DALTON
FULL PAPER

Nucleophilic addition and substitution reactions on the sulfur atoms bound to two Ir atoms. Conversion of a hydrosulfido complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}SH)_3]Cl$ into a series of diiridium complexes with bridging thiolato ligands

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The hydrosulfido-bridged diiridium complex $[Cp^*Ir(\mu\text{-}SH)_3IrCp^*]Cl$ **2** ($Cp^* = \eta^5\text{-}C_5Me_5$) reacted with an excess of CH_2=CHX (X = COMe, SO_2Ph, COOMe, CN) in the presence of NEt_3 (4 equiv) in MeCN to afford the diiridium complexes $[Cp^*Ir(\mu\text{-}SCH_2CH_2X)_3IrCp^*]Cl$ **4**, which contain three bridging thiolato ligands derived from the Michael addition of the μ-SH ligands in **2** to the activated alkenes. In contrast, when only 2 equiv of CH_2=CHX (X = SO_2Ph, CN) were allowed to react with **2** under analogous conditions, sulfido–thiolato complexes $[Cp^*Ir(\mu\text{-}S)(\mu\text{-}SCH_2CH_2X)_2IrCp^*]$ **5** were obtained exclusively. Reaction of **5d** (X = CN) with neat $ClCH_2CH_2Cl$ and that of **2** with CH_2=CHCN in $ClCH_2CH_2Cl$ in the presence of NEt_3 both gave a mixed-thiolato complex $[Cp^*Ir(\mu\text{-}SCH_2CH_2Cl)(\mu\text{-}SCH_2CH_2CN)_2IrCp^*]Cl$ **6**. Diiridium complexes with bridging dithiolato ligands were also obtainable from **2**, which include $[Cp^*Ir(\mu\text{-}SCH_2CH_2S)(\mu\text{-}SCH_2CH_2Cl)IrCp^*]Cl$ **7** from the reaction with $ClCH_2CH_2Cl/NEt_3$ along with $[Cp^*Ir\{\mu\text{-}SCH_2CH_2CH(OH)S\}(\mu\text{-}SCH_2CH_2CHO)IrCp^*]Cl$ and $[Cp^*Ir\{\mu\text{-}SCHPhCH_2CH(OH)S\}(\mu\text{-}S)IrCp^*]$ **9** afforded by treatment with α,β-unsaturated aldehydes CH_2=CHCHO and PhCH=CHCHO, respectively. Reaction of **2** with ethylene sulfide in the presence of NEt_3 also yielded a diiridium complex with bridging dithiolato ligands $[Cp^*Ir(\mu\text{-}SCH_2CH_2S)_2IrCp^*]$ **10**. Detailed structures have been determined by X-ray analyses for **4b** (X = SO_2Ph), **5d**, **9**, and **10**, as well as the PF_6 salts of **6** and **7**.

Introduction

Previous studies on the syntheses and reactivities of dinuclear Ru, Ir, and Rh complexes with two or three bridging thiolato ligands such as $[Cp^*MCl(\mu\text{-}SR)_2MCp^*Cl]$ (M = Ru,[1] Ir,[2] Rh;[2,3] R = alkyl; $Cp^* = \eta^5\text{-}C_5Me_5$), $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]Cl$ (R = aryl),[1] $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]$ (R = alkyl, aryl),[4] and $[Cp^*Ir(\mu\text{-}SEt)_3IrCp^*]Cl$[2] have been extended more recently to those on their hydrosulfido analogues, $[Cp^*MCl(\mu\text{-}SH)_2MCp^*Cl]$ **1** (M = Ru,[5] Ir, Rh[6]) and $[Cp^*M(\mu\text{-}SH)_3MCp^*]Cl$ (M = Ir **2**, Rh **3**).[6] Hydrosulfido complexes are of particular interest because of their possible relevance to the species playing an important role in certain industrial and biological catalysis, *e.g.* hydrodesulfurization of petroleum distillates[7] and enzymatic nitrogen fixation.[8] However, the chemistry of hydrosulfido complexes[9] has been explored poorly, as compared to that of thiolato complexes.

Reactions of the hydrosulfido ligands can be characterised by the facile cleavage of their S–H bonds. We have demonstrated in previous papers that **1** can serve as versatile precursors in the preparation of a variety of sulfido-bridged homo- and heterometallic clusters.[10] For example, treatment of **1** with excess NEt_3 affords readily the cubane-type clusters $[(Cp^*M)_4(\mu_3\text{-}S)_4]$ through dehydrochlorination of **1** followed by dimerization of the coordinatively unsaturated species $\{(Cp^*M)_2(\mu\text{-}S)_2\}$ generated *in situ*.[11] Furthermore, since this dimerization is considerably slower for M = Ru than for M = Rh and Ir, treatment of **1** (M = Ru) with NEt_3 in the presence of alkynes RC≡CR′ results in the formation of dinuclear dithiolene complexes $[(Cp^*Ru)_2(\mu\text{-}S_2C_2RR')]$,[11a] although **1** (M = Rh, Ir) also gives the cubane-type cluster under these conditions through the rapid dimerization of the dehydrochlorinated species.

Although reactions of **2** and **3** under the analogous conditions are elusive, it has been found that, in the presence of excess NEt_3, **2** reacted with a range of activated alkenes to give the corresponding thiolato-bridged diiridium complexes, resulting from the addition of the hydrosulfido groups in **2** to the C=C double bond of the alkenes. In this paper, we wish to describe the details of these reactions along with the characterization of the produced diiridium complexes. Part of this work has appeared recently as a communication.[12]

Results and discussion

Formation of diiridium complexes with three bridging thiolato ligands

Treatment of **2** with 4 equiv of vinyl compounds CH_2=CHX in MeCN at −40 °C in the presence of 4 equiv of NEt_3 smoothly afforded red reaction mixtures, which were gradually converted into yellow solutions during continuous stirring at room temperature. Work-up of these mixtures afforded the corresponding yellow diiridium complexes $[Cp^*Ir(\mu\text{-}SCH_2CH_2X)_3IrCp^*]Cl$ (X = COMe **4a**, SO_2Ph **4b**) in high yields (Scheme 1). Reaction of **2** with methyl acrylate (X = COOMe) required more forcing reaction conditions (40 °C) to complete this Michael-type addition of three SH ligands, whose product was isolated in 58% yield as a PF_6 salt, $[Cp^*Ir(\mu\text{-}SCH_2CH_2COOMe)_3IrCp^*][PF_6]$ **4c′**, after anion metathesis with $[NH_4][PF_6]$ (Scheme 1). In the absence of NEt_3, **2** did not react with these alkenes.

