

Syntheses of a series of trinuclear MIr_2 or pentanuclear MIr_4 bimetallic bis(selenido) and selenido–sulfido clusters ($\text{M} = \text{Pd}, \text{Pt}, \text{Fe}, \text{Co}$) from diiridium μ -bis(hydroselenido) and μ -hydroselenido–hydrosulfido complexes $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\}_2(\mu\text{-SeH})(\mu\text{-EH})]$ ($\text{E} = \text{Se}, \text{S}$)

Shoken Nagao^a, Hidetake Seino^a, Masanobu Hidai^b, Yasushi Mizobe^{a,*}

^a Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan

^b Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

Received 25 November 2002; received in revised form 10 December 2002; accepted 26 December 2002

Abstract

Reactions of a diiridium μ -bis(hydroselenido) complex $[\text{Cp}^*\text{IrCl}(\mu\text{-SeH})_2\text{IrCp}^*\text{Cl}]$ (**1a**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{cod} = 1,5\text{-cyclooctadiene}$), FeCl_2 , and CoCl_2 readily afforded the bimetallic selenido clusters containing a trinuclear or a pentanuclear cores $[(\text{Cp}^*\text{Ir})_2(\text{MCl}_2)(\mu_3\text{-Se})_2]$ ($\text{M} = \text{Pd}, \text{Pt}$ (**5**), Fe (**6**)) and $[(\text{Cp}^*\text{Ir})_4\text{Co}(\mu_3\text{-Se})_4][\text{CoCl}_3(\text{MeCN})_2]$ (**8**). Cluster **6** was converted to the latter-type bow-tie cluster $[(\text{Cp}^*\text{Ir})_4\text{Fe}(\mu_3\text{-Se})_4][\text{BPh}_4]_2$ (**7**) by treatment with an additional amount of **1a** and excess NaBPh_4 . Novel μ -hydroselenido–hydrosulfido complex $[\text{Cp}^*\text{IrCl}(\mu\text{-SeH})(\mu\text{-SH})\text{IrCp}^*\text{Cl}]$ (**3**) was obtained by the reaction of $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2\text{IrCp}^*\text{Cl}]$ with one equiv of H_2Se generated in situ from a NaSeH/HCl aq. mixture, followed by that with H_2S gas. Treatment of **3** with a range of transition metal compounds has shown that **3** can serve as a good precursor to synthesize a series of mixed-chalcogenido clusters in a rational manner; selenido–sulfido clusters derived from **3** include $[(\text{Cp}^*\text{Ir})_2(\text{MCl}_2)(\mu_3\text{-Se})(\mu_3\text{-S})]$ ($\text{M} = \text{Pd}, \text{Pt}, \text{Fe}$ (**14**)), $[(\text{Cp}^*\text{Ir})_2\{\text{PtCl}(\text{PPh}_3)\}(\mu_3\text{-Se})(\mu_3\text{-S})]\text{Cl}$ (**13**), $[(\text{Cp}^*\text{Ir})_4\text{Co}(\mu_3\text{-Se})_2(\mu_3\text{-S})_2][\text{CoCl}_3(\text{MeCN})_2]$ (**15**), and $[(\text{Cp}^*\text{Ir})_4\text{Fe}(\mu_3\text{-Se})_2(\mu_3\text{-S})_2][\text{BPh}_4]_2$. To determine the detailed structures, X-ray analyses have been undertaken for **5**·1/2 $\text{ClCH}_2\text{CH}_2\text{Cl}$, **6**, **7**, **8**, **13**· CH_2Cl_2 , **14**, and **15**· CH_2Cl_2 .

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Bimetallic selenido clusters; Trinuclear and pentanuclear cores; Diiridium hydroselenido complexes

1. Introduction

Our extensive studies on the exploration of the rational routes leading to the high-yield synthesis of homo- and hetero-metallic sulfido clusters with desired

core structures and atom compositions [1] have recently been extended to those of the corresponding selenido clusters. Thus, we have reported the syntheses of a diiridium μ -tetraselenido complex $[\text{Cp}^*\text{Ir}(\mu\text{-Se}_4)_2\text{IrCp}^*]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) [2] along with dinuclear μ -hydroselenido complexes such as $[\text{Cp}^*\text{MCl}(\mu\text{-SeH})_2\text{MCp}^*\text{Cl}]$ ($\text{M} = \text{Ir}$ (**1a**), $\text{M} = \text{Rh}$ (**1b**)) [3] and $[\text{CymRuCl}(\mu\text{-SeH})_2\text{RuCymCl}]$ ($\text{Cym} = p\text{-cymene}$) [4], and these dinuclear complexes have proved to serve as good precursors to a range of new homo- and hetero-metallic

* Corresponding author. Tel.: +81-3-5452-6360; fax: +81-3-5452-6361.

E-mail address: ymizobe@iis.u-tokyo.ac.jp (Y. Mizobe).

clusters with μ -selenido ligands. These include the $\text{Ir}_2\text{Pd}_2\text{Se}_3$ and $\text{Ir}_2\text{Pd}_3\text{Se}_5$ clusters obtained from the former iridium tetraselenido complex [2a] and the cubane-type M_4Se_4 clusters ($\text{M} = \text{Ir}, \text{Rh}, \text{Ru}$) derived from the latter hydroselenido complexes [3,4].

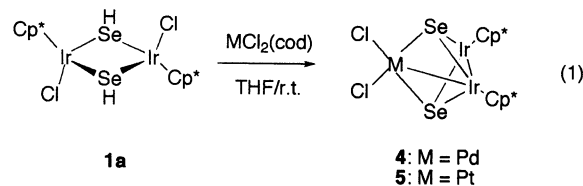
Since our previous studies have already shown that the μ -hydrosulfido complexes $[\text{Cp}^*\text{MCl}(\mu\text{-SH})_2\text{MCp}^*\text{Cl}]$ (**2**; $\text{M} = \text{Ru}, \text{Ir}, \text{Rh}$) are quite versatile for preparing not only the cubane-type tetranuclear clusters but also numerous trinuclear and pentanuclear sulfido clusters [5], conversion of **1a**, which is the selenium analogue of **2a** ($\text{M} = \text{Ir}$), into the bimetallic selenido clusters with triangular cores or pentanuclear bow-tie cores has been investigated in this study. Furthermore, we have succeeded in preparing a new diiridium complex having both the hydroselenido and hydrosulfido ligands $[\text{Cp}^*\text{IrCl}(\mu\text{-SeH})(\mu\text{-SH})\text{IrCp}^*\text{Cl}]$ (**3**), which has proved to be an excellent starting complex to obtain the mixed-chalcogenido clusters containing both the selenido and sulfido ligands. This represents one of the still rare pathways leading to the formation of tailored mixed-chalcogenido clusters and its details are also reported herein.

2. Results and discussion

2.1. Reactions of **1a** with transition metal compounds

As reported already, $[\text{Cp}^*\text{MCl}(\mu\text{-SH})_2\text{MCp}^*\text{Cl}]$ ($\text{M} = \text{Ir}$ (**2a**), Rh (**2b**), Ru (**2c**)) readily react with various metal compounds accompanied by dehydrochlorination to give a trinuclear clusters with two capping sulfido ligands, which are formulated as $[(\text{Cp}^*\text{M})_2(\text{M}'\text{L}_m)(\mu_3\text{-S})_2]^n$ (e.g. $\text{M} = \text{Ir}$: $\text{M}'\text{L}_m = \text{PdCl}_2$, $\text{PdCl}(\text{PPh}_3)$ [5a], $\text{RuCl}_2(\text{PPh}_3)$; $\text{M} = \text{Ir}, \text{Rh}$: $\text{M}'\text{L}_m = \text{Rh}(\text{cod})$ ($\text{cod} = 1,5$ -cyclooctadiene) [5c], FeCl_2 [5d]; $\text{M} = \text{Ru}$: $\text{M}'\text{L}_m = \text{RuCl}(\text{PPh}_3)_2(\mu\text{-H})$ [5e], $\text{RhCl}_2(\text{PPh}_3)(\mu\text{-H})$ [5f]; etc.). In the preceding paper [3], we described the syntheses of the Ir and Rh μ -hydroselenido analogues **1** and the subsequent transformations of the Rh complex **1b** into triangular $\text{Rh}_3(\mu_3\text{-Se})_2$ clusters such as $[(\text{Cp}^*\text{Rh})_2(\text{RhL}_2)(\mu_3\text{-Se})_2]^+$ ($\text{L} = \text{CO}, \text{PPh}_3$) and $[(\text{Cp}^*\text{Rh})_3(\mu_3\text{-Se})_2]^{2+}$ along with the condensation of two molecules of **1** to afford the cubane-type tetranuclear clusters $[(\text{Cp}^*\text{M})_4(\mu_3\text{-Se})_4]$ ($\text{M} = \text{Ir}, \text{Rh}$).

