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Dithioethers as ligands in pentamethylcyclopentadienylrhodium(III) and iridium(III) complexes. Crystal structures of $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2\{\mu\text{-}(MeS)_2CH_2\}](BF_4)_2{\cdot}H_2O$ and $[(\eta^5\text{-}C_5Me_5)IrCl_2\{\eta^1\text{-}(PhS)_2CH_2\}]$

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Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

Abstract

Reactions of complexes $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ (M = Rh, Ir) with the ligand $(MeS)_2CH_2$ in CH_2Cl_2 solution led to the neutral dinuclear complexes of the general formula $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2\{\mu\text{-}(MeS)_2CH_2\}]$ [M = Rh (**1**), Ir (**2**)]. Compound **1** reacts in CH_2Cl_2 solution with silver tetrafluoroborate in 1:2 molar ratio to yield the dinuclear cationic complex $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2\{\mu\text{-}(MeS)_2CH_2\}](BF_4)_2{\cdot}H_2O$ (**3**). Compound **2** reacts with silver salts in analogous conditions to give the mononuclear cationic complex $[(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(MeS)_2CH_2\}]BF_4$ (**4**). Reactions of the starting complexes $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ with the ligand $(PhS)_2CH_2$ afforded the mononuclear complexes $[(\eta^5\text{-}C_5Me_5)MCl_2(\eta^1\text{-}(PhS)_2CH_2)]$ [M = Rh (**5**), Ir (**6**)]. All the complexes have been characterised by analytical and spectroscopic means, and the fluxional behaviour of **4**, in solution, has been studied. The crystal structures of complexes **3** and **6** have been established by X-ray crystallography. Complex **3** crystallised in space group $P2_1/n$, $a = 11.848(2)$, $b = 12.693(2)$, $c = 21.608(4)$ Å, $\beta = 95.18(2)°$ and $Z = 4$. The complex cation consists of two $(\eta^5\text{-}C_5Me_5)Rh$ moieties connected by two chloride atoms and one dithioether group. The two rhodium atoms are separated by 3.6093(10) Å. Complex **6** crystallised in space group $P2_1/c$, $a = 8.366(1)$, $b = 16.011(3)$, $c = 17.911(2)$ Å, $\beta = 100.28(1)°$ and $Z = 4$. The iridium atom has a distorted octahedral co-ordination with a $\eta^5\text{-}C_5Me_5$ group occupying the centre of three octahedral sites, two chloride atoms and a sulphur of a monodentate bis(phenylthio)methane ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dithioethers; Rhodium; Iridium; Dinuclear complexes; Synthesis

1. Introduction

There is considerable interest in the synthesis of mono and bimetallic complexes containing short-bite bidentate ligands such as $Ph_2ACH_2BPh_2$ (A = B = P; A = B = As; A = P, B = As) [1], $2\text{-}(Ph_2P)Py$ [2], Ph_2PCH_2SR (R = Me [3], Ph [4], CH_2Ph [5]) and $(RS)_2CH_2$ (R = Me [6], Ph [7]). In particular, the use of $(Ph_2P)_2CH_2$(dppm) as a bridging ligand has been extensively studied due to the fact that it can form very strong metal–phosphorus bonds and can lock together the two metal atoms in close proximity promoting reactions which involve the two metal centres [1a].

On the other hand, the P and S donor sites ligands are described as monodentate P-donor, bidentate chelate and bidentate bridging ligands. These types of ligands are of interest because when the phosphorus and thioether functions are co-ordinated to a metal, the thioether is expected to be more labile permitting the formation of a vacant site at the metal centre. These ligands can form bimetallic complexes with similar or dissimilar metal centres, acquiring a head-to-tail arrangement where the metal centres are connected with a metal-metal bond [3–5].

A limited number of metal complexes containing related dithioether ligands, of the type $(RS)_2CH_2$ (R = Me, Ph), have been reported. These ligands have a

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single methylene interdonor linkage that disfavour the chelation to a metal centre due to the ring strain, promoting monodentate [6] or bridging bonding modes [7,8]. However, it was recently described the synthesis and crystal structure of the complex [SnCl$_4$(η^2-{MeS)$_2$CH$_2$}] that shows the ligand in the unexpected chelate co-ordination fashion [9].

