

Syntheses of diiridium complexes with two bridging tetrachalcogenide ligands [$\{\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-E}_4)_2$] ($\text{E} = \text{Se}$ or S) and their reactions with alkynes forming mono- or di-nuclear dichalcogenolene complexes

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Treatment of $[\text{ClCp}^*\text{Ir}(\mu\text{-Cl})_2\text{IrCp}^*\text{Cl}]$ **1** ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with 2 equivalents of Li_2Se_4 in THF at 50 °C afforded a diiridium complex with two bridging tetraselenide ligands $[\text{Cp}^*\text{Ir}(\mu\text{-Se}_4)_2\text{IrCp}^*]$ **2**. The sulfur analog $[\text{Cp}^*\text{Ir}(\mu\text{-S}_4)_2\text{IrCp}^*]$ **3** was also obtained by either the reaction of **1** with Li_2S_4 or treatment of a mixture of $[\text{ClCp}^*\text{Ir}(\mu\text{-SH})_2\text{IrCp}^*\text{Cl}]$ and S_8 with NEt_3 . When treated with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (DMAD), **2** afforded the diselenolene complexes $[\text{Cp}^*\text{Ir}(\mu\text{-Se}_4)\{\mu\text{-Se}_2\text{C}_2(\text{CO}_2\text{Me})_2\}\text{IrCp}^*]$ and $[\text{IrCp}^*\{\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ as well as the DMAD adduct to the latter $[\text{IrCp}^*\{\text{Se}_2\text{C}_4(\text{CO}_2\text{Me})_4\}]$. Analogous treatment of **2** with $\text{HC}\equiv\text{CCO}_2\text{Me}$ (MAMC) resulted in formation of diiridium complexes with bridging diselenolene ligand(s) $[\text{Cp}^*\text{Ir}(\mu\text{-Se}_4)\{\mu\text{-Se}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}\text{IrCp}^*]$ and $[\text{Cp}^*\text{Ir}\{\mu\text{-Se}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}\text{IrCp}^*]$ but no complex corresponding to $[\text{IrCp}^*\{\text{Se}_2\text{C}_4(\text{CO}_2\text{Me})_4\}]$. Reactions of **3** with these alkynes were also carried out for comparison, which led to exclusive formation of the mononuclear complexes: $[\text{IrCp}^*\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ and $[\text{IrCp}^*\{\text{S}_2\text{C}_4(\text{CO}_2\text{Me})_4\}]$ for DMAD and $[\text{IrCp}^*\{\text{S}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}]$ for MAMC, respectively. X-Ray analyses were undertaken to clarify the detailed structures of seven complexes.

Introduction

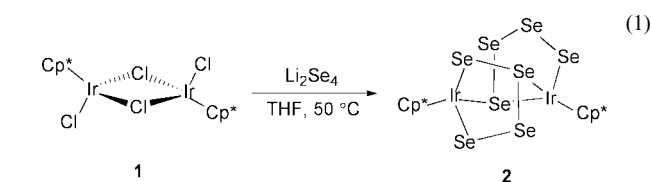
Metal polychalcogenides have been attracting much attention because of their potential as synthetic reagents or catalysts as well as new materials.¹ Although the chemistry of metal polysulfides has extensively been studied, that of metal polyselenides is still poorly advanced. We have briefly reported² that the diiridium complex $[\text{IrCp}^*\text{Cl}(\mu\text{-Cl})_2\text{IrCp}^*\text{Cl}]$ **1** ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) reacts with Li_2Se_4 to give a diiridium complex containing two bridging Se_4 ligands $[\text{Cp}^*\text{Ir}(\mu\text{-Se}_4)_2\text{IrCp}^*]$ **2**. Interestingly, treatment of **2** with $[\text{Pd}(\text{PPh}_3)_4]$ resulted in the formation of bimetallic clusters with the unique $\text{Ir}_2\text{Pd}_2\text{Se}_3$ or $\text{Ir}_2\text{Pd}_2\text{Se}_5$ core, $[(\text{IrCp}^*)_2\{\text{Pd}(\text{PPh}_3)\}_2(\mu_3\text{-Se})_2(\mu\text{-Se})]$ and $[(\text{IrCp}^*)_2\{\text{Pd}(\text{PPh}_3)\}_3(\mu_3\text{-Se})_3(\mu_3\text{-Se}_2)]$.² Since mixed-metal selenide clusters have rarely been documented owing presumably to the lack of convenient synthetic methods, it is noteworthy that **2** serves as a precursor to bimetallic selenide clusters.

Now we have found that complex **2** reacts with the activated alkynes $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (dimethyl acetylenedicarboxylate; DMAD) and $\text{HC}\equiv\text{CCO}_2\text{Me}$ (methyl acetylenemonocarboxylate; MAMC) to give a series of mono- and di-nuclear diselenolene complexes. For comparison, the reaction of the sulfur analog $[\text{Cp}^*\text{Ir}(\mu\text{-S}_4)_2\text{IrCp}^*]$ **3**,³ derived analogously from **1** and Li_2S_4 in the present work, with these alkynes has been investigated. In this paper we summarize the results of these studies along with details of the synthesis and characterization of **2**.

Results and discussion

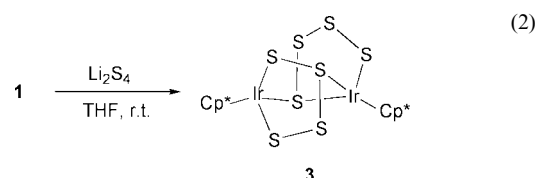
Synthesis of complexes **2** and **3**

At present employment of alkali metal polychalcogenides most successfully leads to the formation of metal-heavy chalcogenide compounds.^{1b} Thus, we have attempted to prepare iridium complexes containing polyselenido ligands by treating halide complexes of Ir with polyselenide anions Li_2Se_n ($n = 2-5$). Actually, **2** is obtained in moderate yield from the reaction of **1** with 2 equivalents of Li_2Se_4 in THF at 50 °C (eqn. 1).



Complex **2**, isolated as dark brown crystals after recrystallization from benzene-methanol, was characterized by spectroscopic and microanalytical data along with single-crystal X-ray diffraction (see below). When other polyselenides Li_2Se_n ($n \neq 4$) were used, desired iridium complexes with Se_n ligand(s) were not isolable, although the formation of **2** in low yield was observed in each reaction.

The sulfur analog **3** is also available in moderate yield from **1** and Li_2S_4 by the same procedure as that for **2** (eqn. 2). Complex



3 was characterized spectroscopically and by microanalysis.⁴ The synthesis of **3** reported previously by Herberhold *et al.* is not straightforward; the complex $[\text{Cp}^*\text{Ir}(\text{CO})_2]$ was first treated

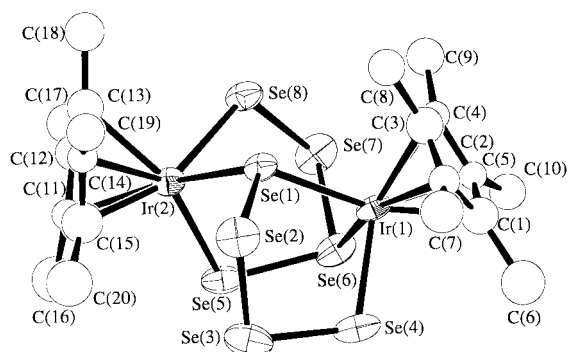
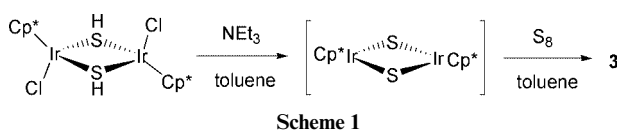


