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# Reactions of hydrosulfido- and hydroselenido-bridged dinuclear Ir, Rh, and Ru complexes with $SbCl_3$ and $BiCl_3$ affording mixed-metal sulfido and selenido clusters containing both noble metals and Group 15 metals

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**Abstract**

A new versatile method to synthesize a series of noble metal-Group 15 metal chalcogenido clusters has been found. Thus, treatment of the hydrosulfido- or hydroselenido-bridged dinuclear complexes $[Cp^*MCl(\mu\text{-}EH)_2MCp^*Cl]$ (M = Ir, Rh; E = S, Se; $Cp^* = \eta^5\text{-}C_5Me_5$), $[Cp^\circ RuCl(\mu\text{-}SH)_2RuCp^\circ Cl]$ ($Cp^\circ = \eta^5\text{-}C_5EtMe_4$), and $[Ru(L)Cl(\mu\text{-}SH)_2Ru(L)Cl]$ ($L = \eta^6\text{-}C_6Me_5H$) with $M'Cl_3$ (M′ = Sb, Bi) in THF at room temperature afforded smoothly the clusters $[Cp^*MCl(\mu\text{-}EM'Cl_2)_2MCp^*Cl]$, $[Cp^\circ RuCl(\mu\text{-}SM'Cl_2)_2RuCp^\circ Cl]$, and $[Ru(L)Cl(\mu\text{-}SM'Cl_2)_2Ru(L)Cl]$ through dehydrochlorination. The X-ray analyses of eleven new clusters clarified the details of their structures consisting of the cubane-type $M_2M'_2E_2Cl_2$ cores resulting from the presence of weak $MCl\cdots M'$ bonding interactions in addition to the normal M–E, M–Cl, and M′–E bonds.

*Keywords:* Mixed-metal cluster; Chalcogenido cluster; Group 15 metals; Noble metals; X-ray structure

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## 1. Introduction

Our recent studies on the reactivities of hydrosulfido- and hydroselenido-bridged dinuclear $M^{III}$ complexes of the type $[Cp^*MCl(\mu\text{-}EH)_2MCp^*Cl]$ (E = S: M = Ir (**1a**), Rh (**2a**), Ru(**3**); E = Se: M = Ir (**1b**), Rh (**2b**); $Cp^* = \eta^5\text{-}C_5Me_5$) have revealed that these can serve as potential precursors to synthesize a variety of homo- and heterometallic sulfido and selenido clusters with the nuclearities varying from 3 to 5 [1]. Thus, as summarized in Scheme 1, reactions with certain late transition metal complexes proceed with concurrent loss of the μ-EH hydrogens as HCl or $H_2$ to give the $M'M_2(\mu_3\text{-}E)_2$ and $M'M_4(\mu_3\text{-}E)_4$ cores [2], while dimerization of the dehydrochlorinated **1**–**3** yields the cubane-type $M_4(\mu_3\text{-}E)_4$ clusters [3]. Dehydration between **1**–**3** and the dinuclear complex with a $Mo(=O)(\mu\text{-}S)_2Mo(=O)$ core also leads to the cubane-type $Mo_2M_2(\mu_3\text{-}S)_2(\mu_3\text{-}E)_2$ clusters [4]. However, reactions of **1**–**3** with other early transition metal compounds are elusive, and those with main group metal compounds are still unknown.

Now we have found that dinuclear complexes **1**, **2**, and the Cp° analogue of **3**, $[Cp^\circ RuCl(\mu\text{-}SH)_2RuCp^\circ Cl]$ (**3′**; $Cp^\circ = \eta^5\text{-}C_5EtMe_4$), react with $SbCl_3$ and $BiCl_3$ to give new $Ir_2M'_2$, $Rh_2M'_2$, and $Ru_2M'_2$ mixed-metal clusters (M′ = Sb, Bi) through dehydrochlorination between the μ-EH ligands and $M'Cl_3$. Reactions with $M'Cl_3$ proceeded similarly for the $Ru^{II}$ complex $[Ru(L)Cl(\mu\text{-}SH)_2Ru(L)Cl]$ (**4**; $L = \eta^6\text{-}C_6Me_5H$), which is isoelectronic and essentially isomorphous with **1** and **2**.

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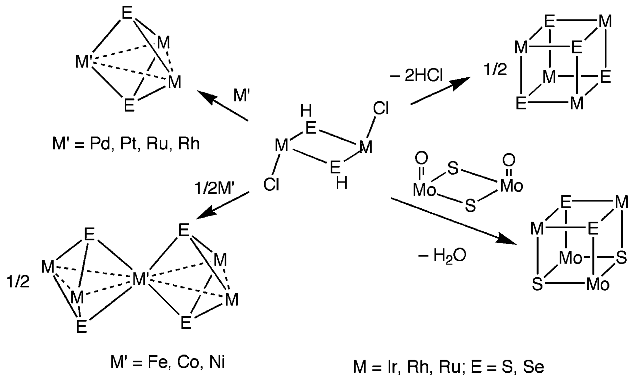
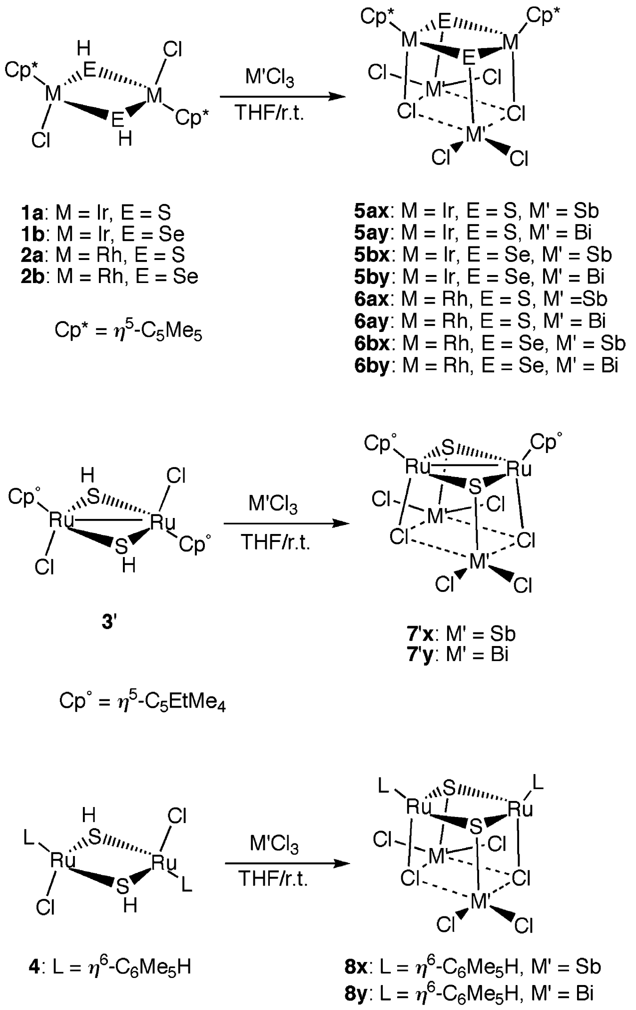