In this paper, we describe the preparation of new binuclear complexes of formula [(η^5-C$_5$Me$_5$)MCl$_2${μ-(MeS)$_2$CH$_2$}] [M = Rh (**1**), Ir (**2**)] and [{(η^5-C$_5$Me$_5$)Rh}$_2$(μ-Cl)$_2${μ-(MeS)$_2$CH$_2$}](BF$_4$)$_2$·H$_2$O (**3**), and the mononuclear derivatives [(η^5-C$_5$Me$_5$)IrCl{η^2-(MeS)$_2$CH$_2$}]BF$_4$ (**4**) and [(η^5-C$_5$Me$_5$)MCl$_2${η^1-(PhS)$_2$CH$_2$}] [M = Rh (**5**), Ir (**6**)]. The crystal structure of complexes [{(η^5-C$_5$Me$_5$)Rh}$_2$(μ-Cl)$_2${μ-(MeS)$_2$CH$_2$}]-(BF$_4$)$_2$·H$_2$O (**3**) and [(η^5-C$_5$Me$_5$)IrCl$_2${η^1-(PhS)$_2$CH$_2$}] (**6**), determined by single-crystal X-ray diffraction, are also reported.

2. Experimental

2.1. General

All reactions were carried out by Schlenk techniques under purified nitrogen. The starting complexes [{(η^5-C$_5$Me$_5$)MCl$_2$}$_2$] (M = Rh, Ir) were prepared by published procedures [10]. Dithioethers and reagent grade solvents were purchased from Aldrich and Fisher Scientific, respectively, and were used as received.

Elemental analyses (C, H and S) were made with a Fisons EA 1108 microanalyser. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. Conductivities were measured in ca. 5×10^{-4} mol l^{-1} acetone solutions using a WTW LF-521 conductimeter. ^{1}H (200 MHz) spectra were recorded on a Bruker AC-200P spectrometer and the chemical shifts are reported in ppm relative to Me$_4$Si as internal standard. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode; ions were produced with the standard Cs$^+$ gun at ca. 30 kV and 3-nitrobenzylalcohol (NBA) was used as the matrix. Thermogravimetric measurements were carried out with a Mettler TA-3000 calorimetric system equipped with a TC-10A processor and a TG-50 thermobalance.

*2.2. Preparation of [{(η^5-C$_5$Me$_5$)MCl$_2$}$_2${μ-(MeS)$_2$CH$_2$}] [M = Rh (**1**), Ir (**2**)]*

To a solution of the binuclear complex [{(η^5-C$_5$Me$_5$)MCl$_2$}$_2$] (0.2 mmol) in dichloromethane (10 cm^3) a slight excess of the ligand (MeS)$_2$CH$_2$ (0.45 mmol; 49 mg) in dichloromethane solution was added dropwise. During the addition a decrease in the colour intensity of the solution was observed. After stirring at room temperature (r.t.) for 8 h, the solution was filtered through cellulose and concentrated to a small volume. Solid complexes were obtained by adding n-pentane. Compound **1**: orange–red solid, yield: 134 mg, 92% (Found: C, 38.4; H, 5.3; S, 8.0. C$_{23}$H$_{38}$Cl$_4$Rh$_2$S$_2$ requires: C, 38.0; H, 5.3; S, 8.8%). δ_H (CDCl$_3$) 1.71 (s, 30 H, Me, C$_5$Me$_5$), 2.42 (s, 6 H, Me) and 4.21 ppm (s, 2 H, CH). MS (FAB$^+$, *m*/*z*, %): 581, 100% [M$^+$–Cl–(MeS)$_2$CH$_2$]. Compound **2**: yellow solid, yield: 165 mg, 91% (Found: C, 30.3; H, 4.0; S, 7.3. C$_{23}$H$_{38}$Cl$_4$Ir$_2$S$_2$ requires: C, 30.5; H, 4.3; S, 7.1%). δ_H (CDCl$_3$) 1.70 (s, 30 H, Me, C$_5$Me$_5$), 2.61 (s, 6 H, Me) and 4.37 ppm (s, 2 H, CH). MS (FAB$^+$, *m*/*z*,%): 761, 12%[M$^+$–Cl–(MeS)$_2$CH$_2$].

