

## Synthesis and structural characterisation of some triangular and tetrahedral mixed metal platinum–gold clusters

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### Abstract

The compounds  $[\text{Pt}_2(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_2]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_2(\text{CNxylyl})_2(\text{PCy}_3)_3]$  react with one mole of  $[\text{Au}(\text{PCy}_3)\text{Cl}]$  to give  $[\text{Pt}_2\text{Au}(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_3]^+ \text{PF}_6^-$  (I) and  $[\text{Pt}_3\text{Au}(\mu\text{-SO}_2)_2(\mu\text{-CNxylyl})(\text{PCy}_3)_4]^+ \text{PF}_6^-$  (II), respectively. The molecular structure of I has been determined by single crystal X-ray techniques, and found to be based on a nearly perfect equilateral triangle of the three metal atoms. The Pt–Pt bond is bridged by an  $\text{SO}_2$  ligand, and the two platinum atoms are also coordinated to one xylyl-isocyanide ligand each. The coordination environments about each metal are completed by a tricyclohexylphosphine ligand. NMR studies ( $^{31}\text{P}\text{-}\{^1\text{H}\}$  and  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ ) have confirmed that this structure persists in solution. The molecular structure of II was established from IR,  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR and FAB mass spectroscopic studies, as a tetrahedral structure with only one xylyl isocyanide bridging the two equivalent platinum atoms. There are two  $\text{SO}_2$  ligands bridging the other Pt–Pt bonds in the triangle and the coordination environment about each metal is completed by a tricyclohexylphosphine ligand.

### Introduction

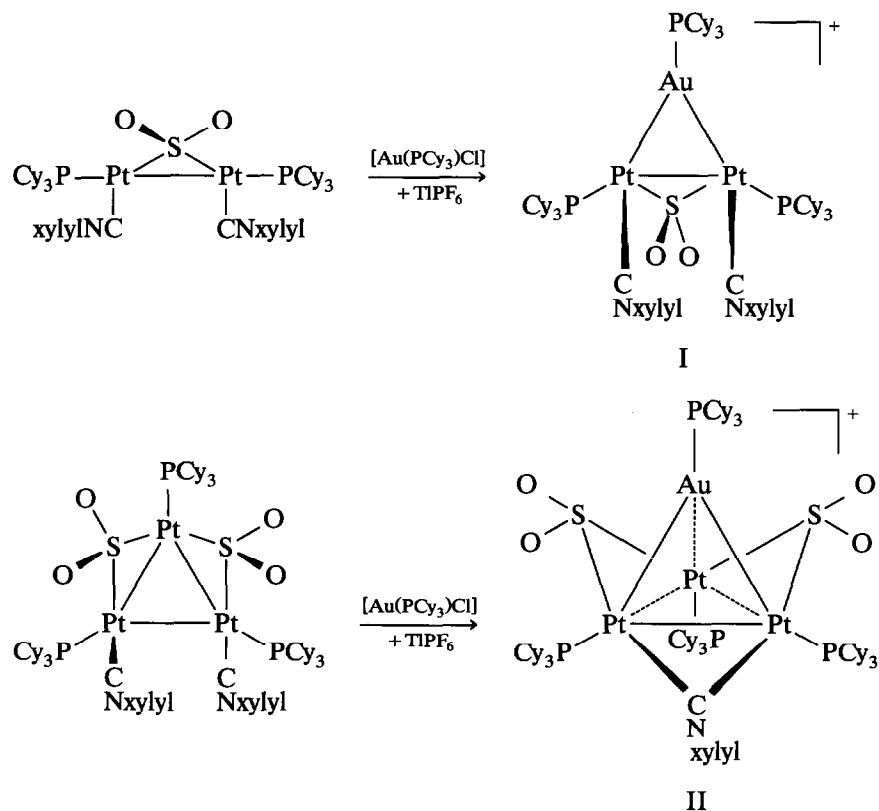
Heterometallic cluster compounds containing gold have attracted wide interest in recent years and many types of cluster compounds with platinum have been reported [1–3]. The recent report of two new platinum cluster compounds containing isocyanide ligands  $[\text{Pt}_2(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_2]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_2(\text{CNxylyl})_2(\text{PCy}_3)_3]$  [4] afforded the opportunity of studying the possibility of utilizing these compounds as precursors for heteronuclear platinum–gold cluster compounds. The reactions of the triangular platinum cluster were of particular interest, since each face is partially blocked by a xylyl isocyanide group. It was thus of interest to determine whether the  $[\text{AuPCy}_3]^+$  fragment could approach the sterically shielded platinum atoms.

