Platinum(II) and Palladium(II) Complexes of Some Chelating Polyfluoroalkyldithioethanes

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Platinum(II) halide complexes of the chelating ligands $CF_3SCH_2CH_2SCF_3$, $CF_3SCHMeCH_2SCF_3$, and $C_6F_5SCH_2CH_2SC_6F_5$ and platinum(II) and palladium(II) complexes of $CF_3SCH_2CH_2SCH_3$, $CH_3SCF_2CH_2SCH_3$, $CH_3SCH(CF_3)CH_2SCH_3$, $CH_3SCH(CF_3)CH(CF_3)SCH_3$, and $C_6F_5SCH_2CH_2SCH_3$ are described. N.m.r. spectroscopy shows the presence of isomers for each complex with rapid ring-conformational changes but slow inversion at sulphur on an n.m.r. time scale. Detailed ^{19}F n.m.r. studies allow specific isomers to be identified in many cases. Low-temperature ^{19}F n.m.r. studies on $[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$ show a barrier to ring-conformational changes, the first such barrier observed for five-membered chelate rings.

MANY complexes of 1,2-bis(alkylthio)ethanes are known [1] and in some of the formally square-planar platinum(II) and palladium(II) derivatives it has been shown that the dithioether is chelated to the metal and that in solution at room temperature there are isomers present which arise because of the relative positions of the sulphur substituents with respect to the plane of the metal co-ordination. The ring is puckered at the carbon atoms but, as is usual with five-membered rings, there is rapid ring inversion in all species investigated to date.

The preparation of some platinum(II) complexes of dithioethers containing fluorine on either the terminal or the bridge atoms has been described briefly.[2] *X*-Ray crystallography confirmed chelation (with weak dimerisation in the solid state through interaction between electron-deficient sulphur and electron-rich chlorine) through sulphur [3] in $[PtCl_2(CF_3SCHMeCH_2SCF_3)]$. Some isomers of trifluoromethylthio-derivatives showed long-range fluorine–fluorine coupling and this was associated with a *syn* configuration of the sulphur substituents.[2] In the present paper we describe the details of the preparation and some spectroscopic properties of platinum(II) and palladium(II) complexes of some fluorine-containing dithioethers. Details of the ^{195}Pt n.m.r. parameters of these complexes will be published separately; the mass spectra of the complexes have already been described.[4] Fluorine-containing diselenoethers and their platinum(II) and palladium(II) complexes have been prepared recently [5] and their properties are similar to those described here.

The electron-withdrawing effects of the fluorine atoms on the chelating ligands are likely to reduce the availability of the sulphur lone pairs for σ co-ordination to the metal but to facilitate π bonding from the metal to the sulphur. The trifluoromethylthio-group can readily act as a bridge between metal atoms [6] and there is ample evidence that the fluorine substituents do not reduce completely the donor ability of sulphur ligands.

RESULTS AND DISCUSSION

Most of the dithioethers studied react with platinum(II) and palladium(II) chlorides to give 1 : 1 complexes as shown in Table 1. 1,1,1,3,3,6,6,6-Octafluoro-2,5-dithiahexane, $CF_3SCF_2CH_2SCF_3$, did not give complexes with either platinum or palladium chloride and this level of fluorine substitution seems to have removed the ability to form complexes in this potential ligand. The monothioethers CH_3SCF_3 and CF_3SCF_3 also failed to give complexes under the conditions used to form the dithioether derivatives, a result in accordance with those

TABLE 1

Complexes of fluorinated dithioethers

Ligand	Ratio ligand : MX_2	Colour					
		Platinum			Palladium		
		Cl	Br	I	Cl	Br	I
$CF_3SCF_2CH_2SCF_3$	[a]						
$CF_3SCH_2CH_2SCF_3$	1 : 1	Yellow	Yellow				
$CF_3SCHMeCH_2SCF_3$	1 : 1	Yellow	Yellow				
$C_6F_5SCH_2CH_2SC_6F_5$	1 : 1	Yellow	Yellow	Yellow-brown			
$CH_3SCF_2CH_2SCH_3$	1 : 1	Yellow	Yellow	Yellow-brown	Yellow	Orange	Violet
$CH_3SCH(CF_3)CH_2SCH_3$	1 : 1	Yellow	Yellow-brown	Brown	Yellow	Orange	Violet
$CH_3SCH(CF_3)CH(CF_3)SCH_3$	1 : 1	Yellow	Yellow-brown	Brown	Yellow	Orange	Violet
$CF_3SCH_2CH_2SCH_3$	1 : 1	Yellow			Orange-brown [b]		
	2 : 1 [c]	Yellow					
$C_6F_5SCH_2CH_2SCH_3$	1 : 1	Yellow	Yellow				
	2 : 1 [c]	Yellow	Yellow	Yellow-brown	Orange-red	Red	Violet

[a] No complexes formed. [b] Dimer. [c] *cis* and *trans* isomers.