Fig. 1 Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity in all the structures shown.

with S_8 under photo-irradiation to afford either $[(OC)Cp^*Ir(\mu-S)_2IrCp^*(CO)]$ **4** or $[IrCp^*(CO)(S_4)]$, which were then converted into **3** upon treatment of the former with an excess of S_8 or by photolysis or thermolysis of the latter.^{3b} Based on the spectral data, the structure of **3** was proposed by these authors to be analogous to that of the fully characterized rhodium complex $[Cp^*Rh(\mu-S)_2RhCp^*]$ **5** derived from $[Rh_2Cp^*_2(CO)_2]$ and S_8 .⁵ Independently, Chen and Angelici isolated **3** from the reactions of the 2,5-dimethylthiophene complexes $[IrCp^*(\eta^4-Me_2C_4H_2S)]$ or $[IrCp^*(C,S-Me_2C_4H_2S)]$ with S_8 , and confirmed its structure by X-ray crystallography.^{3a}

We have reported that treatment of the hydrosulfide-bridged dinuclear complexes $[ClCp^*M(\mu-SH)_2MCp^*Cl]$ ($M = Ir, Rh$ or Ru) with NEt_3 affords the co-ordinatively unsaturated species $[Cp^*M(\mu-S)_2MCp^*]$ *in situ*, which dimerizes to give homo-metallic cubane-type M_4S_4 clusters.⁶ Since Herberhold showed that the sulfide bridged diiridium complex **4** reacts with S_8 to form **3**, the reaction of the *in situ* generated $[Cp^*Ir(\mu-S)_2IrCp^*]$ with S_8 has been attempted. As expected, this resulted in the formation of **3** in satisfactory yield according to Scheme 1.



Scheme 1

Under analogous conditions, the reactions of the rhodium complex $[ClCp^*Rh(\mu-Cl)_2RhCp^*Cl]$ with Li_2E_n ($E = Se$ or S ; $n = 2, 4$ or 5) were conducted. However, no tractable products were isolated from the reaction mixtures except for the case using Li_2S_5 , which afforded the known tetrasulfide complex **5** in low yield as the only characterizable product.

Structure of complex **2**

The ORTEP⁷ drawing of complex **2** is depicted in Fig. 1, while important bond lengths and angles are listed in Table 1. Complex **2** consists of two Cp^*Ir units with a chelating Se_4 ligand, which are connected by two Ir–Se bonds. Hence, the total geometry around the Ir atoms is a three-legged piano stool with the Se–Ir–Se angles in the range 78–97°. The structure of **2** is not symmetrical; Ir(1) binds to the β -Se atom (Se(6)) in the Se_4 chain around Ir(2), whereas Ir(2) is bonded to the α -Se atom (Se(1)) in that around Ir(1). Accordingly the 1H NMR spectrum shows two singlets attributable to two Cp^* methyl protons. As expected from the 18-electron count satisfied by the two iridium(III) centers, there exists no bonding interaction between the two Ir atoms (Ir...Ir distance: 4.179(3) Å).

Each $IrSe_4$ ring has the envelope geometry, one being folded along the Se(1)–Se(3) vector with the Se(2) atom at the *exo* position and the other along the Se(5)–Se(7) vector with the *endo* Se(6) atom. The dihedral angle between the least-squares plane defined by the Ir(1), Se(1), Se(3), and Se(4) atoms and the

Table 1 Bond distances (Å) and angles (°) in complex **2**

Ir(1)–Se(1)	2.456(5)	Ir(1)–Se(4)	2.468(5)
Ir(1)–Se(6)	2.423(4)	Ir(1)–C(Cp*)	2.14(5)–2.25(4)
Ir(2)–Se(1)	2.454(5)	Ir(2)–Se(5)	2.423(5)
Ir(2)–Se(8)	2.496(5)	Ir(2)–C(Cp*)	2.01(5)–2.20(5)
Se(1)–Se(2)	2.405(7)	Se(2)–Se(3)	2.285(7)
Se(3)–Se(4)	2.309(8)	Se(5)–Se(6)	2.312(7)
Se(6)–Se(7)	2.391(7)	Se(7)–Se(8)	2.325(7)
Se(1)–Ir(1)–Se(4)	97.0(2)	Se(1)–Ir(1)–Se(6)	94.1(2)
Se(4)–Ir(1)–Se(6)	82.7(2)	Se(1)–Ir(2)–Se(5)	93.1(2)
Se(1)–Ir(2)–Se(8)	77.9(2)	Se(5)–Ir(2)–Se(8)	95.2(2)
Ir(1)–Se(1)–Ir(2)	116.7(2)	Ir(1)–Se(1)–Se(2)	101.2(2)
Ir(2)–Se(1)–Se(2)	109.5(2)	Se(1)–Se(2)–Se(3)	96.8(2)
Se(2)–Se(3)–Se(4)	99.7(3)	Ir(1)–Se(4)–Se(3)	108.5(2)
Ir(2)–Se(5)–Se(6)	104.2(2)	Ir(1)–Se(6)–Se(5)	109.0(2)
Ir(1)–Se(6)–Se(7)	107.5(2)	Se(5)–Se(6)–Se(7)	94.7(3)
Se(6)–Se(7)–Se(8)	96.7(2)	Ir(2)–Se(8)–Se(7)	108.4(2)

Se(1)–Se(2)–Se(3) plane is 122.3°, while that between the planes defined by the Ir(2), Se(5), Se(7), and Se(8) atoms and Se(5)–Se(6)–Se(7) is 121.3°. The Ir–Se bond lengths in the range 2.42–2.50 Å are comparable to those in $[IrCp^*(PMe_3)(Se_4)]$ (2.468(2) and 2.472(2) Å)⁸ and slightly shorter than that in $[Ir(Me_2PCH_2CH_2PMe_2)_2(Se_4)]Cl$ (2.542(3) Å).⁹ The Se–Se bond distances varying from 2.28 to 2.41 Å are unexceptional when compared with those in chelating tri- to penta-selenide ligands previously reported.

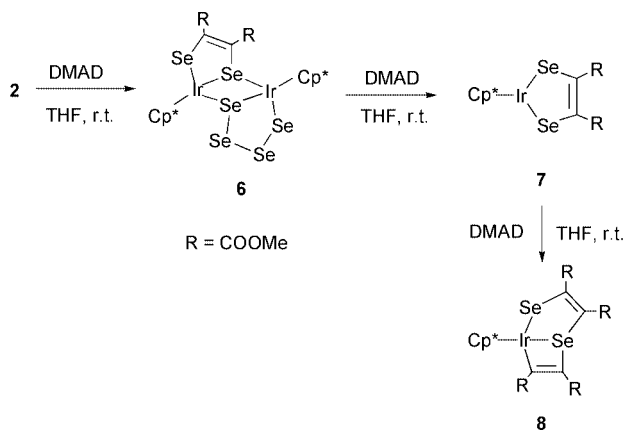
The structure demonstrated for complex **2** is in good agreement with that manifested previously for the sulfur analog **3**^{3a} except that the Ir–Se and Se–Se bond distances shown above are considerably longer than the corresponding Ir–S and S–S bond lengths in **3**, varying from 2.31 to 2.41 Å and from 2.02 to 2.11 Å, respectively. This results in a larger Ir–Ir separation in **2** than that in **3** (3.994(2) Å⁴). The S–Ir–S angles observed in **3** fall in the range 77–94°.