Scheme 1.



Scheme 2.

For the *p*-cymene analogue of **4**, it has been confirmed previously that the formation of the cubane-type $Ru_4(\mu\text{-}S)_4$ cluster occurs readily as observed for **1–3** [5].

These reactions of the dinuclear μ-hydrochalcogenido complexes **1–4** demonstrate a new versatile method to prepare the mixed-metal chalcogenido clusters containing both the noble metals M and the Group 15 metals M′. Incorporation of Group 15 elements into cluster cores has been attracting significant attention [6]. The molecular clusters containing transition metals as well as Group 16 and Group 15 elements [7] are known to be derived from, e.g., the reactions of transition metal omplexes with Group 16–Group 15 aggregates or those of transition metal chalcogenides with Group 15 atom compounds. However, those using the hydrochalcogenido complexes as precursors are not precedented. It is also to be noted that the clusters of this type containing heavier Group 15 elements are quite rare.

## 2. Results and discussion

### 2.1. Preparation of cubane-type $M_2M'_2E_2Cl_2$ clusters ($M' = Sb$, $Bi$; $E = S$, $Se$)

When a suspension of the hydrosulfido-bridged $Ir_2$ complex **1a** in THF was treated with ca. 2 equiv of $SbCl_3$ at room temperature, dehydrochlorination between the hydrosulfido ligands and $SbCl_3$ took place smoothly. Thus, workup of the orange-yellow reaction mixture gave the $Ir_2$ complex with the bridging $SSbCl_2$ ligands $[Cp^*IrCl(\mu\text{-}SSbCl_2)_2IrCp^*Cl]$ (**5ax**) as orange-yellow crystals in 85% yield. Reaction of **1a** with only one equiv of $SbCl_3$ at room temperature afforded a mixture of **5ax** and unreacted **1a** in a ratio of 1:1. In contrast, reactions of **1a** with transition metal (M′) species generally result in the formation of trinuclear $M'Ir_2(\mu^3\text{-}S)_2$ cores, as reported previously [2]. Similarly, by treatment of **1a**, **2a**, **3′**, and **4** with 2 equiv of $SbCl_3$ or $BiCl_3$ in THF at room temperature, the $Ir_2$, $Rh_2$, and $Ru_2$ complexes containing two bridging $SM'Cl_2$ ligands $[Cp^*MCl(\mu\text{-}SM'Cl_2)_2MCp^*Cl]$ (M = Ir: M′ = Bi (**5ay**); M = Rh: M′ = Sb (**6ax**), Bi (**6ay**)), $[Cp^\circ RuCl(\mu\text{-}SM'Cl_2)_2RuCp^\circ Cl]$ (M′ = Sb (**7′x**), Bi (**7′y**)), and $[Ru(L)Cl(\mu\text{-}SM'Cl_2)_2Ru(L)Cl]$ (M′ = Sb (**8x**), Bi (**8y**)), respectively, were obtained in moderate to high yields as summarized in Scheme 2.

Hydroselenido complexes **1b** and **2b** also reacted readily with $SbCl_3$ and $BiCl_3$ at room temperature to give the corresponding $\mu\text{-}SeM'Cl_2$ complexes $[Cp^*MCl(\mu\text{-}SeM'Cl_2)_2MCp^*Cl]$ (M = Ir: M′ = Sb (**5bx**), Bi (**5by**); M = Rh: M′ = Sb (**6bx**), Bi (**6by**)) (Scheme 2).

Out of 12 new complexes **5–8** obtained here, 11 were characterized crystallographically, which disclosed, interestingly, that these $\mu\text{-}EM'Cl_2$ complexes have the cubane-type cores consisting of four different elements: transition metal, Group 15 metal, chalcogen, and chlorine, as described below. Spectroscopic and microanalytical data are consistent with these structures.

Table 1
Selected interatomic distances in new complexes **5**, **6**, **7′** and **8**

