

Platinum Complexes with Non-Symmetric Fluorodithioethers. Molecular Structures of *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)] (R_f = C₆F₅, C₆H₄F-3) and *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂]

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Este trabalho descreve a síntese e caracterização dos ligantes não simétricos CH₃SCH₂CH₂SR_f (R_f = C₆F₅, C₆HF₄-4, C₆H₄F-2, C₆H₄F-3, C₆H₄F-4) bem como seus derivados de platina(II) *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)] (R_f = C₆F₅, C₆HF₄-4, C₆H₄F-2, C₆H₄F-3, C₆H₄F-4) e *trans*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂] (R_f = C₆F₅, C₆HF₄-4). O espectro de RMN de ¹⁹F desses complexos mostra os isômeros *syn* e *anti*, consistente com um rápido dobramento do anel metalacíclico e uma inversão lenta de configuração nos átomos de enxofre do tioéter. As estruturas molecular e cristalina dos compostos *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)], *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] e *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂], resolvida por difração de raios-X, são também descritas.

This paper describes the synthesis and characterization of the non-symmetric ligands CH₃SCH₂CH₂SR_f (R_f = C₆F₅, C₆HF₄-4, C₆H₄F-2, C₆H₄F-3, C₆H₄F-4) as well as their platinum(II) derivatives *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)] (R_f = C₆F₅, C₆HF₄-4, C₆H₄F-2, C₆H₄F-3, C₆H₄F-4) and *trans*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂] (R_f = C₆F₅, C₆HF₄-4). ¹⁹F NMR of these complexes show the presence of *syn* and *anti* isomers, consistent with a fast flipping of the metallacycle ring and a slow inversion of configuration at the dithioether sulfur atoms. The molecular and crystalline structures of the compounds *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)], *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] and *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂], solved by X-ray diffraction are also described.

Keywords: fluorodithioethers, platinum, ¹⁹F NMR, X-ray diffraction

Introduction

The co-ordination chemistry of sulfur containing ligands-thiolates, thioethers etc, is a traditional area still growing at a fast speed. Its interest stems from the importance of these compounds in catalytic processes, oil dehydrodesulfurization, biological systems and chemical synthesis amongst others. The equivalent chemistry involving fluoro-containing ligands,^{1,2} is younger, proportionally less known, but not less interesting. Fluorinated compounds are becoming of increasing importance in modern pharmacology,³ design of new materials⁴ and catalysis of fluorinated organic compounds.⁵

Substitution of hydrogen by fluorine has two general consequences. The first one is topological, as a result of the different dimensions between hydrogen and fluorine atoms. The second is an electronic one, caused by the difference on the electroattractor character of these two elements. It is possible to generalize in a broad sense, by stating that a fluorinated molecule is stereochemically similar to its normal hydrogenated analogue but considerably different as far as its electronic properties is concerned. The chemical reactivity derived from morphological changes is hardly altered whereas chemical behavior depending on electronic parameters is profoundly affected.

We have been interested in the chemistry of transition metal compounds with fluorinated ligands for a long time.⁶ One of the areas that has particularly attracted our attention

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is that related with sulfur containing polydentate ligands, especially those systems in which each sulfur atom has a different coordinating ability. In this paper we describe the synthesis and characterization of the non-symmetric ligands $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SR}_f$ ($R_f = \text{C}_6\text{F}_5$ **L1**, C_6HF_4 -4 **L2**, $\text{C}_6\text{H}_4\text{F}$ -2 **L3**, $\text{C}_6\text{H}_4\text{F}$ -3 **L4** and $\text{C}_6\text{H}_4\text{F}$ -4 **L5**) as well as their platinum(II) derivatives *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)] ($R_f = \text{C}_6\text{F}_5$ **1**, C_6HF_4 -4 **2**, $\text{C}_6\text{H}_4\text{F}$ -2 **3**, $\text{C}_6\text{H}_4\text{F}$ -3 **4** and $\text{C}_6\text{H}_4\text{F}$ -4 **5**) as chelating ligands and *trans*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂] ($R_f = \text{C}_6\text{F}_5$ **6** and C_6HF_4 -4 **7**) as monodentate ligands. The ¹⁹F NMR spectra of complexes **1-5**, show the presence of *syn* and *anti* isomers, consistent with a fast flipping of the metallacycle ring and a slow inversion of configuration at the dithioether sulfur atoms. The molecular and crystalline structures of the compounds *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1**, *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] **4** and *trans* [PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6**, solved by X-ray diffraction are also described.