Reactions of complex **2** with alkynes

Complex **2** reacts with DMAD or MAMC in THF at room temperature to give a series of diselenolene complexes. Unactivated alkynes such as *p*-tolylacetylene did not react even in refluxing THF. Dichalcogenolene complexes are of much interest owing to their unique physical properties leading to development of high performing materials. However, in contrast to the rich chemistry of dithiolene complexes rapidly progressing,¹⁰ studies on diselenolene complexes are relatively scarce.¹¹

When treated with equimolar DMAD for 1 day at room temperature, complex **2** gave a mixture of the dinuclear diselenolene complex $[Cp^*Ir(\mu-Se_4)\{\mu-Se_2C_2(CO_2Me)_2\}IrCp^*]$ **6** and the mononuclear diselenolene complex $[IrCp^*\{Se_2C_2(CO_2Me)_2\}]$ **7** together with unchanged **2**, whose molar ratio was determined to be *ca.* 6:4:3 from the 1H NMR spectrum of the resultant reaction mixture. Complex **6** was isolated in 10% yield and well characterized. By treatment of **2** with 2 equivalents of DMAD at room temperature a mixture was obtained, which contained **6**, **7**, and the DMAD adduct to **7**, $[IrCp^*\{Se_2C_4(CO_2Me)_4\}]$ **8**, in the molar ratio of **6**:**7**:**8** = 3:9:1. Complex **7** was isolated in 28% yield from this reaction mixture in a pure form and characterized unambiguously. On the other hand, the reaction of **2** with 10 equivalents of DMAD gave **8** in moderate yield. These products are illustrated in Scheme 2.† The stepwise conversion of **2** into **8** via **6** and then **7** has been manifested by following the change in the ratio of these compounds in the reaction mixture

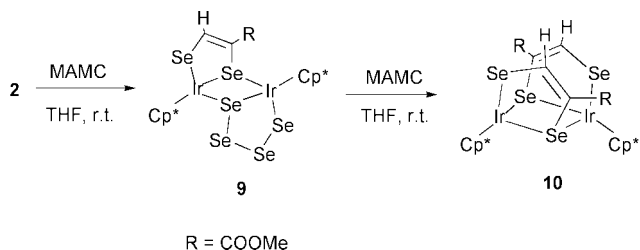
† Quite recently it has been reported¹² that the reactions of $[PtSe_4(dppe)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) with $RO_2CC\equiv CCO_2R$ ($R = Me$ or Et) give the diselenolene complexes $[Pt\{Se_2C_2(CO_2R)_2\}(dppe)]$; using excess of DMAD the presence of a product in low concentration has been detected which can be characterized spectroscopically to be $[Pt\{Se_2C_4(CO_2Me)_4\}(dppe)]$.



Scheme 2

using ^1H NMR spectroscopy. Herberhold and co-workers have reported recently that the mononuclear polyselenide complexes $[\text{IrCp}^*(\text{PMe}_3)(\text{Se}_n)]$ ($n = 2$ or 4) react with DMAD to give $[\text{IrCp}^*(\text{PMe}_3)\{\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ and either sulfur-induced phosphine loss or thermolysis of this diselenolene complex affords **7**, although the latter could not be isolated in a pure form by these procedures.¹³ Reaction of the tetraselenido complex $[\text{WSe}(\text{Se}_4)_2]^{2-}$ with DMAD also results in the formation of the diselenolene complex $[\text{W}\{\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2\}_3]^{2-}$.¹⁴

When complex **2** was treated with 1 equivalent of MAMC at room temperature a mixture of the tetraselenide–diselenolene complex $[(\text{IrCp}^*)_2(\mu\text{-Se}_4)\{\mu\text{-Se}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}]$ **9** and the diselenolene complex $[\text{Cp}^*\text{Ir}\{\mu\text{-Se}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}_2\text{IrCp}^*]$ **10** was obtained (Scheme 3). Complex **9** is isolable in low yield from the



Scheme 3

reaction mixture was characterized by spectroscopic data and preliminary X-ray analysis. On the other hand, **10** formed in satisfactory yield upon treatment of **2** with an excess of MAMC. Interestingly, the X-ray analysis revealed its dimeric structure in solid form in contrast to the monomeric **7**. At present, it is uncertain whether the dimeric structure of **10** is retained in solution. However, since the ^{77}Se NMR spectrum of its CDCl_3 solution showed resonances at δ 846 and 771 and the monomeric **7** dissolved in CDCl_3 exhibited a signal at δ 857, **10** is presumed to be present as a monomer in solution. It is also to be noted that **10** did not react further with MAMC even under more forcing conditions (Scheme 3). This also presents a sharp contrast to the reactivity of the DMAD adduct **7**.

Reactions of complex 3 with alkynes

The reactions of the tetrasulfide complex **3** with DMAD and MAMC were also investigated for comparison, which demonstrated that these alkynes react with **3** more slowly than **2**. Thus, treatment of **3** with 2 equivalents of DMAD at room temperature for 2 days gave a mixture containing only the mononuclear dithiolene complex $[\text{IrCp}^*\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ **11** in *ca.* 30% yield and unchanged **3** (*ca.* 60%). Complex **11** was isolated from the reaction mixture obtained after a longer reaction time, and fully characterized. In contrast, when the reaction was carried out in the presence of 10 equivalents of DMAD in THF at room temperature for a week, the ^1H NMR spectrum of the

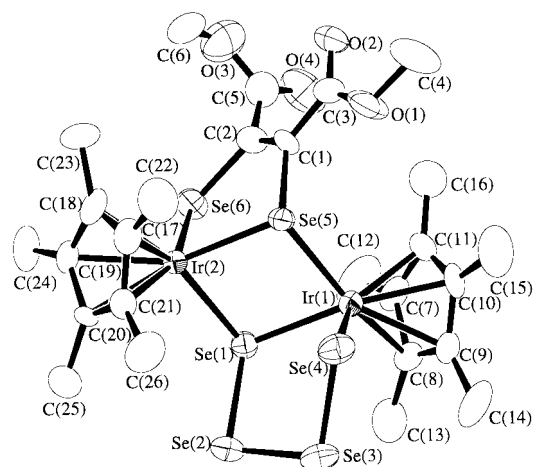
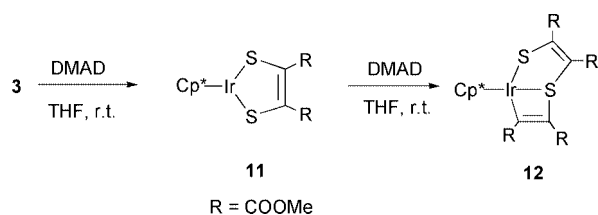


Fig. 2 Molecular structure of complex **6**.

reaction mixture showed the presence of $[\text{IrCp}^*\{\text{S}_2\text{C}_4(\text{CO}_2\text{Me})_4\}]$ **12** as the only characterizable product, which was isolated in 44% yield as orange-red crystals (Scheme 4). It

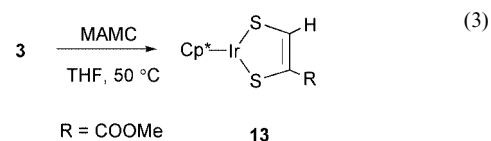


Scheme 4

was previously observed that the rhodium dithiolene complex $[\text{RhCp}\{\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2\}]$ undergoes addition of DMAD analogously at the Rh–S bond to give $[\text{RhCp}\{\text{S}_2\text{C}_4(\text{CO}_2\text{Me})_4\}]$.¹⁵

Formation of **11** from the related polysulfide complexes has been described previously, which includes the reactions of $[\text{IrCp}^*(\text{PMe}_3)(\text{S}_n)]$ ($n = 6, 5$ or 4) with DMAD followed by the removal of PMe_3 . However, further reaction of **11** with DMAD has not been reported.¹³

In the reactions of complex **3** with MAMC no other products than the mononuclear dithiolene complex $[\text{IrCp}^*\{\text{S}_2\text{C}_2\text{H}(\text{CO}_2\text{Me})\}]$ **13** were obtained or detected. Thus, **13** was isolated in moderate yield by treatment of **3** with 2–4 equivalents of MAMC at 50°C for 4 days (eqn. 3) and further reaction of MAMC with **13** did not take place.



