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THE FORMATION OF POLYFLUOROPHENYLPLATINUM(II) COMPOUNDS BY SULPHUR DIOXIDE ELIMINATION REACTIONS *

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Summary

The organoplatinum compounds, PtR_2L_2 ($R = C_6F_5$ or p-HC_6F_4, L_2 = *trans*-$(py)_2$; $R = C_6F_5$, L_2 = 2,2′-bipyridyl (bipy)) have been prepared by reaction of the corresponding $PtCl_2L_2$ complexes and barium polyfluorobenzenesulphinates in boiling pyridine. Similar reactions gave $PtCl(C_6F_5)$phen (phen = 1,10-phenanthroline), $Pt(p\text{-}HC_6F_4)_2$bipy, $PtCl(p\text{-}HC_6F_4)$bipy, $Pt(p\text{-}HC_6F_4)_2$phen, and $PtCl(p\text{-}HC_6F_4)$phen either impure or in mixtures. Reaction of $Ba(O_2S\text{-}o\text{-}HC_6F_4)_2$ with *trans*-$PtCl_2(py)_2$ in boiling pyridine gave *trans*-$PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$, which lost SO_2 at 210–215°C to give *trans*-$PtCl(o\text{-}HC_6F_4)(py)_2$. Treatment of *trans*-$PtCl_2(py)_2$ with thallous pentafluorobenzenesulphonate in boiling pyridine did not result in desulphonation but $[Pt(py)_4](O_3SC_6F_5)_2$ was obtained.

Introduction

The comparatively high thermal stability of organoplatinum compounds [1] suggests scope for their synthesis by thermally induced CO_2, SO_2 or SO_3 elimination reactions, and we have recently prepared polyfluorophenylplatinum(II) complexes with heterocyclic nitrogen donor ligands [2] or phosphine ligands [3] by thermal decarboxylation reactions between appropriate chloroplatinum(II) complexes and thallous polyfluorobenzoates in boiling pyridine. Very limited use has been made of sulphur dioxide elimination reactions in the synthesis of organoplatinum(II) compounds [4,5], though organopalladium(II) species are believed to be intermediates in the palladium-catalysed desulphination of arenesulphinic acids and their salts [6]. It has been recently shown that thermal rearrangement of platinum(II) *S*-sulphinates into chelating *O*-sulphinates is a barrier to desulphination [7]. We now report a study of the use of sulphur dioxide elimination in the synthesis of polyfluorophenyl-

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platinum(II) complexes, together with an attempt to achieve an analogous desulphonation (SO_3 elimination) reaction.

Results and discussion

Desulphination reactions

Details of reactions of $PtCl_2L_2$ (L_2 = *trans*-$(py)_2$, 2,2′-bipyridyl (bipy), or 1,10-phenanthroline (phen)) complexes with barium polyfluorobenzenesulphinates, $Ba(O_2SR)_2$ (R = C_6F_5 or *p*-HC_6F_4) in boiling pyridine are given in Table 1. In each case, there was substantial elimination of sulphur dioxide and either the corresponding PtR_2L_2 complex (R = C_6F_5, L_2 = *trans*-$(py)_2$ or bipy; R = *p*-HC_6F_4, L_2 = *trans*-$(py)_2$), the $PtCl(R)L_2$ complex (R = C_6F_5, L_2 = phen), or a mixture of the two [R = *p*-HC_6F_4; L_2 = bipy or phen) was obtained.

$$PtCl_2L_2 + Ba(O_2SR)_2 \rightarrow PtR_2L_2 + BaCl_2 + 2SO_2 \quad (1)$$

$$2PtCl_2L_2 + Ba(O_2SR)_2 \rightarrow 2PtCl(R)L_2 + BaCl_2 + 2SO_2 \quad (2)$$

Use of an excess of the barium sulphinate favours the formation of pure PtR_2L_2 in good yield (Table 1). Inspection of the results suggests that further adjustment of the reaction stoichiometry could lead to elimination of product mixtures, at least for R = *p*-HC_6F_4, L_2 = bipy. The difficulty in achieving substantial conversion into PtR_2L_2 complexes using a stoichiometric amount of the barium sulphinate may be partly attributed to the low solubility of the barium salts in pyridine. In addition, traces of water which could not be removed were present in these reactants (cf. earlier preparations [8]) and could have led to some hydrolysis during desulphination. The choice of the barium salts as reagents is based on their superior stability in pyridine to the more accessible lithium salts [8], unsuccessful attempts to obtain the corresponding silver salts [8], and an easier preparation of the barium derivatives than possible routes to the thallium(I) salts. The formation of identifiable organoplatinum compounds in the reactions of $PtCl_2$phen (Table 1) is of particular interest, since treatment of this complex with thallous pentafluorobenzoate in boiling pyridine gives a blue-black mixture of unidentifiable products despite near quantitative decarboxylation [2].