| Complex | M | E | M···M | M–E | M–Cl | M′–E | M′–Cl | M′···Cl |
|---|---|---|---|---|---|---|---|---|
| (a) M′ = Sb | | | | | | | | |
| **5ax** | Ir | S | 3.6824(8) | 2.396(3)[b] | 2.434(3)[a] | 2.451(3)[a] | 2.404(4)[b] | 3.041(3)–3.099(4) |
| **6ax** | Rh | S | 3.6457(6) | 2.411(1)[b] | 2.436(1)[a] | 2.439(1)[a] | 2.420(2)[b] | 2.929(2)–3.095(2) |
| **7′x** | Ru | S | 2.866(2) | 2.317(4)[b] | 2.445(4)[a] | 2.493(4)[a] | 2.413(6)[b] | 2.944(5)–3.000(4) |
| **8x** | Ru | S | 3.658(1) | 2.416(2)[b] | 2.433(2)[a] | 2.447(2)[a] | 2.416(3)[b] | 2.943(2)–3.072(3) |
| **5bx** | Ir | Se | 3.7981(8) | 2.504(1)[a] | 2.425(3)[a] | 2.595(1) | 2.408(3)[a] | 3.004(2), 3.047(3) |
| **6bx** | Rh | Se | 3.7746(8) | 2.5057(7)[a] | 2.429(2)[a] | 2.5802(6) | 2.423(2)[a] | 2.988(1), 3.033(1) |
| (b) M′ = Bi | | | | | | | | |
| **5ay** | Ir | S | 3.659(1) | 2.396(3)[a] | 2.446(5)[a] | 2.562(3) | 2.514(4)[a] | 2.972(3), 3.057(3) |
| **7′y** | Ru | S | 2.858(2) | 2.315(5)[b] | 2.472(5)[a] | 2.593(5)[a] | 2.522(6)[b] | 2.934(5)–3.002(5) |
| **8y** | Ru | S | 3.642(1) | 2.412(3)[b] | 2.450(3)[a] | 2.547(2)[a] | 2.538(4)[b] | 2.972(3)–3.035(3) |
| **5by** | Ir | Se | 3.792(1) | 2.501(2)[a] | 2.443(5)[a] | 2.675(2) | 2.519(5)[a] | 2.994(3), 3.070(3) |
| **6by** | Rh | Se | 3.774(2) | 2.505(2)[b] | 2.462(3)[a] | 2.654(2)[a] | 2.539(5)[b] | 3.002(4)–3.060(4) |

[a] Average of two independent values.
[b] Average of four independent values.

### 2.2. X-ray structures of cubane-type $M_2M'_2E_2Cl_2$ clusters ($M' = Sb, Bi$; $E = S, Se$)

Selected interatomic distances for the 11 analyzed clusters are listed in Table 1, while the ORTEP drawings are shown only for **5ax**, **7′x**, and **8y** in Figs. 1–3, respectively.

As depicted in these Figures, the structures of the new complexes reported here are quite analogous: two noble metal centers are connected with two bridging $EM'Cl_2$ moieties, forming the distorted cubane-type $M_2M'_2E_2Cl_2$ cores. The M···M separations in the range 3.64–3.87 Å for these complexes indicate the absence of any metal–metal bonding interactions except for the $Ru^{III}$ complexes **7′**, for which the observed Ru–Ru distances at 2.866(2) and 2.858(2) Å for **7′x** and **7′y** suggest the presence of a metal–metal single bond between two $d^5$ Ru centers. Indeed, by assuming the Ru–Ru single bond, the EAN rule is satisfied for both Ru centers in **7′** and their diamagnetic nature becomes plausible. Two Cl ligands on M are mutually *cis*, as are the two Cp*, Cp°,

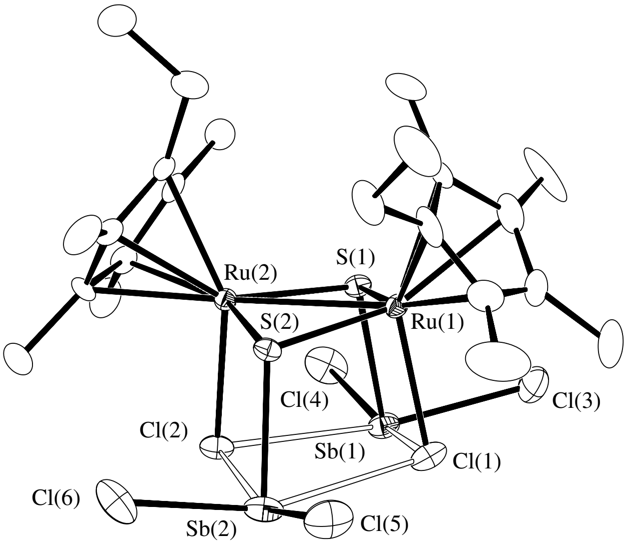


Fig. 2. Structure of **7′x**. Hydrogen atoms are omitted for clarity.

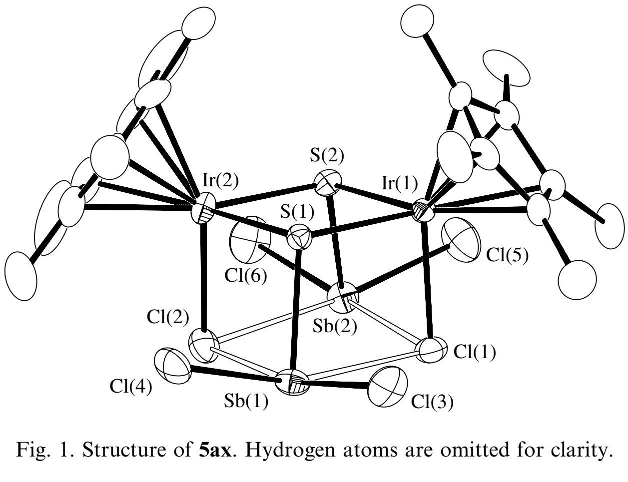


Fig. 1. Structure of **5ax**. Hydrogen atoms are omitted for clarity.

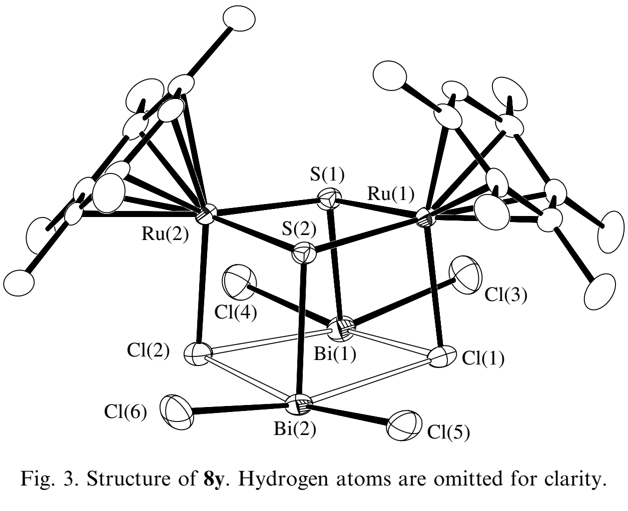


Fig. 3. Structure of **8y**. Hydrogen atoms are omitted for clarity.