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## Results and discussion

The compounds  $[\text{Pt}_2\text{Au}(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_3]^+\text{PF}_6^-$  (I), and  $[\text{Pt}_3\text{Au}(\mu\text{-SO}_2)_2(\mu\text{-CNxylyl})(\text{PCy}_3)_4]^+\text{PF}_6^-$  (II), were synthesized from  $[\text{Pt}_2(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_2]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_2(\text{CNxylyl})_2(\text{PCy}_3)_3]$  respectively, with  $[\text{Au}(\text{PCy}_3)\text{Cl}]$  in  $\text{CH}_2\text{Cl}_2$  and tetrahydrofuran (THF) solutions, in the presence of  $\text{TIPF}_6$  (Scheme 1). One major product was isolated from each reaction.  $\text{TI}^+$  was used as a halide abstractor to promote the formation of the intermediate fragment  $[\text{Au}(\text{PCy}_3)]^+$ . Compound I is a *triangulo*-cluster with the  $[\text{Au}(\text{PCy}_3)]^+$  fragment bridging the Pt–Pt bond. It is produced in > 90% yield. Compound II is a tetrahedral cluster with the  $[\text{Au}(\text{PCy}_3)]^+$  fragment capping the Pt<sub>3</sub> triangle in a  $\mu_3$  fashion. It is produced in a smaller yield. In the parent compound the isocyanide ligands project above and below the triangular plane and therefore the approach of the  $[\text{Au}(\text{PCy}_3)]^+$  fragment is sterically hindered. One of these ligands is lost in the capping process. Cluster degradation products are observed if the reactions proceed for long periods of time.

Compound I is a yellow microcrystalline solid and its IR spectrum indicates the presence of terminal isocyanide ( $2137\text{ cm}^{-1}$ ) and bridging sulphur dioxide ( $1174$  and  $1056\text{ cm}^{-1}$ ) ligands. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum illustrated in Fig. 1(a) is consistent with an asymmetric  $\text{Pt}_2\text{AuP}_3$  triangle with  $C_{2v}$  symmetry. A satisfactory computer simulation of this spectrum has been achieved on the basis of the



Scheme 1.