Treatment of *trans*-$PtCl_2(py)_2$ with slightly greater than an equimolar amount of barium bis(2,3,4,5-tetrafluorobenzenesulphinate) resulted in some desulphination (Table 1), but $PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$ and not an organoplatinum(II) compound was the principal product.

$$2PtCl_2(py)_2 + Ba(O_2S\text{-}o\text{-}HC_6F_4)_2 \rightarrow 2PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2 + BaCl_2 \quad (3)$$

The same product was also obtained in good yield from reaction of $PtCl_2$bipy with the barium sulphinate (Table 1).

$$2PtCl_2\text{bipy} + Ba(O_2S\text{-}o\text{-}HC_6F_4)_2 + 4py \rightarrow 2PtCl(O_2S\text{-}o\text{-}HC_6F_4)_2(py)_2 + BaCl_2 + 2\text{bipy} \quad (4)$$

Formation of $PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$ (reaction 3) rather than $Pt(O_2S\text{-}o\text{-}HC_6F_4)_2(py)_2$ despite the initial stoichiometry (Table 1) can be related to formation of $PtCl(R)L_2$ rather than PtR_2L_2 complexes (above), and may be attributed to the low solubility of the barium sulphinate. The occurrence of ligand exchange in

reaction 4 presumably owing to the large excess of pyridine, has precedent in formation of some *trans*-$Pt(C_6F_5)_2(py)_2$ in the decarboxylation synthesis of $PtBr(C_6F_5)$bipy [2] in pyridine. Besides the sulphinato complex, the interaction of $Ba(O_2S\text{-}o\text{-}HC_6F_4)_2$ and $PtCl_2$bipy also gave two 2,3,4,5-tetrafluorophenylplatinum(II) complexes, probably $Pt(o\text{-}HC_6F_4)_2$bipy and $PtCl(o\text{-}HC_6F_4)$bipy (next section). Thus, at least some desulphination leading to organoplatinum compounds occurs in this reaction. This contrasts with decarboxylation syntheses of organoplatinum(II) compounds [2] where two fluorines *ortho* to the carboxyl are necessary for elimination of CO_2 to occur. To further illustrate the wider scope of desulphination, pyrolysis of $PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$ under nitrogen resulted in SO_2 elimination and formation of a 2,3,4,5-tetrafluorophenylplatinum(II) compound, albeit in low yield.

$$PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2 \rightarrow PtCl(o\text{-}HC_6F_4)(py)_2 + SO_2$$

Despite this evidence of increased scope, desulphination appears less synthetically useful at this stage than decarboxylation, mainly because thallous carboxylate reagents are more readily accessible than barium sulphinates.

Identification and stereochemistry of desulphination products

Characterization of a number of organoplatinum products was straightforward since the authentic compounds were available from decarboxylation reactions (see Experimental). Even though isolated impure or as mixtures, the phenanthroline complexes were identified unambiguously because of the close similarity of their ^3J(PtF) and ^3J(PtH) coupling constants and, for PtCl(R)phen complexes, their

TABLE 1

REACTIONS OF HALOGENOPLATINUM(II) COMPLEXES WITH BARIUM BIS(POLYFLUOROBENZENESULPHINATES) IN BOILING PYRIDINE (10 cm^3)

$PtCl_2L_2$		$Ba(O_2SR)_2$		Time (min)	Organoplatinum product	Yield [a] (%)	Yield SO_2 [b] (%)
L_2	mmol	R	mmol				
trans-(py)$_2$	0.50	C_6F_5	1.00	30	*trans*-$Pt(C_6F_5)_2(py)_2$	79	> 40
bipy	0.50	C_6F_5	1.00	105	$Pt(C_6F_5)_2$bipy	58	38
phen	0.50	C_6F_5	0.50	55	$PtCl(C_6F_5)$(phen) [c]	14	62
trans-(py)$_2$	0.50	*p*-HC_6F_4	0.53	90	*trans*-$Pt(p\text{-}HC_6F_4)_2(py)_2$	45	48
bipy	0.50	*p*-HC_6F_4	0.59	70	$Pt(p\text{-}HC_6F_4)_2$bipy [d]	14	56
					$PtCl(p\text{-}HC_6F_4)$bipy [d]	42	
phen	0.50	*p*-HC_6F_4	0.55	80	$Pt(p\text{-}HC_6F_4)_2$phen [d]	5	46
					$PtCl(p\text{-}HC_6F_4)$phen [d]	19	
					$Pt(O_2S\text{-}p\text{-}HC_6F_4)_2$phen [d]	8	
trans-(py)$_2$	0.50	*o*-HC_6F_4	0.55	120	*trans*-$PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$	62	> 26
bipy	0.50	*o*-HC_6F_4	0.75	120	*trans*-$PtCl(O_2S\text{-}o\text{-}HC_6F_4)(py)_2$	54	25
					$Pt(o\text{-}HC_6F_4)_2$bipy [e]		
					$PtCl(o\text{-}HC_6F_4)$bipy [e]		