Complexes **4** have been characterized spectroscopically and by elemental analyses, and their structures have been confirmed by the X-ray analysis of **4b**·2MeCN. The ^1H NMR spectra of **4**

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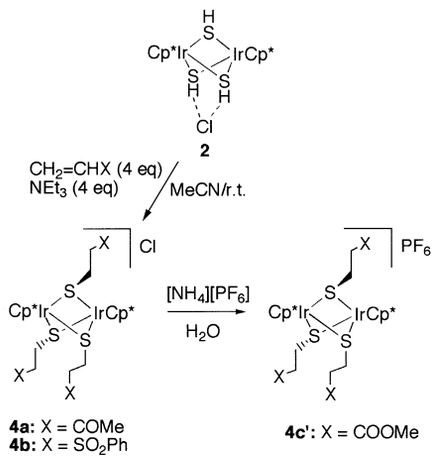
Table 1 Selected interatomic distances (Å) and angles (°) in complex **4b**

Ir(1) ··· Ir(2)	3.3300(4)		
Ir(1)–S(1)	2.398(2)	Ir(1)–S(3)	2.395(2)
Ir(1)–S(5)	2.395(2)	Ir(2)–S(1)	2.400(2)
Ir(2)–S(3)	2.384(2)	Ir(2)–S(5)	2.397(2)
S(1)–Ir(1)–S(3)	75.63(6)	S(1)–Ir(1)–S(5)	77.61(5)
S(3)–Ir(1)–S(5)	77.57(5)	S(1)–Ir(2)–S(3)	75.80(6)
S(1)–Ir(2)–S(5)	77.55(6)	S(3)–Ir(2)–S(5)	77.75(5)
Ir(1)–S(1)–Ir(2)	87.90(5)	Ir(1)–S(3)–Ir(2)	88.34(5)
Ir(1)–S(5)–Ir(2)	88.04(5)		



Scheme 1

show only one singlet due to the Cp* protons, indicating that the two Cp*Ir units are equivalent. Furthermore, appearance of only one set of resonances assignable to the thiolato protons suggests clearly that the three thiolato ligands are also equivalent.

An X-ray analysis has been carried out for **4b** and its structure has been determined in detail (Fig. 1 and Table 1). The

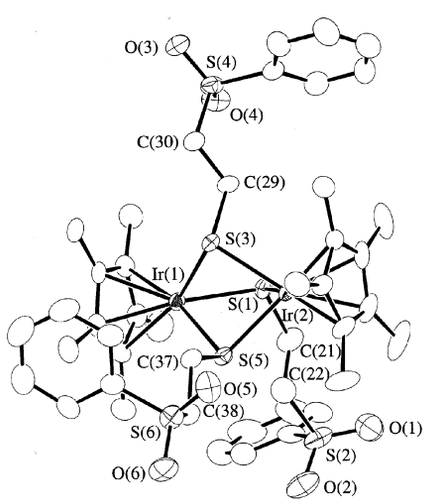


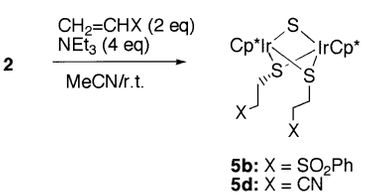
Fig. 1 Structure of the cation in complex **4b**.

cation in **4b** consists of two Cp*Ir units bridged by three $SCH_2CH_2SO_2Ph$ ligands. The two Cp* planes are almost parallel with a dihedral angle of 4.0°. The Ir–Ir distance at 3.3300(4) Å is comparable to that at 3.2954(7) Å in **2**, which is indicative of the absence of any bonding interactions between the two Ir centers. The Ir–S bond lengths ranging from 2.384(2) to 2.400(2) Å are essentially the same as those in **2** (2.395(4)–2.411(4) Å).[6] The orientation of the substituents on the three bridging S atoms is mutually *anti* with respect to the all-adjacent thiolato pairs, *i.e.* the three thiolato ligands are equivalent. In contrast to the dinuclear Ir and Rh complexes bridged by only two thiolato ligands ubiquitously known, those with three thiolate bridges are still rare. For Ir, $[Cp^*Ir(\mu\text{-}SR)_3IrCp^*]Cl$ (R = CF_3, *p*-FC_6H_4,[13] Et[2]) are precedented, but none of their X-ray structures have been reported, although the related Rh cations $[Cp^*Rh(\mu\text{-}SR)_3RhCp^*]^+$ (R = C_6F_5,[13] Me[3]) and the Ir–Rh complex $[Cp^*Ir(\mu\text{-}SPh)_3Rh(L)][ClO_4]_2$ (L = 1,4,7-trithiacyclononane)[14] have been fully characterized. In all of these X-ray analyzed complexes, the three thiolato ligands have C_3 symmetry around the M–M vector and in the latter Ir–Rh complex the Ir–S bond distances are reported to be 2.389(6)–2.405(7) Å with an Ir ··· Rh separation of 3.244(2) Å. Similar triply bridged cores are found in Ru complexes such as $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]^{n+}$ (n = 1, R = aryl;[1a] n = 0, R = alkyl, aryl[4]) and $[(C_6Me_6)Ru(\mu\text{-}SPh)_3Ru(C_6Me_6)]Cl$.[15] It is also noteworthy that the triply bridged species $[\{CpMo(MeCN)\}(\mu\text{-}SMe)_3\{CpMo(MeCN)\}]^+$ is known and extensive reactivities of its dimolybdenum site towards various substrate molecules have been demonstrated.[16]

Related reactions of the bridging hydrosulfido ligands with C=C double bonds reported previously include the treatment of $[\{Fe(CO)_3\}_2(\mu\text{-}SH)_2]$ with CH_2=CHX (X = CN, COMe, COOMe) in the presence of piperidine affording $[\{Fe(CO)_3\}_2(\mu\text{-}SCH_2CH_2X)_2]$[17] as well as the formation of $[(CpMo)_2(\mu,\eta^2\text{-}SCH_2S)(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)]^+$ from $[(CpMo)_2(\mu,\eta^2\text{-}SCH_2S)(\mu\text{-}S)(\mu\text{-}SH)]^+$ and CH_2=CHCN.[18] Analogous addition of the μ-SH group in $[Cp^*Rh(\mu\text{-}CH_2)_2(\mu\text{-}SH)RhCp^*]^+$ to the activated alkynes $R^1C{\equiv}CR^2$ is also known, which yields the alkenylthiolato complexes $[Cp^*Rh(\mu\text{-}CH_2)_2(\mu\text{-}SCR^1{=}CHR^2)RhCp^*][BPh_4]$ ($R^1 = R^2$ = COOMe; R^1 = H, R^2 = COOMe or COOPh).[19]

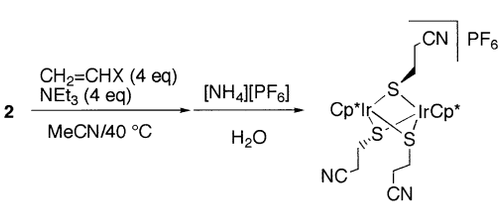
Formation of diiridium sulfido–thiolato complexes