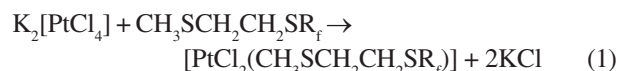
Results and Discussion

CH₃SCH₂CH₂SR_f

Reactions of CH₃SCH₂CH₂Cl with lead fluorothiolates Pb(SR_f)₂ ($R_f = \text{C}_6\text{F}_5$, ⁷ C_6HF_4 -4, $\text{C}_6\text{H}_4\text{F}$ -2, $\text{C}_6\text{H}_4\text{F}$ -3 and $\text{C}_6\text{H}_4\text{F}$ -4) yield the corresponding dithioethers CH₃SCH₂CH₂SR_f ($R_f = \text{C}_6\text{F}_5$ **L1**, C_6HF_4 -4 **L2**, $\text{C}_6\text{H}_4\text{F}$ -2 **L3**, $\text{C}_6\text{H}_4\text{F}$ -3 **L4** and $\text{C}_6\text{H}_4\text{F}$ -4 **L5**) as clear, dense oils. IR, ¹H and ¹⁹F NMR as well as EI-MS data, shown in Table 1, confirm the identity of each ligand.

[PtCl₂(CH₃SCH₂CH₂SR_f)]

The reactions of bisulphides CH₃SCH₂CH₂SR_f, **L1-L5**, with alcohol-water solutions of K₂[PtCl₄], reaction 1, yield the compounds *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)], ($R_f = \text{C}_6\text{F}_5$ **18**, C_6HF_4 -4 **2**, $\text{C}_6\text{H}_4\text{F}$ -2 **3**, $\text{C}_6\text{H}_4\text{F}$ -3 **4** and $\text{C}_6\text{H}_4\text{F}$ -4 **5**), as air stable, yellow microcrystalline solids, soluble in acetone and dichloromethane. As expected for planar platinum(II) complexes, compounds **1-5** are diamagnetic. Physical and spectroscopic data for compounds **1-7** are collected in Table 2.



Infrared spectra

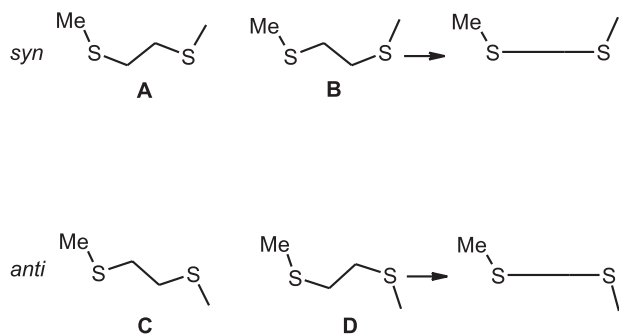
As expected for a *cis* configuration, IR spectra of compounds **1-5**, show two absorptions in the 330-310 cm⁻¹ range, assigned to the symmetric and asymmetric Pt-Cl vibrations. $\Delta\nu = \nu_{\text{sym}} - \nu_{\text{asym}}$, span from 11 to 15 cm⁻¹ but without apparent correlation with the fluorinated substituent at the sulfur atom. The IR spectra are useful in terms of characterization since they exhibit the absorptions associated to both the ligands and the *cis*-PtCl₂ fragment. Unfortunately since absorptions are relatively wide, this spectroscopy is insensitive to structural changes and therefore, for identification purposes, only characteristic bands are reported for compounds **1** to **7**.