[a] Yields based on the platinum reagent. [b] Based on the barium sulphinate. [c] Impure product. [d] Mixture of products. Yields determined using ^{19}F NMR spectroscopy. [e] Mixture, yields not determined.

ν(Pt–Cl) frequencies to those of the corresponding known [2] 2,2′-bipyridyl complexes (Table 2). The distinction between PtCl(*p*-HC_6F_4)phen and Pt(*p*-$HC_6F_4)_2$phen, obtained as a mixture, was confirmed by comparison of the F(2,6) chemical shifts (Experimental section) with those of the bipyridyl complexes [2]. All the phenanthroline complexes showed characteristic [9] intense infrared absorption near 840 cm^{-1}. Assignment of *trans* stereochemistry for PtCl(*o*-HC_6F_4)$(py)_2$ is based on the similarity of ^3J(PtH) and ν(Pt–Cl) to those of *trans*-PtCl(C_6F_5)$(py)_2$ and their wide difference from those of the necessarily *cis*-PtCl(C_6F_5)bipy (Table 2). In addition, observation of a single infrared absorption in the region 500–440 cm^{-1}, viz. 471w, which can be assigned to a coupled ring mode and ν(Pt–N) vibration [10], is consistent with *trans* stereochemistry [10]. Comparison of ^3J(PtF) with those of *trans*-PtCl(C_6F_5)$(py)_2$ and PtCl(C_6F_5)bipy does not provide a clear indication of stereochemistry. This is not surprising because ^3J(MF) values for C_6F_5 and *o*-HC_6F_4 complexes can differ markedly [8,11,12]. The *trans*-stereochemistry of PtCl(O_2S-*o*-HC_6F_4)$(py)_2$ is evident from ^3J(PtH) and ν(Pt–Cl) values (Table 2). In this case, the 500–440 cm^{-1} spectrum cannot be used diagnostically since Ba(O_2S-*o*-$HC_6F_4)_2$ has two bands in the region. The $\nu(SO_2)$ frequencies of the platinum sulphinate (Experimental section) are clearly indicative [13] of *S*-sulphinate coordination. Chemical shift values (Experimental section) reveal that two minor products obtained in addition to *trans*-PtCl(O_2S-*o*-HC_6F_4)$(py)_2$ from $PtCl_2$bipy and Ba(O_2S-*o*-$HC_6F_4)_2$ are 2,3,4,5-tetrafluorophenylplatinum(II) compounds and are consistent with 2,2′-bipyridyl rather than pyridine as the uncharged ligand.

An attempted desulphonation

Reaction of thallous pentafluorobenzenesulphonate with *trans*-$PtCl_2(py)_2$ in an attempt to yield *trans*-Pt($C_6F_5)_2(py)_2$ by desulphonation was unsuccessful, giving instead a tetrapyridineplatinum(II) derivative.

$$trans\text{-}PtCl_2(py)_2 + 2TlO_3SC_6F_5 + 2py \rightarrow [Pt(py)_4](O_3SC_6F_5)_2 + 2TlCl$$

Thus, use of desulphonation in organometallic synthesis still remains restricted to mercury [14,15].