Now it has been found that the reactions of **1a** with one equiv of $[\text{PdCl}_2(\text{cod})]$ or $[\text{PtCl}_2(\text{cod})]$ in THF proceed in an analogous manner to those of **2a** to give the trinuclear bimetallic selenido clusters $[(\text{Cp}^*\text{Ir})_2(\text{MCl}_2)(\mu_3\text{-Se})_2]$ ($\text{M} = \text{Pd}$ (**4**), Pt (**5**)) as green crystals (Eq. (1)).



It is noteworthy that the reactions occur more smoothly for **1a** as compared to those of the hydrosulfido analogue **2a**. Thus, the reactions of **1a** yielding **4** and **5** complete in several hours at room temperature, whereas to convert all **2a** cleanly into the corresponding sulfido clusters higher reaction temperatures (e.g. 50°C) were required. Single-crystal X-ray analysis has been carried out for **5** to confirm the structures of these products, the results of which are shown in Fig. 1.

The reaction of **1a** with an equimolar amount of FeCl_2 in THF at room temperature also gave a trinuclear selenido cluster $[(\text{Cp}^*\text{Ir})_2(\text{FeCl}_2)(\mu_3\text{-Se})_2]$ (**6**) as black crystals (Scheme 1). Subsequent treatment of paramagnetic **6** with one equiv of **1a** in the presence of NaBPh_4 in THF at room temperature resulted in the formation of the diamagnetic pentanuclear complex with a bow-tie core $[(\text{Cp}^*\text{Ir})_4\text{Fe}(\mu_3\text{-Se})_4][\text{BPh}_4]_2$ (**7**) as red crystals (Scheme 1). Cluster **7** was also obtained by reacting **6** with only NaBPh_4 , presumably via the degradation of the Ir_2Fe core of part of **6**. Both **6** and **7** have been fully characterized by the X-ray analyses, whose structures are depicted in Figs. 2 and 3, respectively. Analogous reactions of **1a** were also carried out with CoCl_2 and NiCl_2 , which showed that only the pentanuclear cluster $[(\text{Cp}^*\text{Ir})_4\text{Co}(\mu_3\text{-Se})_4][\text{CoCl}_3(\text{MeCN})]_2$ (**8**) was isolable by treatment with the former, the product(s) from **1a** and NiCl_2 being intractable. Although the reaction of equimolar amounts of **1a** and

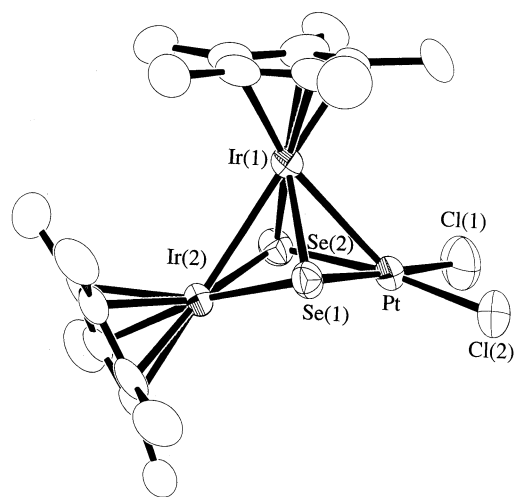
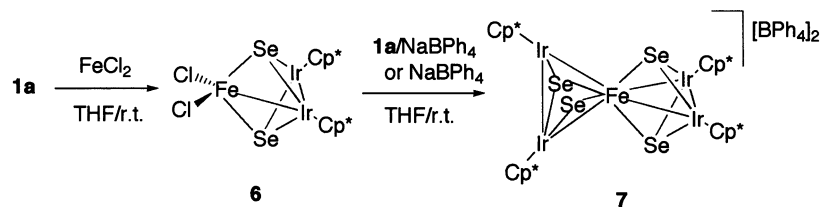
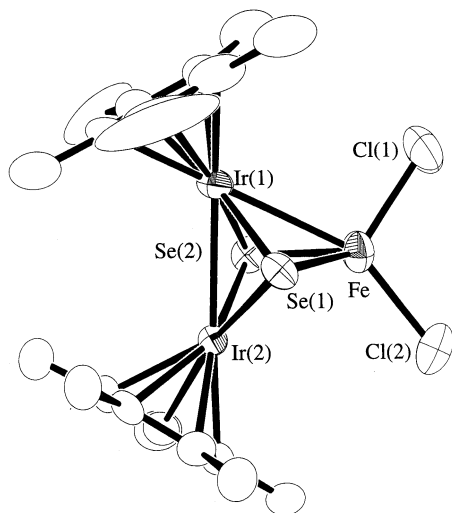
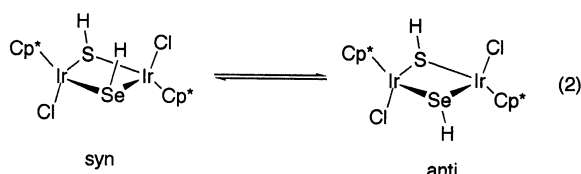
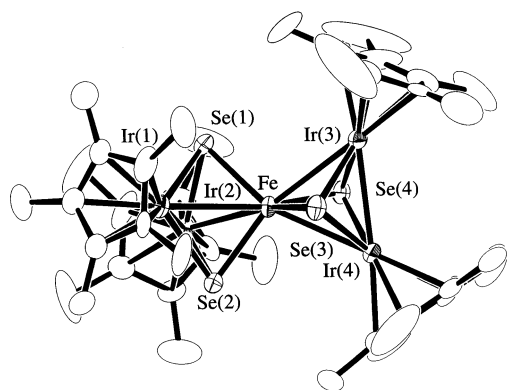
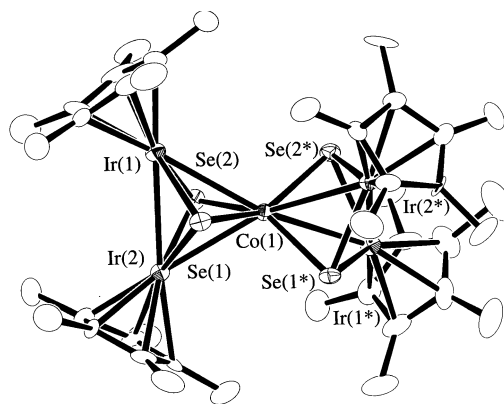


Fig. 1. An ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvating $\text{ClCH}_2\text{CH}_2\text{Cl}$ are omitted for clarity.



Scheme 1.

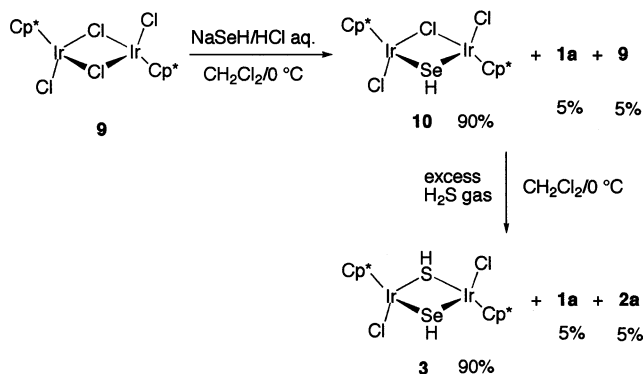
Fig. 2. An ORTEP drawing of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.Fig. 3. An ORTEP drawing of **7**. Thermal ellipsoids are drawn at the 30% probability level. The anions and hydrogen atoms are omitted for clarity.Fig. 4. An ORTEP drawing of **8**. Thermal ellipsoids are drawn at the 30% probability level. The anions and hydrogen atoms are omitted for clarity.

CoCl_2 directly gave **8**, the yield was quite low. However, when treated with 1.5 equivalents of CoCl_2 as required from the Co:Ir ratio of 3:4 in **8**, **1a** was converted into **8** in satisfactory yield. These results on the reactions of **1a** with FeCl_2 and CoCl_2 are analogous to those of the hydrosulfido complex **2a** previously observed [5d]. By contrast, although the NiIr_4 sulfido cluster was also available from **2a** and NiCl_2 under more forcing conditions, somehow the corresponding Se cluster could not be obtained from the reactions using **1a**. Cluster **8** has been characterized by the X-ray analysis as depicted in Fig. 4.