or L ligands. The $M_2E_2$ rings are close to planar with the dihedral angles between two $M_2E$ planes in the range 1–6° for the Ir, Rh, and Ru complexes without M–M bonds, whereas those in **7′** are folded significantly with the dihedral angles of 12–16°. Orientation of the two $EM'Cl_2$ moieties is syn-axial. These structural features are comparable to those of the chalcogenolato analogues such as $[Cp^*IrCl(\mu\text{-}SPr^i)_2IrCp^*Cl]$ [8], $[Cp^*\text{-}RhCl(\mu\text{-}SMe)_2RhCp^*Cl]$ [9], $[Cp^*RuCl(\mu\text{-}SEt)_2RuCp^*Cl]$ [2e], and $[Cp^*RuCl(\mu\text{-}EFc)_2RuCp^*Cl]$ (E = S, Se; Fc = ferrocenyl) [10], but contrast to those of the μ-hydrochalcogenido complexes **1** [11], **2** [11,1c], **3** [2e], and **4** [5] having the trans configuration in a solid state as illustrated in Scheme 2.

The interatomic distances around M, viz., M···M, M–E, and M–Cl lengths, listed in Table 1 are comparable to those in the related hydrochalcogenido and thiolato complexes. As observed for the pairs **5ax/5bx**, **6ax/6bx**, and **5ay/5by**, replacement of S by Se results in the elongation of the M–E distances by ca. 0.09–0.11 Å.

With respect to the interatomic distances around M′, the Sb–S and Bi–S bond lengths in the new complexes shown in Table 1 fall in the range 2.43–2.50 and 2.54–2.60 Å, while the distances of the Sb–Se and Bi–Se bonds are 2.58 and 2.60 Å, and 2.65 and 2.68 Å, respectively. These as well as the observed Sb–Cl and Bi–Cl bond lengths in the range 2.40–2.43 and 2.51–2.54 Å are all in good agreement with the values calculated as the sum of the covalent radii [12]: Sb–S, 2.45; Bi–S, 2.56; Sb–Se, 2.58; Bi–Se, 2.69; Sb–Cl, 2.40; Bi–Cl, 2.51 Å. For comparison, the Sb(III)–μ-S bond lengths reported previously for the transition metal clusters are from 2.35 to 2.53 Å in, e.g., $[Fe_2(CO)_6(Sb_2S_6)][SbF_6]_2$ [13], $[Mn_2(EtNH_2)_2(Sb_2S_5)]$ [14], $[\{Fe(N(CH_2CH_2NH_2)_3)\}\text{-}\{FeSbS_4\}]^-$ [15], and $[Cr(H_2NCH_2CH_2NH_2)_2SbS_3]$ [16], while the Sb(III)–μ-Se bond lengths are in the range 2.52–2.66 Å as demonstrated for $[PPh_4]_2[Fe_2(CO)_4\text{-}(SbSe_4)_2]$ [17], and the antimony selenide anions such as $[Sb_2Se_4]^{2-}$ [18], $[Sb_2Se_5]^{4-}$ [19], and $[Sb_2Se_6]^{2-}$ [20]. To the best of our knowledge, few Bi(III)–μ-sulfide or Bi(III)–μ-selenide bond lengths in the molecular M–Bi–E or Bi–E aggregates to be comparable have been reported.

For all complexes reported here, the geometry of the $M'ECl_2$ moiety is a trigonal pyramid with one M′–E and two M′–Cl bonds, where the E–M′–Cl and Cl–M′–Cl angles are all close to 90°. Interesting feature is the presence of the weaker but significant bonding interactions between M′ and the Cl atoms bonded to M, which constitute the remaining four edges of the cubane-type $M_2M'_2E_2Cl_2$ core. The M′···Cl separations fall in the range 2.96–3.04 Å (Table 1), which are apparently larger than the sums of the covalent radii shown above but smaller than those of the van der Waals radii: Sb, 2.2; Bi, 2.4; Cl, 1.8 Å [21]. By taking these two long M′···Cl bonds into account, the geometry around M′ is a distorted square pyramid with four Cl atoms in the basal plane and one apical E atom. Such secondary bonding interactions between heavier Group 15 elements and halogens have often been claimed [22] and analogous geometry around Sb was demonstrated for, e.g., $[PPh_4][Sb_2SCl_5]$ and $[PPh_4]_2[Sb_2SCl_6]$ [*d*(Sb–S), 2.41–2.43; *d*(short Sb–Cl), 2.38–2.54; *d*(long Sb–Cl), 2.70–3.12 Å] [23].

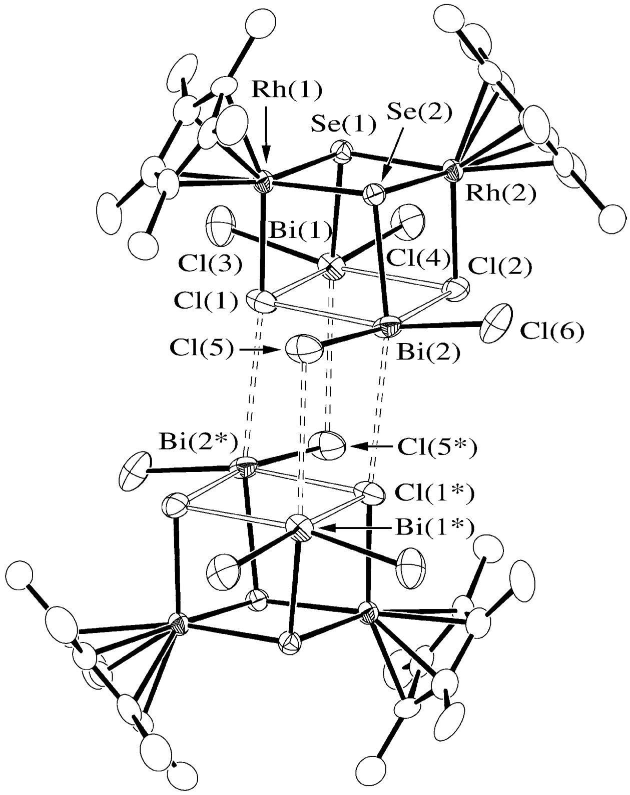


Fig. 4. Packing of two molecules of **6by** in the crystal, showing the weak intermolecular Bi–Cl bonding interactions with the dashed lines. Interatomic distances: Bi(1)···Cl(5*), 3.588(4); Bi(2)···Cl(1*), 3.343(3) Å.