*2.3. Preparation of [{(η^5-C$_5$Me$_5$)Rh}$_2$(μ-Cl)$_2${μ-(MeS)$_2$CH$_2$}](BF$_4$)$_2$·H$_2$O (**3**)*

To a solution of the binuclear complex [{(η^5-C$_5$Me$_5$)RhCl$_2$}$_2$] (124 mg; 0.2 mmol) in dichloromethane (10 cm^3) was added a solution of AgBF$_4$ (78 mg; 0.4 mmol) in acetone (2 cm^3). After stirring the mixture for 1 h at r.t., in the absence of light, a slight excess of (MeS)$_2$CH$_2$ (0.30 mmol) was added and the mixture was stirred again for 6 h. The precipitated silver chloride was removed by filtration through Kieselguhr, the solution was evaporated to a small volume and the complex precipitated by adding diethyl ether. Red crystals were obtained from acetone–diethyl ether. Yield: 106 mg, 64% (Found: C, 32.02; H, 4.92, S, 7.30. C$_{23}$H$_{38}$B$_2$Cl$_2$F$_8$Rh$_2$S$_2$·H$_2$O requires: C, 32.62; H, 4.76; S, 7.57%). δ_H (CD$_3$NO$_2$) 1.76 (s, 30 H, Me, C$_5$Me$_5$), 2.88 (s, 6 H, Me) and 4.51 ppm (s, 2 H, CH). $\Lambda_M = 173\ \Omega$ mol^{-1} cm^{-1} (acetone).

*2.4. Preparation of [(η^5-C$_5$Me$_5$)IrCl{η^2-(MeS)$_2$CH$_2$}]BF$_4$ (**4**)*

A mixture of the dinuclear complex [{(η^5-C$_5$Me$_5$)IrCl$_2$}$_2$] (120 mg; 0.15 mmol) and AgBF$_4$ (59 mg; 0.30 mmol), in acetone (15 cm^3), was stirred for 1 h at r.t., in the absence of light. The precipitated silver chloride was removed by filtration through Kieselguhr and, to the resulting solution, (MeS)$_2$CH$_2$ (32 mg; 0.30 mmol) was added. After stirring the mixture for 4 h, the solution was evaporated to dryness and the residue chromatographed on Kieselgel using acetone as eluent. The solution obtained was concentrated to a small volume and the complex precipitated by adding diethyl ether. The product was recrystallised as yellow crystals from dichloromethane–diethyl ether. Yield: 88 mg, 53% (Found: C, 28.3; H, 4.45; S, 11.9. C$_{13}$H$_{23}$BClF$_4$IrS$_2$ requires: C, 28.0; H, 4.2; S, 11.5%). δ_H (CD$_3$NO$_2$) 1.85 (s, 15 H, Me, C$_5$Me$_5$), 2.60 (s, br, Me), 2.90 (s, br, Me), 5.56 [d, br, 1 H, CH, $^2J(HH) = 12.3$ Hz] and 7.28 [d, br, 1 H, CH, $^2J(HH) = 12.3$ Hz]. $\Lambda_M = 127\ \Omega\ mol^{-1}\ cm^{-1}$ (acetone).

*2.5. Preparation of [(η⁵-C₅Me₅)MCl₂(η¹-(PhS)₂CH₂)] [M = Rh (**5**), Ir (**6**)]*

To a solution of the dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ (0.2 mmol) in dichloromethane (10 cm^3) was added a solution of the ligand $(PhS)_2CH_2$ (0.4 mmol) in dichloromethane (7 cm^3). The resulting solution was stirred at r.t. for 24 h and then evaporated to a small volume (3–5 cm^3). The addition of *n*-hexane caused the precipitation of a solid, which was filtered off, washed with *n*-hexane and crystallised from dichloromethane–*n*-hexane. Compound **5**: red crystals, yield: 178 mg, 61% (Found: C, 50.5; H, 5.7; S, 12.3. $C_{23}H_{27}Cl_2RhS_2$ requires: C, 51.0; H, 5.0; S, 11.8%). δ_H (CDCl$_3$) 1.57 (s, 15 H, Me, C$_5$Me$_5$), 4.53 (s, 2 H, CH), 7.27 (m, 6 H, Ph) and 7.49 ppm (m, 4 H, Ph). Compound **6**: orange crystals, yield: 181 mg, 50% (Found: C, 44.0; H, 4.2; S, 10.4. $C_{23}H_{27}Cl_2IrS_2$ requires: C, 43.8; H, 4.3; S, 10.2%). δ_H (CDCl$_3$) 1.43 (s, 15 H, Me, C$_5$Me$_5$), 5.08 (s, 2 H, CH), 7.29 (m, 6 H, Ph) and 7.62 ppm (m, 4 H, Ph).

