Synthesis, Reactivity, and Fluorine-19 Nuclear Magnetic Resonance Spectra of Binuclear Trifluoromethylthio-complexes of Platinum and Palladium

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The preparation of $[M_2(SCF_3)_2(PR_3)_4]X_2$ complexes (M = Pd or Pt; R = Et or Ph; X = BF_4 or ClO_4) is described. ^{19}F N.m.r. spectra of these complexes are used to assign structures and to demonstrate the existence of *syn*- and *anti*-isomers. Bridge-cleavage reactions with PR_3, pyridine, *p*-toluidine, or chloride give monomeric species, *cis*-$[Pt(SCF_3)(L)(PR_3)_2]X$ or *cis*-$[PtCl(SCF_3)(PR_3)_2]$, and demonstrate the weakness of the SCF_3 bridge compared to SR bridges (where R = hydrocarbon radical). The preparation of the unusual complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ is also described.

CONSIDERABLE effort has been devoted to the synthesis and characterisation of transition-metal complexes containing bridging organothio-groups. However comparatively little attention has been paid to platinum-group metals and, in particular, to such complexes also containing tertiary phosphines. Chatt and Hart [1,2] have inserted EtS^- directly into Pt–Cl–Pt bridges by an elimination reaction, utilising EtSH, to give the complexes $[Pt_2Cl_2(\mu\text{-}SEt)_2(PR_3)_2]$. More recently $[M(SC_6X_5)_2]$ complexes (M = Pt and Pd; X = F [3] and Cl [4]) have been made by a similar type of reaction, starting with $PtCl_2$ and HSC_6X_5. These complexes are polymeric and can be cleaved by PPh_3 to give monomeric $[M(SC_6X_5)_2(PPh_3)_2]$. In a previous paper [5] we described preparations of the complexes $[M(SCF_3)_2(PPh_3)_2]$ and $[MCl(SCF_3)(PPh_3)_2]$ (M = Pt and Pd).

In this paper we describe the preparation and ^{19}F n.m.r. spectra of binuclear complexes containing SCF_3 as a bridging group. The results show a number of interesting features. For the first time the existence of *syn*- and *anti*-isomers has been demonstrated in square-planar complexes. The equilibrium between these isomers does not appear to be labile under normal conditions, but the ease of bridge cleavage by donor ligands shows that the SCF_3 bridges are rather weak, in sharp contrast with the strong bridging abilities of alkyl and aryl sulphides.

RESULTS AND DISCUSSION

Binuclear Complexes.—Two synthetic methods [equations (1) and (2)] were used to prepare the binuclear

$$2[MCl(SCF_3)(PPh_3)_2] + 2AgX \longrightarrow [M_2(SCF_3)_2(PPh_3)_4]X_2 + 2AgCl \quad (1)$$

$$[M_2Cl_2(PPh_3)_4]X_2 + 2AgSCF_3 \longrightarrow [M_2(SCF_3)_2(PPh_3)_4]X_2 + 2AgCl \quad (2)$$

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complexes ($M = Pd$ or Pt and $X = BF_4$ or ClO_4). Reactions similar to (2) also yielded $[M_2(SCF_3)_2(PEt_3)_4]X_2$ complexes ($M = Pd$ and $X = BF_4$; $M = Pt$, $X = BF_4$ or ClO_4). All these preparations proceeded smoothly in dichloromethane or acetone solution * giving high yields and almost quantitative precipitation of silver(I) chloride. I.r. spectra of the products showed the absence of bands due to ν(Pt–Cl), very strong but poorly resolved ν(C–F) modes, and the appropriate anion absorptions. Conductivity measurements in nitromethane gave values in the range appropriate for 1 : 2 electrolytes.[6] Characterisation data are summarised in the Table and structures are assigned mainly on the basis of the n.m.r. spectra discussed below.