Table 1. NMR, IR and MS data for compounds CH₃SCH₂CH₂SR_f, **L1** to **L5**

Compound	¹ H NMR (ppm)	¹⁹ F NMR (ppm)	IR (cm ⁻¹)	MS (m/z)
L1 CH ₃ SC ₂ H ₄ SC ₆ F ₅	3.13, m, CH ₂ SMe	-162.11, m, F _m	2922, 1638, 1514,	274[M] ⁺ , 10%
	2.68, m, CH ₂ SR _f	-154.12, m, F _p	1486, 1374, 1292,	199[SC ₆ F ₅] ⁺ , 80%
	2.10, s, CH ₃	-132.75, m, F _o	1090, 980, 862	75[CH ₃ SC ₂ H ₄] ⁺ , 100%
L2 CH ₃ SC ₂ H ₄ SC ₆ HF ₄ -4	7.51, tt, H _p	-135.99, m, F _m	3073, 1630, 1488,	256[M] ⁺ , 10%
	3.21, m, CH ₂ SMe	-131.39, m, F _o	1378, 1232, 1174,	181[SC ₆ HF ₄] ⁺ , 10%
	2.71, m, CH ₂ SR _f		916, 891, 712	75[CH ₃ SC ₂ H ₄] ⁺ , 100%
	2.11, s, CH ₃			
L3 CH ₃ SC ₂ H ₄ SC ₆ H ₄ F-2	6.8-7.2, m, H _{arom}	-112.02, m, F _o	3058, 1588, 1570,	202[M] ⁺ , 100%
	3.10, m, CH ₂ SMe		1468, 1378, 1320,	127[SC ₆ H ₄ F] ⁺ , 80%
	2.66, m, CH ₂ SR _f		1265, 1047, 744	75[CH ₃ SC ₂ H ₄] ⁺ , 80%
	2.07, s, CH ₃			
L4 CH ₃ SC ₂ H ₄ SC ₆ H ₄ F-3	6.7-7.2, m, H _{arom}	-114.25, m, F _m	3062, 1598, 1578,	202[M] ⁺ , 100%
	3.24, m, CH ₂ SMe		1322, 1216, 1168,	127[SC ₆ H ₄ F] ⁺ , 75%
	2.74, m, CH ₂ SR _f		880, 776, 678	75[CH ₃ SC ₂ H ₄] ⁺ , 80%
	2.14, s, CH ₃			
L5 CH ₃ SC ₂ H ₄ SC ₆ H ₄ F-4	6.87, m, H _m 7.16, m, H _o	-112.70, m, F _p	3058, 2915, 1583,	202[M] ⁺ , 100%
	3.31, m, CH ₂ SMe		1489, 1395, 1320,	127[SC ₆ H ₄ F] ⁺ , 70%
	2.67, m, CH ₂ SR _f		1227, 828	75[CH ₃ SC ₂ H ₄] ⁺ , 80%
	2.09, s, CH ₃			

Table 2. Physical and spectroscopic data for compounds [PtCl₂(CH₃SCH₂CH₂SR₁)], **1** to **5** and [PtCl₂(CH₃SCH₂CH₂SR₁)₂], **6** and **7**

Compound	Yield(%)	mp(°C)	Analyses		¹⁹ F NMR	IR (cm ⁻¹)	MS (<i>m/z</i>)
			Found(%)	Calculated(%)			
1 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ F ₅)]	86	243-245	C 20.44, H 1.55, S 11.93 C 20.03, H 1.29, S 11.87		isomer A -156.63, m, F _m -143.56, m, F _p -127.00, m, F _o isomer B -156.79, m, F _m -143.93, m, F _p -127.35, m, F _o A:B, 1:1.	1642, 1514, 1483, 1091, 1027, 974, 860, 632, 338, 316	539[M] ⁺ 504[M-Cl] ⁺ 469[M-2Cl] ⁺ 274[M-PtCl ₂] ⁺
2 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ HF ₄ -4)]	76	236-237	C 20.44, H 1.55, S 11.93 C 20.73, H 1.54, S 12.28		isomer A -134.34, m, F _p -128.68, m, F _o isomer B -134.55, m, F _p -129.12, m, F _o A:B, 1:1	1609, 1497, 1440, 1381, 1178, 1127, 922, 913, 847, 710, 334, 319	521 [M] ⁺ 486 [M-Cl] ⁺ 451 [M-2Cl] ⁺ 256 [M-PtCl ₂] ⁺
3 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ H ₄ F-2)]	81	255-257	C 22.8, H 2.1, S 13.6 C 23.1, H 2.4, S 13.7		isomer A -104.36, m, F _o isomer B -103.77, m, F _o A:B, 1:1	3058, 1588, 1570, 1468, 1378, 1320, 1265, 1047, 744, 674, 337, 323	467 [M] ⁺ 432 [M-Cl] ⁺ 397 [M-2Cl] ⁺ 202 [M-PtCl ₂] ⁺
4 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ H ₄ F-3)]	81	234-236	C 23.1, H 2.1, S 13.5 C 23.1, H 2.4, S 13.7		isomer A -106.86, m, F _m isomer B -106.37, m, F _m A:B, 2:1	3061, 1602, 1582, 1482, 1322, 1166, 1101, 1071, 889, 798, 654, 516, 331, 320	467 [M] ⁺ 432 [M-Cl] ⁺ 397 [M-2Cl] ⁺ 202 [M-PtCl ₂] ⁺
5 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ H ₄ F-4)]	81	215-217	C 22.9, H 2.2, S 13.6 C 23.1, H 2.4, S 13.7		isomer A -105.916, m, F _p isomer B -106.43, m, F _p A:B, 2:1	2924, 1583, 1488, 1217, 829, 629, 524, 336, 322	467 [M] ⁺ 432 [M-Cl] ⁺ 397 [M-2Cl] ⁺ 202 [M-PtCl ₂] ⁺
6 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ F ₅) ₂]	86	<290 d.	C 26.4, H 1.5, S 15.6 C 26.57, H 1.72, S 15.74		-154.72, m, F _m -143.29, m, F _p -126.12, m, F _o	1644, 1513, 1481, 1092, 1026, 978, 863, 639, 340	813[M] ⁺ 778[M-Cl] ⁺ 743[M-2Cl] ⁺
7 [PtCl ₂ (CH ₃ SCH ₂ CH ₂ SC ₆ HF ₄ -4)]	88	<290 d.	C 27.3, H 2.1, S 16.48 C 27.8, H 2.06, S 16.47		-135.63, m, F _p -129.13, m, F _o	1609, 1497, 1440, 1381, 1178, 1127, 922, 913, 847, 710, 334, 319	777[M] ⁺ 742[M-Cl] ⁺ 707[M-2Cl] ⁺