Although the reaction of **2** with 4 equiv of CH_2=CHCN was carried out similarly in the presence of 4 equiv of NEt_3 at room temperature, the red solution initially obtained did not change in color even after 24 h. Work-up of this reaction mixture has shown that not a triply bridged thiolato complex but a sulfido–thiolato complex $[Cp^*Ir(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)_2IrCp^*]$ **5d** is formed as a major product. As expected, when **2** was reacted with only 2 equiv of CH_2=CHCN at room temperature in the presence of 4 equiv of NEt_3, the reaction proceeded more cleanly to give **5d** exclusively, which was isolated as red crystals in 70% yield. In an analogous manner, $[Cp^*Ir(\mu\text{-}S)(\mu\text{-}SCH_2CH_2SO_2Ph)_2IrCp^*]$ **5b** was obtained in 60% yield (eqn. (1)). By



(1)

contrast, when the reaction with 4 equiv of CH_2=CHCN was carried out at 40 °C, a diiridium complex with three thiolato ligands $[Cp^*Ir(\mu\text{-}SCH_2CH_2CN)_3IrCp^*]Cl$ **4d** formed in significant yield. Thus, from the reaction mixture obtained after 70 h followed by anion metathesis by $[NH_4][PF_6]$, **4d′**, a PF_6 salt of **4d**, was isolated in 36% yield along with **5d** in 41% yield (eqn. (2)). Spectroscopic data for **4d′** is consistent with a structure similar to that of **4a**, **4b**, and **4c′**.



(2)

Table 2 Selected interatomic distances (Å) and angles (°) in complex **5d**

Ir(1) ··· Ir(2)	3.324(1)		
Ir(1)–S(1)	2.387(2)	Ir(1)–S(2)	2.395(2)
Ir(1)–S(3)	2.388(3)	Ir(2)–S(1)	2.382(2)
Ir(2)–S(2)	2.394(2)	Ir(2)–S(3)	2.384(2)
S(1)–Ir(1)–S(2)	78.65(7)	S(1)–Ir(1)–S(3)	73.53(9)
S(2)–Ir(1)–S(3)	78.25(8)	S(1)–Ir(2)–S(2)	78.76(8)
S(1)–Ir(2)–S(3)	73.67(8)	S(2)–Ir(2)–S(3)	78.35(8)
Ir(1)–S(1)–Ir(2)	88.36(8)	Ir(1)–S(2)–Ir(2)	87.90(7)
Ir(1)–S(3)–Ir(2)	88.28(8)		

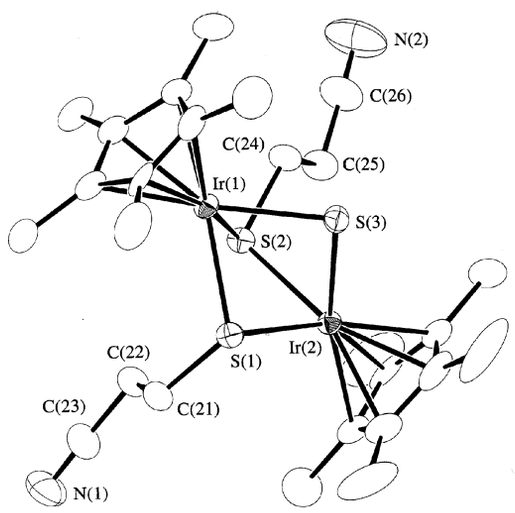


Fig. 2 Molecular structure of complex **5d**.

As described already in a foregoing communication,[12] **5d** has been characterized by X-ray crystallography, whose results are shown in Fig. 2 and Table 2. The core structure of **5d** is quite analogous to that of **4b**. Thus, the two Cp* ligands are almost parallel with a dihedral angle of 9.6°, and the Ir ··· Ir distance at 3.324(1) Å as well as the Ir–S bond lengths in the range 2.382(2)–2.395(2) Å are in good agreement with those in **4b**. As for the Ir–S bond lengths and the Ir–S–Ir angles, no significant differences are observed between those around the thiolato S atoms S(1) and S(2) and those around the sulfido atom S(3). However, with respect to the mutual separations between these three S atoms, the S(1) ··· S(3) distance at 2.858(3) Å is considerably shorter than the other two (S(1) ··· S(2) 3.303(3), S(2) ··· S(3) 3.018(3) Å), because the two cyanoethyl groups with an *anti* configuration are directed towards the site between the S(1) and S(2) atoms and that between the S(2) and S(3) atoms and the remaining site between the S(1) and S(3) atoms is sterically less hindered.

The ^{1}H NMR spectra of **5b** and **5d** exhibit one sharp singlet assignable to the Cp* protons as expected from the X-ray structure clarified for **5d**. In the spectrum of **5b** recorded in C_6D_6 at room temperature, the methylene protons of the two thiolato ligands appear as four signals with the same intensities, which is diagnostic of the *anti* configuration as elucidated by X-ray crystallography for **5d**. However, since these signals are significantly broadened, the orientation of the bridging thiolato ligands in **5b** is presumed to be somewhat non-rigid. For **5d**, the methylene protons were observed as only two broad signals under the similar conditions, which sharpened considerably and separated into four broad signals with the same intensities when recorded at −20 °C in THF-d_8. This indicates that the fluxionality of the two thiolato ligands becomes more rigid at lower temperatures. Non-rigid features of the bridging thiolato ligands are ubiquitously observed for a number of thiolato-bridged multinuclear complexes, which include a closely related diiridium bis(thiolato)–chloro complex $[Cp^*Ir(\mu\text{-}SPr^i)_2(\mu\text{-}Cl)IrCp^*]^+$.[20]

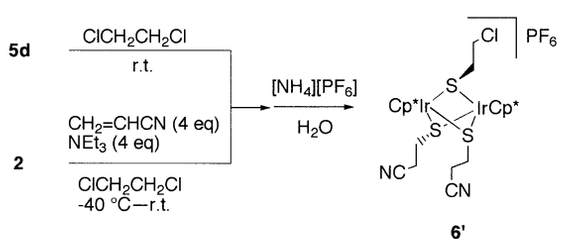
Table 3 Selected interatomic distances (Å) and angles (°) in complex **6′**