2.2. Synthesis of diiridium μ -hydroselenido–hydrosulfido complex **3**

Since the diiridium complexes with two bridging hydrochalcogenido ligands **1a** and **2a** have turned out to be quite excellent precursors to synthesize a variety of chalcogenido clusters, attempts have been made to prepare a diiridium mixed-hydrochalcogenido complex, aiming at derivatizing mixed-chalcogenido clusters in a rational manner.

Now we have found that when $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2\text{IrCp}^*\text{Cl}]$ (**9**) was treated with one equiv of H_2Se , which was generated in situ from one equiv of NaSeH and 1.15 equivalents of HCl aq. in CH_2Cl_2 at 0°C , a μ -hydroselenido complex $[\text{Cp}^*\text{IrCl}(\mu\text{-SeH})(\mu\text{-Cl})\text{IrCp}^*\text{Cl}]$ (**10**) was obtained as a major product (Scheme 2). Thus, the $^1\text{H-NMR}$ spectrum of the reaction mixture



Scheme 2.

showed the presence of **10**, bis(hydroselenido) complex **1a**, and the unreacted **9** in a ratio of 18:1:1, indicating clearly that the initial replacement of the Cl ligand in **9** forming **10** is much faster than the following substitution reaction converting **10** into **1a** at room temperature. By contrast, treatment of **9** under similar conditions with one equiv of H₂S generated analogously from NaSH and HCl aq. has resulted in the formation of a mixture containing [Cp*IrCl(μ-SH)(μ-Cl)IrCp*Cl], bis(hydrosulfido) complex **2a**, and the unreacted **9** in a ratio of 2:1:1.

Since the isolation of **10** in pure form was unsuccessful, the resultant reaction mixture containing **10** as the major component was successively treated with an excess of H₂S gas at 0 °C, which afforded a mixture containing the desired mixed-hydrochalcogenido complex **3** (90%) along with impurities **1a** (5%) and **2a** (5%) (Scheme 2). This result indicates that the replacement of the μ-SeH ligand by the SH anion does not take place under these conditions. Attempts to isolate analytically pure **3** were unsuccessful, the following syntheses of the mixed chalcogenido clusters were conducted by the use of this product without further purification.

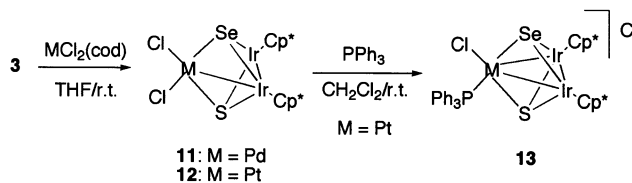
As observed previously for the precedent μ-hydroselenido and μ-hydrosulfido complexes **1** and **2**, the ¹H-NMR spectrum showed that **3** exists as a mixture of *syn* and *anti* forms with respect to the two μ-EH (E = S, Se) groups in solution (Eq. (2)). Thus, previous work has shown that both **1a** and **2a** are present in C₆D₆ at room temperature as a mixture of the *syn* and *anti* forms in a ratio of 3:2, which was easily determined on the basis of the intensity ratio of the Cp* resonances assignable to these two isomers: two singlets with the same intensities for the *syn* isomers and one singlet for the *anti* isomers. By contrast, for **3** both the *syn* and *anti* forms contain two inequivalent Cp* groups and show two Cp* resonances. Hence, the signals due to the two isomers are unable to be assigned unambiguously. However, also for the hydroselenido–hydrosulfido complex **3**, two sets of the Cp* signals appeared in an intensity ratio of 3:2 as observed for the bis(hydroselenido) complex **1a** and the

bis(hydrosulfido) complex **2a**. Furthermore, the difference in the chemical shifts of the two Cp* singlets due to the predominant isomer of **3** (0.21 ppm), which is much larger than that of the minor isomer (0.04 ppm), is in good agreement with those observed for the *syn* isomers of both **1a** (0.19 ppm) [3] and **2a** (0.23 ppm) [5c,6]. These data might suggest that the predominant form in solution might be assignable to be *syn* also for **3**.

2.3. Syntheses of mixed-metal mixed-chalcogenido clusters

Reactions of **3** with a range of transition metal compounds were carried out in an analogous manner to those of **1a**. Thus, when **3** was allowed to react with one equiv of [MCl₂(cod)] (M = Pd, Pt), expected selenido–sulfido clusters [(Cp*Ir)₂(MCl₂)(μ₃-Se)(μ₃-S)] (M = Pd (**11**), Pt (**12**)) were obtained as green crystals in moderate yields. Cluster **12** was further reacted with an equimolar amount of PPh₃ to afford a cationic cluster [(Cp*Ir)₂{PtCl(PPh₃)}(μ₃-Se)(μ₃-S)]Cl (**13**) (Scheme 3), whose structure was determined unequivocally by the X-ray analysis (Fig. 5). Despite the use of a starting complex **3** contaminated with **1a** and **2a**, these products are pure from the ¹H-NMR criteria and the elemental analyses also gave the satisfactory results.

Complex **3** also reacted with FeCl₂ and CoCl₂ under the conditions essentially analogous to those for preparing **6** and **8** from **1a**, yielding paramagnetic [(Cp*Ir)₂(FeCl₂)(μ₃-Se)(μ₃-S)] (**14**) and [(Cp*Ir)₄Co(μ₃-Se)₂(μ₃-S)₂][CoCl₃(MeCN)]₂ (**15**), respectively. The former was convertible to an expected diamagnetic bow-tie



Scheme 3.

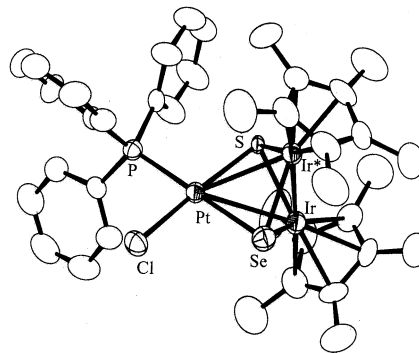


Fig. 5. An ORTEP drawing of **13**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvating CH₂Cl₂ are omitted for clarity.

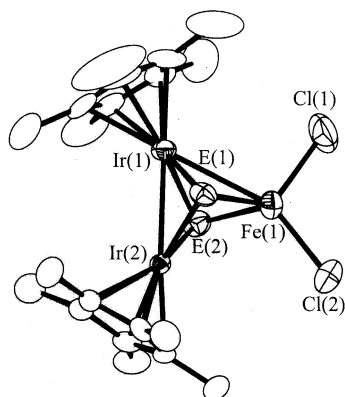


Fig. 6. An ORTEP drawing of **14**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

cluster $[(\text{Cp}^*\text{Ir})_4\text{Fe}(\mu_3\text{-Se})_2(\mu_3\text{-S})_2][\text{BPh}_4]_2$ (**16**) similarly (Scheme 4). In the FAB-MS spectrum of **14**, the peak assignable to the ion $[\mathbf{14}-\text{Cl}]^+$ appeared, whereby those arising from the bis(selenido) and bis(sulfido) analogues of **14** were not detectable. This also indicates that only the selenido–sulfido cluster **14** was isolated in a pure form. Clusters **14** and **15** have been characterized by the X-ray diffraction as shown in Figs. 6 and 7.

Reactivities displayed at the multinuclear metal–sulfido sites and their selenido analogues are currently attracting increasing interest in relevance to certain biological and industrial catalysis, and the mixed-chalcogenido clusters are of considerable importance because of their potential as good models to clarify the site selectivity exhibited at the multimetallic mixed-chalcogenido site. However, although a range of sulfido–selenido, sulfido–telurido, and selenido–telurido clusters are known, which include, for example, those derived from $[\text{Fe}_2(\mu\text{-EE})(\text{CO})_6]$ ($\text{E}, \text{E}' = \text{S}, \text{Se}, \text{Te}$) [7], well-defined mixed-chalcogenido clusters are still rare and little is known about the methods to prepare such clusters in a reliable manner [8]. The reactions