Crystal structures of diselenolene complexes

X-Ray analyses have been carried out to clarify the detailed structures for the diselenolene complexes and their derivatives shown above. Figs. 2–5 depict the ORTEP drawings for **6**, **7**, **8**, and **10**, respectively, while selected bond distances and angles in **6–8** are listed in Table 2 and those for **10** are in Table 3.

Complex **6** has a dinuclear structure in which the $\text{Cp}^*\text{Ir}(\text{Se}_4)$ and $\text{Cp}^*\text{Ir}\{\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2\}$ units are connected by two Ir–Se bonds. The Ir_2Se_2 unit is essentially planar. The two Ir atoms have a three-legged piano stool geometry with the Se–Ir–Se angles varying from 78 to 92° for Ir(1) and from 81 to 86° for Ir(2). There exists no bonding interaction between the two Ir atoms, separation $3.756(1)$ Å, as expected from the 18-electron count for both iridium atoms. For the former Ir tetraselenide moiety, the α -Se atom (Se(1)) bridges the other Ir atom as

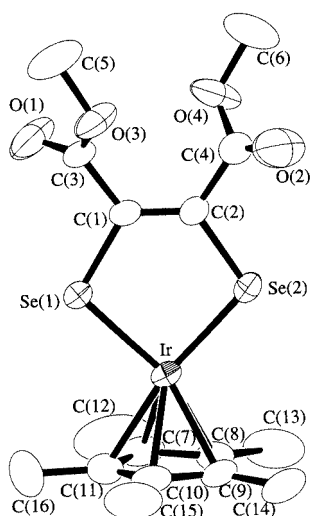


Fig. 3 Molecular structure of complex 7.

observed for the Se(1) atom in the Se(1)–Se(4) chain of **2**. However, in contrast to the IrSe₄ ring having an envelope structure folded about the Se(1)–Se(3) vector in **2**, the corresponding five-membered ring in **6** is folded around the Ir(1)–Se(3) vector with a dihedral angle of 118.0° between the Ir(1)–Se(3)–Se(4) plane and the least-squares plane defined by atoms Ir(1) and Se(1)–Se(3). With respect to the iridium diselenolene, the IrSe₂C₂ ring is not planar but bent around the Se(5)–Se(6) vector: the angle between the IrSe₂ plane and the least-squares plane defined by atoms Se(5), Se(6), C(1), and C(2) is 151.8°. From the two Ir–Se distances of the iridium diselenolene, the bridging Se(5) atom is closer to Ir(2) than the terminal Se(6) atom but only slightly (2.458(1) vs. 2.477(2) Å). The distances of the Ir–Se bonds combining the iridium tetraselenide and the Ir diselenolene units (Ir(1)–Se(5) 2.510(2); Ir(2)–Se(1) 2.490(2)) are longer than the other four Ir–Se distances involved in these two units. In the dimeric palladium diselenolene complex [Pd₂(PPh₃)₂(SeCR=CR′Se)₂] (R,R′ = (CH₂)₆), it has also been found that the Pd–Se bridges are considerably longer than the Pd–Se bonds in the diselenolene units. However, among the two Pd–Se bond distances in the diselenolene fragments the terminal Se atoms are closer to the Pd atoms than the bridging Se atoms.^{11a}

In complex **7** the Ir–Se(1) and Ir–Se(2) distances at 2.3494(7) and 2.3520(7) Å, respectively, are significantly shorter than the Ir–Se distances in **2** and **6** having 18-electron iridium centers. This is interpreted in terms of delocalization of the lone pair electron density of the Se atoms towards the 16-electron Ir through the pπ(Se)–dπ(Ir) interaction. The Ir, Se(1), Se(2), and C(1)–C(4) atoms are coplanar with deviations of less than 0.06 Å from their least-squares plane and this iridium diselenolene ring is nearly perpendicular to the Cp* plane with an angle of 89.4°. Planarity of metal–diselenolene moieties is ubiquitous for mononuclear diselenolene complexes.

Complex **8** has a structure in which DMAD is added to one of the Ir–Se bonds in the iridium diselenolene unit. The Ir, Se(1), Se(2), C(1), and C(2) atoms are essentially coplanar. The two Ir–Se bond distances at 2.4683(4) and 2.4787(4) Å differ only slightly, but are much longer than those in the 16-electron diselenolene complex **7** and comparable to those in the 18-electron complexes **2** and **6**.

In complex **10** two iridium diselenolene units are connected by two Ir–Se bonds in such a manner that the molecule has C₂ symmetry around the axis perpendicular to the Ir–Ir vector. The absence of any metal–metal interaction is demonstrated by the long Ir···Ir distance of 3.745(1) Å. The Ir₂Se₂ ring is puckered only slightly with the dihedral angle between the two Ir₂Se₂ planes of 168.3°, where the two Se atoms are shifted toward the direction opposite to the Cp* ligands. The Ir, Se(1),

