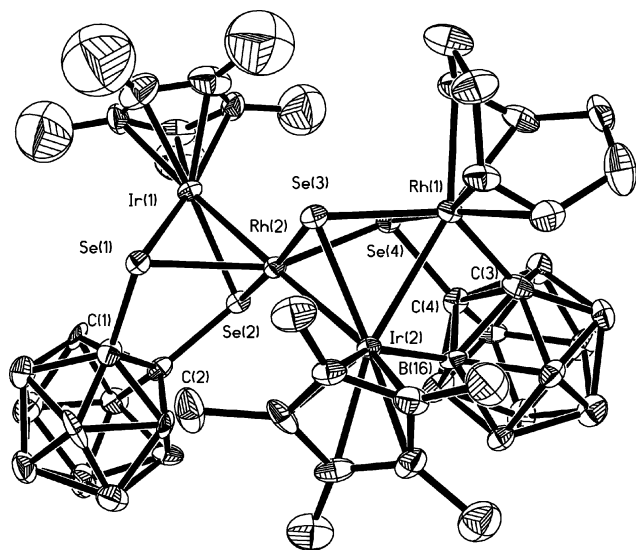


Fig. 3 Molecular structure of the tetranuclear complex **3b**.

“pseudo-aromatic” iridadiseleno ring in $\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]$ (**1b**) (2.3753(9) and 2.3656(9) Å).⁹

Conclusion

In this work, we carried out the reactions of 16-electron coordinatively unsaturated iridium dichalcogenolato complexes **1a**, **1b** with $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$. Two novel tetranuclear cluster complexes were prepared and fully characterized. The resultant clusters **3a**, **3b** feature an Ir_2Rh_2 core containing three Ir–Rh metal bonds.

Experimental

General information

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl (toluene, hexane, dichloromethane) and distilled just before use. $\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]$ (**1a**),^{4,9} $\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]$ (**1b**)⁹ and $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ ¹⁶ were prepared by methods reported previously. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer, whereas ¹H (500 MHz) and ¹¹B (160 MHz) NMR spectra were obtained on a Bruker DMX-500 spectrometer in CDCl_3 solution. Elemental analyses were performed on an Elementar vario EI Analyzer.

Synthesis of $\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}$ (2a**) and $\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}$ (**3a**).** $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ (51 mg, 0.1 mmol) was added to a green solution of **1a** (106 mg, 0.2 mmol) in toluene (30 mL). The mixture was stirred for 24 h at room temperature; and the color changed from green to dark-red. After removal of the solvent, the residue was chromatographed on silica gel. Elution with hexane gave **2a** (42 mg, 18%) as a violet zone. Recrystallization from hexane afforded air-stable dark-violet crystals. Elemental analysis. Calc. for $\text{C}_{24}\text{H}_{50}\text{B}_{20}\text{S}_4\text{Ir}_2\text{Rh}$ (%): C, 24.63; H, 4.31. Found (%): C 24.59, H 4.30. Spectroscopic data as reported previously.⁵ Elution with

toluene–hexane (1 : 2) gave **3a** (91 mg, 30%) as a dark-red band. Recrystallization from CH_2Cl_2 –hexane afforded red crystals. Elemental analysis. Calc. for $\text{C}_{32}\text{H}_{61}\text{B}_{20}\text{S}_4\text{Ir}_2\text{Rh}_2\text{S}_4$ (%): C 25.47, H 4.08. Found (%): C 25.16, H 3.89. ¹H NMR (25 °C, TMS): δ 1.58 (m, 4H, CH_2), 1.83 (m, 4H, CH_2), 2.07 (s, 15H, C_5Me_5), 2.19 (s, 15H, C_5Me_5), 4.02 (m, 2H, $\text{CH}=\text{}$), 4.29 (m, 2H, $\text{CH}=\text{}$). ¹¹B NMR (25 °C, $\text{BF}_3\cdot\text{Et}_2\text{O}$): δ –3.2, –6.7, –9.0, –11.1, –13.6, –15.8, –20.2; IR (KBr disk): 2573, 2588 cm^{-1} ($\nu_{\text{B-H}}$).