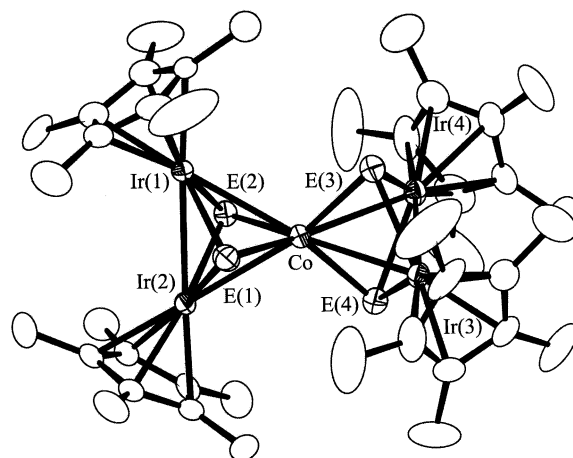


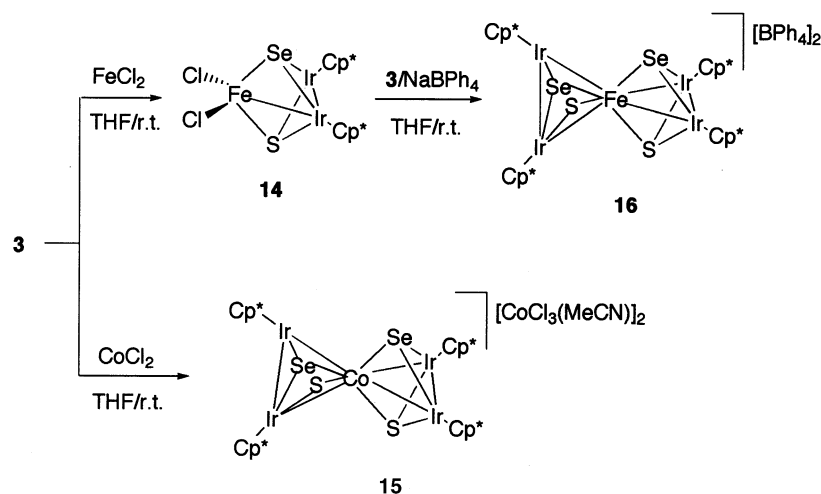
Fig. 7. An ORTEP drawing of **15**. Thermal ellipsoids are drawn at the 30% probability level. The anions and hydrogen atoms along with solvating CH_2Cl_2 are omitted for clarity.

using the μ -hydroselenido–hydrosulfido complex **3** reported here may therefore represent quite a powerful method to obtain mixed selenido–sulfido clusters numerous. Reactivities of new selenido–sulfido clusters are now under investigation and the results will be described elsewhere.

2.4. Description of the X-ray structures of bis(selenido) and selenido–sulfido clusters

The X-ray analyses have been carried out to determine the detailed structures for diselenido clusters **5**, **6**, **7** and **8** as well as selenido–sulfido clusters **13**, **14** and **15**. Pertinent bonding parameters in these clusters are listed in Tables 1–7, respectively.

As shown in Fig. 1, **5** has a triangular core, for which the Ir–Ir distance at 2.913(1) Å and one Pt–Ir distance at 2.751(1) Å fall in the range of the metal–metal single bond lengths, whereas the remaining Pt–Ir distance is



Scheme 4.

Table 1
Selected bond lengths (Å) and bond angles (°) in **5**

<i>Bond lengths</i>			
Pt–Ir(1)	2.751(1)	Pt···Ir(2)	3.487(1)
Ir(1)–Ir(2)	2.913(1)	Pt–Se(2)	2.411(2)
Pt–Se(1)	2.408(2)	Pt–Cl(2)	2.366(5)
Pt–Cl(1)	2.352(5)	Ir(1)–Se(2)	2.424(2)
Ir(1)–Se(1)	2.435(2)	Ir(2)–Se(2)	2.410(2)
Ir(2)–Se(1)	2.413(2)		
<i>Bond angles</i>			
Pt–Ir(1)–Ir(2)	75.94(3)	Se(1)–Pt–Cl(1)	175.1(2)
Se(1)–Pt–Se(2)	83.99(7)	Se(2)–Pt–Cl(1)	91.1(2)
Se(1)–Pt–Cl(2)	92.5(1)	Cl(1)–Pt–Cl(2)	92.4(2)
Se(2)–Pt–Cl(2)	172.6(2)	Se(1)–Ir(2)–Se(2)	83.88(7)
Se(1)–Ir(1)–Se(2)	83.12(6)	Pt–Se(1)–Ir(2)	92.64(7)
Pt–Se(1)–Ir(1)	69.21(5)	Pt–Se(2)–Ir(1)	69.36(5)
Ir(1)–Se(1)–Ir(2)	73.84(5)	Ir(1)–Se(2)–Ir(2)	74.09(5)
Pt–Se(2)–Ir(2)	92.65(7)		

Table 2
Selected bond lengths (Å) and bond angles (°) in **6**

<i>Bond lengths</i>			
Fe–Ir(1)	2.926(2)	Fe···Ir(2)	3.120(2)
Ir(1)–Ir(2)	2.8520(6)	Fe–Se(2)	2.444(2)
Fe–Se(1)	2.455(2)	Fe–Cl(2)	2.252(4)
Fe–Cl(1)	2.230(5)	Ir(1)–Se(2)	2.422(1)
Ir(1)–Se(1)	2.425(1)	Ir(2)–Se(2)	2.413(1)
Ir(2)–Se(1)	2.415(1)		
<i>Bond angles</i>			
Fe–Ir(1)–Ir(2)	65.35(4)	Se(1)–Fe–Cl(1)	120.1(2)
Se(1)–Fe–Se(2)	89.14(6)	Se(2)–Fe–Cl(1)	114.2(1)
Se(1)–Fe–Cl(2)	110.4(1)	Cl(1)–Fe–Cl(2)	107.9(2)
Se(2)–Fe–Cl(2)	114.6(1)	Se(1)–Ir(2)–Se(2)	90.84(4)
Se(1)–Ir(1)–Se(2)	90.39(4)	Fe–Se(1)–Ir(2)	79.68(5)
Fe–Se(1)–Ir(1)	73.68(5)	Fe–Se(2)–Ir(1)	73.92(5)
Ir(1)–Se(1)–Ir(2)	72.22(4)	Ir(1)–Se(2)–Ir(2)	72.30(3)
Fe–Se(2)–Ir(2)	79.92(6)		

elongated to a non-bonding one at 3.487(1) Å. Thus, the PtIr₂Se₂ core has rather a square pyramidal structure with the Ir(1) atom at the apex than a trigonal bipyramid with two apical Se atoms. Analogous square pyramidal cores have been demonstrated for the M₃Se₂ clusters of e.g. M = Fe, Ru [9]. Inequivalency was also observed for the two Fe–Ir distances in **6** (2.926(2) and 3.120(2) Å) but apparently the difference is much smaller than that in **5**, and the geometry of the FeIr₂Se₂ core in **6** is close to a trigonal bipyramid as depicted in Fig. 2. It is also noteworthy that both of the two Fe–Ir bonds are longer than the Ir–Ir bond at 2.8520(6) Å, indicating the weaker interactions present between Fe and Ir atoms. In the related sulfido cluster [(Cp*Ir)₂(FeCl)₂(μ₃-S)₂] (**17**) [5d], the Fe–Ir distances are 2.880(3) and 3.006(3) Å, displaying the comparable inequivalency but both being slightly shorter than those in the selenido cluster **6**.

Table 3
Selected bond lengths (Å) and bond angles (°) in **7**

<i>Bond lengths</i>			
Fe–Ir(1)	2.742(2)	Fe–Ir(2)	2.759(3)
Fe–Ir(3)	2.770(3)	Fe–Ir(4)	2.758(2)
Ir(1)–Ir(2)	2.8121(9)	Ir(3)–Ir(4)	2.799(1)
Fe–Se(1)	2.279(3)	Fe–Se(2)	2.282(3)
Fe–Se(3)	2.280(3)	Fe–Se(4)	2.274(3)
Ir(1)–Se(1)	2.394(2)	Ir(1)–Se(2)	2.395(2)
Ir(2)–Se(1)	2.393(2)	Ir(2)–Se(2)	2.398(2)
Ir(3)–Se(3)	2.394(2)	Ir(3)–Se(4)	2.403(2)
Ir(4)–Se(3)	2.404(2)	Ir(4)–Se(4)	2.383(2)
<i>Bond angles</i>			
Ir(1)–Fe–Ir(2)	61.49(5)	Fe–Ir(1)–Ir(2)	59.57(5)
Fe–Ir(2)–Ir(1)	58.95(5)	Se(1)–Fe–Se(2)	98.6(1)
Se(1)–Fe–Se(3)	127.2(1)	Se(1)–Fe–Se(4)	104.2(1)
Se(2)–Fe–Se(3)	105.0(1)	Se(2)–Fe–Se(4)	126.3(1)
Se(3)–Fe–Se(4)	98.5(1)	Se(1)–Ir(1)–Se(2)	92.46(6)
Se(1)–Ir(2)–Se(2)	92.41(7)	Se(3)–Ir(3)–Se(4)	92.01(7)
Se(3)–Ir(4)–Se(4)	92.25(7)	Fe–Se(1)–Ir(1)	71.80(8)
Fe–Se(1)–Ir(2)	72.36(8)	Ir(1)–Se(1)–Ir(2)	71.95(6)
Fe–Se(2)–Ir(1)	71.72(8)	Fe–Se(2)–Ir(2)	72.21(8)
Ir(1)–Se(2)–Ir(2)	71.84(5)	Fe–Se(3)–Ir(3)	72.64(8)
Fe–Se(3)–Ir(4)	72.10(8)	Ir(3)–Se(3)–Ir(4)	71.37(5)
Fe–Se(4)–Ir(3)	72.56(8)	Fe–Se(4)–Ir(4)	72.57(8)
Ir(3)–Se(4)–Ir(4)	71.56(5)		