**Figure 1.** Isomers *syn* (**A**, **B**) and *anti* (**C**, **D**) derived from a flipping fragment SCH₂CH₂S and the observable *syn* and *anti* isomers from an averaged SCH₂CH₂S fragment.

NMR spectra

Compounds with general formulae [PtX₂(RSCH₂CH₂SR)] can give rise to different isomers depending, as shown in Figure 1, on the relative position of the sulfur substituents -*syn* and *anti*- and also, depending of the relative configuration of the PtS₂C₂ cycle, **A**, **B**, **C** and **D** isomers.

In solution at room temperature, the **A**, **B** or **C**, **D** isomers are, in general, NMR indistinguishable because flipping of the PtS₂C₂ ring is too fast on the time scale of this spectroscopy. There are some examples, with large R substituents, that allow distinct configurations of the

SCR₂CR₂S- skeleton to be measured at low temperatures.⁸ Normally however, all one can detect is a dynamic average between both stereoisomers shown in Figure 1.

Isomers *syn* and *anti* -Figure 1- can also interconvert to each other through a process known as inversion of configuration⁹ at the sulfur atoms. This inversion requires energies between 40 and 80 kJ mol⁻¹ and therefore at room temperature both isomers can, normally, be experimentally detected by NMR.¹⁰

Each of the sulfur substituents used in this work show second order magnetic systems. Experimentally the expected multiplicity for each absorption has been obtained. ¹⁹F NMR parameters for compounds **1** to **5** are shown in Table 2.

Compounds **1** to **5** show NMR spectra consistent with the presence of *syn* and *anti* isomers. As an example, Figure 2 shows the spectrum of *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1**. The presence of only two absorptions (isomers) requires fast (in the NMR time scale) conformational changes at