TABLE 2

SPECTROSCOPIC PROPERTIES OF SOME PtR_2L_2 AND $PtCl(R)L_2$ COMPLEXES

Compound	$^3J(^{195}PtF)$ (Hz)	$^3J(^{195}PtH)$ (Hz)	ν(Pt–Cl) (cm^{-1})
PtCl(C_6F_5)phen	354	22 [a]	353
PtCl(C_6F_5)bipy [b]	355	21 [c]	349
PtCl(*p*-HC_6F_4)phen	350	22 [a]	353
PtCl(*p*-HC_6F_4)bipy [b]	355	20 [c]	350
Pt(*p*-$HC_6F_4)_2$phen	455	[d]	–
Pt(*p*-$HC_6F_4)_2$bipy [b]	443	[d]	–
trans-PtCl(*o*-HC_6F_4)$(py)_2$	364	48	292
trans-PtCl(C_6F_5)$(py)_2$ [b]	385	46	297
trans-PtCl(O_2S-*o*-HC_6F_4)$(py)_2$	–	44	315
$[Pt(py)_4](O_3SC_6F_5)_2$	–	40	–

[a] ^3J(PtH(2)); N(1) is *cis* to Cl. Coupling to H(9) is not resolvable. [b] From Ref. 2. [c] ^3J(PtH(6)); N(1) is *cis* to Cl. Coupling to H(6′) not resolvable. [d] Not resolvable.

Experimental

(a) General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Thallium(I) was determined with potassium iodate under Andrew's conditions [16]. Sulphur dioxide was determined by absorption in an acidified standard iodine solution followed by titration of residual iodine with sodium thiosulphate [8]. Infrared, mass and NMR spectra were determined as described previously [2]. Listed IR bands (below) are restricted to those of strong intensity in the region 1700–650 cm^{-1}, whilst ν(Pt–Cl) frequencies are in Table 2 *. In mass spectra, clusters for platinum-containing ions showed correct isotope patterns. Only the most intense peak (containing ^{195}Pt or ^{231}(PtCl)) of clusters with intensity $\geqslant 10\%$ (except for parent ions) of that of the base peak cluster [PtL_2^+ or $Ptpy^+$] at $m/z >$ base peak values are listed *. Proton and fluorine chemical shifts are in ppm downfield from internal Me_4Si and upfield of internal $CFCl_3$ respectively. The solvent was $(CD_3)_2CO$ unless indicated otherwise. Because of resolution difficulties and complexity in some cases, aromatic resonances are given to only one decimal place. Integrations were satisfactory and are given only for unidentified impurity features. For PtCl(R)phen complexes, the hydrogens in the ring *cis* to chlorine are designated H(2–4). Platinum–fluorine and platinum–hydrogen coupling constants are given in Table 2.

(b) Solvents and reagents

Purification methods for pyridine, acetone and petroleum ether and preparations of platinum reactants have been given [2]. Ether and tetrahydrofuran were distilled from and stored over sodium wire. Barium bis(pentaflurobenzenesulphonate) hydrate was from Bristol Organics. Barium bis(pentafluorobenzenesulphinate) and bis(2,3,5,6-tetrafluorobenzenesulphinate) were prepared by the reported method [8] but using more concentrated solutions of the aqueous reagents. The compounds could not be obtained completely anhydrous (IR ca. 3400w(br)).

Barium bis(2,3,4,5-tetrafluorobenzenesulphinate). Mixing concentrated aqueous solutions of the lithium salt [17] (10 mmol) and barium chloride (8.2 mmol) deposited the required compound (44%), m.p. > 300°C (Found: C, 25.0; H, 0.3; F, 26.5. $C_{12}H_2BaF_8O_4S_2$ calcd.: C, 25.6; H, 0.4; F, 27.0%) cf. an earlier unsuccessful synthesis by this method [8]. IR 1628s, 1527 and 1519s, 1468vs, 1092s, 1006vs [$\nu_{as}(SO_2)$], 986vs [$\nu_s(SO_2)$], 871s, 678s cm^{-1}. In addition, 3380w(br) suggested slight hydration. ^{19}F NMR spectrum (D_2O): 136.9, m, F(5); 145.0, m, F(2); 152.3, m, F(4); 153.7, m, F(3).

(c) Preparations and attempted preparations of organoplatinum(II) compounds by desulphination

General method. Mixtures of the appropriate halogenoplatinum(II) compound and barium bis(polyfluorobenzenesulphinate) in pyridine (10 cm^3) were heated under reflux. Purified (BASF R3/11 catalyst and molecular sieves) nitrogen was slowly passed over the reaction mixture and then through standard iodine solution (section (a)). After reaction, the pyridine was evaporated under vacuum at room

* More complete spectral details are available from the authors.

temperature. Extraction of the residue with boiling acetone, filtration, addition of petroleum ether (b.p. 60–80°), and crystallization gave the organoplatinum product. Amounts of reagents, reaction conditions, and yields of products are given in Table 1.