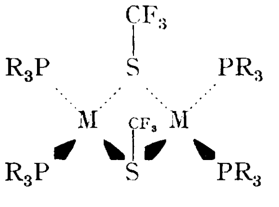
Characterisation data

Complex	M.p. (t/°C)	Analyses (%) C Calc.	C Found	H Calc.	H Found	Molar conductance [a] Ω^{-1} cm^2	δ [c]	^{19}F N.m.r. [b] $^3J_{PtF}$	$^4J_{PF}$ (*trans*)
$[Pd_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$	188—193 (decomp.)	53·4	54·2	3·6	3·8	158	23·33		5·5
							23·57		5·5
$[Pd_2(SCF_3)_2(PPh_3)_4](BF_4)_2$	176—181 (decomp.)	54·3	54·4	3·7	3·9	152	22·85		5·5
							23·14		5·5
$[Pd_2(SCF_3)_2(PEt_3)_4](BF_4)_2$	158—162	29·4	29·2	5·7	5·7	181	21·25		5·0
$[Pd_2Cl_3(SCF_3)(PPh_3)_3]$ (III)	124—130	54·7	52·7	3·8	4·0	89	27·43		
$[Pd_2Cl_3(SCF_3)(PPh_3)_3]$ (IV)	154—156	54·7	54·1	3·8	4·5	80	22·60		10·0
$[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$	237—240	48·3	49·1	3·3	3·4	161	27·40	61	5·0
$[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$	205—215 (decomp.)	49·0	50·7	3·3	3·7	152	26·90	59	5·0
							27·15	61	5·0
$[Pt_2(SCF_3)_2(PEt_3)_4](ClO_4)_2$	208—212	24·7	24·9	4·8	4·8	188	26·20	52	5·0
$[Pt_2(SCF_3)_2(PEt_3)_4](BF_4)_2$	189—193	25·2	25·7	4·9	5·1	195	26·20	52	5·0
$[Pt(SCF_3)(ClO_4)(PPh_3)_2]$	173—177	48·3	48·3	3·3	3·7	60 [d]	26·12	58	10·5
cis-$[Pt(SCF_3)(py)(PPh_3)_2]BF_4$ [e]	200—203	51·1	51·5	3·6	3·8	95	25·80	56	9·5
cis-$[Pt(SCF_3)(py)(PEt_3)_2]BF_4$ [f]	189—195	31·0	30·2	5·1	5·1	89	23·60	53	9·0
cis-$[Pt(SCF_3)(p\text{-toluidine})(PPh_3)_2]BF_4$ [g]	195—200 (decomp.)	52·1	51·9	3·9	3·8	100	26·00	57	10·0
cis-$[Pt(SCF_3)(p\text{-toluidine})(PEt_3)_2]BF_4$	Not isolated						22·70	57	8·5
$[Pt(SCF_3)(PEt_3)_3]BF_4$	Not isolated						21·60	64	10·0
$[Pt(SCF_3)(PPh_3)_3]BF_4$	Not isolated						23·01	58	7·5

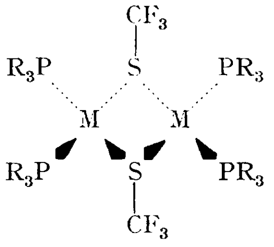
[a] Nitromethane solution at 25 °C. [b] Coupling constants in Hz; chemical shifts in CH_2Cl_2 solution in p.p.m. upfield from $CFCl_3$ as external reference. $^4J_{PF}(cis) < 1$ Hz in all cases except $[Pt(SCF_3)(PR_3)_3]BF_4$ [R = Et (1·5 Hz), R = Ph (3·0 Hz)]. [c] *syn*-Isomer probably resonates at lower field in the platinum complexes; distinction could not be made in the palladium complexes. [d] 22 and 90 Ω^{-1} cm^2 in CH_2Cl_2 and acetone solution respectively. [e] N (Found: 1·3. Calc.: 1·4%). [f] N (Found: 1·5. Calc.: 2·0%). [g] N (Found: 0·8. Calc.: 1·4%).

The ^{19}F n.m.r. spectrum of the complex $[Pd_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$, prepared by route (1), consisted of two triplets (δ 23·33 and 23·57 p.p.m. upfield from external CCl_3F, relative intensities *ca.* 20 : 1). Coupling within the triplets was 5·5 Hz in both cases and the tetrafluoroborate salt prepared by the same route had a similar spectrum except that the high-field triplet was the most intense (δ 22·85 and 23·14 p.p.m., relative intensities *ca.* 1 : 5).

In bridged di-μ-organothio-complexes geometrical isomers are possible depending on the arrangement of the organo-substituents relative to one another. Such isomerism is well known for complexes with octahedral or trigonal-bipyramidal co-ordination of the central metal atoms [7-13] but its occurrence has not been established for square-planar complexes. Although Chatt and Hart [2] did discuss this type of isomerism for $[Pt_2Cl_2(SR)_2(PPr^n{}_3)_2]$ complexes, they had only dipole-moment evidence and were consequently unable to reach any definite conclusions. For our $[M_2(SCF_3)_2(PR_3)_4]^{2+}$ cations the two possible geometrical isomers are (I) and (II). Both isomers belong to the AA′A″A‴X_3X_3' spin system (A = ^{31}P, X = ^{19}F) and, although this is too complex for our computer program,† we were able to obtain approximate simulated spectra using an AA′A″A‴XX′ model. The results are valid for the X region of the spectrum provided $J_{XX'}$ is small. Assuming $^4J_{PF}(trans) = 5$ Hz, variable $^2J_{PP}$, and all other $J = 0$.



(I)
syn-Isomer



(II)
anti-Isomer

the simulations show that small values of $^2J_{PP}$ (<2 Hz) give triplet spectra changing to quintets for large values

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* Choice of solvent was critical in some cases (see Experimental section).

† The UEAITR program used here has a limit of seven nuclei having a maximum product of multiplicities of 216.