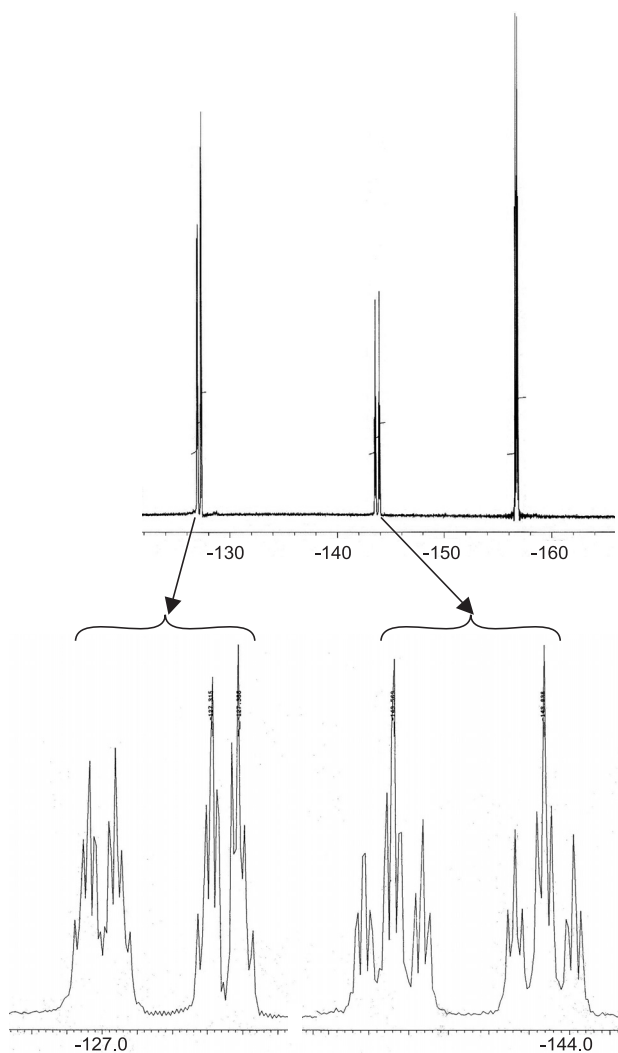


Figure 2. ¹⁹F NMR spectrum of *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1** at room temperature.

the metallacycle otherwise up to four isomers would have been detected, see Figure 1.

At room temperature both isomers are in equilibrium with nearly equal abundances for compounds **1** to **4** and with a *ca.* 2:1 relative abundance for compound **5**. It is worth mentioning that the presence of both isomers implies that inversion of configuration could not be only and simultaneously at both sulfur atoms.

From NMR data it is not possible to assign unambiguously a set of signals to a particular isomer (*syn* or *anti*). It has been suggested before¹¹ that the more abundant isomer corresponds frequently to the *anti* isomer, since this geometry minimizes the steric interactions. This does not seem to be the case for the complexes studied in this work, since they do not show significant differences between the relative *syn:anti* proportions observed. The relative sizes of both substituents -CH₃ and R₁- are similar for all **1** to **5** complexes and apparently the steric hindrance of the methyl group has no effect on the orientation adopted by the fluorinated benzene ring.

¹⁹F NMR spectrum of compound [PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1**, Figure 2, exhibits two sets of absorptions arising from the *syn* and *anti* isomers -magnetic system A₂B₂C- with nearly equal relative intensities. Each group includes three absorptions corresponding to fluorine nuclei at *ortho*, *meta* and *para* positions with relative intensities of 2:2:1 respectively.

[PtCl₂(CH₃SCH₂CH₂SC₆F₄H)] **2** exhibits a ¹⁹F NMR spectrum with two groups of signals assigned to the *syn* and *anti* isomers -magnetic system A₂B₂X- with 1:1 relative intensities. Each set shows two absorptions arising from the fluorine nuclei in *ortho* and *meta* positions with nearly equal relative intensities. ¹⁹F NMR spectra of compounds [PtCl₂(CH₃SCH₂CH₂SC₆H₄F)] **3** to **5**, with a single fluorine atom in *ortho*, *meta* or *para* positions display the expected single absorption for each isomer.

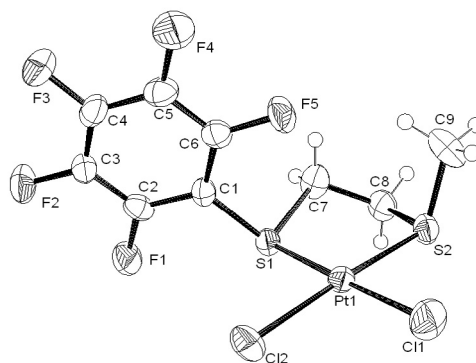


Figure 3. ORTEP diagram of compound *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1** with vibrational ellipsoids at 50%. Hydrogen atoms are represented by spheres of arbitrary size.

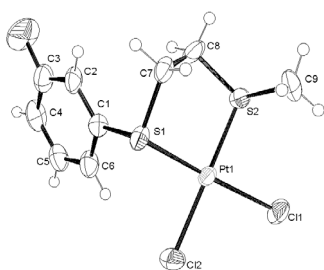


Figure 4. ORTEP diagram of compound *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] **4** with vibrational ellipsoids at 50%. Hydrogen atoms are represented by spheres of arbitrary size.

Molecular structures

cis-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1** and *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] **4** were studied by X-ray diffraction methods. Table 3 shows the principal bond angles and distances from these molecules. ORTEP diagrams are shown in Figures 3 and 4.