from previous attempts to form complexes with CF_3SCH_3 and $HOC_2H_4SCF_2CFClH$.[7] Palladium(II) chloride shows much less ability to form complexes than platinum(II) species [8] and complexes could only be isolated in the case of ligands with *S*-methyl substituents. This is in accord with weaker π bonding in the case of palladium as compared with platinum.[8]

Reaction of the chloro-complexes with alkali-metal bromide or iodide gives bromo- or iodo-complexes in most cases (see Table 1), but although chloro- and bromo-complexes are formed by platinum(II) with $CF_3SCH_2CH_2SCF_3$ and $CF_3SCHMeCH_2SCF_3$ the iodo-complexes have not been isolated and addition of iodide to, for example, $[PtCl_2(CF_3SCH_2CH_2SCF_3)]$ gives free ligand and PtI_2. There is no reaction between $CF_3SCH_2CH_2SCF_3$ and $K_2[PtI_4]$. The ***trans*** effect for halides, and the order of π-back bonding to the halide, varies in the order $I^- > Br^- > Cl^-$,[9] and thus introduction of iodide for chloride should result in a weakening of the ***trans***-Pt–S π bond. The compound $C_6F_5SCH_2CH_2SC_6F_5$ forms a platinum(II) iodide complex; the pentafluorophenyl group is much less electronegative than the trifluoromethyl group.[10] Intermediate mixed halides $[MX(X')L]$ (L = chelate ligand) are formed in solution and have been characterised by n.m.r. spectroscopy; their detailed properties will be described elsewhere.

The ligands $CF_3SCH_2CH_2SCH_3$ and $C_6F_5SCH_2CH_2SCH_3$ differ from the more heavily fluorinated derivatives in forming (*cis* and ***trans***) 2 : 1 complexes with $PtCl_2$ and PdX_2 in addition to the 1 : 1 chelated complexes. The ^{19}F n.m.r. spectra of the 2 : 1 platinum complexes show no fluorine–platinum coupling suggesting that the trifluoromethyl-sulphur atoms are not co-ordinated to platinum and that the ligand is bonded to platinum through the methyl sulphur only. The methyl protons show coupling to platinum.

Substitution of bromide into $[PtCl_2(CH_3SCH_2CH_2SCF_3)]$ does not give the expected bromine chloride or dibromide species. The reaction of the dichloride proceeds directly (with no apparent difference in the rate of reaction of the ***syn*** or ***anti*** isomer) to a product which has a single ^{19}F n.m.r. resonance at -39.7 p.p.m. showing no platinum–fluorine spin–spin coupling. This chemical shift is very similar to that of *cis*-$[PtCl_2(CH_3SCH_2CH_2SCF_3)_2]$ (-41.0 p.p.m.) which we consider to have two non-bonded trifluoromethyl-sulphur atoms. We believe that bromide substitution releases the trifluoromethyl sulphur.

The formation of hydrocarbon dithioether complexes of platinum(II) and palladium(II) of the type $[MX_2L]$ generally proceeds [11] through intermediate ionic species of type $[ML_2][MX_4]$. In the present reactions between chlorometallates(II) and dithioethers containing polyfluorinated substituents no such intermediates were observed, although as the precipitation and crystallisation of the complexes $[PtX_2L]$ was slow, intermediate ionic species cannot be ruled out.

As has been mentioned previously the n.m.r. spectra of square-planar platinum(II) halide complexes of dithioethers show the presence of isomers. The ^{19}F n.m.r. spectra of some of the platinum complexes prepared in the present work will now be discussed in detail. The palladium complexes gave broadly similar spectra (but without coupling to palladium). The pentafluorophenyl derivatives of both platinum and palladium gave rather complex n.m.r. spectra which were consistent with the presence of isomers similar to those discussed below. The ^1H n.m.r. spectra were complex and it was not possible to interpret the spectra fully.

The numbers of isomers detected in particular series of complexes are recorded in Table 2. With the exception of the complexes of $CH_3SCH(CF_3)CH(CF_3)SCH_3$ the number of isomers detected at ambient temperature can be explained simply in terms of the relative orientation of the sulphur and methylene substituents assuming rapid conformational changes of the rings and slow configurational changes of the sulphur substituents. On lowering the temperature the spectra of complexes of $CH_3SCH(CF_3)CH(CF_3)SCH_3$ change markedly and we attribute this to a slowing down of the conformational changes in the ring; no other complexes show such changes on lowering the temperature.