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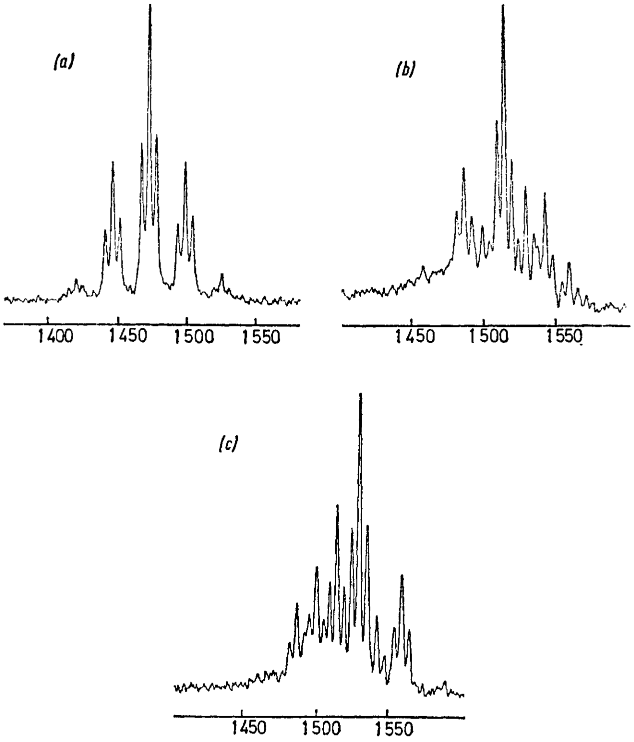
($\geqslant$20 Hz). The coupling within the triplets is $^4J_{PF}(trans)$ and within the quintets it is *ca.* $\frac{1}{2}\,^4J_{PF}(trans)$ {actually $\frac{1}{2}[^4J_{PF}(trans) + {}^4J_{PF}(cis)]$}. We therefore conclude that the two triplets observed for the complexes $[Pd_2(SCF_3)_2(PPh_3)_4]X_2$, prepared by route (1), are due to a mixture of *syn*- and *anti*-isomers, each having $^4J_{PF}(trans) = 5{\cdot}5$, $^4J_{PF}(cis) < 1$, and $^2J_{PP} < 2$ Hz. Preparations of these complexes by route (2) resulted in similar isomer mixtures with relative intensities of the low-field : high-field resonances being *ca.* 3 : 2 (ClO_4^- salt) and *ca.* 5 : 1 (BF_4^- salt). A preparation of the complex $[Pd_2(SCF_3)_2(PEt_3)_4](BF_4)_2$ by this route gave only a single isomer.

^{19}F Spectra of the analogous platinum complexes are complicated by coupling to ^{195}Pt (33·8% abundant, $I = \frac{1}{2}$). Any particular $[Pt_2(SCF_3)_2(PR_3)_4]^{2+}$ ion may have zero, one, or two magnetically active ^{195}Pt nuclei and the respective probabilities are 4/9, 4/9, and 1/9. If the spectrum in the absence of ^{195}Pt coupling is a triplet, as in the palladium cases, then overlapping of the resultant triplet of triplets, doublet of triplets, and single triplet gives an overall spectrum consisting of a 1 : 8 : 18 : 8 : 1 quintet of triplets. The spectrum of the complex $[Pt_2(SCF_3)_2(PEt_3)_4](ClO_4)_2$ [Figure (*a*)] was of this type and the BF_4^- salt had a similar spectrum, showing that both salts have a single isomeric form of the cation. Similar spectra were also obtained for the $[Pt_2(SCF_3)_2(PPh_3)_4]^{2+}$ cation prepared by route (1) (BF_4^- salt: $^3J_{PtF}$ 59 Hz, δ 26·9 p.p.m.; ClO_4^- salt: $^3J_{PtF}$ 61 Hz, δ 27·4 p.p.m.), but the slightly different chemical shifts and coupling constants suggest that one salt has a *syn*- and the other an *anti*-cation. Preparation of the complex $[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$ by route (2) again gave the high-field isomer ($^3J_{PtF}$ 61 Hz) but the corresponding BF_4^- salt gave a more complex spectrum [Figure (*b*)]. After 1 week in dichloromethane solution the spectrum had changed [Figure (*c*)] and the patterns may be interpreted as due to mixtures of *syn*- and *anti*-isomers ($^3J_{PtF}$ 59 and 61 Hz, δ 26·9 and 27·15 p.p.m., relative intensities *ca.* 3 : 1 changing to *ca.* 2 : 3). The isomer having $^3J_{PtF} = 61$ Hz may be the *anti*-form (see discussion below), but an unambiguous assignment is not possible.



^{19}F N.m.r. spectra at 56·4 MHz: (*a*), $[Pt_2(SCF_3)_2(PEt_3)_4](ClO_4)_2$; (*b*), mixture of *syn*- and *anti*-$[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$; and (*c*), (*b*) after 1 week at 25 °C. The spectra were recorded in CH_2Cl_2 solution and the scale is in Hz upfield from external $CFCl_3$

No general pattern of isomer preferences is apparent from these results but some features call for comment. First, the ability to isolate various mixtures of isomers, and in some cases pure isomers, shows that the *syn*–*anti*-equilibrium is not labile under ordinary conditions. Although some slow interconversion does occur for the complex $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$, the general situation is in contrast to the labile, dynamic equilibrium postulated previously [2] on the basis of the dipole moment of $[Pt_2Cl_2(S{\cdot}C_6H_4{\cdot}NO_2)_2(PPr^n_3)_2]$. Secondly, all the triethylphosphine complexes and platinum perchlorate salts give products which are single isomers.[*] Presumably, some form of Pt–S bond fission is involved in isomer interconversions and this may be facilitated by the higher *trans*-influence of triethylphosphine. For the perchlorates the co-ordinating ability of the anion may labilise the interconversion by fission of one Pt–S bond [†] or it may influence the steric course of the preparative reaction. In these cases it is not clear whether the single product is the thermodynamically favoured isomer or whether there is some steric effect on the ease of bridge cleavage by solvent or anion in the *syn*- and *anti*-forms (see discussion of bridge-cleavage reactions below).