Molecules **1** and **4** have platinum atoms bonded to both sulfur atoms of the chelating ligands with practically equal Pt-S bond lengths. **1**: Pt-S1 2.244(2), Pt-S2 2.252(2) and **4**: Pt-S1 2.257(3), Pt-S2 2.252(3) Å. Despite the presumed electronic differences between C₆F₅ and C₆H₄F-3 there is no evidence of *cis*-effect since the Pt-S1 and Pt-S2 are practically equal for both compounds.

In contrast, *trans* bond distances, **1**: Pt-Cl1 2.306(2), Pt-Cl2 2.330(2) and **4**: Pt-Cl1 2.318(3), Pt-Cl2 2.322(3) Å, are significantly different and probably reflect a larger *trans*-influence of the SC₆F₅ as compared with that of SC₆H₄F-3. Bond angles around the central platinum atoms as well as bond distances with sulfur and chlorine ligands define an almost perfect square.

Both substituents at the sulfur atoms are located above the S₂Cl₂ plane, adopting a *syn* configuration, probably as a result of crystal packing effects. Similar *anti* isomers are found in the solid state structures of [PtCl₂(CF₃SCH(CH₃)CH₂SCF₃)],¹² [PtCl₂(CH₃SCH(CF₃)CH(CF₃)SCH₃)],¹³ [Pt(SC₆F₅)₂(CH₃SCH(CF₃)CH(CF₃)SCH₃)],¹⁴ and [PtCl₂(CH₃SCF₂CH₂SCH₃)].¹⁵

H₃C9-S-Pt and R_fCl-S-Pt bond angles (108°, average)

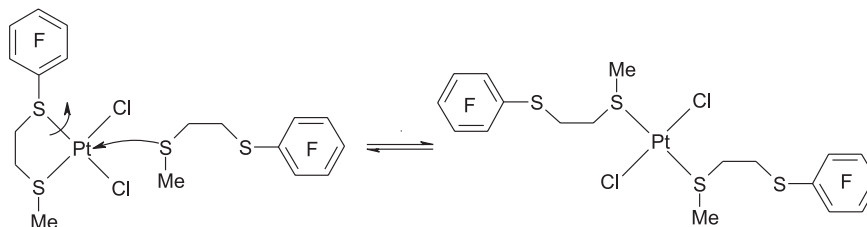


Figure 5. Displacement of the labile R_fS-Pt moiety by an incoming MeS group.

Table 3. Bond lengths (Å) and angles (°) for compounds [PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1** and [PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] **4**

	Compound 1	Compound 4
Pt(1)-S(1)	2.244(2)	2.257(3)
Pt(1)-S(2)	2.252(2)	2.252(3)
Pt(1)-Cl(1)	2.306(2)	2.318(3)
Pt(1)-Cl(2)	2.330(2)	2.322(3)
S(1)-C(1)	1.787(8)	1.796(12)
S(1)-C(7)	1.842(9)	1.833(14)
S(2)-C(9)	1.775(11)	1.808(14)
S(2)-C(8)	1.815(9)	1.828(14)
S(1)-Pt(1)-S(2)	90.29(8)	91.01(13)
S(1)-Pt(1)-Cl(1)	178.36(10)	172.54(12)
S(2)-Pt(1)-Cl(1)	88.39(10)	87.65(13)
S(1)-Pt(1)-Cl(2)	88.65(9)	91.48(13)
S(2)-Pt(1)-Cl(2)	175.17(9)	174.24(12)
Cl(1)-Pt(1)-Cl(2)	92.75(10)	90.54(14)
C(1)-S(1)-C(7)	102.0(4)	102.9(6)
C(1)-S(1)-Pt(1)	108.3(3)	109.6(4)
C(7)-S(1)-Pt(1)	103.7(3)	101.1(4)
C(9)-S(2)-C(8)	102.2(5)	101.7(8)
C(9)-S(2)-Pt(1)	108.6(4)	107.3(5)
C(8)-S(2)-Pt(1)	102.8(3)	102.9(5)

suggest the geometry around the sulfur atoms is pyramidal, close to a tetrahedral arrangement (109.5°) and therefore each sulfur atom could be considered as having sp³ hybridization.

A noticeable feature on these structures is that the crystal seems to be stabilized by intermolecular interactions in which the *ortho*-fluorine atoms of C₆F₅ in a molecule have short contacts with the *para*-fluorine atoms of C₆F₅ in a neighbor molecule.