Characterization of products. The complexes, *trans*-bis(pentafluorophenyl)dipyridineplatinum(II), 2,2′-bipyridylbis(pentafluorophenyl)platinum(II), and *trans*-dipyridinebis(2,3,5,6-tetrafluorophenyl)platinum(II) had IR, mass and ^{19}F and ^{1}H NMR spectra in agreement with those of authentic samples prepared by decarboxylation [2].

2,2′-Bipyridylbis(2,3,5,6-tetrafluorophenyl)platinum(II) and 2,2′bipyridylchloro(2,3,5,6-tetrafluorophenyl)platinum(II), obtained as a mixture (Table 1), had ^{19}F NMR spectra identical with those of authentic samples [2].

Chloropentafluorophenyl(1,10-phenanthroline)platinum(II). The compound was obtained impure, dec. temp. 300°C. IR: 1505vs, 1456 and 1443vs, 1065vs, 950vs, 840s, 802s, 710s, cm^{-1}. ^{19}F NMR spectrum: 119.1, m, F(2,6); 163.3, m, F(4); 165.6, m, F(3,5). Impurity (19% of main product): 118.1, m, 1F (no PtF satellites observable); 161.8, m, 1F; ca. 165, m, 1F. ^{1}H NMR spectrum: 7.9, m, H(3,8); 8.3, s, H(5,6); 8.9, m, H(9); 9.1, m, H(4,7); 9.8, m, H(2). *m/z* 578 [42%, M^+], 542 [21, $PtC_6F_5(phen)^+$], 411 [11, $PtCl(phen)^+$].

Chloro-1,10-phenanthroline(2,3,5,6-tetrafluorophenyl)platinum(II) (i) and 1,10-Phenanthrolinebis(2,3,5,6-tetrafluorophenyl)platinum(II) (ii). Desulphination (Table 1) gave a mixture of the title compounds and 1,10-phenanthrolinebis(2,3,5,6-tetrafluorobenzenesulphinato)platinum(II) (iii). ^{19}F NMR spectrum: (i) 120.6, m, F(2,6); ca. 142, m, F(3,5). (ii) 119.8, m, F(2,6); ca. 142, m, F(3,5). (iii) 138.3, m, and 140.4, m, F(2,3,5,6). ^{1}H NMR spectrum: (i) 7.0, m, HC_6F_4; 8.0, m, H(3,8); 8.3, s, H(5,6); 8.8, m, H(9); 9.1, m, H(4.7); 9.8, m, H(2). No resonances specifically attributable to (ii) or (iii) could be distinguished though additional poorly resolved features were present. IR 1453vs, 1160s, 890vs, 842s, 712s cm^{-1}. *m/z* 560 [33%, $PtCl(C_6HF_4)phen^+$], 524 [44, $Pt(C_6HF_4)phen^+$].

trans-Chlorodipyridine(2,3,4,5-tetrafluorobenzenesulphinato)platinum(II). Despite partial desulphination (Table 1), the usual work-up gave the title compound, m.p. 222°C (dec.) (Found: C, 32.3; H, 1.8; F, 12.3; S, 4.9. $C_{16}H_{11}ClF_4N_2O_2SPt$ calcd.: C, 31.9; H, 1.8; F, 12.6; S, 5.3%). IR: 1613s, 1514s, 1479vs, 1458vs, 1321s, 1232vs [$\nu_{as}(SO_2)$], 1090vs, 1071vs [$\nu_s(SO_2)$], 1051s, 1010s, 770s, 697 and 690s cm^{-1}. ^{19}F NMR spectrum: 139.4, m, F(2 or 5); 140.1, m, F(2 or 5); 153.0, m, F(4); 154.1, m, F(3). ^{1}H NMR spectrum: 6.7, m, HC_6F_4, 7.6, m, H(3,5); 8.1, m, H(4); 8.8, m, H(2,6). *m/z* 602 [4%, M^+], 538 [11, $PtCl(C_6HF_4)(py)_2^+$], 459 [10, $PtCl(C_6HF_4)(py)^+$], 389 [59, $PtCl(py)_2^+$]. The complex (spectroscopic identification) was also obtained as the major product from reaction of $PtCl_2$bipy with $Ba(O_2S\text{-}o\text{-}HC_6F_4)_2$ (Table 1). After collection of this compound, evaporation of the filtrate gave a mixture of (tentatively assigned) 2,2′-bipyridylbis(2,3,4,5-tetrafluorophenyl)platinum(II), ^{19}F NMR spectrum: 121.0, m, F(2); 139.3, m, F(5); 154.1 or 156.2, m, F(3); 159.8 or 160.7, m, F(4), 2,2′-bipyridylchloro(2,3,4,5-tetrafluorophenyl)platinum(II), ^{19}F NMR spectrum: 121.8, m, F(2); 140.7, m, F(5); 154.1 or 156.2, m, F(3); 159.8 or 160.7, m, F(4) and an unidentified species, ^{19}F NMR spectrum: 142.8, m, 1F; 144.5, m, 1F; 164.5, m, 1F; 166.8, m, 1F. No PtF satellites could be resolved for the first two compounds.