Further evidence that the co-ordinating ability of perchlorate is important in these systems comes from the reaction of the complex $[Pt_2Cl_2(PPh_3)_4](ClO_4)_2$ with $AgSCF_3$. In acetone as reaction solvent the high-field isomer of the complex $[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$ was formed but in dichloromethane the reaction also gave a product showing a 1 : 4 : 1 triplet of doublets in the ^{19}F n.m.r. spectrum. Reaction in nitromethane gave a product showing only the triplet of doublets. The presence of only three doublets and their intensity ratios show that the signals are due to a monomeric platinum complex with a phosphorus atom *trans* to the SCF_3 group. The product analyses as $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ and its conductivities in nitromethane or

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[*] Probably *anti* (see discussion under bridge-cleavage reactions).

[†] Complete bridge cleavage with fission of two bonds is improbable in view of failure of the complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ to dimerise.

acetone indicate that it is a 1 : 1 electrolyte,* although the values (60 and 90 Ω^{-1} cm^2, respectively) are amongst the lowest recorded suggesting that dissociation is not complete.[6] Unfortunately the presence or absence of co-ordinated perchlorate cannot be corroborated by i.r. evidence as C–F modes obscure the critical ClO_4^- modes. Several reactions of the complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ confirm our formulation. Stirring with 48% aqueous HBF_4 resulted in the high-field isomer of the complex $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ together with *ca.* 30% of a hydrolysed product, $[Pt_2(OH)(SCF_3)(PPh_3)_4](BF_4)_2$. The latter was characterised by its ^{19}F n.m.r. spectrum which consisted of a quintet of quintets [δ 22·82 p.p.m., $^3J_{PtF}$ 40, $^4J_{PF}(trans)$ 5·0 Hz, see discussion of $AA'BB'X_3$ system below] and by the occurrence of ν(O–H) at 3 450 cm^{-1} in the i.r.[14] Addition of 100% excess of triphenylphosphine or pyridine (py) to solutions of the complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ in dichloromethane gave *ca.* 20% conversion to $[Pt(SCF_3)(PPh_3)_3]ClO_4$ or 100% conversion to *cis*-$[Pt(SCF_3)(py)(PPh_3)_2]ClO_4$, both complexes being identified by their first-order ^{19}F n.m.r. spectra (see Table).

Co-ordinated perchlorate has been observed before in a number of cases,[15,16] including some platinum and palladium complexes[17] and an iridium complex, $[Ir(ClO_4)(CO)(PPh_3)_2]$,[18] which is very similar to our example. The failure of the complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ to yield sulphur-bridged species in solution is however very surprising, as is the reaction of $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ with excess of $NaClO_4$ to give only $[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$ with no evidence for bridge-cleaved products. Construction of Courtaulds molecular models shows that all these complexes are very seriously constrained by interactions between the CF_3 and phenyl groups and it is reasonable to postulate a steric barrier to interconversion of the complexes $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ † and $[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$.

Reactions of the complexes $[Pt_2Cl_2(PPh_3)_4](BF_4)_2$ or $[Pt_2Cl_2(PEt_3)_4](ClO_4)_2$ with $AgSCF_3$ gave only binuclear species with no evidence for bridge-cleaved products and in the absence of mechanistic data it is not possible to reach definite conclusions as to why $[Pt_2Cl_2(PPh_3)_4](ClO_4)_2$ behaves differently or why the reaction is solvent dependent. However, it is clear that a delicate balance exists between steric effects, co-ordinating abilities of the anion and solvent, and the rather weak bridging ability (see discussion below) of the SCF_3 group. For example, one possible first step in route (2) is cleavage of the chloride bridge by SCF_3^- followed by a reaction identical to route (1). Perchlorate might inhibit this in some circumstances by competing for axial co-ordination sites and thus promoting an alternate reaction path such as chloride abstraction by silver(I) ion.