Table 4
Selected bond lengths (Å) and bond angles (°) in **8**

<i>Bond lengths</i>			
Co(1)–Ir(1)	2.913(1)	Co(1)–Ir(2)	2.804(1)
Ir(1)–Ir(2)	2.873(1)	Co(1)–Se(2)	2.293(3)
Co(1)–Se(1)	2.302(3)	Ir(1)–Se(2)	2.422(2)
Ir(1)–Se(1)	2.395(2)	Ir(2)–Se(2)	2.397(2)
Ir(2)–Se(1)	2.415(2)		
<i>Bond angles</i>			
Ir(1)–Co(1)–Ir(2)	60.30(2)	Co(1)–Ir(1)–Ir(2)	57.96(4)
Co(1)–Ir(2)–Ir(1)	61.74(4)	Se(1)–Co(1)–Se(1*)	95.7(2)
Se(1)–Co(1)–Se(2)	95.19(8)	Se(2)–Co(1)–Se(2*)	96.4(2)
Se(1)–Co(1)–Se(2*)	143.48(7)	Se(1)–Ir(2)–Se(2)	89.66(7)
Se(1)–Ir(1)–Se(2)	89.55(7)	Co(1)–Se(1)–Ir(2)	72.90(6)
Co(1)–Se(1)–Ir(1)	76.65(8)	Co(1)–Se(2)–Ir(1)	76.27(6)
Ir(1)–Se(1)–Ir(2)	73.36(6)	Ir(1)–Se(2)–Ir(2)	73.19(6)
Co(1)–Se(2)–Ir(2)	73.38(8)		

The Ir–Se bond lengths in **5** and **6** are essentially the same (2.410(2)–2.435(2) Å), which are longer than the Ir–S bond distances in **17** (2.280(5)–2.328(6) Å) as expected from the difference in the single-bond covalent radius of Se at 1.17 Å and that of S at 1.04 Å [10]. For comparison, the Ir(III)–Se distances in the selenido clusters reported previously are, e.g. 2.402(1)–2.409(2) Å in [(Cp*Ir)₃(μ₃-Se)₂][PF₆]₂ [3] and 2.482(2)–2.501(2) Å in [(Cp*Ir)₄(μ₃-Se)₄] [11]. The Pt in **5** and the Fe in **6** are each bonded to two Cl anions, and if the metal–metal bonds are ignored, the geometry around the Pt is essentially square planar, while that around the Fe is almost tetrahedral. The Pt–Se bond lengths in **5** are 2.408(2) and 2.411(2) Å, which are shorter than the Fe–

Table 5
Selected bond lengths (Å) and bond angles (°) in **13**

<i>Bond lengths</i>			
Pt–Ir	3.041(1)	Ir–Ir*	2.935(1)
Pt–Se	2.470(1)	Pt–S	2.350(2)
Pt–Cl	2.351(3)	Pt–P	2.262(3)
Ir–S	2.347(2)		
<i>Bond angles</i>			
Ir–Pt–Ir*	57.71(2)	Pt–Ir–Ir*	61.15(1)
Se–Pt–S	85.99(7)	Se–Pt–Cl	90.63(9)
Se–Pt–P	179.40(9)	S–Pt–Cl	176.6(1)
S–Pt–P	93.41(9)	Cl–Pt–P	90.0(1)
Se–Ir–S	87.30(5)	Ir–Se–Ir*	74.80(4)
Pt–Se–Ir	76.97(4)	Ir–S–Ir*	77.40(7)
Pt–S–Ir	80.70(7)		

Table 6
Selected bond lengths (Å) and bond angles (°) in **14**

<i>Bond lengths</i>			
Fe–Ir(1)	2.898(1)	Fe···Ir(2)	3.056(1)
Ir(1)–Ir(2)	2.826(1)	Fe–E(2)	2.398(2)
Fe–E(1)	2.414(2)	Fe–Cl(2)	2.251(3)
Fe–Cl(1)	2.227(3)	Ir(1)–E(2)	2.376(1)
Ir(1)–E(1)	2.399(1)	Ir(2)–E(2)	2.364(1)
Ir(2)–E(1)	2.386(1)		
<i>Bond angles</i>			
Fe–Ir(1)–Ir(2)	64.52(4)	E(1)–Fe–Cl(1)	120.0(1)
E(1)–Fe–E(2)	89.05(6)	E(2)–Fe–Cl(1)	113.3(1)
E(1)–Fe–Cl(2)	110.69(9)	Cl(1)–Fe–Cl(2)	107.6(1)
E(2)–Fe–Cl(2)	115.63(9)	E(1)–Ir(2)–E(2)	90.52(4)
E(1)–Ir(1)–E(2)	89.90(4)	Fe–E(1)–Ir(2)	79.09(5)
Fe–E(1)–Ir(1)	74.03(4)	Fe–E(2)–Ir(1)	74.75(5)
Ir(1)–E(1)–Ir(2)	72.40(4)	Ir(1)–E(2)–Ir(2)	73.19(4)
Fe–E(2)–Ir(2)	79.84(5)		

Se bond distances in **6** at 2.444(2) and 2.455(2) Å. For comparison, the Pt–Se bond distances in the Pt(II)₃ cluster [{Pt(PPh₃)₂]₂{Pt(cod)}(μ₃-Se)] [PF₆]₂ are in the range 2.431(1)–2.474(1) Å [12] and those in the Pt(II)₂ complex [{Pt(PPh₃)₃]₂(μ₂-Se)₂] are 2.433(1) and 2.465(1) Å [13], all being slightly longer than those in **5**. The Fe–Se bond distances in the selenido clusters containing lower valent Fe centers are e.g. 2.318(3)–2.326(3) Å for [(Ph₃P)₂N]₂[Fe₃(μ₃-Se)(CO)₉] [14] and 2.34(2)–2.37(2) Å for [Fe₃(μ₃-Se)₂(CO)₉] [15].

In the pentanuclear bow-tie clusters **7** and **8**, the M–Ir distances (M = Fe, Co, Ir) in the range 2.742(2)–2.913(1) Å are all indicative of the presence of metal–metal bonding interactions between these atoms. The Ir–Se bond lengths in these two vary from 2.383(2) to 2.422(2) Å. The Fe–Se bond lengths in **7** from 2.274(3) to 2.282(3) Å are considerably shorter than those in the trinuclear cluster **6**, while the Co–Se bond lengths in 79e[−] **8** are 2.293(3) and 2.302(3) Å, which are longer only slightly than those in a 78e[−] cluster **7**. The Co–Se bond lengths reported previously are, for example,

Table 7
Selected bond lengths (Å) and bond angles (°) in **15**

<i>Bond lengths</i>			
Co(1)–Ir(1)	2.796(2)	Co(1)–Ir(2)	2.755(2)
Co(1)–Ir(3)	2.803(2)	Co(1)–Ir(4)	2.773(2)
Ir(1)–Ir(2)	2.840(1)	Ir(3)–Ir(4)	2.825(1)
Co(1)–E(1)	2.274(2)	Co(1)–E(2)	2.287(2)
Co(1)–E(3)	2.275(2)	Co(1)–E(4)	2.282(2)
Ir(1)–E(1)	2.375(2)	Ir(1)–E(2)	2.375(2)
Ir(2)–E(1)	2.367(2)	Ir(2)–E(2)	2.394(2)
Ir(3)–E(3)	2.390(2)	Ir(3)–E(4)	2.373(2)
Ir(4)–E(3)	2.360(2)	Ir(4)–E(4)	2.387(2)
<i>Bond angles</i>			
Ir(1)–Co(1)–Ir(2)	61.54(4)	Co(1)–Ir(1)–Ir(2)	58.51(4)
Co(1)–Ir(2)–Ir(1)	59.95(4)	Ir(3)–Co(1)–Ir(4)	60.89(4)
Co(1)–Ir(3)–Ir(4)	59.03(4)	Co(1)–Ir(4)–Ir(3)	60.09(4)
E(1)–Co(1)–E(2)	96.39(8)	E(1)–Co(1)–E(3)	103.70(9)
E(1)–Co(1)–E(4)	131.1(1)	E(2)–Co(1)–E(3)	129.07(9)
E(2)–Co(1)–E(4)	104.96(9)	E(3)–Co(1)–E(4)	96.09(9)
E(1)–Ir(1)–E(2)	91.39(7)	E(1)–Ir(2)–E(2)	91.13(7)
E(3)–Ir(3)–E(4)	90.73(7)	E(3)–Ir(4)–E(4)	91.33(7)
Co(1)–E(1)–Ir(1)	73.91(7)	Co(1)–E(1)–Ir(2)	72.78(7)
Ir(1)–E(1)–Ir(2)	73.57(6)	Co(1)–E(2)–Ir(1)	73.70(7)
Co(1)–E(2)–Ir(2)	72.07(7)	Ir(1)–E(2)–Ir(2)	73.11(6)
Co(1)–E(3)–Ir(3)	73.82(7)	Co(1)–E(3)–Ir(4)	73.45(7)
Ir(3)–E(3)–Ir(4)	73.00(6)	Co(1)–E(4)–Ir(3)	74.02(7)
Co(1)–E(4)–Ir(4)	72.98(7)	Ir(3)–E(4)–Ir(4)	72.97(6)