Molecule 1			
Ir(1) ··· Ir(2)	3.335(1)		
Ir(1)–S(1)	2.407(6)	Ir(1)–S(2)	2.409(7)
Ir(1)–S(3)	2.400(7)	Ir(2)–S(1)	2.380(6)
Ir(2)–S(2)	2.408(7)	Ir(2)–S(3)	2.395(7)
S(1)–Ir(1)–S(2)	77.1(2)	S(1)–Ir(1)–S(3)	77.0(2)
S(2)–Ir(1)–S(3)	76.4(2)	S(1)–Ir(2)–S(2)	77.6(2)
S(1)–Ir(2)–S(3)	77.6(2)	S(2)–Ir(2)–S(3)	76.6(2)
Ir(1)–S(1)–Ir(2)	88.3(2)	Ir(1)–S(2)–Ir(2)	87.6(3)
Ir(1)–S(3)–Ir(2)	88.1(2)		
Molecule 2			
Ir(3) ··· Ir(4)	3.323(1)		
Ir(3)–S(4)	2.399(6)	Ir(3)–S(5)	2.380(7)
Ir(3)–S(6)	2.375(7)	Ir(4)–S(4)	2.408(6)
Ir(4)–S(5)	2.386(7)	Ir(4)–S(6)	2.382(7)
S(4)–Ir(3)–S(5)	76.3(2)	S(4)–Ir(3)–S(6)	78.2(2)
S(5)–Ir(3)–S(6)	76.7(3)	S(4)–Ir(4)–S(5)	76.0(2)
S(4)–Ir(4)–S(6)	77.9(3)	S(5)–Ir(4)–S(6)	76.4(3)
Ir(3)–S(4)–Ir(4)	87.5(2)	Ir(3)–S(5)–Ir(4)	88.4(3)
Ir(3)–S(6)–Ir(4)	88.6(2)		

For comparison, the reaction of the bis(hydrosulfido) complex **1** (M = Ir) with CH_2=CHCN in the presence of NEt_3 was also attempted. However, the product was the cubane-type cluster $[(Cp^*Ir)_4(\mu_3\text{-}S)_4]$, which is readily available from the reaction of **1** with NEt_3 in the absence of CH_2=CHCN as described above.[11b]

Reactions of sulfido–thiolato complex 5d. The reaction of the isolated sulfido–thiolato complex **5d** with 2 equiv of CH_2=CHCN in the presence of $[NEt_3H]Cl$ was undertaken. The ^{1}H NMR spectrum of this reaction mixture showed the formation of **4d** in high yield, indicating unambiguously that **5d** is the intermediate stage for the conversion of **2** into **4d**.

Meanwhile, it has turned out that **5d** readily reacts with $ClCH_2CH_2Cl$ at room temperature at the considerably nucleophilic sulfido ligand to yield a mixed-thiolato complex $[Cp^*Ir(\mu\text{-}SCH_2CH_2Cl)(\mu\text{-}SCH_2CH_2CN)_2IrCp^*]Cl$ **6**. Complex **6** was also available straightforwardly from **2**, by conducting the reaction with 4 equiv of CH_2=CHCN and NEt_3 at room temperature in $ClCH_2CH_2Cl$ (Scheme 2). Complex **6** has been



Scheme 2

characterized by X-ray analysis using a single crystal of its PF_6 salt (**6′**). Thus, the asymmetric unit contains two independent molecules of **6′**, whose structures are essentially identical. The results are summarized in Table 3 and an ORTEP[21] drawing of one of these two molecules is depicted in Fig. 3. Pertinent bonding parameters associated with the Ir_2S_3 core are nearly the same as those in **4b** containing three $SCH_2CH_2SO_2Ph$ ligands; *e.g.* in **6′**, the Ir ··· Ir distances are 3.335(1) and 3.323(1) Å, while the Ir–S bond lengths vary from 2.380(6)–2.409(7) and 2.375(7)–2.408(6) Å in molecules 1 and 2, respectively.

Subsequent studies on the reactivities of **5d** with other metal complexes have revealed that several homo- and hetero-metallic clusters with bridging sulfido and thiolato ligands can be pre-

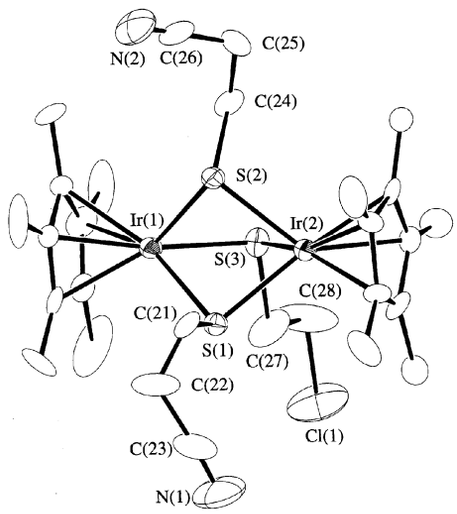
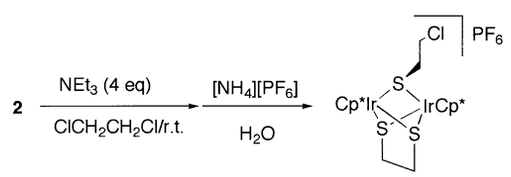


Fig. 3 Structure of the cation in complex **6′**. One of the two independent cations is shown.

pared from **5d**, including $[Cp^*_3RuIr_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)_2Cl]$ previously described briefly.[12] Details of these clusters will be reported separately elsewhere.[22]

Formation of diiridium complexes with bridging dithiolato ligands

Treatment of **2** with 4 equiv of NEt_3 in $ClCH_2CH_2Cl$ at room temperature,yieldedthediiridiumcomplex[Cp*Ir(μ-SCH_2CH_2S)-(μ-SCH_2CH_2Cl)IrCp*]Cl **7**, which was isolated as a PF_6 salt (**7′**) in 67% yield (eqn. (3)). The X-ray analysis of **7′** has shown



clearly that the two Cp*Ir moieties are joined by the three bridging S atoms in the 1,2-ethanedithiolato and chloroethanethiolato ligands (Fig. 4). The pertinent interatomic

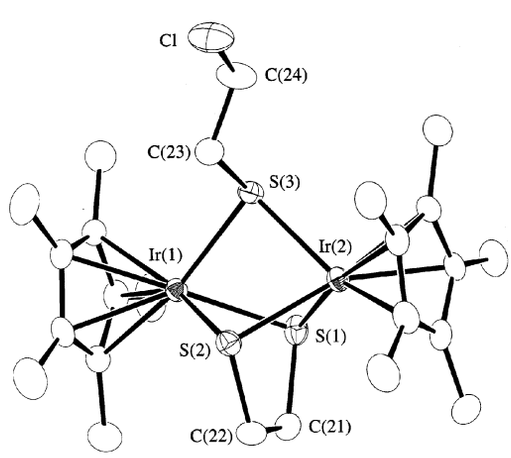


Fig. 4 Structure of the cation in complex **7′**.