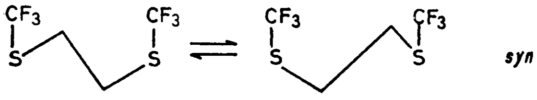
TABLE 2

Number of isomers detected by n.m.r. spectroscopy

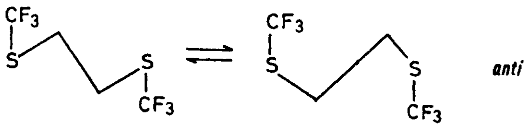
Complex	Number of isomers
$[PtX_2(CF_3SCH_2CH_2CF_3)]$	2
$[PtX_2(CF_3CHMeCH_2SCF_3)]$	4
$[PtX_2(CH_3SCF_2CH_2SCH_3)]$	2
$[PtX_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$	4
$[PtCl_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$	4
$[PtBr_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$	5
$[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$	4
$[PtX_2(CH_3SCH_2CH_2SCF_3)]$	2

Thus for complexes of $CF_3SCH_2CH_2SCF_3$ the isomers present may be represented as in (IA) and (IB) where the PtX_2 unit lies perpendicular to the paper and in the plane defined by the sulphur atoms. The proton-decoupled ^{19}F n.m.r. spectrum of $[PtCl_2(CF_3SCH_2CH_2SCF_3)]$ (Table 3) shows two triplets arising from the two isomers (relative abundance 35 : 65). The triplets arise from coupling to ^{195}Pt ($I = \frac{1}{2}$, abundance 34%). The ^{13}C satellites of the low-field signal are singlets whereas those of the high-field signal are quartets arising from ^{19}F–^{19}F coupling between two trifluoromethyl groups

(IA)



(IB)



rendered non-equivalent by the presence of only one ^{13}C nucleus.

A crystal-structure determination [2,3] on one (*syn*) form of $[PtCl_2(CF_3SCHMeCH_2SCF_3)]$ has shown that in the particular complex studied there is a relatively close approach of the fluorine atoms of the two trifluoromethyl groups (2.83 Å compared with a van der Waals radius for fluorine of 1.35 Å). If the ^{19}F–^{19}F coupling occurs predominantly by a through-bond mechanism it seems unlikely that the coupling constant over six bonds would be as large as observed and we, therefore, conclude that coupling is mainly through space and that the isomer showing the high-field ^{19}F signal and the ^{19}F–^{19}F coupling should be assigned the *syn* configuration. The complex $[PtBr_2(CF_3SCH_2CH_2SCF_3)]$ is similar; the less abundant isomer with the high-field ^{19}F signal shows ^{19}F–^{19}F coupling. If $[PtCl_2(CF_3SCH_2CH_2SCF_3)]$ is treated in acetone with an equimolar amount of alkali-metal bromide new signals are observed which are assigned to the mixed-halide complex $[PtBrCl(CF_3SCH_2CH_2SCF_3)]$. In this complex the trifluoromethyl groups are chemically non-equivalent so that ^{19}F–^{19}F coupling, if present, can be observed directly. As expected, only one of the two isomers present shows such coupling (J = 3.7 Hz).

TABLE 3

Complex		Relative abundance (%)	$\delta(^{19}F)$	J(FF)
$[PtCl_2(CF_3SCH_2CH_2SCF_3)]$	*syn*	35	−44.7	4
	anti	65	−44.1	0
$[PtBrCl(CF_3SCH_2CH_2SCF_3)]$	*syn*	35	−44.3, −44.5	3.7
	anti	65	−43.8, −43.9	0
$[PtBr_2(CF_3SCH_2CH_2SCF_3)]$	*syn*	28	−44.2	3.7
	anti	72	−43.7	0
$[PtCl_2(CH_3SCH_2CH_2SCF_3)]$	*syn*	30	−41.8	
	anti	70	−41.6	

TABLE 4

	Isomer			
	syn-syn (A)	*syn-anti* (B)	*anti-syn* (C)	*anti-anti* (D)
$[PtCl_2(CF_3SCHMeCH_2SCF_3)]$				
Relative abundance (%)	4	6	78	12
J(FF)	4.6	0	4.6	0
$\delta(^{19}F)$	−38.5 −45.1	−37.9 −43.9	−44.0 −44.4	−42.1 −43.7
$[PtBr_2(CF_3SCHMeCH_2SCF_3)]$				
Relative abundance (%)	10	17	65	8
J(FF)	4.6	0	4.6	0
$\delta(^{19}F)$	−38.2 −45.0	−37.5 −43.8	−43.9 −44.4	−43.4 −43.5
$[PtCl_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				
Relative abundance (%)	4	8	57	31
$\delta(^{19}F)$	−62.6	−62.6	−66.0	−66.0
$[PtBr_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				
Relative abundance (%)	6	13	53	28
$\delta(^{19}F)$	−62.2	−62.2	−65.8	−65.7
$[PtI_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				
Relative abundance (%)	5	19	52	24
$\delta(^{19}F)$	−62.0	−61.7	−65.6	−65.5

Molecular models suggest strongly that steric interaction in an *anti* configuration, (IB), is much less than in the *syn* configuration (IA), thus providing independent evidence from amounts of isomers for the assignment of the isomer showing the high-field ^{19}F shift to the *syn* configuration of the sulphur substituents.

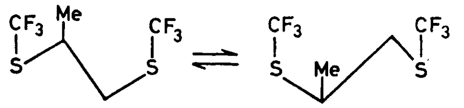
The ^{19}F n.m.r. spectrum of $[PtCl_2(CF_3SCH_2CH_2SCF_3)]$ in $MeO(CH_2)_2O(CH_2)_2OMe$ solution was studied at various temperatures. There are virtually no changes in the spectrum on lowering the temperature, but on raising the temperature to 403 K the signals from the two isomers have coalesced to a triplet (arising from coupling to ^{195}Pt), the process essentially involving inversion at sulphur as has previously been postulated for dithioether complexes at such temperatures.[1,12] The coalescence temperature for $[PtCl_2(CH_3SCH_2CH_2SCH_3)]$ is 373 K,[12] which is appreciably lower than in the fluorinated derivative.