Finally, packings of the cubane-type cores in the crystals are shown in Fig. 4. Due to the intermolecular M′···Cl bondings which are further weaker than the intramolecular M′···Cl bondings, cluster molecules in the crystals are connected to exhibit four types of aggregation modes. For example, Fig. 4 shows one of these four that was observed for **6by**, which occurs also in the crystals of **7′y** and **8y**.

## 3. Experimental

### *3.1. General*

All manipulations were carried out under $N_2$ using standard Schlenk techniques. Complexes **1** and **2** were prepared as described previously [11,1c], while the synthesis of **3′** and **4** was done as described for its Cp* and *p*-cymene analogues [2e,5]. Other reagents were commercially obtained and used as received.

NMR spectra were measured on a JEOL alpha-400 spectrometer and elemental analyses were done with a Perkin–Elmer 2400 series II CHN analyzer.

### *3.2. [Cp*IrCl(μ-SSbCl$_2$)$_2$IrCp*Cl] (**5ax**)*

To a suspension of **1a** (140 mg, 0.177 mmol) in THF (12 mL) was added SbCl$_3$ (85 mg, 0.34 mmol), and the mixture was stirred at room temperature for 12 h. The resulting orange-yellow mixture was filtered and the residue was extracted with THF (5 mL). Hexane (30 mL) was added slowly to the combined extracts, affording **5ax** as orange-yellow plates (178 mg, 85% yield). Found: C, 20.48; H, 2.45. $C_{20}H_{30}Cl_6Sb_2S_2Ir_2$ requires C, 20.44; H, 2.57. $\delta_H$ (CDCl$_3$): 1.60 (s, Cp*).

### *3.3. [Cp*IrCl(μ-SBiCl$_2$)$_2$IrCp*Cl] (**5ay**)*

A suspension of **1a** (229 mg, 0.289 mmol) and BiCl$_3$ (182 mg, 0.578 mmol) in THF (20 mL) was stirred at room temperature for 18 h and the resulting red solution was filtered. Hexane was added to the concentrated filtrate, affording **5ay** · 1/2THF as red-brown crystals (336 mg, 84% yield). Found: C, 19.21; H, 2.39. $C_{22}H_{34}O_{0.5}S_2Cl_6Ir_2Bi_2$ requires C, 19.07; H, 2.47. $\delta_H$ (CDCl$_3$): 1.61 (s, 30H, Cp*), 1.85, 3.75 (m, 2H each, THF).

### *3.4. [Cp*IrCl(μ-SeSbCl$_2$)$_2$IrCp*Cl] (**5bx**)*

A suspension of **1b** (50 mg, 0.056 mmol) and SbCl$_3$ (26 mg, 0.11 mmol) in THF (6 mL) was stirred at room temperature overnight. The resulting yellow-brown mixture was dried up in vacuo and the residue was extracted with CH$_2$Cl$_2$ (3 mL) twice. Addition of hexane (20 mL) to the combined and concentrated extracts (ca. 4 mL) gave **5bx** · 1/2CH$_2$Cl$_2$ as red-brown crystals in 68% yield. Found: C, 18.72; H, 2.36. $C_{20.5}H_{31}Cl_7Sb_2Se_2Ir_2$ requires C, 18.77; H, 2.38. $\delta_H$ (CDCl$_3$): 1.62 (s, 30H, Cp*), 5.30 (s, 1H, CH$_2$Cl$_2$).

### *3.5. [Cp*IrCl(μ-SeBiCl$_2$)$_2$IrCp*Cl] (**5by**)*

The red mixture obtained from **1b** (50 mg, 0.056 mmol) and BiCl$_3$ (35 mg, 0.11 mmol) similarly was dried up and the residue was extracted with acetone (3 mL) twice. The combined extracts were dried up and the residue was redissolved in THF (4 mL). Addition of hexane (20 mL) afforded **5by** · 1/2THF as red needles in 43% yield. Found: C, 17.93; H, 2.30. $C_{22}H_{34}O_{0.5}Cl_6Bi_2Se_2Ir_2$ requires C, 17.86; H, 2.32. $\delta_H$ (CDCl$_3$): 1.62 (s, 30H, Cp*), 1.85, 3.75 (m, 2H each, THF).

### *3.6. [Cp*RhCl(μ-SSbCl$_2$)$_2$RhCp*Cl] (**6ax**)*

This complex was prepared from **2a** by the similar procedure to that for **5ax** as orange-red crystals in 80% yield. Found: C, 24.20; H, 2.93. $C_{20}H_{30}Cl_6Sb_2S_2Rh_2$ requires C, 24.10; H, 3.03. $\delta_H$ (CDCl$_3$): 1.63 (s, Cp*).

### *3.7. [Cp*RhCl(μ-SBiCl$_2$)$_2$RhCp*Cl] (**6ay**)*

This complex was prepared from **2a** by the similar procedure to that for **5ay** as orange crystals in 83% yield. Found: C, 20.61; H, 2.55. $C_{20}H_{30}S_2Cl_6Rh_2Bi_2$ requires C, 20.58; H, 2.58. $\delta_H$ (CDCl$_3$): 1.59 (s, 30H, Cp*).

### *3.8. [Cp*RhCl(μ-SeSbCl$_2$)$_2$RhCp*Cl] (**6bx**)*

This complex was prepared from **2b** by the same method as that for **5bx**. The product **6bx** · 1/2CH$_2$Cl$_2$ was isolated as red-black crystals in 67% yield. Found: C, 21.58; H, 2.77. $C_{20.5}H_{31}Cl_7Sb_2Se_2Rh_2$ requires C, 21.73; H, 2.76. $\delta_H$ (CDCl$_3$): 1.66 (s, 30H, Cp*), 5.30 (s, 1H, CH$_2$Cl$_2$).