Trans-[PtCl₂(CH₃SCH₂CH₂SR_f)₂]

Reactions of compounds *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1** and *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆H₄F-4)] **2** with additional stoichiometric amounts of CH₃SCH₂CH₂SC₆F₅ or CH₃SCH₂CH₂SC₆H₄F-4, respectively, in acetone and room temperature yield the *trans* compounds [PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6** and [PtCl₂(CH₃SCH₂CH₂SC₆H₄F-4)] **7**. Clearly, the presence of free ligand allows the donor sulfur atoms in CH₃S- and R_fS- to compete. Despite the chelating effect, the more basic CH₃S group displaces the labile R_fS moiety and *trans*-

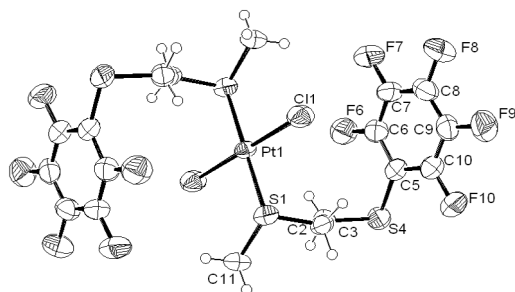


Figure 6. ORTEP diagram of compound *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6** with vibrational ellipsoids at 50%. Hydrogen atoms are represented by spheres of arbitrary size.

Table 4. Bond lengths (Å) and angles (°) for compound *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6**

Bond	(Å)	Angle	(°)
Pt(1)-Cl(1)	2.3004(13)	Cl(1)-Pt(1)-S(1)	85.06(5)
Pt(1)-S(1)	2.3121(12)	C(2)-S(1)-Pt(1)	104.24(16)
S(1)-C(11)	1.805(5)	C(2)-C(3)-S(4)	112.7(4)
S(1)-C(2)	1.815(5)	C(11)-S(1)-Pt(1)	111.9(2)
C(3)-S(4)	1.820(5)	C(3)-C(2)-S(1)	114.2(3)
C(2)-C(3)	1.507(7)	C(5)-S(4)-C(3)	99.5(2)
S(4)-C(5)	1.772(5)	C(6)-C(5)-S(4)	121.9(4)
		C(10)-C(5)-S(4)	121.2(4)
		C(11)-S(1)-C(2)	101.0(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, -y, -z.

[PtCl₂(CH₃SCH₂CH₂SR_f)₂] compounds are formed predominantly as shown in Figure 5.

X-ray diffraction data for compound *trans*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6** are shown in Table 2. The corresponding ORTEP diagram is shown in Figure 6.

Experimental

All reactions were carried out under an atmosphere of oxygen-free dinitrogen using Schlenk techniques. Solvents were purified and degassed prior to use according to published methods.¹⁶ Thin-layer chromatography (TLC) (Merck, silica gel 60 F₂₅₄ and neutral aluminium oxide 60 F₂₅₄) was used to monitor the progress of the reactions under study. All reagents were purchased from Aldrich and used as received.

CH₃SCH₂CH₂SC₆F₅,⁷ [PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂]⁸ and the lead thiolates Pb(SR_f)₂ (R_f = C₆F₅, SC₆HF₄-4, SC₆H₄F-2, SC₆H₄F-3 and SC₆H₄F-4,^{17,18} were synthesized following published reports.

Infrared spectra were recorded on a 750 Nicolet Fourier Transform Magna-IR Spectrometer over the 4000-300 cm⁻¹ range on CsI. Elemental Analyses were determined by Galbraith Laboratories Inc., USA. ¹H and ¹⁹F-¹H nuclear magnetic resonance spectra were recorded on a Varian Unity INOVA-300 spectrometer operating at 300 MHz and 282.23

MHz respectively. Chemical shifts are in ppm positive at low field, relative to TMS=0 ppm for ¹H and CFCl₃=0 ppm for ¹⁹F.

FAB⁺ mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating with an acceleration voltage of 10 KV. Samples were desorbed from a 3-nitrobenzyl alcohol matrix using 3KeV xenon atoms. FAB⁺ mass measurements were carried out with resolution of 3000 using magnetic field scan and the matrix ions as reference or as electric field scan with the sample peak flanked by two poly(ethylene glycol) or CsI ions as reference.