The ^{19}F n.m.r. spectrum of the complex $[PtCl_2(CH_3SCH_2CH_2SCF_3)]$ (Table 3) shows the presence of the two isomers as expected from the above arguments. The ^{19}F signals of the two isomers are closer than in the bis(trifluoromethyl)dithioether complexes but again the high-field signal isomer is present in the smaller amount in agreement with its assignment to the *syn* isomer.

The complexes $[PtX_2(CF_3SCHMeCH_2SCF_3)]$ should show four isomers (see below) as is observed clearly for the chloride. (In the naming of these isomers, *e.g. syn-syn*, the first configuration refers to the relationship of the trifluoromethyl and *gem* methylene substituent and the second to the relationship of the two trifluoromethyl groups; the methyl groups are axial or equatorial with respect to the ring.) In these complexes (Table 4) the trifluoromethyl groups are again chemically distinct so that ^{19}F–^{19}F coupling can be observed directly. Such coupling is observed only in two isomers and, following the previous discussion, these would be identified with (IIA) or (IIC) which have a *syn* configuration of the two sulphur substituents. Molecular models indicate extensive steric interactions between the sulphur substituents and the methyl group with further interaction between sulphur substituents; interactions appear to be in the order C < D < B < A. In agreement with this order, in which the least hindered isomer is predicted to have *syn*-sulphur substituents, the most abundant isomer for both the chloro-(78%) and bromo-complexes (65%) shows measurable $^{19}F-^{19}F$ coupling. An *X*-ray crystallographic examination was carried out on a crystal of $[PtCl_2(CF_3SCHMeCH_2SCF_3)]$ picked from a mixture and again the structure found [2,3] was that of isomer C. The remaining isomers have structures assigned in decreasing order of non-bonding interactions; the two least abundant isomers have very similar abundances but assignment of structure may be made on the basis of the observation of $^{19}F-^{19}F$ coupling in the *syn-syn* case (IIA).

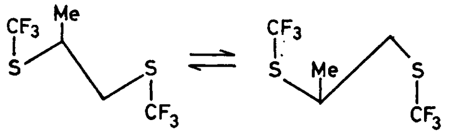
It is notable that the ^{19}F chemical shifts for two of the isomers of the chloro-complex show similar values for the two trifluoromethyl groups whilst two of the isomers show rather differing shifts.

(IIA)



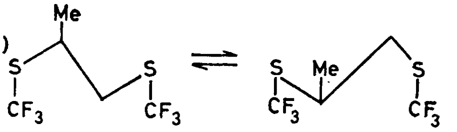
syn–syn

(IIB)



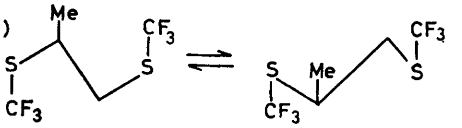
syn–anti

(IIC)



anti–syn

(IID)



anti–anti

The ^{19}F n.m.r. spectrum of $[PtBr_2(CF_3SCHMeCH_2SCF_3)]$ (Table 4) shows six signals but from the shifts and coupling constants two of the weaker signals originate from species of different structure from those being discussed here. The most common isomer (65%) shows $^{19}F-^{19}F$ coupling and similar ^{19}F shifts and is assigned the *anti-syn* configuration C. The next most common isomer (17%) shows no $^{19}F-^{19}F$ coupling and hence is either configuration B or D. The ^{19}F shifts of the trifluoromethyl groups are dissimilar and hence we assign B for the structure although steric effects would suggest D. The least abundant isomer (8%) has very close ^{19}F shifts for the trifluoromethyl groups and hence is assigned structure D. It is not clear why the bromide has behaved differently in the distribution of isomers as compared with the chloride.

Platinum(II) halide complexes of $CH_3SCH(CF_3)CH_2SCH_3$ should show an isomer pattern corresponding to that of the complexes of $CF_3SCHMeCH_2SCF_3$ (IIA)—(IID) and four isomers are clearly observed from the $^{19}F-\{^1H\}$ spectrum (Table 4).

Direct n.m.r. evidence on the assignment of configuration is not available as $^1H-^1H$ coupling between the methyl groups is not observable. Assignment of structure purely on the basis of the relative abundances of isomers, the structure with least steric interactions being given to the most abundant isomer, results in the n.m.r. parameters in Table 4. These assignments lead to further internal consistences in that the ^{19}F trifluoromethyl shifts of isomers C and D are similar but differ from those of isomers A and B which are, however, similar to each other; this pattern is similar to that observed for the various isomers of $[PtX_2(CF_3SCHMeCH_2SCF_3)]$.