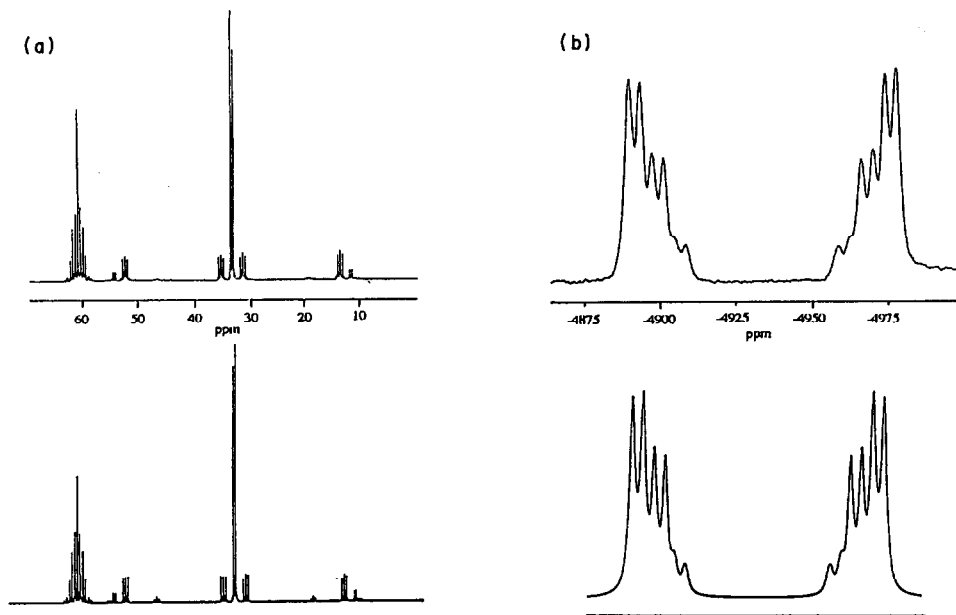


Fig. 1. (a) Observed (upper) and calculated  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra for compound I. (b) Corresponding observed and calculated  $^{195}\text{Pt}\{-^1\text{H}\}$  NMR spectra.

isotopomers  $\text{A}_2\text{B}$  (44.0% abundance, no  $^{195}\text{Pt}$  nuclei),  $\text{AA}'\text{BX}$  (44.7% abundance, one  $^{195}\text{Pt}$  nucleus, X),  $\text{AA}'\text{BXX}'$  (11.3% abundance, two  $^{195}\text{Pt}$  nuclei, X and X').

The  $^{195}\text{Pt}\{-^1\text{H}\}$  spectrum consists of one resonance centred at  $-4931.92$  ppm with respect to  $\text{Na}_2\text{PtCl}_6$  and is illustrated in Fig. 1(b). It has been interpreted using the spin systems described above and is consistent with the proposed structure of a  $\text{C}_{2v}$   $\text{Pt}_2\text{AuP}_3$  triangle. The coupling constants derived from the computer simulations of the  $^{31}\text{P}\{-^1\text{H}\}$  and  $^{195}\text{Pt}\{-^1\text{H}\}$  spectra are given in Table 1.

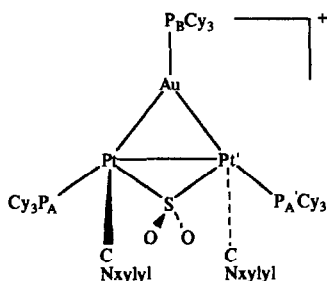
Compound II is an orange microcrystalline solid. The IR spectrum shows the presence of an isocyanide ligand, with stretching frequency intermediate between terminal and bridging coordination ( $1980\text{ cm}^{-1}$ ). A similar isocyanide stretching mode has been reported in the compound  $[\text{Pd}_2\text{Cl}_2(\mu\text{-CNxylyl})_2(\text{Py})_2]$  at  $1976\text{ cm}^{-1}$  [5] synthesized by Yamamoto and Yamozaki, and also in  $[\text{Pd}_5(\mu\text{-SO}_2)_3(\mu\text{-CNxylyl})_2(\text{CNxylyl})_5]$  ( $2047$  and  $1990\text{ cm}^{-1}$ ) [6]. These molecules are known to have a linear C–N–C geometry, and the same geometry was postulated for II. The compound also possesses bridging sulphur dioxide ligands ( $1176$  and  $1078\text{ cm}^{-1}$ ). The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of II is illustrated in Fig. 2(a). The spectrum has been satisfactorily simulated using a computer analysis based on the isotopomers  $\text{A}_2\text{BC}$  (29.1% abundance, no  $^{195}\text{Pt}$ ),  $\text{AA}'\text{BCX}$  (29.6% abundance, one  $^{195}\text{Pt}$  nucleus, X),  $\text{A}_2\text{BCY}$  (14.8% abundance, one  $^{195}\text{Pt}$  nucleus, Y),  $\text{AA}'\text{BCXX}'$  (7.5% abundance, two  $^{195}\text{Pt}$  nuclei, X and X'),  $\text{AA}'\text{BCXY}$  (15.1% abundance, two  $^{195}\text{Pt}$  nuclei, X and Y),  $\text{AA}'\text{BCXX}'\text{Y}$  (3.8% abundance, three  $^{195}\text{Pt}$  nuclei, X, X' and Y).