Table 2 Bond distances (Å) and angles (°) in complexes **6**, **7** and **8**

6			
Ir(1)–Se(1)	2.469(2)	Ir(1)–Se(4)	2.471(2)
Ir(1)–Se(5)	2.510(2)	Ir(1)–C(Cp*)	2.19(2)–2.22(2)
Ir(2)–Se(1)	2.490(2)	Ir(2)–Se(5)	2.458(1)
Ir(2)–Se(6)	2.477(2)	Ir(2)–C(Cp*)	2.18(2)–2.22(1)
Se(1)–Se(2)	2.423(2)	Se(2)–Se(3)	2.339(3)
Se(3)–Se(4)	2.323(3)	Se(5)–C(1)	1.96(1)
Se(6)–C(2)	1.90(2)	C(1)–C(2)	1.34(2)
Se(1)–Ir(1)–Se(4)	91.56(6)	Se(1)–Ir(1)–Se(5)	81.32(5)
Se(4)–Ir(1)–Se(5)	78.82(6)	Se(1)–Ir(2)–Se(5)	81.95(5)
Se(1)–Ir(2)–Se(6)	82.91(6)	Se(5)–Ir(2)–Se(6)	86.09(5)
Ir(1)–Se(1)–Ir(2)	98.49(5)	Ir(1)–Se(1)–Se(2)	107.45(7)
Ir(2)–Se(1)–Se(2)	109.27(7)	Se(1)–Se(2)–Se(3)	101.95(8)
Se(2)–Se(3)–Se(4)	100.74(9)	Ir(1)–Se(4)–Se(3)	99.18(8)
Ir(1)–Se(5)–Ir(2)	98.21(5)	Ir(1)–Se(5)–C(1)	107.6(4)
Ir(2)–Se(5)–C(1)	100.8(4)	Ir(2)–Se(6)–C(2)	100.9(5)
Se(5)–C(1)–C(2)	119(1)	Se(5)–C(1)–C(3)	119(1)
C(2)–C(1)–C(3)	121(1)	Se(6)–C(2)–C(1)	124(1)
Se(6)–C(2)–C(5)	112(1)	C(1)–C(2)–C(5)	122(1)
7			
Ir–Se(1)	2.3494(7)	Ir–Se(2)	2.3520(7)
Ir–C(Cp*)	2.140(6)–2.187(6)	Se(1)–C(1)	1.885(6)
Se(2)–C(2)	1.880(6)	C(1)–C(2)	1.339(8)
Se(1)–Ir–Se(2)	89.22(2)	Ir–Se(1)–C(1)	104.2(2)
Ir–Se(2)–C(2)	103.7(2)	Se(1)–C(1)–C(2)	120.7(5)
Se(1)–C(1)–C(3)	114.2(4)	C(2)–C(1)–C(3)	125.0(5)
Se(2)–C(2)–C(1)	122.1(4)	Se(2)–C(2)–C(4)	113.7(4)
C(1)–C(2)–C(4)	124.2(6)		
8			
Ir–Se(1)	2.4683(4)	Ir–Se(2)	2.4787(4)
Ir–C(7)	2.039(4)	Ir–C(Cp*)	2.187(4)–2.242(4)
Se(1)–C(1)	1.873(4)	Se(2)–C(2)	1.937(4)
Se(2)–C(8)	1.928(4)	C(1)–C(2)	1.340(5)
C(7)–C(8)	1.336(6)		
Se(1)–Ir–Se(2)	86.18(1)	Se(1)–Ir–C(7)	87.9(1)
Se(2)–Ir–C(7)	68.9(1)	Ir–Se(1)–C(1)	103.2(1)
Ir–Se(2)–C(2)	104.1(1)	Ir–Se(2)–C(8)	77.5(1)
C(2)–Se(2)–C(8)	99.2(2)	Se(1)–C(1)–C(2)	126.5(3)
Se(1)–C(1)–C(3)	112.3(3)	C(2)–C(1)–C(3)	121.2(4)
Se(2)–C(2)–C(1)	118.2(3)	Se(2)–C(2)–C(4)	117.7(3)
C(1)–C(2)–C(4)	124.1(4)	Ir–C(7)–C(8)	109.9(3)
Ir–C(7)–C(9)	125.5(3)	C(8)–C(7)–C(9)	124.6(4)
Se(2)–C(8)–C(7)	103.1(3)	Se(2)–C(8)–C(10)	120.7(3)
C(7)–C(8)–C(10)	135.9(4)		

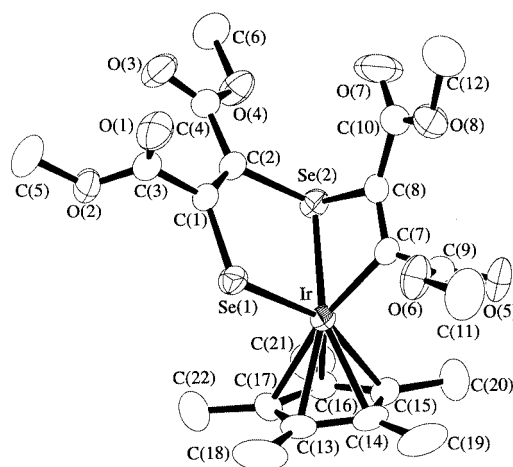
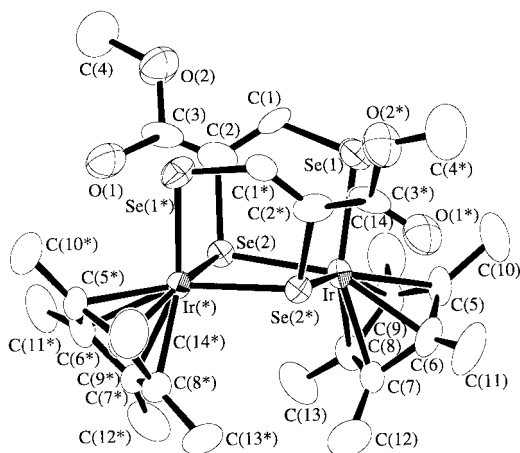


Fig. 4 Molecular structure of complex 8.

Se(2), C(1), and C(2) atoms are essentially coplanar with deviations less than 0.44 Å. The two diselenolene rings are not parallel; for example, the dihedral angle between the Ir–Se(1)–Se(2)

Table 3 Bond distances (Å) and angles (°) in complex **10**

Ir–Se(1)	2.451(2)	Ir–Se(2)	2.461(2)
Ir–Se(2*)	2.496(1)	Ir–C(Cp*)	2.19(1)–2.22(1)
Se(1)–C(1)	1.91(2)	Se(2)–C(2)	1.97(1)
C(1)–C(2)	1.36(2)		
Se(1)–Ir–Se(2)	88.32(5)	Se(1)–Ir–Se(2*)	95.83(5)
Se(2)–Ir–Se(2*)	81.37(5)	Ir–Se(1)–C(1)	102.2(5)
Ir–Se(2)–Ir(*)	98.12(5)	Ir–Se(2)–C(2)	102.7(5)
Ir(*)–Se(2)–C(2)	110.0(4)	Se(1)–C(1)–C(2)	123(1)
Se(2)–C(2)–C(1)	119(1)	Se(2)–C(2)–C(3)	115(1)

**Fig. 5** Molecular structure of complex **10**.

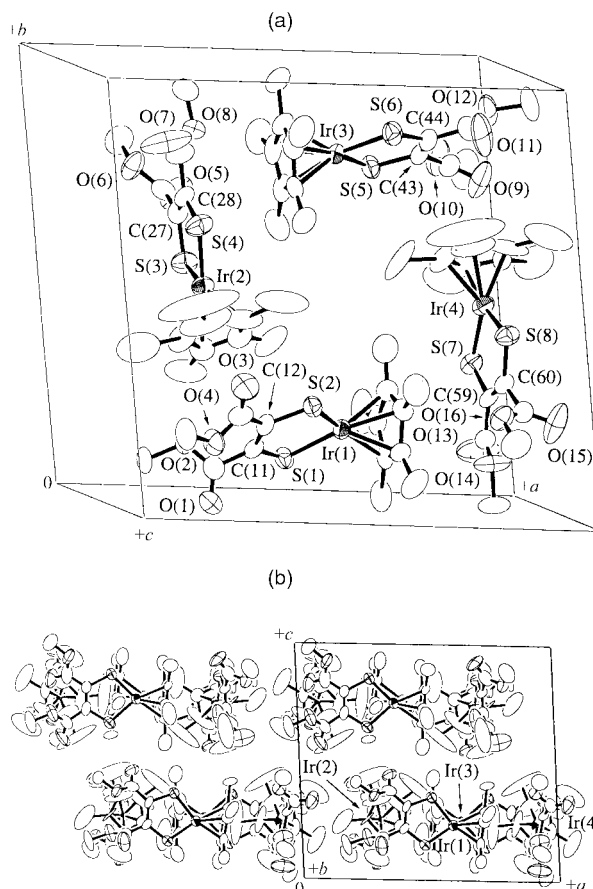
and Ir*–Se(1)*–Se(2)* planes is 19°. The Ir atom has a three-legged piano stool geometry. The two Ir–Se bond lengths in the diselenolene unit are identical (2.451(2) and 2.461(2) Å), and slightly shorter than that connecting the two diselenolene units (2.496(1) Å). These bond lengths as well as the Se–Ir–Se angles varying from 81.4 to 95.8° are not unusual.