Spectra of $[Pt_2(SCF_3)_2(PPh_3)_4]X_2$ complexes from route (1) showed the presence of *ca.* 15% impurity which appeared as a 1 : 8 : 18 : 8 : 1 quintet of poorly resolved quintets with apparent couplings 20 and 2·5 Hz respectively. The intensity ratios of the quintets show that the complex is binuclear and, since we have experienced difficulty in obtaining *cis*-$[PtCl(SCF_3)(PPh_3)_2]$ free from *cis*-$[PtCl_2(PPh_3)_2]$, we suggest that the minor product is $[Pt_2Cl(SCF_3)(PPh_3)_4]X_2$, produced by reaction (3) (X = BF_4 or ClO_4). The complexes belong to the

$$[PtCl_2(PPh_3)_2] + [PtCl(SCF_3)(PPh_3)_2] + 2AgX \longrightarrow [Pt_2Cl(SCF_3)(PPh_3)_4]X_2 + 2AgCl \quad (3)$$

$AA'BB'X_3$ spin system (A = B = ^{31}P, X = ^{19}F) and computer simulation [assuming $^4J_{PF}(trans)$ 5 Hz, variable $^2J_{PP}$, all other $J = 0$] showed that as $^2J_{PP}$ increases the spectra change from triplets [coupling = $^4J_{PF}(trans)$] to quintets [apparent coupling = $\frac{1}{2}$ $^4J_{PF}(trans)$] with intermediate spectra occurring when $\delta_{P_A} - \delta_{P_B} \simeq {}^2J_{PP}$. Our experimental data therefore give $^4J_{PF}(trans)$ 5·0, $^3J_{PtF}$ 40 Hz, and, if $^2J_{PP}$ is small (<10 Hz), as is expected from data on di-μ-SCF_3-complexes, then $\delta_{P_A} - \delta_{P_B}$ is also small, probably <5 Hz.

Attempts to synthesise $[Pt_2Cl(SCF_3)(PPh_3)_4]X_2$ complexes by reactions between equimolar quantities of $[Pt_2Cl_2(PPh_3)_4](BF_4)_2$ with $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ or $AgSCF_3$ were unsuccessful. A by-product in the preparation of the complexes $[Pd_2(SCF_3)_2(PPh_3)_4]X_2$ by route (2) is an ether-soluble red material. This also formed when the complex *trans*-$[PdCl(SCF_3)(PPh_3)_2]$ was set aside in acetone for several weeks. Chromatography of this material on deactivated silica gave two components, one (the minor fraction) yellow and the other orange-red. Both complexes analysed close to $Pd_2Cl_3(SCF_3)(PPh_3)_3$, and measurements of their molar conductivities in $MeNO_2$ showed them to be 1 : 1 electrolytes based on a molecular weight of 1 207. Molecular-weight measurements gave values *ca.* 690 indicating almost complete dissociation. I.r. spectra of both complexes showed intense but poorly resolved ν(C–F) bands at *ca.* 1 100 cm^{-1} and a weak broad absorption at *ca.* 300 cm^{-1}. The latter region could be associated with either bridging or terminal Pd–Cl groups since the *trans*-influence of SCF_3 or PPh_3 ligands causes a lowering of terminal ν(Pd–Cl) frequencies into the region normally associated with bridging chloride.[5] The ^{19}F n.m.r. spectrum of the red complex consisted of a single peak, whereas the yellow complex showed a doublet. On this basis we tentatively suggest that the red and yellow compounds have structures (III) and (IV) respectively.

Bridge-cleavage Reactions.—Recent discussions of the relative bridging abilities of various ligands[19,20] have

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* It also conducts in dichloromethane (22 Ω^{-1} cm^2), but values for various electrolyte types have not been established in this solvent.

† Or a corresponding solution species in which the perchlorate group is replaced by a solvent molecule.

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[19] J. Chatt and B. Heaton, *J. Chem. Soc. (A)*, 1968, 2745.

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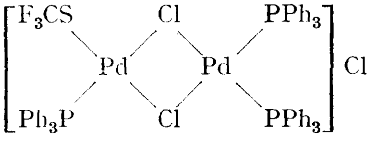
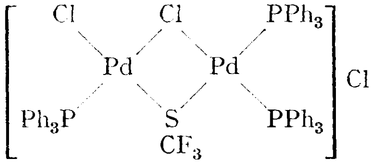
suggested that SR is a very strong bridging group. The comparative rarity of terminal SR groups (R = hydrocarbon radical) confirms this view. However, introduction of an electronegative fluorocarbon group[10,21] is expected to markedly reduce the bridging ability of the sulphur and it was consequently of interest to investigate the susceptibility of SCF_3 bridges to cleavage reactions. Under conditions chosen to parallel those used in the corresponding reactions of the complexes $[Pt_2Cl_2(PR_3)_4](BF_4)_2$,[22,23] we found that the mixture of *syn*- and *anti*-isomers of $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ readily underwent bridge cleavage by Cl^-, py, or *p*-toluidine to yield the known *cis*-$[PtCl(SCF_3)(PPh_3)_2]$[5] and the new products *cis*-$[Pt(SCF_3)L(PPh_3)_2]BF_4$ (L = py or *p*-toluidine). These bridge-cleaved products were characterised by their first-order ^{19}F n.m.r. spectra which consisted of 1 : 4 : 1 triplets of doublets due to coupling to ^{195}Pt and the *trans* phosphorus atom respectively. Retention of stereochemistry on cleavage is consistent with our studies on other bridge-cleavage reactions.[22]


(III)


(IV)