The  $^{195}\text{Pt}\{-^1\text{H}\}$  spectrum consists of two resonances, one centred at  $-4399.85$  ppm, with respect to  $\text{Na}_2\text{PtCl}_6$ , corresponding to the two equivalent platinum atoms, and one centred at  $-4991.58$  ppm, corresponding to the unique platinum atom. The observed and simulated spectra are illustrated in Figs. 2(b) and (c).

Table 1

Chemical shifts and coupling constants for compound I. The  $^1J$  Pt-Pt coupling constant (starred) was calculated from the computer simulation

	$\delta$ (ppm)	$J$ (Hz)			
		$P_{A'}$	$P_B$	Pt'	Pt
$P_A$	33.24	51	41	395	3920
$P_{A'}$	33.24	—	41	3920	395
$P_B$	61.15	—	—	195	195
Pt'	—	—	—	—	820 *



They have been interpreted using the spin systems described above and the coupling constants derived from the computer simulation are given in Table 2.

The fast atom bombardment (FAB) mass spectrum of II is shown in Fig. 3 and an interpretation is given in Table 3. A parent ion  $[Pt_3Au(\mu-SO_2)_2(\mu-CNxylyl)(PCy_3)_4]^+$  is observed at  $m/z = 2163$  and the fragmentation pattern is dominated by the loss of  $SO_2$ , CNxylyl, and  $PCy_3$  ligands. The presence of only one isocyanide ligand, is supported by the elemental analysis, details of which are given in the Experimental section. It is proposed that this ligand is bridging, in a  $\mu_2$  fashion, between the two equivalent platinum atoms. This is consistent with the

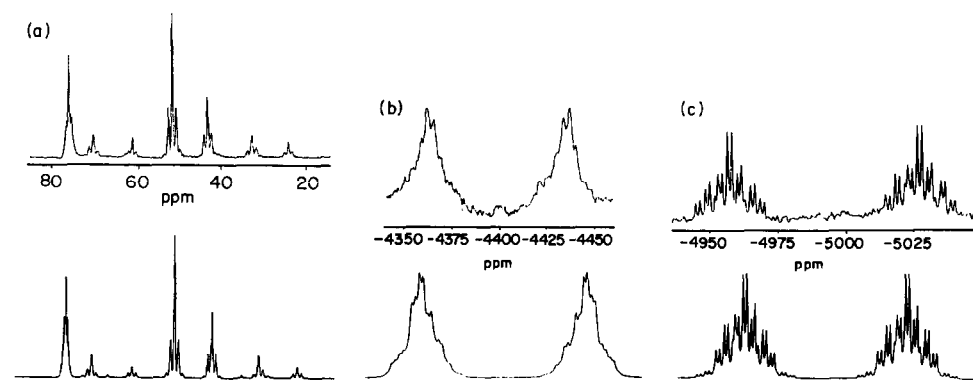


Fig. 2. (a) Observed (upper) and calculated  $^{31}P\{-^1H\}$  NMR spectra for compound II. (b) Observed (upper) and calculated resonances for the two equivalent Pt atoms in the  $^{195}Pt\{-^1H\}$  spectrum of compound II. (c) Observed and calculated  $^{195}Pt\{-^1H\}$  spectra for the remaining unique Pt atom.