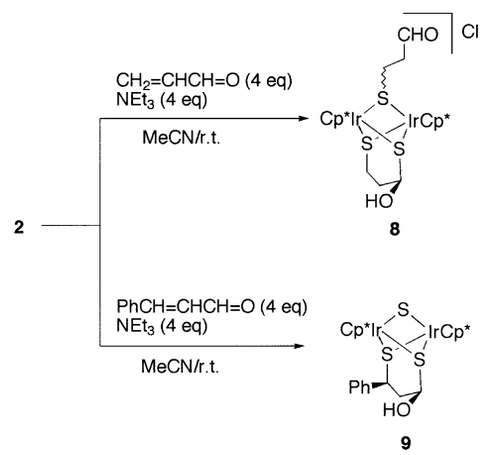
parameters around the Ir and S atoms in **7′** (Table 4) are comparable to those in the bridging thiolato complexes **4b** and **6′** except that the S(1) ··· S(2) distance associated with the chelating ethaneditiolato ligand 2.857(2) Å is considerably smaller

Table 4 Selected interatomic distances (Å) and angles (°) in complex **7′**

Ir(1) ··· Ir(2)	3.3233(6)		
Ir(1)–S(1)	2.398(2)	Ir(1)–S(2)	2.380(2)
Ir(1)–S(3)	2.376(2)	Ir(2)–S(1)	2.397(2)
Ir(2)–S(2)	2.383(2)	Ir(2)–S(3)	2.383(2)
S(1)–Ir(1)–S(2)	73.43(6)	S(1)–Ir(1)–S(3)	77.31(6)
S(2)–Ir(1)–S(3)	79.71(6)	S(1)–Ir(2)–S(2)	73.41(6)
S(1)–Ir(2)–S(3)	77.20(6)	S(2)–Ir(2)–S(3)	79.51(6)
Ir(1)–S(1)–Ir(2)	87.75(5)	Ir(1)–S(2)–Ir(2)	88.50(6)
Ir(1)–S(3)–Ir(2)	88.56(6)		

than the other two; S(1) ··· S(3) 2.982(2), S(2) ··· S(3) 3.048(2) Å. The S(1), S(2), C(21), and C(22) atoms are almost coplanar, and the least-squares plane defined by these four atoms is almost parallel to the Cp* rings with dihedral angles of 0.5 and 0.8°.

It has also been found that the reactions of certain α,β-unsaturated aldehydes with **2** afford diiridium complexes containing a 1,3-propanedithiolato ligand (Scheme 3). Thus, **2** was



Scheme 3

treated with 4 equiv of CH_2=CHCHO in the presence of NEt_3 at room temperature to give [Cp*Ir{μ-$SCH_2CH_2CH(OH)S$}-(μ-SCH_2CH_2CHO)IrCp*]Cl **8** in 47% yield. In this reaction, two acrolein molecules are bound to two bridging S atoms at the β-C atom of the C=C double bond and one of these acrolein moieties further reacts with the remaining third S atom at the carbonyl group to form an hydroxythiolato CH(OH)S chromophore. In the ^{1}H NMR spectrum, the alcoholic and aldehydic protons are each recorded as two signals at δ 7.81 and 7.84 and at δ 9.81 and 9.82, respectively, which is interpreted in terms of the presence of two stereoisomers arising from the orientation of the β-formylethyl group, *viz*. the isomers in which the β-formylethyl substituent is directed toward the remaining S atom with or without the hydroxy group at the α-position. With respect to the other protons in the $CH_2CH_2CH(OH)$ moiety, two sets of signals appeared. The ratio of these two isomers at room temperature is estimated to be *ca.* 1 : 1 from the intensities of these ^{1}H NMR signals. In each of the two diastereomers, the two Cp* ligands are inequivalent to give in total four singlets due to the Cp* protons in the ^{1}H NMR spectrum, although two of these are accidentally overlapping.

Cinnamaldehyde also reacted with **2** under the same conditions. However, only one PhCH=CHCHO molecule was incorporated into the diiridium core (Scheme 3). One bridging S atom binds to the β-C atom of the C=C double bond and then the second bridging S atom reacts with the carbonyl C atom, yielding the corresponding 1,3-propanedithiolato ligand, whereas the third S atom remains as the μ-sulfide. The steric crowding of the Ph group attached to the β-C atom might inhibit the binding of the third S atom to the second

Table 5 Selected interatomic distances (Å) and angles (°) in complex **9**

Ir(1) ··· Ir(2)	3.3328(6)		
Ir(1)–S(1)	2.389(2)	Ir(1)–S(2)	2.371(3)
Ir(1)–S(3)	2.388(3)	Ir(2)–S(1)	2.378(3)
Ir(2)–S(2)	2.354(3)	Ir(2)–S(3)	2.386(3)
S(1)–Ir(1)–S(2)	76.62(9)	S(1)–Ir(1)–S(3)	75.42(9)
S(2)–Ir(1)–S(3)	76.26(10)	S(1)–Ir(2)–S(2)	77.16(9)
S(1)–Ir(2)–S(3)	75.65(9)	S(2)–Ir(2)–S(3)	76.61(9)
Ir(1)–S(1)–Ir(2)	88.71(8)	Ir(1)–S(2)–Ir(2)	89.73(9)
Ir(1)–S(3)–Ir(2)	88.56(9)		

PhCH=CHCHO molecule. Thus, when the product [Cp*Ir{μ-SCHPhCH$_2$CH(OH)S}(μ-S)IrCp*] **9** was treated further with one equiv of sterically unencumbered CH$_2$=CHCHO in the presence of [NEt$_3$H]Cl, the ^{1}H NMR spectrum of the reaction mixture showed that the addition of CH$_2$=CHCHO to the sulfido ligand took place in an expected manner to afford [Cp*Ir{μ-SCHPhCH$_2$CH(OH)S}(μ-SCH$_2$CH$_2$CHO)IrCp*].

Complex **9** has been characterized by an X-ray diffraction study, whose results are shown in Fig. 5 and Table 5. In **9**, the

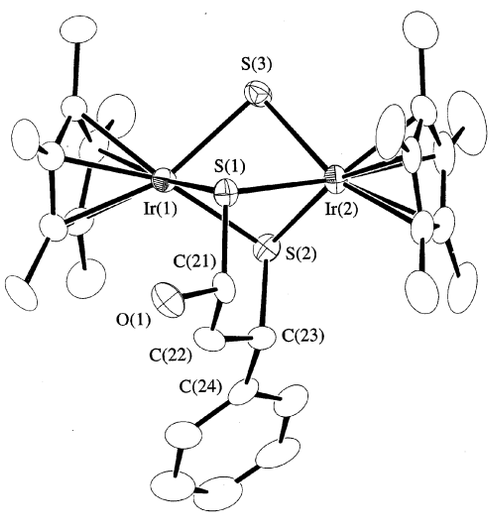
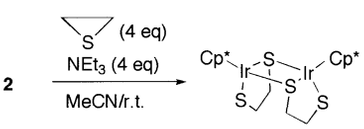


Fig. 5 Molecular structure of complex **9**.

Ir centers separated by 3.3328(6) Å are bridged by the 1,3-propanedithiolato and sulfido ligands. The geometry of the phenyl and hydroxy groups in the propanedithiolato ligand is shown to be mutually *syn*. The ^{1}H NMR spectrum of the reaction mixture also indicated the absence of the other *anti* isomer, *viz*. the present reaction proceeds in a strictly stereoselective manner.