Table 1
Crystal data and structure refinement for complexes **3** and **6**

Complex	**3**	**6**
Empirical formula	$C_{23}H_{40}B_2Cl_2F_8ORh_2S_2$	$C_{23}H_{27}Cl_2IrS_2$
Formula weigth	847.01	630.67
Temperature (°K)	293(2)	297(2)
Wavelength (Å)	Mo–K$_\alpha$ (0.71073)	Mo–K$_\alpha$ (0.71073)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P21/c$
Unit cell dimensions		
a (Å)	11.848(2)	8.366(1)
b (Å)	12.693(2)	16.011(3)
c (Å)	21.608(4)	17.911(2)
β (°)	95.18(2)	100.28(1)
Volume (Å^3)	3236.3(10)	2360.6(6)
Z	4	4
D_{calc} (Mg m^{-3})	1.738	1.775
Absorption coefficient (mm^{-1})	1.378	6.066
$F(000)$	1696	1232
Crystal size (mm)	0.18 × 0.14 × 0.10	0.26 × 0.24 × 0.18
θ Range for data collection(°)	1.89–25.05	1.72–27.56
Index ranges	$0 \leq h \leq 14$, $0 \leq k \leq 15$, $-25 \leq l \leq 25$	$0 \leq h \leq 10$, $0 \leq k \leq 20$, $-23 \leq l \leq 22$
Reflections collected	6020	5765
Independent reflections	5725 ($R_{int} = 0.0261$)	5408 ($R_{int} = 0.0322$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5725/0/355	5408/0/253
Goodness-of-fit on F^2	0.927	0.895
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0467$, $wR_2 = 0.1163$	$R_1 = 0.028$, $wR_2 = 0.061$
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.1276$	$R_1 = 0.045$, $wR_2 = 0.064$
Largest difference peak and hole (e Å^{-3})	1.468 and −0.646	0.479 and −0.731

*2.6. X-ray crystallography of complexes [{(η⁵-C₅Me₅)Rh}₂(μ-Cl)₂{μ-(MeS)₂CH₂}](BF₄)₂·H₂O(**3**) and [(η⁵-C₅Me₅)IrCl₂{η¹-(PhS)₂CH₂}](**6**)*

Suitable crystals for the X-ray structure determinations were grown up by slow diffusion of diethyl ether into an acetone and dichloromethane solution of complexes **3** and **6**, respectively. Intensity data were collected on a Siemens R3m/V diffractometer in $\theta/2\theta$ scan mode, using graphite-monochromated Mo–K$_\alpha$ radiation. Semi-empirical corrections, via psi-scans, were applied for absorption.

Crystal data and relevant refinement parameters for both complexes are summarised in Table 1. The structures were solved by direct methods and refined by least-squares methods with SHELX-97 [11]. A riding model was applied to all H atoms, placed at geometrically idealised positions with C–H = 0.96 Å, with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of their corresponding parent C atoms. Methyl groups in complex **3** were treated as rotating groups as well, BF$_4$ anions were constrained to be regular tetrahedrons with B–F = 1.37 Å and refined as rigid groups.

3. Results and discussion

3.1. Synthesis and characterisation of the new complexes

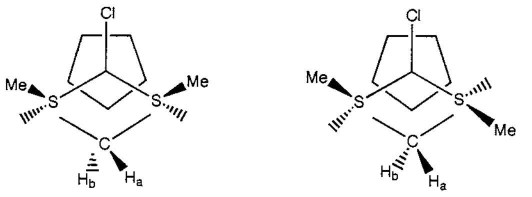
The dinuclear complexes $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ (M = Rh, Ir) react with the ligand bis(methylthio)methane, $(MeS)_2CH_2$, in dichloromethane solution by cleavage of the chlorine bridges to yield bimetallic complexes with the ligand acting as bidentate bridging ligand, in accord with the general equation:

$$[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2] + (MeS)_2CH_2$$

$$\rightarrow [\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2\{\mu\text{-}(MeS)_2CH_2\}]$$