Table 2

Chemical shifts and coupling constants for compound II. Those starred were calculated from the simulation

	$\delta$ (ppm)	$J$ (Hz)					
		$P_{A'}$	$P_B$	$P_X$	$Pt_A$	$Pt_{A'}$	$Pt_B$
$P_A$	51.55	9.7	28.2	19.7	4588.6	231.4	229.3
$P_{A'}$	51.55	—	28.2	19.7	231.4	4588.6	229.3
$P_B$	43.01	—	—	18.2	212.7	212.7	4509.5
$P_X$	76.28	—	—	—	105.0 *	105.0 *	103.0
$Pt_A$	—	—	—	—	—	700.0 *	1067.7
$Pt_{A'}$	—	—	—	—	—	—	1067.7

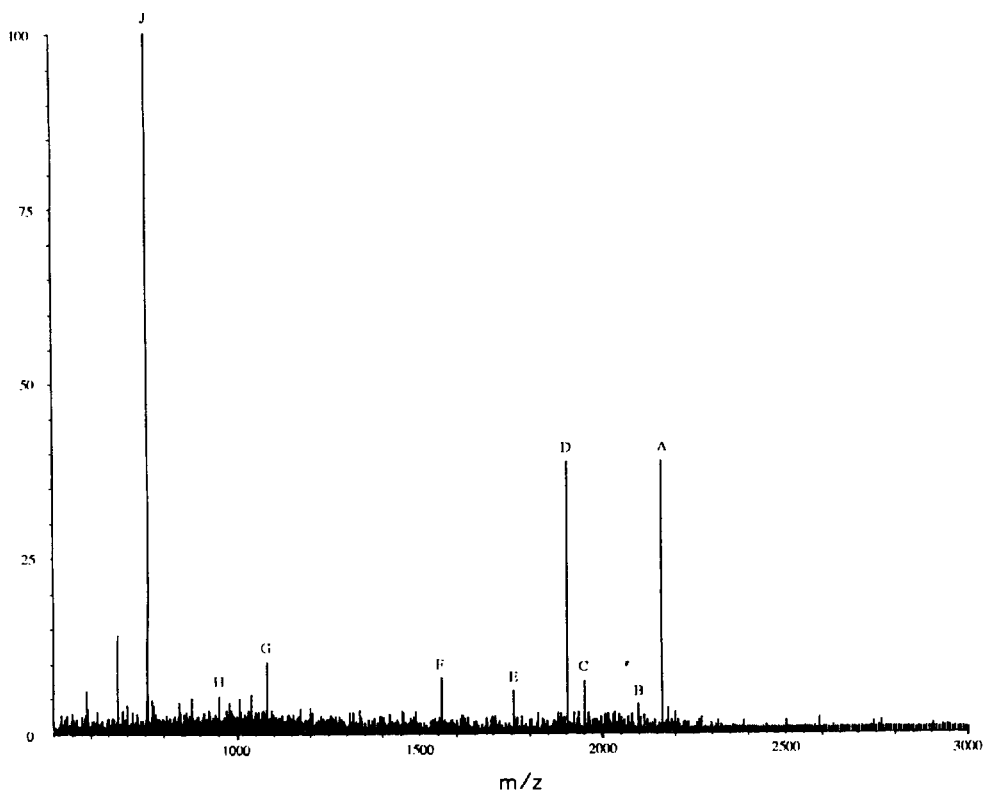
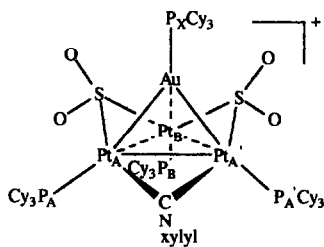


Fig. 3. Fast atom bombardment (FAB) mass spectrum for compound II (see Table 3 for interpretation).