For both, dithioethers -CH₃SCH₂CH₂SR_f- and platinum(II) derivatives -*cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂] and *trans*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂]- a detailed experimental procedure is described.

CH₃SCH₂CH₂SR_f, LI-L5

CH₃SCH₂CH₂Cl (0.88g, 8 mmol) in acetone (25 mL) were added to a solution of Pb(SR_f)₂ (4.0 mmol) in acetone (25 mL) and refluxed overnight. The white precipitate (PbCl₂) was filtered off and the solvent transferred under vacuum. The oily colorless products were purified through a chromatographic column with silica and (CH₃)₂CO/CH₃COOEt 1:1 as eluent. Yields: 97-98%.

cis-[PtCl₂(CH₃SCH₂CH₂SR_f)₂], 1-5

CH₃HSCH₂CH₂SR_f (0.242 mmol) in acetone (20 mL) was added dropwise to (100.0mg, 0.242mmol) of K₂[PtCl₄] dissolved in a 1:1 water-acetone mixture (20 mL). The color changes slowly from red to yellow and after 24 h at room temperature the solvent was evaporated under vacuum. The yellow solid of *cis*-[PtCl₂(CH₃SCH₂CH₂SR_f)₂] was washed with cold water and dried under vacuum at room temperature 4 h.

trans-[PtCl₂(CH₃SCH₂CH₂SR_f)₂], 6-7

CH₃SCH₂CH₂SC₆F₅ **L1** (0.28mg, 1 mmol), dissolved in acetone (10 mL) was added to [PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **1** (0.540g, 1 mmol) dissolved in acetone (10 mL). The color solution changes between yellow tones and after 24 h at room temperature the solvent was evaporated to obtain *cis*-[PtCl₂(CH₃SCH₂CH₂SC₆F₅)₂] **6** (0.710g, 0.88 mmol).

X-ray diffraction data

Air stable single crystals of complexes **1**, **4**, and **6** were obtained by slow evaporation of saturated solutions. Crystal data and other crystallographic parameters are listed in Table

5. The diffraction data for **1** was collected at room temperature on a Enraf CAD4 diffractometer using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) and $\theta/2\theta$ or ω scan mode with variable scan speed. Structures was solved and refined using routine procedures¹⁹ on the basis of absorption-corrected data (ψ -scans). Structure **1** was refined without restraints. H atoms were placed on idealized positions and final least-squares cycles were carried-out using anisotropic displacement parameters for non-H atoms.

The diffraction data for **4** and **6** were collected at room temperature on a Siemens P4/PC 20,²⁰ diffractometer using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) and $\theta/2\theta$ or ω scan mode with variable scan speed. Structures were solved and refined using routine procedures¹⁹ on the basis of absorption-corrected data (ψ -scans). Structures **4** and **6** were refined without restraints. H atoms were placed on idealized positions and final least-squares cycles were carried-out using anisotropic displacement parameters for non-H atoms.

Table 5. Crystallographic data for compounds [PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **1**, [PtCl₂(CH₃SCH₂CH₂SC₆H₄F-3)] **4** and [PtCl₂(CH₃SCH₂CH₂SC₆F₅)] **6**

	1	4	6
Formula	C ₉ H ₇ Cl ₂ F ₅ S ₂ Pt	C ₉ H ₁₁ Cl ₂ F ₅ S ₂ Pt	C ₁₈ H ₁₄ Cl ₂ F ₁₀ S ₄ Pt
Group	P2(1)/c	P	P
<i>a</i> , Å	11.4095(5)	8.121(5)	7.5978(7)
<i>b</i> , Å	7.8309(3)	8.704(5)	7.6467(7)
<i>c</i> , Å	16.0595(7)	10.387(5)	11.4709(15)
α , deg	90	113.460(5)	104.670(9)
β , deg	106.9970(10)	104.516(5)	103.384(9)
γ , deg	90	94.360(5)	90.773(8)
<i>V</i> , Å ³	1372.19(10)	639.1(6)	625.36(12)
<i>Z</i>	4	2	2
ρ_{calc} gcm ⁻³	2.958	2.433	2.163
μ , cm ⁻¹	11.352	11.698	6.239
<i>R</i> ₁ ^a %	3.50	6.74	3.30
<i>wR</i> ₂ ^b %	8.63	15.66	6.51

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad ^b R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Supplementary Information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 265984 (compound **1**), 266404 (compound **4**) and 266807 (compound **6**). Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK ; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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