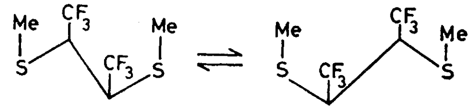
Assignment of structure to the isomers $[PtX_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$ is difficult as not all of the possible isomers are observed, but the situation is helped as in this series of complexes there are marked changes in n.m.r. spectra on lowering the temperature. We associate these changes with a marked slowing in the rate of interchange of ring conformers because of the large steric effects of the trifluoromethyl groups. The possible isomers (III) are shown over (trifluoromethyl groups are actually axial or equatorial) where A, B, and C are complexes derived from the *meso*-dithioether and D, E, and F from the (±)-dithioether. The *meso*- and (±)-ligands are not interchangeable once formed. Within the two series A, B, C, and D, E, F interconversion of isomers would be possible by exchange of position of the sulphur substituents. The ligand $CH_3SCH(CF_3)CH(CF_3)SCH_3$ contains a *ca.* 2 : 1 mixture of isomers. After reaction of excess of ligand with sodium tetrachloroplatinate(II) in ethanol the excess of ligand still showed the same relative proportions of isomers. It is concluded that the complexing abilities of the two forms to platinum(II) are approximately equal and, in view of the high yield, that the ratio of complexes derived from the different ligand diastereoisomers is also *ca.* 2 : 1. Molecular models show that within the two series of complexes the order of steric interactions is: *meso* A > C > B; (±) D > F > E.

At ambient temperature the proton-decoupled ^{19}F n.m.r. spectrum of each platinum(II) halide complex (Table 5) shows three isomers giving singlets; in addition, the chloride and the iodide show one isomer giving rise to two quartets whilst the bromide shows two isomers each giving rise to two quartets. It is considered likely that, as with the other series of complexes described in this paper, isomer formation and distribution within the series chloride, bromide, iodide is fairly similar. The lack of observation of the full predicted set of isomers for this series of complexes is presumably due to the formation of only very small quantities of some isomers.

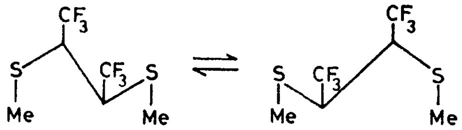
The ^{19}F n.m.r. spectra of all of the complexes change markedly on lowering the temperature. This was studied most fully for the iodo-complex $[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$. The most abundant isomer of this complex shows a singlet at —61.1 p.p.m. at 303 K which broadens on lowering the temperature and finally appears as two equal-intensity quartets at 183 K. The barrier to carbon–carbon rotation in each isomer is likely to be different and it is not surprising that the signals from other isomers do not show such clear-cut changes although changes do occur.

Assuming rapid ring-conformational changes the isomers (III) expected to show singlets in their ^{19}F-$\{^1H\}$ n.m.r. spectra are A, B, D, and E. On freezing the conformational equilibrium the trifluoromethyl groups in (IIIA) and (IIIB) become non-equivalent so that a singlet should transform into two quartets. As the two frozen conformers in either (IIIA) or (IIIB) are mirror images the amounts of each should be equal. For isomers D and E the trifluoromethyl groups in the frozen conformers remain equivalent and there should be no splitting into quartets. Isomers C and F have non-equivalent trifluoromethyl groups whatever the conformational equilibrium, and in frozen conformational equilibrium the trifluoromethyl groups in each conformer would still be non-equivalent.

(IIIA)



(IIIB)



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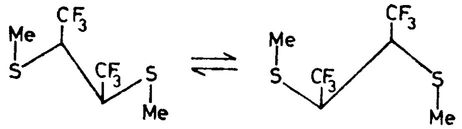
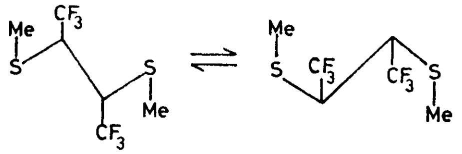
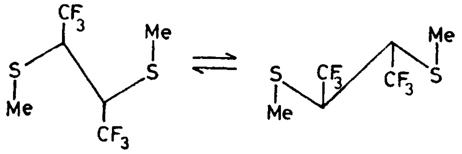


(IIID)



(IIIE)



(IIIF)

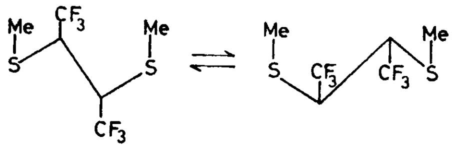


TABLE 5

Complex		Relative abundance (%)	δ(^{19}F)	*J*(FF)
$[PtCl_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				
	a	20	−65.5	0
	b	13	−64.1, −59.8	9.5
	c	0		
	d	64	−61.2	0
	e	3	−60.1	0
$[PtBr_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				
	a	18	−66.0	0
	b	11	−64.1, −59.8	*ca.* 9
	c	18	−61.5, −60.9	*ca.* 9
	d	51	−61.2	0
	e	2	−59.9	0
$[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				
	a	13	−66.2	0
	b	9	−63.9, −59.5	9
	c	0		
	d	73	−61.1	0
	e	5	−59.5	0