2.332(2)–2.350(2) Å for [Co₆(μ₃-Se)₈(CO)₆] [16] and 2.309(1) and 2.310(1) Å in [RuCo₂(μ₃-Se)(CO)₇(μ-Ph₂PCH₂PPh₂)] [17]. For comparison, the Fe–S distances in [(Cp*Ir)₄Fe(μ₃-S)₄][BPh₄]₂ (**18**) are in the range 2.161(4)–2.171(4) Å and the Co–S distances in [(Cp*Ir)₄Co(μ₃-S)₄][CoCl₃(MeCN)]₂ (**19**) are 2.166(6) and 2.183(5) Å with the Ir–S distances from 2.266(3) to 2.298(5) Å [5d]. It is noteworthy that the dihedral angles between two MIr₂ planes differ significantly for M = Fe and Co, the former in **7** being 72.1° with the latter in **8** of 49.0°. This feature was also observed previously for the sulfido analogues, whereby the corresponding dihedral angles were found to be 73.4, 49.9, and 24.3° for **18**, **19** and [(Cp*Ir)₄Ni(μ₃-S)₄][NiCl₄]·CH₂Cl₂ [5d], respectively, the former two being in good agreement with those in the Se analogues **6** and **7**. The previous finding for the latter sulfido clusters was able to be interpreted to some extent in terms of the valence electron counts and molecular orbital calculations of these clusters [5d]. However, more recent results on the X-ray analysis of [(Cp*Ir)₄Co(μ₃-S)₄][BPh₄]₂·CH₂Cl₂ have implicated that the packing effect exerted by the nature of the anion seems to be the important factor to determine these dihedral angles [18] and further studies are needed to rationalize these findings about the structures of a series of metal–chalcogenido bow-tie clusters of this type.

The structure of μ-selenido–sulfido cluster has been clarified unambiguously for **13**. Thus, the X-ray structure of the cationic cluster **13** has a crystallographically

imposed mirror plane defined by a square planar Pt atom together with the Se, S, P, and Cl atoms, which bisects the Ir–Ir* bond. The Pt–Ir and Ir–Ir* bond distances are 3.041(1) and 2.935(1) Å, respectively. We have previously observed the analogous X-ray structure for the PdIr₂S₂ analogue [(Cp*Ir)₂{PdCl(PPh₃)}(μ₃-S)₂]Cl (**20**) with the Pd–Ir and Ir–Ir* bond lengths at 3.001(1) and 2.9002(9) [5a]. This core structure of **13** is quite different from that of the neutral PtIr₂Se₂ cluster **5**, in which two Pt–Ir distances are apparently unequal with the separations of 2.751(1) and 3.487(1) Å (vide supra). It is to be noted, however, that even for **5**, the ¹H-NMR spectrum in CDCl₃ at room temperature shows only one singlet due to the Cp* protons, indicating that two Ir centers become equivalent at this temperature in the NMR time scale.

The X-ray structure of **13** clearly shows that the Cl anion trans to the Se atom in **5** is selectively substituted by PPh₃, reflecting the stronger trans effect exerted by Se^{2–} than S^{2–} bound to the Pt(II) center. The Pt–Se bond length at 2.470(1) is longer than those in **5** (2.408(2) and 2.411(2) Å), while the Pt–S distance at 2.350(2) Å is comparable to those in [(Cp*Ir)₂{Pt(dp-pe)}(μ₃-S)₂][BPh₄]₂ (2.362(5) and 2.347(4) Å) [5a].

For **14** and **15**, the X-ray analyses have also disclosed the presence of the expected trinuclear and pentanuclear core structures. Thus, the Fe–Ir(1) and Fe–Ir(2) distances in **14** at 2.898(1) and 3.056(1) Å, respectively, are inequivalent. This feature and these distances are analogous to those in the bis(selenido) cluster **6** and the bis(sulfido) cluster **17** shown above. On the other hand, the Co–Ir bond lengths in **15** are in the range 2.755(2)–2.803(2) Å. For comparison, the Co–Ir bond lengths in the bis(selenido) cluster **8** are 2.804(1) and 2.913(1) Å, while those in the bis(sulfido) cluster **19** are 2.746(1) and 2.849(1) Å. The dihedral angle between two CoIr₂ planes is 68.2°. In **14** and **15**, since the selenido and sulfido ligands are mutually disordered with the occupancy factor of 0.5, the bonding parameters associated with the chalcogenido ligands are not discussed here.

3. Experimental

3.1. General considerations

All manipulations were carried out under an atmosphere of N₂. IR and NMR spectra were recorded on JASCO FT/IR 420 and JEOL AL-400 spectrometers, respectively. The mass spectra were obtained by a JEOL JMS600H spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 Series II CHN analyzer. Chemicals were commercially obtained and used as received, while compounds **1a** [3], **9** [19], [MCl₂(cod)]

(M = Pd, Pt) [20] were prepared according to the literature methods.

3.2. Preparation of **3**

Ethanol (3.0 cm³) was slowly added to gray Se (80 mg, 1.0 mmol) and NaBH₄ (38 mg, 1.0 mmol) at 0 °C and the mixture was stirred for 1 h at room temperature (r.t.). The resultant mixture was dried up in vacuo and to the residue were added a CH₂Cl₂ solution (40 cm³) of **9** (0.80 g, 1.0 mmol) and then concentrated HCl aq. (120 mg, 1.15 mol) at 0 °C. After stirring for 1 h at this temperature, the resulting solution was dried over MgSO₄. The ¹H-NMR spectrum of this mixture showed the formation of mono(hydroselenido) complex **10** in 90% yield along with a byproduct **1a** (5%). Unreacted **9** (5%) was also detected. The solution was separated from MgSO₄ and then treated with H₂S gas at 0 °C for 5 min. The mixture was evaporated to dryness in vacuo and the residue was washed with acetone and hexane. The yellow solid remained, which contained **3** with a purity of 90% (0.50 g, 60% yield). ¹H-NMR (C₆D₆, ppm): isomer **i**, 1.51, 1.30 (s, 15H each, Cp*), 1.12 (s, 1H, SH), –2.47 (s, 1H, SeH); isomer **ii**, 1.43, 1.39 (s, 15H each, Cp*), 1.23 (s, 1H, SH), –2.37 (s, 1H, SeH); the ratio of isomers **i** and **ii** is 3:2. Two isomers **i** and **ii** may be assigned as *syn* and *anti* forms, respectively (see text).

3.3. Preparation of **4**

A solution containing **1a** (0.44 g, 0.50 mmol) and [PdCl₂(cod)] (0.14 g, 0.50 mmol) in THF (10 cm³) was stirred at r.t. for 5 h. The green suspension was evaporated to dryness in vacuo and the residue was extracted with CH₂Cl₂. Addition of ether to the concentrated extract afforded **4** as green crystals (0.44g, 89% yield). Anal. Calc. for C₂₀H₃₀Cl₂Ir₂PdSe₂: C, 24.26; H, 3.05. Found: C, 24.44; H, 3.25%. ¹H-NMR (CDCl₃, ppm): 2.10 (s, Cp*).

3.4. Preparation of **5**

This complex was obtained from **1a** (0.45 g, 0.50 mmol) and [PtCl₂(cod)] (0.19 g, 0.50 mmol) by the same method as that for **4** as green crystals in 46% yield (0.25 g). Anal. Calc. for C₂₀H₃₀Cl₂Ir₂PtSe₂: C, 22.27; H, 2.80. Found: C, 22.16; H, 3.00%. ¹H-NMR (CDCl₃, ppm): 2.10 (s, Cp*). Single crystals of **5**·1/2ClCH₂CH₂Cl for the X-ray diffraction were available by recrystallization from ClCH₂CH₂Cl–ether.