Reaction with ethylene sulfide

Similar treatment of **2** with 4 equiv of ethylene sulfide in the presence of NEt$_3$ as described above yielded a diiridium complex containing two bridging ethanedithiolato ligands [Cp*Ir(μ-SCH$_2$CH$_2$S)$_2$IrCp*] **10** as orange crystals (eqn. (4)).



(4)

Two bridging S atoms each underwent nucleophilic addition to the ethylene sulfide molecule to give the SCH$_2$CH$_2$S ligand, whereas the fate of the remaining SH group in **2** is uncertain. The X-ray analysis of **10** has disclosed that the molecule has a symmetrical structure with a C_2 axis passing through the center

Table 6 Selected interatomic distances (Å) and angles (°) in complex **10**

Ir ··· Ir	3.6544(4)	Ir–S(2)	2.357(1)
Ir–S(1)	2.362(1)	Ir–S(1*)	2.383(1)
S(1)–Ir–S(1*)	78.99(4)	S(1)–Ir–S(2)	86.97(5)
S(1*)–Ir–S(2)	98.73(5)	Ir–S(1)–Ir	100.74(4)

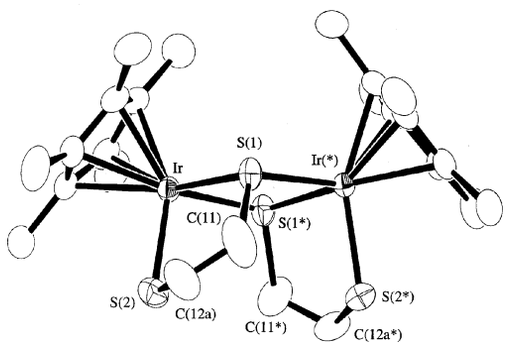


Fig. 6 Molecular structure of complex **10**.

of the Ir–Ir* and S(1)–S(1*) vector (Fig. 6). Thus, **10** has a dimeric structure within the Cp*Ir(η^2-SCH$_2$CH$_2$S) fragment with one S atom coordinating further to the other Ir atom. The Ir–S(1) and Ir–S(2) bond distances are essentially the same (2.362(1) and 2.357(1) Å), but are slightly shorter than the Ir–S(1*) bond length at 2.383(1) Å. The Ir$_2$S$_2$ ring is folded only slightly, the dihedral angle between the two Ir$_2$S planes and that between the two IrS$_2$ planes being 171.3 and 172.8°, respectively. The two Ir atoms are separated by 3.6544(4) Å, indicating the absence of any metal–metal bonding interaction. Important bond distances and angles are summarized in Table 6.

Conclusion

The diiridium complex containing three bridging SH ligands **2** has proved to be an excellent precursor for synthesizing a variety of diiridium complexes with functionalized thiolato bridges. Thus, in the presence of excess NEt$_3$ in MeCN, **2** reacts with CH$_2$=CHX (X = COMe, SO$_2$Ph, COOMe, CN) or α,β-unsaturated aldehydes to afford products formed by the addition of the SH ligands to the C=C and C=O double bonds within these molecules, which include tris(thiolato), sulfido–bis(thiolato), thiolato–dithiolato, or sulfido–dithiolato complexes depending on the nature of the reactants, whereas treatment of **2** with ClCH$_2$CH$_2$Cl in the presence of NEt$_3$ gives a substitution product: diiridium complexes with thiolato–dithiolato bridges.

Experimental

General

All manipulations were carried out under an atmosphere of N$_2$. Solvents were dried by common methods and distilled under N$_2$ just before use. IR and NMR spectra were recorded on JASCO FT/IR 420 and JEOL AL-400 spectrometers, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHN analyzer. Chemicals were commercially obtained and used as received, while **2** was prepared as described previously.[2]

Syntheses

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$COMe)$_3$IrCp*]Cl 4a. To an acetonitrile solution (10 cm^3) of **2** (80 mg, 0.10 mmol) was added CH$_2$=CHCOMe (0.033 cm^3, 0.40 mmol), and the mixture was cooled to −40 °C. Addition of NEt$_3$ (0.056 cm^3, 0.40

mmol) resulted in a spontaneous color change from yellow to red. The mixture was gradually warmed to room temperature and stirred continuously for 24 h. The resultant yellow solution was taken to dryness and the residue was crystallized from MeCN–diethyl ether, affording yellow crystals of **4a**·MeCN (83 mg, 80%). ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 30H, Cp*), 2.00 (s, 3H, MeCN), 2.26 (s, 9H, COMe), 2.75–2.90 (m, 12H, CH_2). IR (KBr): 1705 cm^{-1} [ν(C=O)]. Found: C, 39.09; H, 5.15; N, 1.32. $C_{34}H_{54}NO_3S_3ClIr_2$ requires C, 39.23; H, 5.23; N, 1.35%.

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$SO$_2$Ph)$_3$IrCp*]Cl 4b. This complex was prepared in an analogous manner to that for **4a** from **2** and phenylvinylsulfone in the presence of NEt_3. The yield of **4b**·2MeCN obtained as yellow crystals was 77%. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 30H, Cp*), 2.00 (s, 6H, MeCN), 2.85–2.90, 3.25–3.30 (m, 6H each, CH_2), 7.65–7.93 (m, 15H, Ph). IR (KBr): 1309, 1146 cm^{-1} (SO_2). Found: C, 41.52; H, 4.51; N, 1.57. $C_{48}H_{63}N_2O_6S_6ClIr_2$ requires C, 41.89; H, 4.61; N, 2.04%.

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$COOMe)$_3$IrCp*][PF$_6$] 4c′. Complex **2** (80 mg, 0.10 mmol) was treated with CH_2=CHCOOMe (0.036 cm^3, 0.40 mmol) and NEt_3 (0.056 cm^3, 0.40 mmol) as described above, but the mixture was stirred at 40 °C for 11 h. The product solution was taken to dryness and the residue was redissolved in water. Upon addition of [NH_4][PF_6] (33 mg, 0.20 mmol) with stirring, a yellow solid precipitated, which was filtered off, washed with water, and then dried *in vacuo*. Crystallization from $ClCH_2CH_2Cl$–hexane gave yellow crystals of **4c′** (68 mg, 58%). ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 30H, Cp*), 2.59, 2.87 (t, J = 7.2 Hz, 6H each, CH_2), 3.74 (s, 9H, COOMe). IR (KBr): 1733 [ν(C=O)]; 841, 557 cm^{-1} (PF_6). Found: C, 33.15; H, 4.51. $C_{32}H_{51}O_6PS_3F_6Ir_2$ requires C, 33.21; H, 4.44%.

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$CN)$_3$IrCp*][PF$_6$] 4d′. This complex was prepared from **2** and CH_2=CHCN by the same method as that for preparing **4c′** except for the reaction time which was 70 h. The product **4d′** was obtained as yellow crystals in 36% yield. ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 30H, Cp*), 2.70, 2.95 (t, J = 7.6 Hz, 6H each, CH_2). IR (KBr): 2248 [ν(C≡N)]; 842, 558 cm^{-1} (PF_6). Found: C, 32.76; H, 4.04; N, 4.00. $C_{29}H_{42}N_3PS_3F_6Ir_2$ requires C, 32.91; H, 4.00; N, 3.97%.