### *3.9. [Cp*RhCl(μ-SeBiCl$_2$)$_2$RhCp*Cl] (**6by**)*

This complex was obtained from **2b** and BiCl$_3$ by the same method as that for **5bx** in 51% yield as **6by** · CH$_2$Cl$_2$. Found: C, 18.27; H, 2.21. $C_{21}H_{32}Cl_8Se_2Bi_2Rh_2$ requires C, 18.69; H, 2.39. $\delta_H$ (CDCl$_3$): 1.62 (s, 30H, Cp*), 5.30 (s, 2H, CH$_2$Cl$_2$).

### *3.10. [Cp°RuCl(μ-SSbCl$_2$)$_2$RuCp°Cl] (**7′x**)*

A suspension containing **3′** (63 mg, 0.099 mmol) and SbCl$_3$ (45 mg, 0.20 mmol) in THF (10 mL) was stirred at room temperature for 18 h and the resulting brown mixture was dried up. The residue was crystallized from CH$_2$Cl$_2$-hexane, affording **7′x** as brown crystals. Found: C, 26.24; H, 3.28. $C_{22}H_{34}Cl_6S_2Sb_2Ru_2$ requires C, 25.88; H, 3.36. $\delta_H$ (CDCl$_3$): 1.14 (t, 6H, CH$_2$C*H*$_3$), 1.70, 1.71 (s, 12H each, C$_5$Me), 2.08 (q, 4H, C*H*$_2$CH$_3$).

### *3.11. [Cp°RuCl(μ-SBiCl$_2$)$_2$RuCp°Cl] (**7′y**)*

This complex was obtained from **3′** and BiCl$_3$ in the similar method to that for **7′x** as black crystals in 84% yield. Found: C, 22.39; H, 2.79. $C_{22}H_{34}Cl_6S_2Bi_2Ru_2$ requires C, 22.10; H, 2.87. $\delta_H$ (CDCl$_3$): 1.15 (t, 6H, CH$_2$C*H*$_3$), 1.67, 1.69 (s, 12H each, C$_5$Me), 2.13 (q, 4H, CH$_2$).

### *3.12. [Ru(η$^6$-C$_6$Me$_5$H)Cl(μ-SSbCl$_2$)$_2$Ru(η$^6$-C$_6$Me$_5$H)-Cl] (**8x**)*

This complex was obtained from **4a** by the similar method to that for **5ax** as orange-red crystals of **8x** · 1/