M = Rh (**1**), Ir (**2**)

The ^{1}H-NMR spectra of complexes **1** and **2** are consistent with the proposed formulation, showing three singlet resonances assigned to C$_5$Me$_5$ and to methylene and methyl protons of the dithioether ligand, in the required intensity ratios. The FAB$^+$ mass spectra of these complexes do not show the expected molecular



isomer A (15%)

isomer B (85%)

δ(ppm): 2.60 (s, Me)
5.19 (d, H_a), 7.02 (d, H_b)
$^2J(H_aH_b) = 12.0$ Hz

2.56 (s, Me), 2.93 (s, Me)
5.36 (d, H_a), 7.02 (d, H_b)
$^2J(H_aH_b) = 12.2$ Hz

Fig. 1. Isomers of the cation $[\{(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(MeS)_2CH_2\}]^+$ formed by inversion of sulphur atoms. Proportions and ^{1}H-NMR chemical shifts at 243 K.

ion with the highest ion corresponding to the decomposition compound $[\{(C_5Me_5)M\}_2(\mu\text{-}Cl)_3]^+$.

Reactions of complexes **1** and **2** with $AgBF_4$ in 1:1 molar ratio in dichloromethane solution, in order to obtain the monocationic complex $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)\{\mu\text{-}(MeS)_2CH_2\}]BF_4$, were unsuccessful. In both cases the reactions gave rise to a mixture formed principally by the dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)M\}_2(\mu\text{-}Cl)_3]BF_4$. These products were characterised mainly by comparison of their ^{1}H-NMR spectra with pure samples obtained by reported methods [12].

When these reactions were carried out with $AgBF_4$ in 1:2 molar ratio, different types of compounds were obtained. Thus, treatment of complex **1** with $AgBF_4$ in CH_2Cl_2–Me_2CO solution leads to the formation of a red solid that corresponds to the dicationic complex $[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2\{\mu\text{-}(MeS)_2CH_2\}](BF_4)_2\cdot H_2O$ (**3**). In contrast, the similar reaction using complex **2** as starting material gives a yellow solid characterised as a monocationic complex with the dithioether group acting as chelate bidentate ligand $[\{(\eta^5\text{-}C_5Me_5)IrCl\{\eta^2\text{-}(MeS)_2CH_2\}]BF_4$ (**4**). In both reactions the complexes have been purified by chromatographic methods and were obtained in very low yield. Complexes **3** and **4** can be obtained in high yields by direct reaction of the dinuclear complexes $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ with the silver salt in the presence of a slight excess of the dithioether ligand in a mixture of CH_2Cl_2–Me_2CO. The compounds are soluble in acetone and nitromethane and have a poor solubility in chloroform and dichloromethane.

The IR spectrum of complex **3** in KBr pellets shows the presence of uncoordinated anion, $\nu(BF_4^-)$ ca. 1100 and 520 cm^{-1}, together with the characteristic broad absorption of water, ν(OH) centred at 3447 cm^{-1}. The thermogravimetric analysis (20°C min^{-1}) shows a weight loss of 2% (130–140°C), close to theoretical 2.1% required for the loss of 1 mole of water per mole of complex. Complex **3** behaves as 1:2 electrolytes in acetone solution, in accordance with the dinuclear nature of the complex. The ^{1}H-NMR spectrum in deuterated nitromethane exhibits three singlet signals at δ 1.76, 2.88 and 4.51 ppm assigned to protons of C_5Me_5, MeS and CH_2 groups, respectively. In order to confirm the dinucleating ability of the dithioether ligand, the structure of complex **3** was solved by X-ray methods (see below).

The ^{1}H-NMR spectrum of complex **4**, in nitromethane solution at room temperature (295 K), shows the expected singlet resonance for the co-ordinated C_5Me_5 ring together with two broad singlets and two broad doublets assigned to the protons of non-equivalent methyl groups and methylene protons (H_a, H_b), respectively. The proton endo to the chlorine atom is labelled H_a and it is assigned to the highest resonance [13]. Variable-temperature experiments (243–353 K) reveal the existence of two internal dynamic processes. When cooling the sample at 243 K the spectrum shows that the broad bands sharpen into two groups of resonances attributed to a mixture of the two isomers **A** and **B** (Fig. 1). The isomer **B** has a major percentage population at low temperature.