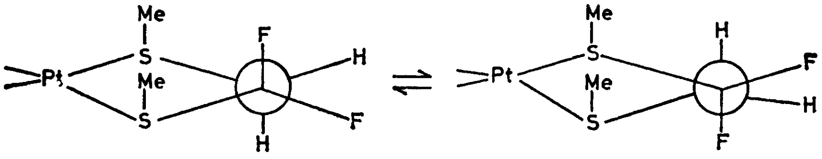
Thus the ^{19}F singlet appearing at —61.1 p.p.m. at ambient temperature must have structure (IIIA) or (IIIB). Structure A has very much greater steric interactions than B and hence this signal (d) almost certainly originates from a structure (IIIB). Thus this isomer is derived from the *meso* isomer of the ligand. In view of the proportion of isomer d (73%) and the 2 : 1 ratio of diastereoisomers in the free ligand this also establishes the more abundant form of the ligand as the *meso* isomer. In addition the proportions of isomers a and b suggest that they must be derived from the (±) isomer of the ligand; therefore isomer b which shows two ^{19}F quartets must have structure (IIIF) and not (IIIC).

On raising the temperature of this complex and continuing to observe the ^{19}F n.m.r. spectra there is broadening and then coalescence of the various signals. These processes are taken to involve inversion of the sulphur methyl groups and equivalence of isomers within either a *meso* or a (±) series of complexes.

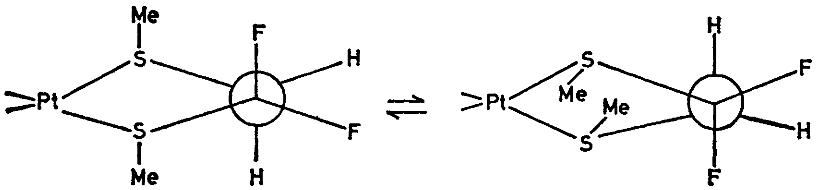
This series of observations, in addition to providing probable structural assignments to two isomers of $[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$, has provided the first clear evidence of a five-membered chelate ring with a barrier to ring inversion high enough to allow n.m.r. detection of a single conformer. The result also provides confirmation of the previous assumptions of low-energy barriers to ring-conformational changes in five-membered rings.

The dibromo-complex $[PtBr_2\{CH_3SCH(CF_3)CH(CF_3)$-

SCH_3}] at ambient temperature shows two isomers (b, c) exhibiting non-equivalent trifluoromethyl groups. The single isomers showing non-equivalent trifluoromethyl groups in the corresponding chloro- and iodo-complexes have a fairly large ^{19}F chemical-shift difference as in b of the bromo-complex and we therefore assign all observed isomers b to a similar structure (IIIF). Isomer c of the bromo-complex must therefore have structure (IIIC), the only other structure which has non-equivalent CF_3 groups. The ^{19}F chemical shifts of the most abundant isomer [structure (IIIB) for the iodide] for each halide are consistent with common structures and, indeed, with the exception of the extra isomer referred to for the bromo-complex, listing the isomers in order of decreasing ^{19}F chemical shift appears to relate isomers with common structures.



syn



anti

TABLE 6

Complex		δ(^{19}F)	J(FF)
[$PtCl_2(CH_3SCF_2CH_2SCH_3)$]	A	−84.6, −82.2	221.0
	B	−83.4, −82.2	204.5
[$PtBr_2(CH_3SCF_2CH_2SCH_3)$]	A	−85.1, −81.3	223.0
	B	−83.2, −83.1	205.1
[$PtI_2(CH_3SCF_2CH_2SCH_3)$]	A	−86.4, −79.8	225.6
	B	−84.7, −82.8	205.9

The complexes [$PtX_2(CH_3SCF_2CH_2SCH_3)$] would be expected to show *syn* and *anti* isomers which are best shown as Newman projections. The ^{19}F n.m.r. spectrum is complex and is not immediately recognisable as arising from two isomers. Assuming coupling between the sulphur-methyl groups and the rest of nuclei to be zero, the expected n.m.r. spectrum for the two isomers should consist of two (possibly superimposed) ABMNX + ABMN patterns ($A = B = {}^{19}F$, $M = N = {}^{1}H$, and $X = {}^{195}Pt$). Heteronuclear proton decoupling would be expected to simplify the spectra to two ABX + AB patterns. Solution of ABX systems is possible[13] and the spectra of these complexes can be interpreted to give the data shown in Table 6. It does not seem possible with the present information to make more precise assignments of structure to the two isomers. The relative amounts of the two isomers are similar.

EXPERIMENTAL

The dithioethers were prepared as previously described or by photochemical addition of bis(trifluoromethyl) disulphide to olefins.[14] Complexes were prepared from dithioethers and tetrachlorometallates(II) (best yields were from potassium salts) in aqueous ethanol and details of the conditions are given in Table 7.