3.5. Preparation of **6**

This complex was obtained as black crystals in 54% yield (50 mg) from **1a** (87 mg, 0.098 mmol) and FeCl₂ (13 mg, 0.10 mmol) in THF (3 cm³) by the same method

as that for **4** except that the evaporated reaction mixture residue was crystallized from CH₂Cl₂–hexane. Anal. Calc. for C₂₀H₃₀Cl₂Ir₂FeSe₂: C, 25.57; H, 3.22. Found: C, 25.55; H, 3.19%.

3.6. Preparation of **7**

(1) Into a suspension of **6** (66 mg, 0.070 mmol) and **1a** (62 mg, 0.070 mmol) in THF (5 cm³) was added NaBPh₄ (96 mg, 0.28 mmol) and the mixture was stirred at r.t. for 6 h. The resultant mixture was dried up in vacuo and the residue was extracted with CH₂Cl₂. Addition of ether to the concentrated extract gave **7**·CH₂Cl₂ as red crystals (140 mg, 83%). Anal. Calc. for C₈₉H₁₀₂B₂Cl₂FeIr₄Se₄: C, 44.45; H, 4.28. Found: C, 44.53; H, 4.20%. ¹H-NMR (CD₂Cl₂, ppm): 1.92 (s, 60H, Cp*), 6.87 (t, 8H, *p*-H of BPh), 7.02 (t, 16H, *m*-H of BPh), 7.29 (m, 16H, *o*-H of BPh). The presence of the solvating CH₂Cl₂ was confirmed by recording ¹H-NMR spectrum in CDCl₃. On the other hand, the single crystal used for the X-ray diffraction study did not contain CH₂Cl₂.

(2) Into a suspension of **6** (57 mg, 0.061 mmol) in THF (5 cm³) was added NaBPh₄ (83 mg, 0.24 mmol) and the mixture was treated analogously. The yield of **7**·CH₂Cl₂ was 51 mg (70% based on Ir atom).

3.7. Preparation of **8**

A suspension containing **1a** (0.18 g, 0.20 mmol) and CoCl₂ (39 mg, 0.30 mmol) in THF (7 cm³) was stirred at r.t. for 1 day. The resultant mixture was filtered off and the black solid remained was extracted with MeCN. Addition of hexane to the concentrated extract afforded black crystals of **8** (0.14 g, 68%). Anal. Calc. for C₄₄H₆₆N₂Cl₆Co₃Ir₄Se₄: C, 25.20; H, 3.17. Found: C, 25.25; H, 3.20%.

3.8. Preparation of **11**

This cluster was prepared from **3** (0.17 g, 0.20 mmol) and [PdCl₂(cod)] (57 mg, 0.20 mmol) as described for preparing **4**. Green crystals (0.13 g, 69% yield). Anal. Calc. for C₂₀H₃₀Cl₂Ir₂PdSSe: C, 25.47; H, 3.21. Found: C, 25.83; H, 3.31%. ¹H-NMR (CDCl₃, ppm): 2.12 (s, Cp*).

3.9. Preparation of **12**

This cluster was obtained from **3** (0.17 g, 0.20 mmol) and [PtCl₂(cod)] (78 mg, 0.21 mmol) similarly. Green crystals (0.12 g, 58% yield). Anal. Calc. for C₂₀H₃₀Cl₂Ir₂PtSSe: C, 23.28; H, 2.93. Found: C, 23.06; H, 2.89%. ¹H-NMR (CDCl₃, ppm): 2.12 (s, Cp*).

3.10. Preparation of **13**

Into a solution of **12** (47 mg, 0.046 mmol) in CH₂Cl₂ (5 cm³) was added PPh₃ (12 mg, 0.046 mmol) and the mixture was stirred for 1 day at r.t. The resultant mixture was dried up in vacuo, and the residue was washed with ether and then extracted with CH₂Cl₂. Addition of hexane to the concentrated extract afforded **13**·CH₂Cl₂ as green crystals (39 mg, 66% yield). Anal. Calc. for C₃₉H₄₇Cl₄Ir₂PPh₃SSe: C, 33.97; H, 3.43. Found: C, 34.27; H, 3.56%. ¹H-NMR (CDCl₃, ppm): 2.07 (s, Cp*), 5.29 (s, 2H, CH₂Cl₂), 7.16 (t, 6H, *o*-H of PPh₃), 7.36 (t, 6H, *m*-H of PPh₃), 7.48 (m, 3H, *p*-H of PPh₃). ³¹P-NMR (CDCl₃, ppm): −0.71 (s).

3.11. Preparation of **14**

This complex was prepared from **3** (0.23 g, 0.27 mmol) and FeCl₂ (35 mg, 0.28 mmol) by an analogous method to that for **6**. Black crystals (0.14 g, 58% yield). Anal. Calc. for C₂₀H₃₀Cl₂FeIr₂SSe: C, 26.91; H, 3.39; S, 3.59. Found: C, 26.66; H, 3.29; S, 3.24%. FABMS *m/z* 857 ([**14**−Cl]⁺).

3.12. Preparation of **15**

This cluster was obtained as **15**·CH₂Cl₂ from the reaction of **3** (0.17 g, 0.20 mmol) and CoCl₂ (40 mg, 0.30 mmol) carried out similarly to that for preparing **8**. Black crystals (79 mg, 39% yield). Anal. Calc. for C₄₄H₆₆N₂Cl₆Co₃Ir₄S₂Se₂: C, 26.38; H, 3.32; N, 1.40. Found: C, 26.18; H, 3.29; N, 1.50%.

3.13. Preparation of **16**

Into a suspension of **14** (0.10 g, 0.11 mmol) and **3** (0.094 g, 0.11 mmol) in THF (8 cm³) was added NaBPh₄ (0.15 g, 0.44 mmol) and the mixture was stirred for 1 day. The resultant mixture was filtered off and the remained solid was extracted with CH₂Cl₂. Addition of hexane to the concentrated extract afforded the red crystals of **16**·CH₂Cl₂ (0.13 g, 50% yield). Anal. Calc. for C₈₉H₁₀₂B₂Cl₂FeIr₄S₂Se₂: C, 46.25; H, 4.45. Found: C, 46.63; H, 4.61%. ¹H-NMR (CD₂Cl₂, ppm): 2.24 (s, 60H, Cp*), 6.87 (t, 8H, *p*-H of BPh), 7.02 (t, 16H, *m*-H of BPh), 7.31 (m, 16H, *o*-H of BPh). The presence of the solvating CH₂Cl₂ was confirmed by recording ¹H-NMR spectrum in CDCl₃.

3.14. X-ray diffraction studies

The X-ray analyses of **5**·1/2ClCH₂CH₂Cl, **6**, **7**, **8**, **13**·CH₂Cl₂, **14**, and **15**·CH₂Cl₂ were carried out at r.t. on a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo−K_α source. Intensity data were corrected for the Lorentz-polarization effect and

Table 8
Crystallographic data for **5**·1/2ClCH₂CH₂Cl, **6**, **7**, **8**, **13**·CH₂Cl₂, **14** and **15**·CH₂Cl₂