The resonances assigned to methyl groups with increasing temperature merge into one broad band at the coalescence temperature (310 K), and finally sharpen to a single band at δ 2.73 ppm (353 K). This result indicates that the isomers interconvert at high temperature by pyramidal inversion of pairs of sulphur atoms [14]. On the other hand, upon heating, the methylene hydrogens (H_a, H_b) become equivalent. Although the high-temperature-limit was not achieved, at 353 K the spectrum showed only a broad resonance at δ 6.17 ppm. This second fluxional process possibly corresponds to a rapid rotation of the ligand through 180°. This type of mechanism (180° pancake rotation) has been proposed for Pt^{IV} complexes, $[PtMe_3X\{MeE(CH_2)_2\text{-}Eme\text{-}E,E\}](E = S, Se)$, and it is considered analogous to the ligand switching movement proposed for binuclear Pt^{IV} complexes [15].

Different results are obtained in the reactions of the starting binuclear complexes $[\{(\eta^5\text{-}C_5Me_5)MCl_2\}_2]$ (M = Rh, Ir) with the ligand bis(diphenylthio)methane, $(PhS)_2CH_2$. In both cases mononuclear neutral complexes with the ligand acting in its monodentate fashion, of the type $[(\eta^5\text{-}C_5Me_5)MCl_2(\eta^1\text{-}(PhS)_2CH_2)]$ [M = Rh (**5**), Ir (**6**)], were isolated. The molecular structure of complex **6** was determined by X-ray diffraction methods. The ^{1}H-NMR spectra of the complexes in deuterated chloroform exhibited the expected three resonances assigned to C_5Me_5 ring, methylene and phenyl protons of the co-ordinated ligand, in the required intensity ratio.

3.2. *Description of the crystal structures*

3.2.1. *$[\{(\eta^5\text{-}C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2\{\mu\text{-}(MeS)_2CH_2\}](BF_4)_2\cdot H_2O$ (3)*

A perspective ORTEP view of the structure of the cation of complex **3** with the labelling of the atoms is shown in Fig. 2. Table 2 lists relevant bond distances and angles. The complex did not crystallise well from dried solvents, but unexpectedly the complex crystallised with one molecule of H_2O from undried solvents. The incorporated water is not involved in any particularly strong interaction with any part of the complex.

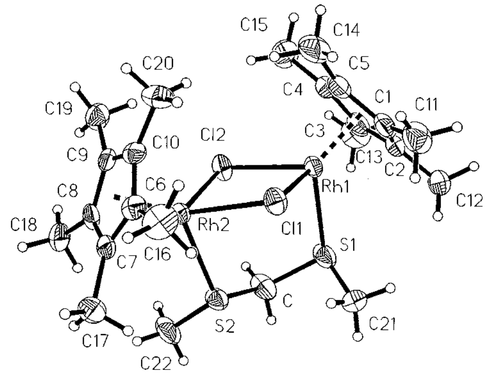


Fig. 2. ORTEP view of the structure of the complex cation **3** with atom numbering scheme (thermal ellipsoids at the 40% probability level).

Table 2
Selected bonds lengths (Å) and angles (°) for complex **3**, with estimated S.D. values in parentheses