Synthesis of $\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}$ (2b**) and $\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}$ (**3b**).** $[\text{Rh}(\text{cod})(\mu\text{-OEt})_2]$ (51 mg, 0.1 mmol) was added to a green solution of **1b** (125 mg, 0.2 mmol) in toluene (30 mL). The mixture was stirred for 48 h at room temperature; and the color changed from green to dark-red. After removal of the solvent, the residue was chromatographed on silica gel. Elution with hexane gave **2b** (46 mg, 16%) as a red zone. Recrystallization from hexane afforded air-stable dark-red crystals. Elemental analysis. Calc. for $\text{C}_{24}\text{H}_{50}\text{B}_{20}\text{Se}_4\text{Ir}_2\text{Rh}$ (%): C, 29.06; H, 5.08. Found (%): C, 28.99; H, 5.07. Spectroscopic data as reported previously.⁵ The second dark-red zone was close to the first band. Elution with toluene–hexane (1 : 2) gave **3a** (91 mg, 30%) as a dark-red band. Recrystallization from CH_2Cl_2 –hexane afforded red crystals. Elemental analysis. Calc. for $\text{C}_{32}\text{H}_{61}\text{B}_{20}\text{S}_4\text{Ir}_2\text{Rh}_2\text{S}_4$ (%): C 25.47, H 4.08. Found (%): C 25.16, H 3.89; ¹H NMR 25 °C, TMS): δ 1.66 (m, 2H, CH_2), 1.81 (m, 4H, CH_2), 2.02 (s, 15H, C_5Me_5), 2.13 (s, 15H, C_5Me_5), 4.10 (m, 2H, $\text{CH}=\text{}$), 4.43 (m, 2H, $\text{CH}=\text{}$); ¹¹B NMR (25 °C, $\text{BF}_3\cdot\text{Et}_2\text{O}$): δ –2.9, –6.1, –8.8, –12.5, –14.7, –19.8; IR (KBr disk): 2577, 2585 cm^{-1} ($\nu_{\text{B-H}}$).

Crystallographic analysis

Dark-red crystals of **3a** and **3b** were grown by slow diffusion from dichloromethane–hexane solution. The data crystals of both compounds were mounted by gluing onto the end of a thin glass fiber. X-Ray intensity data were collected on the CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were included but not refined. All the calculations were carried out the SHELXTL program.¹⁷ Crystal data, data collection parameters, and the results of the analyses of compounds **3a**, **3b** are listed in Table 2.

CCDC reference numbers 281883 and 281884.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512027f

Acknowledgements

This work was supported by the National Science Foundation of China for Distinguished Young Scholars (29925101, 20421303) and by the National Basic Research Program of China (2005CB623802), and is gratefully acknowledged.

Table 2 Crystallographic data for complexes **3a** and **3b**

	3a	3b
Formula	C ₃₂ H ₆₁ B ₂₀ S ₄ Ir ₂ Rh ₂ S ₄ ·CH ₂ Cl ₂	C ₃₂ H ₆₁ B ₂₀ S ₄ Ir ₂ Rh ₂ Se ₄ ·CH ₂ Cl ₂
<i>M</i>	1465.39	1652.99
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	11.066(4)	11.104(3)
<i>b</i> /Å	26.140(8)	26.517(6)
<i>c</i> /Å	18.062(6)	18.003(4)
β/°	98.633(5)	98.155(4)
<i>V</i> /Å ³	5165(3)	5247(2)
<i>Z</i>	4	4
<i>D</i> _c /g cm ⁻³	1.884	2.092
μ(Mo-Kα)/mm ⁻¹	6.057	8.578
Collected reflections	21604	22009
Unique	9083	9264
Parameters	597	595
Goodness of fit	1.020	1.016
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0499	0.0549
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1174	0.1424
Max., min. residual density/e Å ⁻³	1.917, -0.986	1.399, -1.083