trans-Chlorodipyridine(2,3,4,5-tetrafluorophenyl)platinum(II). *trans*-Chlorodipyridine(2,3,4,5-tetrafluorobenzenesulphinato)platinum(II) (0.18 mmol) melted with

effervescence under nitrogen at 210–215°C to give a light brown residue. Extraction with boiling acetone, filtration, and evaporation gave the impure title compound (11%), m.p. 135–170°C (dec.). IR: 1611s, 1505s, 1485s, 1452vs, 1072s, 994s, 768s, 691s cm^{-1}. ^{19}F NMR spectrum: 124.5, m, F(2); 143.2, m, F(5); 159.6, m, F(3); 166.2, m, F(4). Resonances of the reactant (16% of product intensity) and some poorly resolved features were also observed. ^{1}H NMR spectrum: 6.8, m, HC_6F_4; 7.5, m, H(3,5); 8.0, m, H(4); 8.8, m, H(2,6) with additional poorly resolved impurity features. *m/z* 538 [33%, M^+], 502 [10, $Pt(C_6HF_4)(py)_2^+$], 459 [13, $PtCl(C_6HF_4)py^+$], 423 [67, $Pt(C_6HF_4)py^+$], 353 [97, $Pt(py)_2^+$].

(d) Attempted synthesis of a pentafluorophenylplatinum(II) compound by desulphonation

Thallous pentafluorobenzenesulphonate. Dilute sulphuric acid (1.06 mol dm^{-3}; 5.00 cm^3) was added slowly with stirring to barium bis(pentafluorobenzenesulphonate) hydrate (5.3 mmol) in a minimum of water. After filtration of barium sulphate, the resulting solution of pentafluorobenzenesulphonic acid was added to aqueous thallous carbonate (5.3 mmol). The solution was boiled, filtered, and the thallous sulphonate was isolated by evaporation to crystallization (yield, 79%), dec. temp. 296°C (Found: Tl, 44.8. $C_6F_5O_3STl$ calcd.: Tl, 45.3%). IR: 1523s, 1485 and 1470vs, 1220vs [$\nu(SO_3)$], 1193vs [$\nu(SO_3)$], 1112s, 1045s [$\nu(SO_3)$], 981vs, cm^{-1}. ^{19}F NMR spectrum (D_2O): 138.9, m, F(2,6); 149.4, m, F(4); 159.8, m, F(3,5).

Tetrapyridineplatinum(II) bis(pentafluorobenzenesulphonate). *trans*-Dichlorodipyridineplatinum(II) (0.50 mmol) and thallous pentafluorobenzenesulphonate (1.01 mmol) in pyridine or pyridine/xylene (1/1, v/v) (10 cm^3) were heated under reflux for 2 h. Thallous chloride was filtered off and the title compound was precipitated with diethyl ether (yield, 68%), dec. temp. 270°C (Found: C, 38.1; H, 2.1; F, 19.1; N, 5.2. $C_{32}H_{20}F_{10}N_4O_6S_2Pt$ calcd.: C, 38.2. H, 2.0; F, 18.9; N, 5.6%). IR 1612s, 1519s, 1489vs, 1460vs, 1265vs [$\nu(SO_3)$], 1234vs [$\nu(SO_3)$] 1101s, 1044s [$\nu(SO_3)$], 986s, 703s cm^{-1}. ^{19}F NMR spectrum (CD_3OD): 138.7, m, F(2,6); 154.2, m, F(4); 162.9, m, F(3,5). ^{1}H NMR spectrum (CD_3OD): 7.6, m, H(3,5); 8.0, m, H(4); 9.1, m, H(2,6). *m/z*: 768 [21%, $Pt(O_3SC_6F_5)_2py^+$], 688 [32, $Pt(C_6F_5)(O_3SC_6F_5)(py)^+$], 600 [21, $Pt(O_3C_6F_5)(py)_2^+$], 520 [42, $Pt(C_6F_5)(py)_2^+$].

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