Reaction of the complex $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ with PPh_3 did not give $[Pt(SCF_3)(PPh_3)_3]BF_4$. However, the initial mixture of isomers was completely converted into the isomer having the high-field ^{19}F resonance (J_{PtF} 61 Hz) and this suggests that partial bridge cleavage is occurring with consequent labilisation of isomer interconversion. As discussed above for the case of labilisation by the perchlorate group, this is probably fission of a single Pt–S bond, but we also found that $AgSCF_3$ did not react with the ion $[PtCl(PPh_3)_3]^+$ and $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ gave only 20% reaction with PPh_3. Both processes are expected to yield the ion $[Pt(SCF_3)(PPh_3)_3]^+$ and their failure to do so suggests that this species is thermodynamically unstable.* Construction of Courtaulds molecular models shows that it would be extremely sterically crowded and they also show that bridge cleavage of the ion $[Pt_2(SCF_3)_2(PPh_3)_4]^{2+}$ by bulky ligands such as PPh_3 would be inhibited by the CF_3 groups in the *anti*-isomer but permitted in the *syn*-isomer. It is therefore probable that in the reaction of the ion $[Pt_2(SCF_3)_2(PPh_3)_4]^{2+}$ with PPh_3 a small equilibrium percentage of cleaved product is formed from the *syn*-isomer, but it is not clear whether this product is a result of fission of one or two Pt–S bonds. Reformation of the bridges results in *syn*- and *anti*-isomers equally and if the *anti*-isomer is inert to further cleavage the mixture of isomers is gradually converted to pure *anti*-isomer. Alternatively the *anti*-isomer may be the thermodynamically favoured form since molecular models show CF_3–Ph interactions to be less in this configuration, but in either case it is probable that ^{19}F resonances at high field, with $^3J_{PtF} = 61$ Hz, can be assigned to this isomer. A similar set of cleavage reactions was observed for the complex $[Pt_2(SCF_3)_2(PEt_3)_4](BF_4)_2$ with Cl^-, py, *p*-toluidine, and PEt_3. In this case there were no problems with the phosphine reaction which yielded $[Pt(SCF_3)(PEt_3)_3]BF_4$ as expected. However, the product decomposed before it could be isolated and was characterised by its first-order ^{19}F n.m.r. spectrum.

The extreme ease of cleavage of these SCF_3 bridges is in marked contrast to the failure of hydrocarbon thio-bridges to react with any bridge-splitting ligand.[19,20] Although the previous reactions are not strictly comparable since neutral, $[Pt_2Cl_2(SR)_2(PR_3)_2]$, species were used as opposed to our cationic species, the data still demonstrate that the bridging ability of sulphur is considerably reduced by the highly electronegative fluorine atoms. The SCF_3^- ion must therefore be placed very low in the series of relative bridging abilities proposed by Chatt *et al.*[20] for anionic ligands in platinum complexes. In the sequence $SnCl_3^- < SO_2R^- < Cl^- < Br^- < I^- < POR_2^- < SR^- < PR_2^-$, the SCF_3^- ion is probably similar to SO_2R^- in its bridging ability.

EXPERIMENTAL

Data relating to the characterisation of the new complexes are given in the Table. Microanalyses were by Schwartzkopf Microanalytical Laboratory, New York, or by Dr. D. L. McGillivray of this department. The molecular weight of the complex $[Pd_2(PPh_3)_3Cl_2(SCF_3)]Cl$ was determined in dibromomethane solution (*ca.* 3×10^{-3}M solution) at 50 °C using an Hitachi–Perkin-Elmer model 115 vapour-phase osmometer. Molar conductivities were measured in nitromethane solutions at 25 °C on a Radiometer model CDM 3 conductivity meter using a Radiometer CDC324 cell. ^{19}F N.m.r. spectra were recorded at 56·4 MHz on a Varian HA-60 spectrometer with signal-to-noise enhancement using a Northern Scientific NS 500 time-averaging

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* There could also be kinetic reasons but the evidence favours the thermodynamic explanation. We have also studied several related reactions which suggest that this instability is general for $[Pt(SCF_3)(PR_3)_3]^+$ complexes. Thus the complex $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ reacts readily with py to give *cis*-$[Pt(SCF_3)(py)(PPh_3)_2]$, and $AgSCF_3$ with *cis*-$[PtCl(py)(PEt_3)_2]^+$ gives *cis*-$[Pt(SCF_3)(py)(PEt_3)_2]^+$, but *cis*-$[PtCl(PEt_3)_2(PPh_3)]^+$ and $[PtCl(PEt_3)_3]^+$ do not react with $AgSCF_3$. The complex *cis*-$[PtCl(SCF_3)(PR_3)_2]$ with PR_3 and $NaClO_4$ gives $[PtCl(PR_3)_3]^+$ instead of the expected $[Pt(SCF_3)(PR_3)_3]^+$ (R = Et or Ph).

[21] P. Rosenbuch and N. Welcman, *J.C.S. Dalton*, 1972, 1963 and references therein.

[22] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Canad. J. Chem.*, in the press.