(1,1,1,6,6,6-*Hexafluoro*-2,5-*dithiahexane*)*platinum*(II) *Chloride*.—Potassium tetrachloroplatinate(II), $K_2[PtCl_4]$ (0.8 g, 1.9 mmol), was dissolved in a mixture of water (25 cm^3) and ethanol (20 cm^3). The compound $CF_3SCH_2CH_2SCF_3$ (0.5 g, 2.1 mmol) in ethanol (5 cm^3) was added. The colour of the solution slowly changed from red to yellow with deposition of crystals and after 24 h at 0 °C the complex [$PtCl_2(CF_3SCH_2CH_2SCF_3)$] (0.7 g, 1.4 mmol; 70%) was filtered off, washed with cold ethanol, and dried under vacuum at room temperature for 2 h. Bromo- and iodo-complexes were obtained by the reaction of the chloro-species with a large excess of potassium bromide or potassium iodide in acetone. The study of the reaction between [$PtCl_2(CH_3SCH_2CH_2SCF_3)$] (1.5 cm^3, 0.1 mol dm^{-3}) and KBr was carried out in aqueous acetone by successive addition of 0.15-cm^3 portions of 0.1 mol dm^{-3} KBr solution.

Complexes were characterised by i.r. (Perkin-Elmer PE-577 or PE-225 spectrophotometers) and mass spectroscopy. Unless stated otherwise n.m.r. spectra were recorded for [$^2H_6$]acetone solutions at ambient probe temperature on Varian XL-100 or JEOL C-60HL spectrometers. Fluorine-19 chemical shifts are in p.p.m. positive to low field of external CCl_3F. Analyses were by Bernhardt or the Glasgow University Microanalytical Service.