Crystal structures of dithiolene complexes

The structures of the dithiolene complexes **11** and **13** have also been confirmed by X-ray analyses. The X-ray analysis of **11** prepared from [IrCp*(PMe₃)(S₄)] (see above) was reported previously.¹³ However, the two sets of crystallographic data differ significantly. The crystal analysed here contains four essentially identical, but crystallographically independent molecules of **11** in contrast to only one independent molecule in the previous X-ray study. Furthermore, an interesting feature has been found with respect to the packing of the four molecules in the crystal in the present study (see below). The IrS₂C₂ rings are nearly coplanar and these planes are almost perpendicular to the Cp* rings (88–89°); the Ir–S bond distances and S–Ir–S angles are shorter and smaller than the Ir–Se bond lengths and the Se–Ir–Se angle in the congener **7**.

In the crystal of complex **13** there exist two crystallographically independent molecules whose structures are essentially identical. Complex **13** has apparently a monomeric structure, which presents a sharp contrast to its selenium analogue **10** existing as a dimer in a solid state. As summarized in Table 4, the important bonding parameters in **13** are similar to those in **11**. Planar metal dithiolene fragments are commonly observed in many mononuclear dithiolene complexes, although those having a significantly puckered five-membered ring about the S–S vector are also known, e.g. [Ti(MeC₅H₄)₂{S₂C₂(CO₂Me)₂}] and related compounds.¹⁶

Interestingly, in the crystal of complex **11** the four molecules form a square, in which each molecule is oriented in such a manner that the Cp* ring becomes almost parallel to the dithiolene plane in the neighboring molecule with dihedral angles varying from 2 to 7° (Fig. 6a), indicating the presence of π

**Fig. 6** (a) The structures of the four independent molecules of complex **11** in the unit cell. (b) Packing in the crystal viewed along the *b* direction.

stacking between the Cp* and dithiolene groups. The distances of the cyclopentadienyl C atoms from the dithiolene plane are in the range 3.6–4.2 Å. In the crystal this planar unit containing four molecules of **11** is parallel to the *ab* plane and is packed so as to have a layered structure (Fig. 6b). By contrast, in the crystal of **13** two independent molecules are present in close proximity. Similarly, the Cp* ring of one molecule is almost parallel to the dithiolene ring in the other molecule with a dihedral angle of 7° (Fig. 7). The separations of the atoms in the dithiolene ring from the cyclopentadienyl plane are calculated to be 3.4–4.1 Å.

Experimental

General

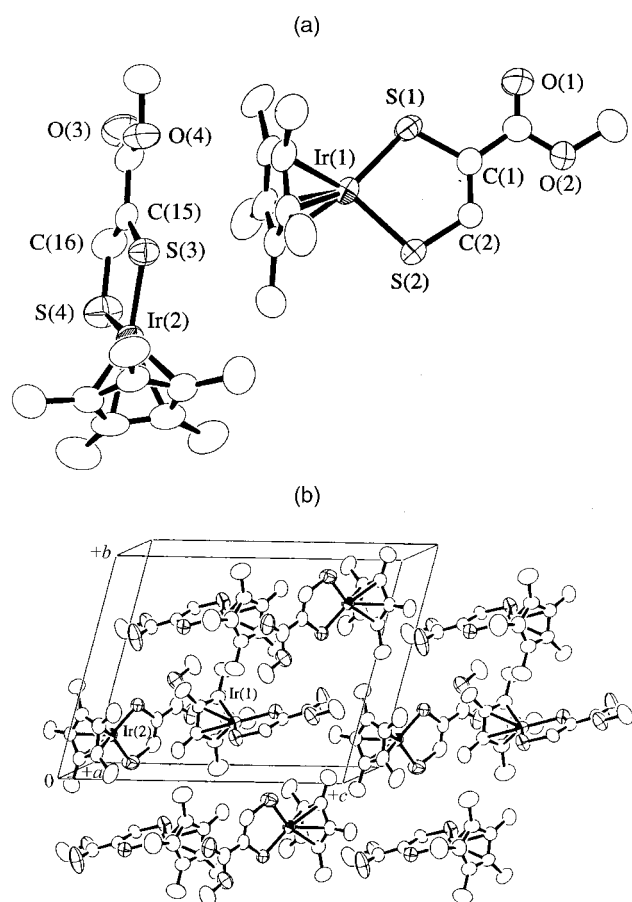
All manipulations were conducted under an atmosphere of nitrogen. IR and NMR spectra were recorded on JASCO FT/IR-420 and JEOL LA-400 spectrometers. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer. Amounts of solvating molecules in the crystals were determined by the X-ray analyses and NMR measurement. Complex **1**, [ClCp*Rh(μ-Cl)₂RhCp*Cl],¹⁷ and Li₂E_{*n*} (E = Se^{16,18} or S¹⁸; *n* = 2–5) were prepared according to the literature methods.

Syntheses

[Cp*Ir(μ-Se₄)₂IrCp*] 2. Gray Se (1.74 g, 22.0 mmol) was suspended in THF (200 cm³) and treated with 1.0 M Li[BHET₃] in THF (11 cm³, 11 mmol) for 1 h at room temperature. The resultant dark brown solution was warmed to 50 °C and complex **1** (1.99 g, 2.50 mmol) was added. After stirring for 1 h at 50 °C, the solvent was removed under reduced pressure and the residue extracted with benzene. Addition of methanol to the con-

Table 4 Selected bond distances (Å) and angles (°) in complexes **11** and **13**

11			
Ir(1)–S(1)	2.238(5)	Ir(1)–S(2)	2.223(5)
Ir(1)–C(Cp*)	2.16(2)–2.20(2)	Ir(2)–S(3)	2.230(5)
Ir(2)–S(4)	2.221(5)	Ir(2)–C(Cp*)	2.10(2)–2.29(2)
Ir(3)–S(5)	2.221(5)	Ir(3)–S(6)	2.235(5)
Ir(3)–C(Cp*)	2.14(2)–2.23(2)	Ir(4)–S(7)	2.213(6)
Ir(4)–S(8)	2.239(5)	Ir(4)–C(Cp*)	2.11(3)–2.16(2)
S(1)–C(11)	1.66(2)	S(2)–C(12)	1.72(2)
S(3)–C(27)	1.74(2)	S(4)–C(28)	1.70(2)
S(5)–C(43)	1.75(2)	S(6)–C(44)	1.70(2)
S(7)–C(59)	1.73(2)	S(8)–C(60)	1.69(2)
C(11)–C(12)	1.42(2)	C(27)–C(28)	1.35(3)
C(43)–C(44)	1.45(3)	C(59)–C(60)	1.38(2)
S(1)–Ir(1)–S(2)	87.4(2)	S(3)–Ir(2)–S(4)	87.6(2)
S(5)–Ir(3)–S(6)	87.2(2)	S(7)–Ir(4)–S(8)	87.3(2)
Ir(1)–S(1)–C(11)	106.2(7)	Ir(1)–S(2)–C(12)	107.3(6)
Ir(2)–S(3)–C(27)	105.8(6)	Ir(2)–S(4)–C(28)	106.2(8)
Ir(3)–S(5)–C(43)	107.5(7)	Ir(3)–S(6)–C(44)	106.7(8)
Ir(4)–S(7)–C(59)	106.8(7)	Ir(4)–S(8)–C(60)	106.4(6)
13			
Ir(1)–S(1)	2.228(2)	Ir(1)–S(2)	2.243(2)
Ir(1)–C(Cp*)	2.152(8)–2.199(8)	Ir(2)–S(3)	2.227(2)
Ir(2)–S(4)	2.241(2)	Ir(2)–C(Cp*)	2.160(8)–2.198(8)
S(1)–C(1)	1.741(7)	S(2)–C(2)	1.700(8)
S(3)–C(15)	1.743(8)	S(4)–C(16)	1.699(9)
C(1)–C(2)	1.336(10)	C(15)–C(16)	1.32(1)
S(1)–Ir(1)–S(2)	87.52(7)	S(3)–Ir(2)–S(4)	87.41(8)
Ir(1)–S(1)–C(1)	105.5(3)	Ir(1)–S(2)–C(2)	105.4(3)
Ir(2)–S(3)–C(15)	105.7(3)	Ir(2)–S(4)–C(16)	105.2(3)