[23] K. R. Dixon and D. J. Hawke, *Canad. J. Chem.*, 1971, **49**, 3252.

computer. Chemical shifts are given in p.p.m. relative to $CFCl_3$ as external reference and positive values denote upfield shifts. Simulated spectra were calculated using the UEAITR program [24] on an IBM 370/145 computer. I.r. spectra were recorded from 4 000 to 250 cm^{-1} as Nujol mulls between caesium-iodide plates on a Beckmann IR20 spectrophotometer. M.p.s were determined as a Reichert hot-stage apparatus and are uncorrected.

Reactions were routinely conducted at 25 °C in an atmosphere of nitrogen, deoxygenated by passage through acidic chromium(II) chloride and dried by calcium chloride and type 4A molecular sieves. Solvents were of Spectrograde quality and were dried and stored over type 4A molecular sieves. Pentane was further purified by distillation from P_2O_5.

Preparations.—The complexes *trans*-$[PdCl(SCF_3)(PPh_3)_2]$,[5] *cis*-$[PtCl(SCF_3)(PPh_3)_2]$,[5] $[M_2Cl_2(PPh_3)_4]X_2$ (M = Pd or Pt; X = BF_4 or ClO_4),[23] $[Pd_2Br_2(PEt_3)_4](BF_4)_2$,[23] $[Pt_2Cl_2(PEt_3)_4]X_2$ (X = BF_4 [23] or ClO_4 [22]), and $AgSCF_3$ [25] were prepared as previously described or, in the case of some ClO_4 salts, by methods exactly analogous to those used for corresponding tetrafluoroborates. $AgClO_4$ and $AgBF_4$ were obtained from B.D.H. and City Chemicals respectively and were used as received.

Route (1). In a typical reaction the complex *trans*-$[PdCl(SCF_3)(PPh_3)_2]$ (0·216 g, 0·281 mmol) in dichloromethane (20 cm^3) was added dropwise to a solution of $AgClO_4$ (0·059 g, 0·285 mmol) in acetone (5 cm^3). After stirring for 30 min and filtering from AgCl, the solution was evaporated to *ca.* 2 cm^3 *in vacuo*. Addition of ether to the cloud point, followed by refrigeration overnight at −20 °C, gave the *complex* $[Pd_2(SCF_3)_2(PPh_3)_4][ClO_4]_2$ (0·143 g, 0·086 mmol). Similar procedures using the complexes *trans*-$[PdCl(SCF_3)(PPh_3)_2]$ or *cis*-$[PtCl(SCF_3)(PPh_3)_2]$ with $AgClO_4$ or $AgBF_4$ gave the following *complexes*: $[Pd_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ (48%); $[Pt_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$ (53%); and $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ (74%). Yields in parentheses are given after crystallisation which is a difficult procedure for these complexes. Much higher yields (80—90%) of crude products were obtained. The crude platinum products also contained the complexes $[Pt_2Cl(SCF_3)(PPh_3)_4]X_2$ (see Results section) and this impurity prevented us from obtaining a good analysis for $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$.

Route (2). Products from reactions (*a*)—(*d*) below were recrystallised by addition of diethyl ether to dichloromethane solutions to the cloud point followed by refrigeration overnight at −20 °C.

(*a*) $[Pd_2(SCF_3)_2(PPh_3)_4](ClO_4)_2$. To a suspension of the complex $[Pd_2Cl_2(PPh_3)_4](ClO_4)_2$ (0·940 g, 0·614 mmol) in nitromethane (25 cm^3) was added $AgSCF_3$ (0·261 g, 1·25 mmol) in acetone (10 cm^3). After stirring overnight filtration gave AgCl (0·142 g, 0·99 mmol) and a lemon-yellow solution. The solution was evaporated to *ca.* 10 cm^3 *in vacuo* whereupon a white impurity precipitated and was removed by filtration. Further evaporation of the filtrate to *ca.* 2 cm^3 followed by addition to stirred diethyl ether (300 cm^3) gave the *complex* (0·750 g, 0·451 mmol) and a red ether-soluble material. The latter was isolated by evaporation of the ether *in vacuo* and by stirring the oily residue in pentane. Chromatography on silica of the solid so obtained gave a small yellow, and a main red, band on elution with 1 : 4 acetone–dichloromethane. The solids obtained on evaporation of solvent were analysed without recrystallisation and their formulation is discussed in the Results section.

(*b*) $[Pd_2(SCF_3)_2(PPh_3)_4](BF_4)_2$. By a procedure similar to (*a*) above, $[Pd_2Cl_2(PPh_3)_4](BF_4)_2$ (0·800 g, 0·531 mmol) in acetone (60 cm^3) and $AgSCF_3$ (0·263 g, 1·26 mmol) in acetone (10 cm^3) gave the *complex* (0·420 g, 0·256 mmol) after a reaction time of 30 min. A red product similar to that in (*a*) was also obtained.

(*c*) $[Pd_2(SCF_3)_2(PEt_3)_4](BF_4)_2$. The complex $[Pd_2Br_2(PEt_3)_4](BF_4)_2$ (0·329 g, 0·323 mmol) in dichloromethane (10 cm^3) was added dropwise to $AgSCF_3$ (0·136 g, 0·651 mmol) in acetone (10 cm^3). After stirring for 30 min and filtration from AgBr, concentration to *ca.* 2 cm^3 followed by addition of diethyl ether to the cloud point gave the *complex* (0·085 g, 0·080 mmol) after refrigeration overnight at −20 °C.