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TABLE 7

Complexes prepared

	Reaction amounts (mmol)					Analysis (%)[a]				
Complex	$K_2[MCl_4]$	ligand	Solvent	Conditions	Yield (%)	C	H	S	X	*M*[a]
$[PtCl_2(CF_3SCH_2CH_2SCF_3)]$	1.9	2.1	H_2O–EtOH (1 : 1)	Stand 24 h	70	9.70 (9.70)	0.85 (0.80)	12.9 (12.9)	14.3 (14.3)	496 (496)
$[PtBr_2(CF_3SCH_2CH_2SCF_3)]$				Metathesis	100	8.40 (8.20)	0.70 (0.70)	27.0 (27.3)	11.2 (11.0)	585 (585)
$[PtCl_2(CF_3SCHMeCH_2SCF_3)]$	2.0	2.0	H_2O–EtOH (1 : 1)	Stand 24 h	71	11.7 (11.7)	1.20 (1.20)	12.5 (12.6)	13.8 (13.9)	510 (510)
$[PtBr_2(CF_3SCHMeCH_2SCF_3)]$				Metathesis	100	9.60 (10.0)	0.80 (1.00)	10.0 (10.7)	25.4 (26.6)	599 (599)
$[PtCl_2(C_6F_5SCH_2CH_2SC_6F_5)]$	2.1	2.1	H_2O–Me_2CO (2 : 5)	Stand 24 h, remove solvent, extract acetone	78	24.5 (24.3)	0.60 (0.55)	9.60 (9.30)	10.2 (10.2)	692 (692)
$[PtBr_2(C_6F_5SCH_2CH_2SC_6F_5)]$				Metathesis	100	21.7 (21.5)	0.75 (0.50)	8.50 (8.20)	20.6 (20.5)	781 (781)
$[PtI_2(C_6F_5SCH_2CH_2SC_6F_5)]$				Metathesis	100	19.4 (19.2)	0.75 (0.45)	7.10 (7.30)	29.3 (29.0)	*b* (875)
$[PtCl_2(CH_3SCF_2CH_2SCH_3)]$	2.0	2.1	H_2O–EtOH (1 : 1)	Stand 24 h	79	11.1 (11.3)	1.70 (1.90)	15.3 (15.1)	16.9 (16.7)	424 (424)
$[PtBr_2(CH_3SCF_2CH_2SCH_3)]$				Metathesis	100	9.30 (9.40)	1.40 (1.55)	12.4 (12.5)	31.1 (31.1)	513 (513)
$[PtI_2(CH_3SCF_2CH_2SCH_3)]$				Metathesis	100	8.30 (7.90)	1.35 (1.30)	10.5 (10.6)	42.2 (41.8)	*b* (607)
$[PdCl_2(CH_3SCF_2CH_2SCH_3)]$	2.0	2.1	H_2O–EtOH (1 : 1)	Stand 24 h	74	14.5 (14.3)	2.15 (2.40)	19.2 (19.1)	21.3 (21.1)	335 (335)
$[PdBr_2(CH_3SCF_2CH_2SCH_3)]$				Metathesis	100	11.3 (11.3)	2.00 (1.90)	15.2 (15.1)	37.6 (37.7)	424 (424)
$[PdI_2(CH_3SCF_2CH_2SCH_3)]$				Metathesis	100	9.20 (9.30)	1.50 (1.55)	12.6 (12.4)	48.4 (49.0)	*b* (518)
$[PtCl_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$	2.0	2.1	H_2O–EtOH (1 : 1)	Stand 24 h	81	13.2 (13.4)	1.95 (2.20)	14.1 (14.3)	15.5 (15.6)	456 (456)
$[PtBr_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				Metathesis	100	11.0 (11.3)	1.65 (1.70)	11.8 (12.0)	29.3 (30.0)	545 (545)
$[PtI_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				Metathesis	100	9.40 (9.60)	1.40 (1.60)	10.0 (11.0)	39.7 (40.7)	*b* (639)
$[PdCl_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$	2.0	2.1	H_2O–EtOH (1 : 1)	Stand 24 h	69	16.3 (16.6)	2.45 (2.60)	17.5 (17.5)	19.3 (19.4)	367 (367)
$[PdBr_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				Metathesis	100	13.1 (13.2)	1.95 (2.00)	14.1 (14.0)	35.0 (34.6)	456 (456)
$[PdI_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				Metathesis	100	10.9 (11.0)	1.65 (1.90)	11.7 (11.7)	46.1 (45.8)	*b* (550)
$[PtCl_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$	2.2	2.2	H_2O–Me_2CO (1 : 1)	Stir for 24 h	81	13.7 (13.9)	1.50 (1.70)	13.5 (13.0)	12.2 (12.8)	524 (524)
$[PtBr_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				Metathesis	100	11.7 (11.6)	1.30 (1.50)	26.1 (26.0)	10.5 (10.6)	613 (613)
$[PtI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				Metathesis	100	10.2 (10.4)	1.15 (1.20)	35.9 (36.6)	9.10 (9.50)	*b* (707)
$[PdCl_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$	2.2	2.2	H_2O–Me_2CO (1 : 1)	Stir for 24 h	76	16.5 (16.6)	1.85 (1.90)	16.3 (16.6)	14.7 (15.0)	435 (435)
$[PdBr_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				Metathesis	100	13.7 (13.9)	1.50 (1.70)	30.5 (30.2)	12.2 (12.5)	524 (524)
$[PdI_2\{CH_3SCH(CF_3)CH(CF_3)SCH_3\}]$				Metathesis	100	11.6 (11.3)	1.30 (1.50)	41.0 (39.8)	10.4 (10.8)	*b* (618)
$[PtCl_2(CH_3SCH_2CH_2SCF_3)]$	4.0	2.4	H_2O–Me_2CO (7 : 1)	Stir for 24 h	63	10.9 (10.9)	1.60 (1.60)	14.7 (14.5)	16.0 (16.0)	442 (442)
$[PtCl_2(CH_3SCH_2CH_2SCF_3)_2]$	2.1	6.1	H_2O–Me_2CO (5 : 1)	Stir for 24 h	66	15.6 (15.5)	2.30 (2.25)	20.4 (20.7)	11.2 (11.5)	618 (618)
$[\{PdCl_2(CH_3SCH_2CH_2SCF_3)\}_2]$	4.0	2.0	H_2O–Me_2CO (7: 1)	Stir	61	13.9 (13.6)	2.10 (2.00)	18.4 (18.2)	19.7 (20.0)	706 (706)
$[PtCl_2(CH_3SCH_2CH_2SC_6F_5)]$	4.3	2.0	H_2O–Me_2CO (7 : 1)	Stir for 24 h	61	20.2 (20.0)	1.50 (1.30)	11.8 (11.9)	13.8 (13.1)	540 (540)
$[PtBr_2(CH_3SCH_2CH_2SC_6F_5)]$				Metathesis		17.4 (17.2)	1.15 (1.10)	10.2 (10.2)	25.6 (25.4)	629 (629)
$[PtCl_2(CH_3SCH_2CH_2SC_6F_5)_2]$	2.2	5.9	H_2O–Me_2CO (5 : 1)	Stir for 24 h	62	26.6 (26.5)	1.65 (1.70)	16.0 (15.8)	8.90 (8.70)	814 (814)
$[PtBr_2(CH_3SCH_2CH_2SC_6F_5)_2]$				Metathesis	100	24.2 (23.9)	1.75 (1.55)	14.5 (14.2)	17.8 (17.7)	903 (903)
$[PtI_2(CH_3SCH_2CH_2SC_6F_5)_2]$				Metathesis	100	21.6 (21.7)	1.55 (1.40)	12.6 (12.8)	25.3 (25.4)	*b* (997)
$[PdCl_2(CH_3SCH_2CH_2SC_6F_5)_2]$	As platinum				72	30.0 (29.8)	2.10 (1.95)	17.9 (17.7)	10.1 (9.80)	725 (725)
$[PdBr_2(CH_3SCH_2CH_2SC_6F_5)_2]$				Metathesis	100	26.7 (26.5)	1.60 (1.70)	15.6 (15.7)	19.8 (19.6)	814 (814)
$[PdI_2(CH_3SCH_2CH_2SC_6F_5)_2]$				Metathesis	100	23.8 (23.8)	1.35 (1.55)	14.3 (14.1)	27.7 (28.0)	*b* (908)

[a] Calculated values are given in parentheses. [b] Parent ions not observed for iodo-complexes.

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