Preparation of [Cp*Ir(μ-S)(μ-SCH$_2$CH$_2$SO$_2$Ph)$_2$IrCp*] 5b. Into an acetonitrile solution (10 cm^3) of **2** (80 mg, 0.10 mmol) and phenylvinylsulfone (30 mg, 0.18 mmol) was added NEt_3 (0.056 cm^3, 0.40 mmol) at −40 °C. The mixture was gradually warmed to room temperature and stirred continuously for 24 h. The resulting red suspension was taken to dryness and the residue was extracted with benzene. The extract was evaporated to dryness again and the remaining solid was crystallized from THF–hexane, affording **5b**·0.5THF as red crystals (68 mg, 60%). ^{1}H NMR (C_6D_6): δ 1.48 (s, 30H, Cp*), 2.76, 3.10, 3.50, 3.64 (br, 2H each, CH_2), 6.97 (br, 6H, Ph), 7.91 (br, 4H, Ph). IR (KBr): 1305, 1147 cm^{-1} (SO_2). Found: C, 40.57; H, 4.66. $C_{38}H_{52}O_{4.5}S_5Ir_2$ requires C, 40.55; H, 4.66%.

Preparation of [Cp*Ir(μ-S)(μ-SCH$_2$CH$_2$CN)$_2$IrCp*] 5d. This complex was prepared by the similar treatment of **2** with CH_2=CHCN and NEt_3. The evaporated reaction mixture residue was extracted with benzene and addition of hexane to the concentrated extract afforded **5d** as red crystals in 70% yield. ^{1}H NMR: (C_6D_6) δ 1.47 (s, 30H, Cp*), 2.23 (br pseudo t, 4H, CH_2), 2.4–3.0 (br, 4H, CH_2); (THF-d_8, −20 °C) δ 2.84, 2.62, 2.60, 2.56 (br pseudo t, 2H each, CH_2). IR (KBr): 2246 cm^{-1} [ν(C≡N)]. Found: C, 36.36; H, 4.55; N, 3.55. $C_{26}H_{38}N_2S_3Ir_2$ requires C, 36.34; H, 4.46; N, 3.26%.

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$Cl)(μ-SCH$_2$CH$_2$CN)$_2$IrCp*][PF$_6$] 6′. *Method (1).* A solution of **2** (80 mg, 0.10 mmol) and CH_2=CHCN (0.026 cm^3, 0.40 mmol) in $ClCH_2CH_2Cl$ (10 cm^3) was cooled to −40 °C and NEt_3 (0.056 cm^3, 0.40 mmol) was added. The mixture changed in color from yellow to red, which was gradually warmed to room temperature and stirred for 24 h. The resultant yellow solution was taken to dryness and the residue was redissolved in water. Upon addition of [NH_4][PF_6] (33 mg, 0.20 mmol), a yellow solid precipitated, which was filtered off, and washed with water. After drying *in vacuo* the residue was crystallized from $ClCH_2CH_2Cl$–hexane, affording **6′** as yellow crystals (56 mg, 52%).

Method (2). Spontaneous color change from red to yellow was observed when **5d** (43 mg, 0.050 mmol) was dissolved in $ClCH_2CH_2Cl$ (5 cm^3). The same work-up of the reaction mixture as that described above in method (1) yielded 27 mg of **6′** (51%). ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 30H, Cp*), 2.71, 2.73 (t, J = 7.0 Hz, 2H each, CH_2), 2.95 (t, J = 7.0 Hz, 4H, CH_2), 2.99, 3.60 (t, J = 7.0 Hz, 2H each, CH_2). IR (KBr): 2247 [ν(C≡N)], 842, 558 cm^{-1} (PF_6). Found: C, 31.49; H, 4.05; N, 2.96. $C_{28}H_{42}N_2PS_3ClF_6Ir_2$ requires C, 31.50; H, 3.96; N, 2.62%.

Preparation of [Cp*Ir(μ-SCH$_2$CH$_2$S)(μ-SCH$_2$CH$_2$Cl)IrCp*][PF$_6$] 7′. A solution of **2** (80 mg, 0.10 mmol) in $ClCH_2CH_2Cl$ (10 cm^3) was cooled to −40 °C and then NEt_3 (0.056 cm^3, 0.40 mmol) was added. A spontaneous color change from yellow to red was observed. The mixture was gradually warmed to room temperature and continuously stirred for 24 h. The resulting yellow solution was taken to dryness and the residue was dissolved in H_2O. Upon addition of [NH_4][PF_6] (33 mg, 0.20 mmol), a yellow solid precipitated, which was filtered off, dried, and then crystallized from $ClCH_2CH_2Cl$–hexane (67 mg, 67% yield). ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 30H, Cp*), 2.60–2.75 (m, 4H, SCH_2CH_2S), 2.90, 3.48 (m, 2H each, SCH_2CH_2Cl). IR (KBr): 841, 557 cm^{-1} (PF_6). Found: C, 29.09; H, 3.83. $C_{24}H_{38}PS_3ClF_6Ir_2$ requires C, 29.19; H, 3.88%.

Preparation of [Cp*Ir{μ-SCH$_2$CH$_2$CH(OH)S}(μ-SCH$_2$CH$_2$CHO)IrCp*]Cl 8. This complex was prepared from **2** (80 mg, 0.10 mmol) and acrolein (0.027 cm^3, 0.40 mmol) by an analogous method to that for preparing **4a** and was obtained as yellow microcrystals (42 mg, 47% yield). ^{1}H NMR ($CDCl_3$) A 1 : 1 mixture of two diastereomers: δ 1.86, 1.87 (s, 7.5H each, Cp*), 1.88 (s, 15H, Cp*), 2.7–3.0 (m, 4H, CH_2CH_2CHO), 9.81, 9.82 (s, 0.5H each, CHO); isomer a 1.50 (dddd, J = 14, 11, 11, and 4 Hz, SCH_2CHH), 2.37 (ddd, J = 14, 14, and 4 Hz, SCHH), 2.7–2.8 (overlapping, SCH_2CHH), 3.03 (ddd, J = 14, 4, and 4 Hz, SCHH), 4.75 (ddd, J = 11, 5, and 4 Hz, SCH(OH)), 7.81 (d, J = 5 Hz, OH); isomer b 1.47 (dddd, J = 14, 11, 11, and 4 Hz, SCH_2CHH), 2.27 (ddd, J = 14, 14, and 4 Hz, SCHH), 2.7–2.8 (overlapping, SCH_2CHH), 3.08 (ddd, J = 14, 4, and 4 Hz, SCHH), 4.84 (ddd, J = 11, 5, and 4 Hz, SCH(OH)), 7.84 (d, J = 5 Hz, OH). IR (KBr): 1711 [ν(C=O)], 2732 cm^{-1} [aldehydic ν(C–H)]. Found: C, 34.78; H, 4.78. $C_{26}H_{41}O_2S_3ClIr_2$ requires C, 34.63; H, 4.58%.