(*d*) $[Pt_2(SCF_3)_2(PPh_3)_4]X_2$ (X = BF_4 *or* ClO_4). By a procedure similar to (*a*) above, $[Pt_2Cl_2(PPh_3)_4](ClO_4)_2$ (0·328 g, 0·192 mmol) in acetone suspension (20 cm^3) or $[Pt_2Cl_2(PPh_3)_4](BF_4)_2$ (1·00 g, 0·594 mmol) in dichloromethane (40 cm^3) and $AgSCF_3$ (0·081 g, 0·388 mol; or 0·34 g, 1·63 mmol) in acetone (10 cm^3) after reaction times of 4 h (X = ClO_4) and 30 min (X = BF_4) gave the *complex* [0·250 g, 0·136 mmol (X = ClO_4) or 0·760 g, 0·419 mmol (X = BF_4)]. Reactions involving similar quantities of reagents but using nitromethane or dichloromethane solutions of the complex $[Pt_2Cl_2(PPh_3)_4](ClO_4)_2$ gave $[Pt(SCF_3)(ClO_4)(PPh_3)_2]$ as described in the Results section. The product from the reaction in nitromethane was isolated in essentially quantitative yield by evaporation of solvent *in vacuo* and recrystallised from methanol by addition of diethyl ether to the cloud point and refrigeration overnight at −20 °C.

(*e*) $[Pt_2(SCF_3)_2(PEt_3)_4](BF_4)_2$. The complex $[Pt_2Cl_2(PEt_3)_4](BF_4)_2$ (0·353 g, 0·319 mmol) in dichloromethane (15 cm^3) was added dropwise to $AgSCF_3$ (0·135 g, 0·646 mmol) in acetone (10 cm^3). After stirring for 1·5 h the solution was filtered from AgCl and evaporated *in vacuo* to leave an amber oil. This was extracted with dichloromethane and the extract re-evaporated to leave a colourless oil. Pumping overnight left a sticky solid which on recrystallisation from acetone, by addition of ether to the cloud point, gave the *complex* (0·305 g, 0·246 mmol) after refrigeration overnight at −20 °C.

(*f*) $[Pt_2(SCF_3)_2(PEt_3)_4](ClO_4)_2$. By a procedure similar to (*e*) above, the complex $[Pt_2Cl_2(PEt_3)_4](ClO_4)_2$ (0·350 g, 0·309 mmol) in dichloromethane (30 cm^3) and $AgSCF_3$ (0·132 g, 0·632 mmol) in acetone (10 cm^3) gave a colourless oil from the dichloromethane extract. Examination of the ^{19}F n.m.r. spectrum of this oil gave no evidence for the presence of bridge-cleaved species as observed in the preparation of $[Pt_2Cl_2(PPh_3)_4](ClO_4)_2$ [see (*d*) above]. Solution of the oil in 100% ethanol, followed by addition of ether to the cloud point, gave an oily solid after setting aside at −20 °C for 1 week. The supernatant liquid was decanted and treated further with ether to give the *complex* (0·090 g, 0·071 mmol) on cooling to −20 °C. The ^{19}F n.m.r. spectrum of the oily solid showed considerable contamination by the complex $[Pt_2Cl(SCF_3)(PEt_3)_4](ClO_4)_2$.

Bridge-cleavage reactions. (a) *Triphenylphosphine complexes*. Generally, the complex $[Pt_2(SCF_3)_2(PPh_3)_4](BF_4)_2$ (1 mol) was stirred in acetone with PPh_3 (2 mol), pyridine

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[24] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Mag. Res.*, 1970, **3**, 84.

[25] H. J. Emeléus and D. E. MacDuffie, *J. Chem. Soc.*, 1961, 2597.

(10 mol), *p*-toluidine (4 mol), or Et_4NCl (2 mol) for 30 min, 20, 20, and 2 h respectively. Reduction of the volume of the acetone solution by 90%, followed by addition to a large volume of diethyl ether, gave *cis*-[Pt(SCF_3)(py)(PPh_3)$_2$]BF_4 (73%) and *cis*-[Pt(SCF_3)(*p*-toluidine)(PPh_3)$_2$]BF_4 (62%). The known complex *cis*-[Pt(SCF_3)Cl(PPh_3)$_2$] was isolated by filtration from Et_4NBF_4, evaporation of the filtrate *in vacuo* and redissolution in dichloromethane before extraction with water, drying of the organic layer ($MgSO_4$), and re-evaporation.

(b) *Triethylphosphine complexes*. Similar reactions to those in (*a*) above carried out in n.m.r. tubes in dichloromethane (or, in the case of Et_4NCl, in acetone) gave products whose spectra indicated complete cleavage of the dimer after setting aside overnight. The complex *cis*-[Pt(SCF_3)(py)(PEt_3)$_2$]BF_4 (85%) was isolated by addition of diethyl ether to the acetone solution. Products of cleavage with PEt_3 and *p*-toluidine decomposed before they could be isolated.

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