**Fig. 7** The structures of two independent molecules of complex **13** (a) and its packing in the crystal (b).

concentrated extract gave dark brown crystals of **2**·C₆H₆ (1.36 g, 40%). ¹H NMR (CDCl₃): δ 1.97 and 1.71 (s, 15 H each, Cp*) and 7.36 (s, 6 H, C₆H₆). Found: C, 22.71; H, 2.64. C₁₃H₁₈IrSe₄ requires C, 22.88; H, 2.66%.

[Cp*Ir(μ-S₄)₂IrCp*] 3. *Method 1.* To a solution of Li₂S₄ prepared from S₈ (642 mg, 2.50 mmol) and Li[BHET₃] in THF (1.0 M, 10 cm³, 10 mmol) were added THF (20 cm³) and then complex **1** (2.00 g, 2.51 mmol). The mixture was continuously stirred at room temperature for 20 h and then evaporated to dryness under reduced pressure. The residue was extracted with CH₂Cl₂ and hexane added to the concentrated extract to give **3**·CH₂Cl₂ as red-brown crystals (1.07 g, 47%). ¹H NMR (CDCl₃): δ 1.97 and 1.73 (s, 15 H each, Cp*) and 5.30 (s, 2 H, CH₂Cl₂). Found: C, 25.69; H, 3.24. C₂₁H₃₂Cl₂Ir₂S₈ requires C, 25.32; H, 3.24%.

Method 2. To a suspension of [ClCp*Ir(μ-SH)₂IrCp*Cl] (79 mg, 0.099 mmol) and S₈ (26 mg, 0.10 mmol) in toluene (10 cm³) was added NEt₃ (0.056 cm³, 0.40 mmol) at –78 °C and the mixture gradually warmed to room temperature with stirring. The resultant red-brown mixture was filtered and the filtrate evaporated to dryness *in vacuo*. The residue was crystallized from benzene–hexane. Yield of **3**·C₆H₆: 53 mg, 58%. Found: C, 31.87; H, 3.60. C₁₃H₁₈IrS₄ requires C, 31.56; H, 3.67%.

[Cp*Rh(μ-S₄)₂RhCp*] 5. To a CH₂Cl₂ solution (5 cm³) of [ClCp*Rh(μ-Cl)₂RhCp*Cl] (249 mg, 0.4 mmol) was added Li₂S₅ (1.0 mmol) prepared from Li[BHET₃] in THF (2.0 mmol; 2 cm³) and sulfur (161 mg, 5.0 mmol) and the mixture stirred for 20 h. The residue upon evaporation was extracted with benzene and hexane added to the extract to give a black oil and red-purple solution. The solution was separated from the oil and kept at –20 °C, giving black crystals of complex **5** in 8% yield after several days. Owing to the presence of a small amount of by-product indicated by the ¹H NMR spectrum, the C analysis was not satisfactory. ¹H NMR (CDCl₃): δ 1.84 and 1.68 (s, 15 H each, Cp*). Found: C, 39.49; H, 4.47. C₁₀H₁₅RhS₄ requires C, 38.51; H, 4.47%.

Reactions of complex 2. *With an equimolar amount of DMAD.* To a THF solution (25 cm³) of complex **2**·C₆H₆ (124 mg, 0.0910 mmol) was added DMAD (0.014 cm³, 0.11 mmol) at 0 °C. The mixture was slowly warmed to room temperature and continuously stirred for 1 day. The resultant mixture was filtered and the filtrate containing **6**, **7**, and unchanged **2** in 6 : 4 : 3 molar ratio by ¹H NMR spectroscopy was concentrated. Careful addition of hexane gave only **6** as dark brown crystals (12 mg, 10%). ¹H NMR (CDCl₃): δ 1.63 and 1.64 (s, 15 H each, Cp*), 3.64 and 3.89 (s, 3 H each, OMe). IR (KBr): 1682 [ν(C=O)]; 1518 [ν(C=C)]; 1243 and 1192 cm^{–1} [ν(C–O)]. Found: C, 24.56; H, 2.70. C₁₃H₁₈IrO₂Se₃ requires C, 24.57; H, 2.86%.

With 2 equivalents of DMAD. Complex **2** (68 mg, 0.050 mmol) was treated with DMAD (0.012 cm³, 0.10 mmol) in THF (7 cm³) in an analogous manner. The ¹H NMR spectrum of the resultant mixture showed the presence of **6**, **7**, and **8** in the molar ratio 3 : 9 : 1. Careful addition of hexane afforded only **7** in a pure form (17 mg, 28%). ¹H NMR (CDCl₃): δ 2.07 (s, 15 H, Cp*) and 3.89 (s, 6 H, OMe). ⁷⁷Se NMR (CDCl₃, relative to Me₂Se): δ 857 (s). IR (KBr): 1708 [ν(C=O)]; 1523 [ν(C=C)] and 1234 cm^{–1} [ν(C–O)]. Found: C, 30.53; H, 3.22. C₁₆H₂₁IrO₄Se₂ requires C, 30.63; H, 3.37%.

With a large excess of DMAD. A THF solution (6 cm³) of complex **2**·C₆H₆ (52 mg, 0.038 mmol) and DMAD (0.046 cm³, 0.38 mmol) was stirred overnight at room temperature. The resultant mixture was filtered and hexane added to the filtrate to deposit **8** as orange crystals (39 mg, 67%). ¹H NMR (CDCl₃): δ 1.88 (s, 15 H, Cp*), 3.63, 3.74, 3.78, and 3.89 (s, 3 H each, OMe). IR (KBr): 1730 and 1694 [ν(C=O)]; 1557 and 1513 [ν(C=C)] and 1243 cm^{–1} [ν(C–O)]. Found: C, 34.18; H, 3.38. C₂₂H₂₇IrO₅Se₂ requires C, 34.34; H, 3.54%.