Preparation of [Cp*Ir{μ-SCHPhCH$_2$CH(OH)S}(μ-S)IrCp*] 9. Complex **2** (80 mg, 0.10 mmol) and cinnamaldehyde (0.050 cm^3, 0.40 mmol) were reacted similarly but the evaporated reaction mixture residue was crystallized from benzene–hexane, affording **9**·0.5C_6H_6 as red crystals (38 mg, 41%). ^{1}H NMR (C_6D_6): δ 1.68, 1.71 (s, 15H each, Cp*), 1.93 (td, J = 12.8 and 10.7 Hz, 1H, CH_2), 2.63 (br, 1H, OH), 2.92 (dt, J = 12.8 and 3.0 Hz, 1H, CH_2), 3.69 (dd, J = 12.8 and 3.0 Hz, 1H, CHPh), 4.46 (dd, J = 10.7 and 3.0 Hz, CHOH), 7.15–7.62 (m, 5H, Ph). Found: C, 41.51; H, 4.68. $C_{32}H_{43}OS_3Ir_2$ requires C, 41.58; H, 4.69%.

Table 7 Crystal data for complexes **4b**·2MeCN, **5d**, **6′**, **7′**, **9**·THF and **10**

	4b·2MeCN	**5d**	**6′**	**7′**	**9**·THF	**10**
Formula	$C_{48}H_{63}N_2O_6S_6ClIr_2$	$C_{26}H_{38}N_2S_3Ir_2$	$C_{28}H_{42}N_2F_6PS_3ClIr_2$	$C_{24}H_{38}F_6PS_3ClIr_2$	$C_{33}H_{48}O_2S_3Ir_2$	$C_{24}H_{38}S_4Ir_2$
M	1376.29	859.22	1067.69	987.60	957.36	839.24
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)	$I4_1/a$ (no. 88)	$C2/c$ (no. 15)
a/Å	11.943(2)	11.384(4)	20.655(4)	11.039(2)	22.375(3)	8.4984(7)
b/Å	22.055(2)	16.097(3)	11.025(5)	11.287(1)	22.375(3)	17.147(2)
c/Å	20.508(2)	16.368(2)	31.223(4)	12.663(3)	27.148(3)	18.213(2)
α/°	90	90	90	92.26(1)	90	90
β/°	90.01(1)	104.93(2)	90	95.68(2)	90	98.384(9)
γ/°	90	90	90	100.85(1)	90	90
U/Å^3	5401(1)	2898(1)	7110(2)	1539.3(5)	13591(3)	2625.7(5)
Z	4	4	4	2	16	4
μ(Mo-Kα)/cm^{-1}	52.63	94.33	78.49	90.53	80.59	104.83
Reflections collected	12409	6650	10539	7064	8354	3019
Unique reflections used [$I > 3.00\sigma(I)$]	7996	5510	5440	5412	4602	2359
R	0.035	0.048	0.050	0.030	0.039	0.022
R_w	0.036	0.061	0.052	0.031	0.039	0.022

Single crystals of **9**·THF suitable for an X-ray diffraction study were obtained by recrystallizing this product from THF–hexane.

Reaction of 9 with CH_2=CHCHO. Complex **9** (0.10 mmol) dissolved in MeCN (10 cm^3) was reacted with CH_2=CHCHO (0.10 mmol) and [NEt_3H]Cl (0.10 mmol) at room temperature for 12 h. The ^{1}H NMR spectrum of the orange product showed the formation of [Cp*Ir{μ-SCHPhCH_2CH(OH)S}(μ-SCH_2CH_2-CHO)IrCp*] as the major product (*ca.* 80% yield), which is a mixture of the two stereoisomers arising from the orientation of the β-formylethyl group as observed for **8**. ^{1}H NMR ($CDCl_3$) A 2 : 1 mixture of two diastereomers: δ 2.7–3.2 (m, CH_2CH_2-CHO), 7.2–7.6 (m, Ph), 8.0 (br, OH); major isomer 1.79, 1.93 (s, 15H each, Cp*), 3.11 (dt, 1H, CHPhC*H*H), 3.68 (dd, 1H, C*H*Ph), 5.03 (dd, 1H, C*H*(OH)), 9.80 (s, 1H, CHO); minor isomer 1.75, 1.91 (s, 15H each, Cp*), 3.28 (dt, 1H, CHPhC*H*H), 3.82 (dd, 1H, C*H*Ph), 4.95 (dd, 1H, C*H*(OH)), 9.83 (s, 1H, CHO). The resonance of one methylene proton in the CHPhCH_2 moiety is presumably overlapping with the Cp* resonances at δ *ca.* 1.9.

Preparation of [Cp*Ir(μ-SCH_2CH_2S)$_2$IrCp*] 10. This compound was obtained as orange crystals (38 mg, 45%) from **2** (80 mg, 0.10 mmol) and ethylene sulfide (0.024 cm^3, 0.40 mmol) by a similar method to that for preparing **9**. ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 30H, Cp*), 1.61 (overlapping with Cp*, 2H, CH_2), 2.17 (ddd, J = 11.6, 7.6 and 5.0 Hz, 2H, CH_2), 3.67 (ddd, J = 11.0, 7.6 and 4.9 Hz, 2H, CH_2), 3.78 (ddd, J = 11.6, 6.7 and 4.9 Hz, 2H, CH_2). Found: C, 34.36; H, 4.66. $C_{24}H_{38}S_4Ir_2$ requires C, 34.35; H, 4.56%.

X-Ray diffraction studies

Single crystal X-ray analyses of complexes **4b**·2MeCN, **5d**, **6′**, **7′**, **9**·THF, and **10** were carried out on a Rigaku AFC7R diffractometer equipped with a Mo-Kα source at room temperature. Details of crystal and data collection parameters are summarized in Table 7.

Structure solution and refinements were performed using the TEXSAN program package.[23] The positions of the non-hydrogen atoms determined by DIRDIF PATTY[24] were refined anisotropically. Hydrogen atoms were placed at ideal positions and included in the final stages of refinements with fixed parameters. In **6′**, one C atom of the SCH_2CH_2Cl ligand in one of the two independent molecules was disordered over two positions with occupancies 0.6 and 0.4, which were refined isotropically. Furthermore, one of the two independent PF_6 anions was also refined as disordered over two positions with occupancies 0.5 and 0.5. The O atom in the solvating THF was found in two disordered positions for **9**·THF, while one methylene C atom in **10** was also disordered over two positions with occupancies 0.6 and 0.4.

CCDC reference numbers 172894 and 178526–178530.

See http://www.rsc.org/suppdata/dt/b2/b200689h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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