Rh(1)–C(1)	2.153(7)	Rh(2)–C(6)	2.152(6)
Rh(1)–C(2)	2.169(7)	Rh(2)–C(7)	2.155(6)
Rh(1)–C(3)	2.152(7)	Rh(2)–C(8)	2.148(6)
Rh(1)–C(4)	2.179(7)	Rh(2)–C(9)	2.176(6)
Rh(1)–C(5)	2.176(7)	Rh(2)–C(10)	2.139(6)
Rh(1)–Cl(1)	2.4427(18)	Rh(2)–Cl(1)	2.4879(18)
Rh(1)–Cl(2)	2.4351(17)	Rh(2)–Cl(2)	2.4425(17)
Rh(1)–S(1)	2.400(2)	Rh(2)–S(2)	2.4164(19)
Rh(1)–Rh(2)	3.6093(10)	C(1)–C(2)	1.400(11)
C(6)–C(7)	1.419(10)	C(2)–C(3)	1.432(10)
C(7)–C(8)	1.449(10)	C(3)–C(4)	1.428(10)
C(8)–C(9)	1.434(9)	C(4)–C(5)	1.413(11)
C(9)–C(10)	1.405(10)	C(5)–C(1)	1.477(10)
C(10)–C(6)	1.415(9)	S(1)–C	1.807(7)
S(2)–C	1.825(7)	S(1)–C(21)	1.808(10)
S(2)–C(22)	1.816(8)		
Rh(1)–Cl(1)–Rh(2)	94.11(6)	Rh(1)–Cl(2)–Rh(2)	95.46(6)
S(1)–Rh(1)–Cl(1)	89.99(7)	S(2)–Rh(2)–Cl(1)	85.68(6)
S(1)–Rh(1)–Cl(2)	90.23(7)	S(2)–Rh(2)–Cl(2)	90.75(7)
Rh(1)–S(1)–C(21)	110.3(3)	Rh(2)–S(2)–C(22)	111.0(3)
Cl(1)–Rh(1)–Cl(2)	85.26(6)	Cl(1)–Rh(2)–Cl(2)	84.13(6)
Rh(1)–S(1)–C	112.0(3)	Rh(2)–S(2)–C	111.9(3)
C–S(1)–C(21)	102.2(4)	C–S(2)–C(22)	94.9(4)
S(1)–C–S(2)	116.0(4)		

The cation consists of two rhodium atoms bridged by one dithioether ligand and two chloride atoms. A η^5-co-ordinated pentamethylcyclopentadienyl ligand completes the pseudo-octahedral co-ordination of the rhodium atoms. The rhodium–rhodium separation of 3.6093(10) Å excludes any significant intermetallic interaction. The distances from the rhodium atoms to the centroid of the corresponding C_5Me_5 ring are 1.792 and 1.781 Å. The methyl substituents stay out of the plane through the five-membered rings, pointing away from the rhodium atoms. The steric requirements of the bridging dithioether ligand hold the two C_5Me_5 rings so that they are not parallel but exhibit a dihedral angle of 116.2°.

The bridging Rh–Cl bonds distances, average 2.4520(18) Å, fall in the range of Rh–Cl distances found in related μ-chloride $(C_5Me_5)Rh^{III}$ compounds [16,17]. The Rh–S bond distances, 2.400(2) and 2.4164(19) Å, are larger than those found in the related rhodium(III)–thioether complexes, $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_2$(1,4,7,10,13,16-hexathiacyclo-octadecane)]$(BPh_4)_2$ [average: 2.3705(9) Å] [18], $(C_5Me_5)Rh(MeSC_3Me_3C(O)Me)](OTf)$ [2.360(1) Å] [19], [Rh(1,4,7-trithiacyclononane)$(PPh_3)I_2]ClO_4$ [average: 2.317(2) Å] [20] and $[(C_5H_5)Rh\{\eta^3\text{-}(S,S,C')\text{-}SC(Z){=}C(Z)S\text{-}C(Z){=}C'\text{-}(Z)\}]$ (Z = COOMe) [average: 2.360(9) Å] [21].

In the co-ordinated dithioether ligand, the S(1)–C [1.808(7) Å] and S(2)–C [1.825(7) Å] distances are longer than those found in related dithioether complexes [19–21]. The bond angle S(1)–C–S(2) [116.0(4)°] reveal the highly distorted tetrahedral environment of the methanide carbon. Angles involving the sulphur atoms reflect a tetrahedral environment, S(1): average 108.2(4)° and S(2): average 105.9(4)°.

3.2.2. *$[(\eta^5\text{-}C_5Me_5)IrCl_2(\eta^1\text{-}(PhS)_2CH_2)]$ (**6**)*

The solid state structure of complex **6** is presented in Fig. 3 together with the atomic numbering scheme. Table 3 lists relevant bonds distances and angles, respectively. The iridium atom has a distorted octahedral co-ordination sphere, commonly referred as a ‘three-legged piano stool’ configuration, with the centroid of the pentamethylcyclopentadienyl ligand occupying the centres of three octahedral sites, the bis(phenylthio)methane ligand bonded to the iridium atom through one sulphur atom and two chloride atoms completing the co-ordination sphere.