Table 2
Details of the X-ray crystallography

| | **5ax** $\cdot$ 1/4$CH_2Cl_2$ | **5ay** $\cdot$ 1/2THF | **5bx** $\cdot$ 1/2$CH_2Cl_2$ | **5by** $\cdot$ 1/2THF | **6ax** | **6bx** $\cdot$ 1/2$CH_2Cl_2$ | **6by** $\cdot$ $CH_2Cl_2$ | **7′x** | **7′y** | **8x** $\cdot$ 1/2$CH_2Cl_2$ | **8y** $\cdot$ $CH_2Cl_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Formula | $C_{20.25}H_{30.5}S_2$-$Cl_{6.5}Sb_2Ir_2$ | $C_{22}H_{34}O_{0.5}S_2$-$Cl_6Ir_2Bi_2$ | $C_{20.5}H_{31}Cl_7$-$Sb_2Se_2Ir_2$ | $C_{22}H_{34}O_{0.5}$-$Cl_6Se_2Ir_2Bi_2$ | $C_{20}H_{30}S_2Cl_6$-$Sb_2Rh_2$ | $C_{20.5}H_{31}Cl_7$-$Sb_2Se_2Rh_2$ | $C_{21}H_{32}Cl_8$-$Se_2Rh_2Bi_2$ | $C_{22}H_{34}S_2$-$Cl_6Sb_2Ru_2$ | $C_{22}H_{34}S_2Cl_6$-$Ru_2Bi_2$ | $C_{22.5}H_{33}Cl_7$-$S_2Sb_2Ru_2$ | $C_{23}H_{34}Cl_8$-$S_2Ru_2Bi_2$ |
| $M$ | 1196.47 | 1385.75 | 1311.50 | 1479.55 | 996.61 | 1132.87 | 1349.80 | 1020.99 | 195.45 | 1061.44 | 1278.37 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $C2/c$ (no. 15) | $C2/m$ (no. 12) | $C2/m$ (no. 12) | $C2/m$ (no. 12) | $P2_1/n$ (no. 14) | $C2/m$ (no. 12) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) | $P2_1/n$ (no. 14) | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) |
| Crystal size (mm) | 0.45 × 0.40 × 0.10 | 0.40 × 0.20 × 0.15 | 0.40 × 0.30 × 0.20 | 0.40 × 0.15 × 0.15 | 0.40 × 0.20 × 0.05 | 0.40 × 0.40 × 0.30 | 0.40 × 0.30 × 0.20 | 0.20 × 0.10 × 0.01 | 0.44 × 0.34 × 0.20 | 0.50 × 0.20 × 0.06 | 0.40 × 0.20 × 0.15 |
| $a$ (Å) | 39.787(4) | 19.201(3) | 19.653(3) | 19.169(4) | 1.996(1) | 19.612(3) | 10.998(3) | 10.728(3) | 11.134(2) | 12.292(1) | 10.731(1) |
| $b$ (Å) | 9.377(5) | 15.958(2) | 15.720(5) | 16.041(3) | 17.536(1) | 5.726(7) | 12.049(4) | 11.126(2) | 16.014(2) | 15.729(1) | 12.045(2) |
| $c$ (Å) | 17.571(4) | 12.004(2) | 12.019(2) | 12.116(2) | 15.551(1) | 12.004(2) | 15.352(7) | 15.443(3) | 18.570(9) | 17.359(1) | 15.549(3) |
| $\alpha$ (°) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 97.66(3) | 75.27(1) | 90.00 | 0.00 | 97.05(1) |
| $\beta$ (°) | 101.03(1) | 113.704(9) | 114.20(1) | 113.822(7) | 06.348(6) | 114.40(1) | 100.86(3) | 73.11(2) | 100.04(3) | 101.837(6) | 98.00(1) |
| $\gamma$ (°) | 90.00 | 90.00 | 90.00 | 90.00 | 0.00 | 90.00 | 113.09(2) | 68.88(2) | 90.00 | 90.00 | 114.376(9) |
| $V$ (Å$^3$) | 6434(3) | 367.6(7) | 3386.9(1) | 3408.1(11) | 3138.9(4) | 3371.3(2) | 1788.7(1) | 1622.0(7) | 3260.3(2) | 3284.7(4) | 1776.3(5) |
| $Z$ | 8 | 4 | 4 | 4 | 4 | 4 | 2 | 2 | 4 | 4 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 2.470 | 2.733 | 2.572 | 2.883 | 2.109 | 2.232 | 2.506 | 2.090 | 2.435 | 2.146 | 2.390 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 106.09 | 89.15 | 121.44 | 207.04 | 33.84 | 52.68 | 133.40 | 31.94 | 122.84 | 32.38 | 114.27 |
| Transmittance factor | 0.16–1.00 | 0.45–1.00 | 0.50–1.00 | 0.23–1.00 | 0.73–1.00 | 0.67–1.00 | 0.37–1.00 | 0.75–1.00 | 0.11–1.00 | 0.72–1.00 | 0.22–1.00 |
| Unique reflections ($R_{int}$) | 7398 (0.059) | 4008 (0.028) | 040 (0.057) | 3959 (0.078) | 7206 (0.021) | 021 (0.012) | 8211 (0.039) | 7441 (0.084) | 7747 (0.048) | 530 (0.061) | 8131 (0.023) |
| Observed reflections | 4542 ($I > 3\sigma(I)$) | 2402 ($I > 3\sigma(I)$) | 2928 ($I > 3\sigma(I)$) | 2430 ($I > 3\sigma(I)$) | 5071 ($I > 3\sigma(I)$) | 3054 ($I > 3\sigma(I)$) | 4279 ($I > 3\sigma(I)$) | 341 | 342 | 325 | 369 |
| Variables | 303 | 189 | 189 | 188 | 290 | 189 | 365 | 2889 ($I > 2\sigma(I)$) | 059 ($I > 2\sigma(I)$) | 5533 ($I > 3\sigma(I)$) | 5868 ($I > 2\sigma(I)$) |
| $R^a$ | 0.046 | 0.039 | 0.040 | 0.047 | 0.030 | 0.025 | 0.040 | 0.047 | 0.062 | 0.049 | 0.049 |
| $R_w$$^b$ or $wR_2$$^c$ | 0.047$^b$ | 0.100$^c$ | 0.102$^c$ | 0.121$^c$ | 0.030$^b$ | 0.084$^c$ | 0.097$^c$ | 0.115$^c$ | 0.134$^c$ | 0.069$^b$ | 0.131$^c$ |
| GOF$^d$ | 1.73 | 1.04 | 0.99 | 1.02 | 1.29 | 1.03 | 0.97 | 1.04 | 1.03 | 1.98 | 1.04 |
| Residuals (e Å$^{-3}$) | 2.25, −2.31 | 0.42, −4.67 | 2.15, −2.22 | 2.76, −1.63 | 0.54, −0.67 | 0.56, −0.54 | 1.09, −1.14 | 0.81, −0.86 | 3.35, −4.91 | 1.52, −1.28 | 4.20, −3.99 |

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

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

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

$2CH_2Cl_2$ in 64% yield. Found: C, 25.36; H, 3.02. $C_{22.5}H_{33}Cl_7S_2Sb_2Ru_2$ requires C, 25.46; H, 3.13. $\delta_H$ ($CDCl_3$): 1.96 (s, 6H,CMe), 2.02, 2.15 (s, 12H each, CMe), 4.91 (s, 2H, $C_6H$), 5.30 (s, 1H, $CH_2Cl_2$).

### 3.13. [Ru($\eta^6$-$C_6Me_5H$)Cl($\mu$-$SBiCl_2$)$_2$Ru($\eta^6$-$C_6Me_5H$)-Cl] (**8y**)

This complex was obtained from **4a** and $BiCl_3$ similarly as black crystals of **8y**·$CH_2Cl_2$ in 77% yield. Found: C, 21.51; H, 2.55. $C_{23}H_{34}Cl_8S_2Ru_2Bi_2$ requires C, 21.61; H, 2.68. $\delta_H$ ($CDCl_3$):, 2.01, 2.05 (s, 12H each, CMe), 2.05 (s, 6H, CMe), 5.04 (s, 2H, $C_6H$), 5.30 (s, 2H, $CH_2Cl_2$).

### 3.14. X-ray crystallography

Single crystals were sealed in glass capillaries under argon and subjected to the X-ray diffraction studies, which were carried out on a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo K$\alpha$ source at room temperature. Data were corrected for Lorentz-polarization effects and for absorption ($\psi$ scans). Details are shown in Table 2.

Structure solution and refinements were performed by using the teXsan program package [24] for **5ax**, **6ax**, and **8x** or CrystalStructure [25] for **5ay, 5bx, 5by, 6bx, 6by**, **7′x**, **7′y**, and **8y**. The positions of non-hydrogen atoms were determined by Patterson methods (PATTY [26] for the formers or SHELXS 97 [27] for the latters), followed by Fourier synthesis (DIRDIF 94 for the formers or DIRDIF 99 for the latters [28]). These were refined anisotropically by using full-matrix least-squares techniques. The hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements with fixed parameters.

## 4. Supplementary material

Listings of atomic coordinates, anisotropic thermal parameters, and extensive interatomic distances and angles for **5ax**, **5ay**, **5bx**, **5by**, **6ax**, **6bx**, **6by**, **7′x**, **7′y**, **8x**, and **8y** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 231558–231568, 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 http://www.ccdc.cam.ac.uk).