Table 5 Crystal data for complexes **2**·C₆H₅Me, **6**, **7**, **8**

	2 ·C ₆ H ₅ Me	6	7	8
Formula	C ₂₇ H ₃₈ Ir ₂ Se ₈	C ₂₆ H ₃₆ Ir ₂ O ₄ Se ₆	C ₁₆ H ₂₁ IrO ₄ Se ₂	C ₂₂ H ₂₇ IrO ₈ Se ₂
<i>M</i>	1378.72	1270.77	627.48	769.59
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	8.519(4)	9.523(1)	11.977(1)	9.951(1)
<i>b</i> /Å	14.081(3)	11.119(1)	11.6244(8)	10.3826(8)
<i>c</i> /Å	14.262(6)	17.255(3)	15.223(1)	12.707
<i>α</i> /°	95.60(2)	100.92(1)		87.707(8)
<i>β</i> /°	94.51(5)	94.12(1)	112.210(6)	87.033(9)
<i>γ</i> /°	91.88(3)	113.82(1)		77.443(7)
<i>U</i> /Å ³	1695(1)	1618.6(5)	1962.2(3)	1279.2(2)
<i>Z</i>	2	2	4	2
<i>μ</i> (Mo-Kα)/cm ^{−1}	164.6	150.1	105.5	81.22
Reflections collected	3458	7882	4695	6200
Unique reflections used [<i>I</i> > 3.00σ(<i>I</i>)]	1658	4823	3435	5017
<i>R</i>	0.057	0.052	0.029	0.034
<i>R</i> _w	0.059	0.055	0.026	0.032

With 1 equivalent of MAMC. A THF solution (4 cm³) of complex **2**·C₆H₆ (137 mg, 0.100 mmol) and MAMC (0.0083 cm³, 0.10 mmol) was stirred at room temperature for 1 day. The resultant mixture was shown to contain **9**, **10**, and unchanged **2** in the molar ratio of 8:4:3 from the ¹H NMR spectrum of the evaporated residue. Complex **9** was isolated in quite low yield as dark brown crystals and characterized by preliminary X-ray analysis (see below) and the spectral data. ¹H NMR (CDCl₃): δ 1.56 and 1.62 (s, 15 H each, Cp*), 3.66 (s, 3 H, OMe) and 9.43 (s, 1 H, CH). IR (KBr): 1682 [ν(C=O)]; 1507 [ν(C=C)] and 1239 cm^{−1} [ν(C–O)].

With a large excess of MAMC. A THF solution of complex **2**·C₆H₆ (137 mg, 0.100 mmol) and MAMC (0.083 cm³, 1.0 mmol) was refluxed for 3 h. The resultant mixture was filtered and hexane added to the concentrated filtrate to precipitate red crystals of **10** (64 mg, 56%). ¹H NMR (CDCl₃): δ 2.09 (s, 30 H, Cp*), 3.86 (s, 6 H, OMe) and 10.16 (s, 2 H, CH). ⁷⁷Se NMR (CDCl₃, relative to Me₂Se): δ 846 and 771 (s, 1Se each). IR (KBr): 1680 [ν(C=O)]; 1519 [ν(C=C)]; 1243 and 1192 cm^{−1} [ν(C–O)]. Found: C, 29.55; H, 3.36. C₁₄H₁₉IrO₂Se₂ requires C, 29.53; H, 3.36%.

Reactions of complex 3. With DMAD. A THF solution (5 cm³) of complex **3**·C₆H₆ (99 mg, 0.10 mmol) and DMAD (0.025 cm³, 0.20 mmol) was stirred at room temperature for 2 days. The ¹H NMR spectrum of the crude products indicated that ca. 60% of **3** remained. Hence, more DMAD (0.037 cm³, 0.30 mmol) was added and the mixture stirred at room temperature for 2 days. From the mixture in which more than 80% of **3** was consumed, the solvent was removed under reduced pressure and the residue crystallized from benzene–hexane, giving **11** as the reddish brown crystals (29 mg, 27%). ¹H NMR (CDCl₃): δ 2.13 (s, 15 H, Cp*) and 3.89 (s, 6 H, OMe). IR (KBr): 1718 and 1707 [ν(C=O)]; 1239 cm^{−1} [ν(C–O)]. Found: C, 36.08; H, 3.90. C₁₆H₂₁IrO₄S₂ requires C, 36.01; H, 3.97%.

With a large excess of DMAD. Complex **3**·C₆H₆ (99 mg, 0.10 mmol) and DMAD (0.123 cm³, 1.0 mmol) in THF (5 cm³) were stirred at room temperature for 7 days. The solvent was removed under reduced pressure and the residue crystallized from benzene–hexane in the presence of an excess of DMAD to give **12** as orange-red crystals (59 mg, 44%). ¹H NMR (CDCl₃): δ 1.87 (s, 15 H, Cp*), 3.85, 3.79, 3.76, and 3.64 (s, 3 H each, OMe). IR (KBr): 1735, 1704, and 1691 [ν(C=O)]; 1569 [ν(C=C)] and 1251 cm^{−1} [ν(C–O)]. Found: C, 39.51; H, 3.84. C₂₂H₂₇IrO₈S₂ requires C, 39.10; H, 4.03%.

With MAMC. A THF solution (5 cm³) containing complex **3**·C₆H₆ (92 mg, 0.093 mmol) and MAMC (0.018 cm³, 0.20 mmol) was stirred at 50 °C for 2 days. Since a significant amount of unchanged **3** remained, an additional amount of

Table 6 Crystal data for complexes **10**, **11**, **13**

	10	11	13
Formula	C ₂₈ H ₃₈ Ir ₂ O ₄ Se ₄	C ₁₆ H ₂₁ IrO ₄ S ₂	C ₁₄ H ₁₉ IrO ₂ S ₂
<i>M</i>	1138.88	533.68	475.64
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbcm</i> (no. 60)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	19.843(5)	16.064(2)	9.237(2)
<i>b</i> /Å	9.233(2)	16.083(2)	12.154(3)
<i>c</i> /Å	17.291(2)	16.387(1)	15.017(3)
<i>α</i> /°		115.234(7)	76.46(2)
<i>β</i> /°		92.887(9)	79.22(1)
<i>γ</i> /°		91.30(1)	87.65(2)
<i>U</i> /Å ³	3167.6(10)	3820.2(7)	1610.2(6)
<i>Z</i>	4	8	4
<i>μ</i> (Mo-Kα)/cm ^{−1}	130.5	72.42	85.69
Reflections collected	4080	18158	7819
Unique reflections used [<i>I</i> > 3.00σ(<i>I</i>)]	2380	8972	4761
<i>R</i>	0.053	0.063	0.034
<i>R</i> _w	0.061	0.081	0.032

MAMC (0.018 cm³, 0.20 mmol) was syringed into the mixture, which was continuously stirred at 50 °C for 2 more days. After the solvent was removed under reduced pressure, the residue was crystallized from toluene–hexane at −20 °C, affording **13** slowly as red crystals (41 mg, 47%). ¹H NMR (CDCl₃): δ 2.15 (s, 15 H each, Cp*), 3.86 (s, 3 H, OMe) and 9.33 (s, 1 H, CH). IR (KBr): 1697 [ν(C=O)]; 1259, 1236, and 1207 cm^{−1} [ν(C–O)]. Found: C, 35.75; H, 3.97. C₁₄H₁₉IrO₂S₂ requires C, 35.35; H, 4.03%.

X-Ray diffraction studies

Single crystal X-ray analyses of complexes **2**, **6**, **7**, **8**, **10**, **11**, and **13** were carried out by a Rigaku AFC7R diffractometer equipped with a Mo-Kα source at room temperature. Details of crystal and data collection parameters are summarized in Tables 5 and 6.

Structure solution and refinements were done by using the TEXSAN program package.¹⁹ The positions of the non-hydrogen atoms determined by DIRDIF PATTY²⁰ were refined anisotropically. For complex **2** all C atoms were treated isotropically. The C(6) atom in **6** found at two disordered positions was refined by use of the occupancies 0.60 for C(6a) and 0.40 for C(6b). Hydrogen atoms were placed at ideal positions and included in the final stages of refinements with fixed parameters.

CCDC reference number 186/2159.

See <http://www.rsc.org/suppdata/dt/b0/b004404k/> for crystallographic files in .cif format.

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