	5 ·1/2ClCH ₂ CH ₂ Cl	6	7	8	13 ·CH ₂ Cl ₂	14	15 ·CH ₂ Cl ₂
Formula	C ₂₁ H ₃₂ Cl ₃ Ir ₂ PtSe ₂	C ₂₀ H ₃₀ Cl ₂ FeIr ₂ Se ₂	C ₉₀ H ₁₀₃ NB ₂ FeIr ₄ Se ₄	C ₄₄ H ₆₆ N ₂ Cl ₆ Co ₃ Ir ₄ Se ₄	C ₃₉ H ₄₇ Cl ₄ Ir ₂ PPtSSe	C ₂₀ H ₃₀ Cl ₂ FeIr ₂ SeS	C ₈₉ H ₁₀₂ B ₂ Cl ₂ CoIr ₄ Se ₂ S ₂
Formula weight	1128.29	939.57	2361.00	2097.26	1379.14	892.67	2314.16
Space group	<i>Pbca</i> (no. 61)	<i>C2/c</i> (no. 15)	<i>P</i> $\bar{1}$ (no. 2)	<i>C2/c</i> (no. 15)	<i>P2₁/m</i> (no. 11)	<i>C2/c</i> (no. 15)	<i>P</i> $\bar{1}$ (no. 2)
Unit cell dimensions							
<i>a</i> (Å)	20.265(5)	33.989(4)	11.391(5)	29.125(4)	14.635(2)	33.725(5)	11.935(2)
<i>b</i> (Å)	16.513(1)	8.919(2)	16.92(1)	8.608(2)	12.635(1)	8.871(2)	16.937(2)
<i>c</i> (Å)	16.375(2)	17.564(2)	23.61(1)	23.951(1)	11.956(1)	17.505(3)	23.752(8)
α (°)	90.00	90.00	76.18(5)	90.00	90.00	90.00	75.98(2)
β (°)	90.00	109.96(1)	77.54(5)	98.18(1)	93.013(8)	109.77(1)	78.32(2)
γ (°)	90.00	90.00	78.29(8)	90.00	90.00	90.00	77.99(1)
<i>V</i> (Å ³)	5479(1)	5004(1)	4258(4)	5943(1)	2207.8(4)	4928.1(1)	4304.5(2)
<i>Z</i>	8	8	2	4	2	8	2
ρ_{calc} (g cm ^{−3})	2.735	2.494	1.841	2.344	2.074	2.406	1.785
μ_{calc} (cm ^{−1})	177.47	143.39	81.64	125.11	103.53	131.68	73.65
Crystal size (mm ³)	0.50 × 0.20 × 0.10	0.40 × 0.20 × 0.10	0.40 × 0.20 × 0.15	0.40 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.30 × 0.25 × 0.20	0.40 × 0.20 × 0.20
Number of data	3610 (<i>I</i> > 3.00σ(<i>I</i>))	3737 (<i>I</i> > 3.00σ(<i>I</i>))	7240 (<i>I</i> > 3.00σ(<i>I</i>))	3465 (<i>I</i> > 3.00σ(<i>I</i>))	4056 (<i>I</i> > 3.00σ(<i>I</i>))	4345 (<i>I</i> > 3.00σ(<i>I</i>))	10815 (<i>I</i> > 3.00σ(<i>I</i>))
Number of variables	262	245	919	285	265	275	1022
Transmission factor	0.1345–0.9991	0.2609–0.9992	0.5026–0.9968	0.0813–0.9976	0.5935–0.9995	0.6339–0.9995	0.7569–0.9988
<i>R</i> ^a	0.049	0.037	0.076	0.063	0.039	0.031	0.048
<i>R</i> _w ^b or <i>wR</i> ₂ ^c	0.050 ^b	0.039 ^b	0.117 ^b	0.065 ^b	0.102 ^c	0.087 ^c	0.114 ^c
GOF ^d	1.71	1.34	1.68	1.81	1.01	0.99	1.09
Residual peaks (e [−] Å ^{−3})	2.58, −1.80	1.48, −1.38	1.95, −1.90	3.71, −3.31	2.69, −2.00	1.22, −1.58	1.58, −1.69

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o^2]^{-1}$).

^c $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^2]^{1/2}$.

^d $\text{GOF} = [\Sigma w(|F_o| - |F_c|)^2 / \{(\text{no. observed}) - (\text{no. variables})\}]^{1/2}$.

for absorption (ψ -scans). Details of crystal and data collection parameters are listed in Table 8.

Structure solution and refinements were conducted by using the TEXSAN program package [21]. The positions of non-hydrogen atoms were determined by DIRDIF PATTY [22] and were refined anisotropically. Hydrogen atoms were placed at ideal positions and included at the final stages of refinements with fixed parameters. For $5 \cdot 1/2\text{ClCH}_2\text{CH}_2\text{Cl}$, half of the solvating dichloroethane molecule is independent, in which the C(21) atom is disordered over two positions with same occupancies. Hydrogen atoms attached to C(21) were not included in the refinements. In **14** and $15 \cdot \text{CH}_2\text{Cl}_2$, the positions of bridging chalcogenido atoms were occupied by the Se and S atoms with the same occupancies. These atoms denoted as E in Figs. 6 and 7 as well as Tables 6 and 7 were refined, assuming the occupancies of 0.735 by only Se.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 201924–201930 for compounds **6**, **5**, **7**, **8**, **14**, **13**, and **15**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support by the JSPS FY 2001 ‘Research for the Future Program’ and the Grant in Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan (No. 14078206) is appreciated.

References

- [1] (a) M. Hidai, S. Kuwata, Y. Mizobe, *Acc. Chem. Res.* 33 (2000) 46;
(b) T. Masumori, H. Seino, Y. Mizobe, M. Hidai, *Inorg. Chem.* 39 (2000) 5002;
(c) S. Kabashima, S. Kuwata, K. Ueno, M. Shiro, M. Hidai, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 1128;
(d) S. Kuwata, S. Kabashima, Y. Ishii, M. Hidai, *J. Am. Chem. Soc.* 123 (2001) 3826;
(e) S. Kuwata, S. Kabashima, N. Sugiyama, Y. Ishii, M. Hidai, *Inorg. Chem.* 40 (2001) 2034;
(f) F. Takagi, H. Seino, Y. Mizobe, M. Hidai, *Organometallics* 21 (2002) 694 (and references therein).
- [2] (a) S. Nagao, H. Seino, Y. Mizobe, M. Hidai, *Chem. Commun.* (2000) 207;
(b) S. Nagao, H. Seino, T. Okada, Y. Mizobe, M. Hidai, *J. Chem. Soc. Dalton Trans.* (2000) 3546.
- [3] H. Seino, Y. Mizobe, M. Hidai, *Organometallics* 19 (2000) 3631.
- [4] H. Seino, Y. Mizobe, M. Hidai, *New J. Chem.* 24 (2000) 907.
- [5] (a) D. Masui, T. Kochi, Z. Tang, Y. Ishii, Y. Mizobe, M. Hidai, *J. Organomet. Chem.* 620 (2001) 69;
(b) T. Kochi, Y. Nomura, Z. Tang, Y. Ishii, Y. Mizobe, M. Hidai, *J. Chem. Soc. Dalton Trans.* (1999) 2575;
(c) Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, M. Hidai, *Organometallics* 16 (1997) 151;
(d) Z. Tang, Y. Nomura, S. Kuwata, Y. Ishii, Y. Mizobe, M. Hidai, *Inorg. Chem.* 37 (1998) 4909;
(e) S. Kuwata, M. Andou, K. Hashizume, Y. Mizobe, M. Hidai, *Organometallics* 17 (1998) 3429;
(f) K. Hashizume, Y. Mizobe, M. Hidai, *Organometallics* 15 (1996) 3303.
- [6] Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, M. Hidai, *Inorg. Chim. Acta* 267 (1998) 73.
- [7] (a) P. Mathur, P. Payra, S. Ghose, Md.M. Hossain, C.V.V. Satyanarayana, F.O. Chicote, P.K. Chadha, *J. Organomet. Chem.* 606 (2000) 176;
(b) P. Mathur, S. Chatterjee, S. Ghose, M.F. Mahon, *J. Organomet. Chem.* 587 (1999) 93 (and references therein).
- [8] H. Seino, M. Hidai, Y. Mizobe, *Chem. Lett.* (2002) 920.
- [9] D. Cauzzi, C. Graiff, C. Massera, G. Predieri, A. Tipicchio, D. Acquotti, *J. Chem. Soc. Dalton Trans.* (1999) 3515.
- [10] J.A. Dean (Ed.), *Lange's Handbook of Chemistry*, Tables 3–10, McGraw Hill, New York, 1985.
- [11] S. Schulz, M. Andruh, T. Pape, T. Heinze, H.W. Roesky, L. Häming, A. Kuhn, R. Herbst-Irmer, *Organometallics* 13 (1994) 4004.
- [12] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, *Inorg. Chem.* 41 (2002) 1194.
- [13] A. Bencini, M.D. Vaira, R. Morassi, P. Stoppioni, F. Mele, *Polyhedron* 15 (1996) 2079.
- [14] R.E. Bachman, K.H. Whitmire, *Inorg. Chem.* 33 (1994) 2527.
- [15] L.F. Dahl, P.W. Sutton, *Inorg. Chem.* 2 (1963) 1067.
- [16] G. Gervasio, S.F.A. Kettle, F. Musso, R. Rossetti, P.L. Stanghellini, *Inorg. Chem.* 34 (1995) 298.
- [17] P. Braunstein, C. Graiff, C. Massera, G. Predieri, J. Rosé, A. Tiripicchio, *Inorg. Chem.* 41 (2002) 1372.
- [18] M. Iwasaki, Private communication (2001).
- [19] R.N. Grimes, *Inorg. Synth.* 29 (1992) 229.
- [20] D. Drew, J.R. Doyle, *Inorg. Synth.* 28 (1990) 346.
- [21] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.
- [22] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Amykall, PATTY: The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.