The methyl substituents are bent away from the iridium atom and the Ir–C(ring) distances span the range of 2.142(5)–2.177(5) Å, and compares well with those found in other pentamethylcyclopentadienyl iridium complexes [4a,22].

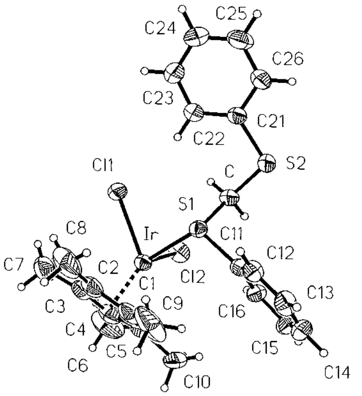


Fig. 3. ORTEP view of the structure of the complex **6** with atom numbering scheme (thermal ellipsoids at the 40% probability level).

Table 3
Selected bond lengths (Å) and angles (°) for complex **6**, with estimated S.D. values in parentheses

Ir–Cl(1)	2.433(1)	Ir–Cl(2)	2.410(1)
Ir–S(1)	2.385(1)	Ir–C(1)	2.156(5)
Ir–C(2)	2.142(5)	Ir–C(3)	2.177(5)
Ir–C(4)	2.160(5)	Ir–C(5)	2.150(5)
S(1)–C	1.837(4)	S(1)–C(11)	1.791(4)
S(2)–C	1.788(5)	S(2)–C(21)	1.774(5)
Cl(1)–Ir–Cl(2)	89.95(5)	Cl(1)–Ir–S(1)	81.30(4)
Cl(2)–Ir–S(1)	90.81(4)	Cl(1)–Ir–C(1)	130.6(2)
Cl(2)–Ir–C(1)	139.4(2)	S(1)–Ir–C(1)	97.1(2)
Ir–S(1)–C	110.4(2)	Ir–S(1)–C(11)	110.7(2)
C–S(1)–C(11)	98.8(2)	C–S(2)–C(21)	103.5(2)
S(1)–C–S(2)	112.3(2)		

The Ir–S bond distance, 2.385(1) Å, is larger than those found in the thioether–iridium(III) complex [IrCl(1,4,8,11-tetrathiocyclotetradecane)]BPh_4 [average: 2.293(4) Å] [23], and it is similar to the distances found in the thioether–phosphine complex [(η^5-C_5Me_5)IrCl(η^2-Ph_2PCH_2SPh–P,S)]BF_4 [2.402(3) Å] [4a], the dithiocarbamate complex [Ir(S_2CNEt_2)$_3$] [average: 2.370(2) Å] [24] and the phosphine sulphide complex [(η^5-C_5Me_5)Ir{PO(OMe)$_2$}{η^2-($SPPh_2$)$_2$$CH_2$}]$BF_4$ [average: 2.398(2) Å] [11b]. The Ir–Cl distances, 2.433(1) and 2.410(1) Å, are similar to those found in related complexes containing the '(C_5Me_5)Ir' moiety, as in the mononuclear complexes [(η^5-C_5Me_5)IrCl(L-prolinate)] [Ir–Cl: 2.417(3) Å] and [(η^5-C_5Me_5)IrCl(L-histidine)]Cl [Ir–Cl: 2.402(5) Å] [25], and larger than that found in the cationic compound [(η^5-C_5Me_5)IrCl(η^2-Ph_2PCH_2SPh–P,S)]BF_4 [2.381(2) Å] [4a].

The S(1)–C bond distance,1.837(4), Å in the co-ordinate monodentate ligand is within the range of expected values and it is larger than the distance S(2)–C, 1.788(5) Å, corresponding to the non co-ordinated sulphur atom [26].

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 14929 for compound [{(η^5-C_5Me_5)Rh}$_2$(μ-Cl)$_2${μ-(MeS)$_2$$CH_2$}](-$BF_4$)$_2$·$H_2O$ (**3**) and CCDC no. 149228 for compound [(η^5-C_5Me_5)$IrCl_2${η^1-(PhS)$_2$$CH_2$}] (**6**). 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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