References

- 1 P. Braunstein and J. Rose, in *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, UK, 1995, vol. 10, ch. 7.
- 2 Selected review: M. Herberhold and G.-X. Jin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 964–966; M. C. Comstock and J. R. Shapley, *Coord. Chem. Rev.*, 1995, **143**, 501–533; L. H. Gade, *Angew. Chem., Int. Ed.*, 2000, **39**, 2658–2678.
- 3 M. Fourmigue, *Coord. Chem. Rev.*, 1998, **178–180**, 823–864.
- 4 M. Herberhold, G.-X. Jin, H. Yan, W. Milius and B. Wrackmeyer, *J. Organomet. Chem.*, 1999, **587**, 252–257; J. Y. Bae, Y. I. Park, J. Ko, K. I. Park, S. I. Cho and S. O. Kang, *Inorg. Chim. Acta*, 1999, **289**, 141–148; J.-H. Won, D.-H. Kim, B. Y. Kim, S.-J. Kim, C. Lee, S. Cho, J. Ko and S. O. Kang, *Organometallics*, 2002, **21**, 1443–1453; X.-F. Hou, X.-C. Wang, J.-Q. Wang and G.-X. Jin, *J. Organomet. Chem.*, 2004, **689**, 2228–2235.
- 5 G.-X. Jin, J.-Q. Wang, Z. Zhang, L. H. Weng and M. Herberhold, *Angew. Chem., Int. Ed.*, 2005, **44**, 259–262; J.-Q. Wang, L. H. Weng and G.-X. Jin, *J. Organomet. Chem.*, 2005, **690**, 249–252; J.-Q. Wang, L. H. Weng and G. X. Jin, *Rev. Inorg. Chem.*, 2005, **25**, 55–66; J.-Q. Wang, X. Hou, L. H. Weng and G.-X. Jin, *Organometallics*, 2005, **24**, 826–830; S. Cai, J.-Q. Wang and G.-X. Jin, *Organometallics*, 2005, **24**, 4226–4231; J.-Q. Wang, S. Y. Cai, L. H. Weng, M. Herberhold and G.-X. Jin, *Chem.-Eur. J.*, 2005, **11**, 7343–7351; W. Li, L.-H. Weng and G.-X. Jin, *Inorg. Chem. Commun.*, 2004, 1174–1177; S. Y. Cai, Y. Lin and G.-X. Jin, *Dalton Trans.*, 2006, DOI: 10.1039/b512027f.
- 6 M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Angew. Chem., Int. Ed.*, 1999, **38**, 3689–3691; M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Chem.-Eur. J.*, 2000, **6**, 3026–3032; M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *J. Chem. Soc., Dalton Trans.*, 2001, 1782–1789.
- 7 M. Nihei, T. Nankawa, M. Kurihara and H. Nishihara, *Angew. Chem., Int. Ed.*, 1999, **38**, 1098–1100.
- 8 F. Teixidor, M. A. Flores, C. Vinas, R. Sillanpaa and R. Kivekas, *J. Am. Chem. Soc.*, 2000, **122**, 1963–1973.
- 9 M. Herberhold, G.-X. Jin, H. Yan, W. Milius and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 1999, 873–875.
- 10 J.-Y. Bae, Y.-J. Lee, S.-J. Kim, J. Ko, S. Cho and S. O. Kang, *Organometallics*, 2000, **19**, 1514–1521; Y.-J. Lee, J.-D. Lee, S.-J. Kim, J. Ko, I.-H. Suh, M. Cheong and S. O. Kang, *Organometallics*, 2004, **23**, 135–143.
- 11 L. J. Farrugia, A. G. Orpen and F. G. A. Stone, *Polyhedron*, 1983, **2**, 171–173; B. Giacomo, S. Gianfranco, R. Renzo, R. Raymond, G. Fabrizia and B. Dario, *Helv. Chim. Acta*, 1993, **76**, 2913–2925; J. R. Galsworthy, A. D. Hattersley, C. E. Housecroft, A. L. Rheingold and A. Waller, *J. Chem. Soc., Dalton Trans.*, 1995, 549–557.
- 12 M. A. F. Hernandez-Gruel, J. J. Perez-Torrente, M. A. Ciriano, F. J. Lanoz and L. A. Oro, *Angew. Chem., Int. Ed.*, 1999, **38**, 2769–2771.
- 13 R. McDonald and M. Cowie, *Inorg. Chem.*, 1990, **29**, 1564–1571.
- 14 F. H. Antwi-Nsiah, O. Oke and M. Cowie, *Organometallics*, 1996, **15**, 1042–1054.
- 15 Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe and M. Hidai, *Organometallics*, 1997, **16**, 151–154.
- 16 G. Pannetier, P. Fougeroux, R. Bonnaire and N. Platzter, *J. Less-Common Met.*, 1971, **24**, 83–92; R. Uson, L. A. Oro and J. A. Cabeza, *Inorg. Synth.*, 1985, **23**, 126–130; L. M. Green and D. W. Meek, *Organometallics*, 1989, **8**, 659–666.
- 17 *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, WI, USA, 2000.