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## References

[1] (a) M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46;
(b) S. Kuwata, M. Hidai, Coord. Chem. Rev. 213 (2001) 211;
(c) H. Seino, Y. Mizobe, M. Hidai, Organometallics 19 (2000) 3631;
(d) M. Hidai, in: C.G. Screttas, B.R. Steele (Eds.), Perspectives in Organometallic Chemistry, Royal Society of Chemistry, Cambridge, 2003, pp. 62–73.
[2] (a) S. Nagao, H. Seino, M. Hidai, Y. Mizobe, J. Organomet. Chem. 669 (2003) 124;
(b) D. Masui, T. Kochi, Z. Tang, Y. Ishii, Y. Mizobe, M. Hidai, J. Organomet. Chem. 620 (2001) 69;
(c) Z. Tang, Y. Nomura, S. Kuwata, Y. Ishii, Y. Mizobe, M. Hidai, Inorg. Chem. 37 (1998) 4909;
(d) Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, M. Hidai, Organometallics 16 (1997) 151;
(e) K. Hashizume, Y. Mizobe, M. Hidai, Organometallics 15 (1996) 3303;
(f) T. Kochi, Y. Nomura, Z. Tang, Y. Ishii, Y. Mizobe, M. Hidai, J. Chem. Soc., Dalton Trans. (1999) 2575.
[3] (a) S. Kuwata, M. Andou, K. Hashizume, Y. Mizobe, M. Hidai, Organometallics 17 (1998) 3429;
(b) See also S. Kabashima, S. Kuwata, K. Ueno, M. Shiro, M. Hidai, Angew. Chem. Int. Ed. 39 (2000) 1128.
[4] (a) H. Seino, M. Hidai, Y. Mizobe, Chem. Lett. (2002) 920;
(b) T. Masumori, H. Seino, Y. Mizobe, M. Hidai, Inorg. Chem. 39 (2000) 5002;
(c) H. Seino, T. Masumori, M. Hidai, Y. Mizobe, Organometallics 22 (2003) 3424.
[5] H. Seino, Y. Mizobe, M. Hidai, New J. Chem. 24 (2000) 907.
[6] (a) K.H. Whitmire, Adv. Organomet. Chem. 42 (1998) 1;
(b) O.J. Scherer, Angew. Chem. Int. Ed. Engl. 29 (1990) 1104;
(c) N.A. Compton, R.J. Errington, N.C. Norman, Adv. Organomet. Chem. 31 (1990) 91;
(d) D. Fenske, J. Ohmer, J. Hachgenei, K. Merzweiler, Angew. Chem. Int. Ed. Engl. 27 (1988) 1277;
(e) A. Herrmann, Angew. Chem. Int. Ed. Engl. 25 (1986) 56.
[7] (a) J. Wachter, Angew. Chem. Int. Ed. 37 (1998) 750;
(b) G.W. Drake, J.W. Kolis, Coord. Chem. Rev. 137 (1994) 131;
(c) R. Hernandez-Molina, M.N. Sokolov, A.G. Sykes, Acc. Chem. Res. 34 (2001) 223.
[8] M. Nishio, H. Matsuzaka, Y. Mizobe, M. Hidai, Inorg. Chim. Acta 263 (1997) 119.
[9] Z. Hou, Y. Ozawa, K. Isobe, Chem. Lett. (1990) 1863.
[10] H. Matsuzaka, J.-P. Qü, T. Ogino, M. Nishio, Y. Nishibayashi, Y. Ishii, S. Uemura, M. Hidai, J. Chem. Soc., Dalton Trans. (1996) 4307.
[11] Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, M. Hidai, Inorg. Chim. Acta 267 (1998) 73.
[12] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 15th ed., McGraw-Hill, Inc., New York, 1999, p. 4.35.
[13] G.W. Drake, G.L. Schimek, J.W. Kolis, Inorg. Chem. 35 (1996) 4534.
[14] M. Shur, C. Näther, W. Bensch, Z. Naturforsch. 56b (2001) 79.
[15] R. Kiebach, W. Bensch, R.-D. Hoffmann, R. Pöttgen, Z. Anorg. Allg. Chem. 629 (2003) 532.
[16] M. Schur, H. Rijnberk, C. Näther, C. Bensch, Polyhedron 18 (1998) 101.

[17] T.M. Martin, G.L. Schimek, D.A. Milsna, J.W. Kolis, Phosphorus, Sulfur, Silicon 93–94 (1994) 93.

[18] (a) T. König, B. Eisenmann, H. Schäfer, Z. Anorg. Allg. Chem. 488 (1982) 126;
(b) D.M. Smith, C.-W. Park, J.A. Ibers, Inorg. Chem. 35 (1996) 6682.

[19] C. Näther, F. Wendland, W. Bensch, Acta Crystallogr. E59 (2003) m119.

[20] D.M. Smith, C.-W. Park, J.A. Ibers, Inorg. Chem. 36 (1997) 3798.

[21] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 13th ed., McGraw-Hill Book Co., New York, 1985, Table 3-120.

[22] (a) G.A. Fisher, N.C. Norman, Adv. Inorg. Chem. 41 (1994) 233;
(b) N.C. Norman, Phosphorus, Sulfur, Silicon 87 (1994) 167.

[23] B. Siewert, U. Müller, Z. Anorg. Allg. Chem. 609 (1992) 89.

[24] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

[25] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, CRYSTALS Issue 10, CrystalStructure 3.00: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, 2000–2002, Chemical Crystallography Laboratory, Oxford, UK.

[26] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, PATTY, The DIRDIF Program System; Technical report of the Crystallography Laboratory: University of Nijmegen, 1992.

[27] G.M. Sheldrick, SHELX 97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.

[28] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, DIRDIF 94: The DIRDIF 94 Program System; Technical report of the Crystallography Laboratory:, University of Nijmegen, Nijmegen, The Netherlands, 1994;
P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, DIRDIF 99: The DIRDIF 99 Program System; Technical report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.