Table 3

Assignment of the peaks in the FAB mass spectrum of compound II.  $[M]^+$  is the molecular ion,  $[\text{Pt}_3\text{Au}(\mu\text{-SO}_2)_2(\mu\text{-CNxylyl})(\text{PCy}_3)_4]^+$

Peak, $m/z$	Fragment
2163, A	$[M]^+$
2098, B	$[M - \text{SO}_2]^+$
2034, C	$[M - 2\text{SO}_2]^+$
1903, D	$[M - 2\text{SO}_2 - \text{CNxylyl}]^+$
1755, E	$[M - 2\text{SO}_2 - \text{PCy}_3]^+$
1560, F	$[M - 2\text{SO}_2 - \text{PCy}_3 - \text{Pt}]^+$
1083, G	$[M - 2\text{SO}_2 - 2\text{PCy}_3 - \text{Pt} - \text{Au}]^+$
953, H	$[M - 2\text{SO}_2 - \text{PCy}_3 - \text{Pt} - \text{Au} - \text{CNxylyl}]^+$
758, J	$[\text{Au}(\text{PCy}_3)_2]^+$

IR and NMR data. The proposed structure of the compound is illustrated in Fig. 4.

In order to confirm the structure of I, a single crystal X-ray crystallographic analysis was completed. Details are summarised in Table 4 and in the Experimental section.

The molecular structure of I is illustrated in Figs. 5 and 6 and consists of a triangular framework of two platinum and one gold atom; each metal atom is coordinated to a tricyclohexylphosphine, with the three phosphorus atoms approximately planar but all displaced slightly below the metal plane. The Pt–Pt bond is typical of those of 44 electron platinum triangles, and thus very similar to those of the parent compound of II. It is slightly longer than those noted for 42 electron triangles, and thus replacing a platinum atom by a gold atom seems to have only a small effect on the Pt–Pt bond. The Pt–Au bond lengths are similar to those found in other platinum gold clusters and are approximately equal to 2.70 Å [1]. The Pt–Pt bond is bridged by a sulphur dioxide ligand which lies on the same side as the plane defined by the phosphine ligands. Two platinum atoms in each molecule are coordinated to terminal xylyl-isocyanide ligands in *cis*-axial sites on the opposite side of the cluster from the other ligands. The planes of the two aromatic

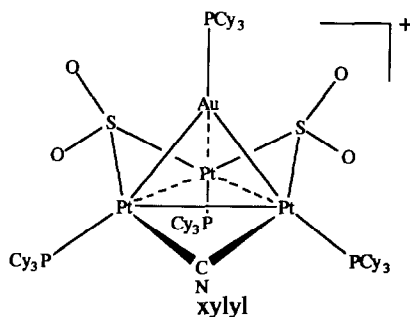


Fig. 4. The proposed structure of compound II.

Table 4  
Structural details, data collection and refinement for I

Compound formula	$2(\text{C}_{72}\text{H}_{117}\text{AuF}_6\text{N}_2\text{O}_2\text{P}_4\text{Pt}_2\text{S}) \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}$
Formula weight	1898.326
Crystal system	monoclinic
Space group	$P2_1/c$
$a$ (Å)	18.545(4)
$b$ (Å)	21.662(5)
$c$ (Å)	41.353(9)
$\alpha$ (°)	90
$\beta$ (°)	92.32(2)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	16598.363
$Z$	4
$D_c$ (g cm <sup>-3</sup> )	1.533
$F(000)$ (electrons)	7636
Linear absorption coefficient (cm <sup>-1</sup> )	53.058
<i>Refinement</i>	
Number of parameters	352
Ratio of data to parameters	15.38
Weighting scheme	unit weights
Method of solution	direct methods (SHELXS-86)
Final $R$	0.0845
Final $R_w$	0.0988
<i>Absorption correction</i>	
Type	azimuthal scan profile
Min/max correction in $\theta$ :	1.00/1.24
<i>Data collection</i>	
X-radiation	Mo- $K_\alpha$ , $\lambda = 0.71069$ Å
$\theta_{\text{min}}$ , $\theta_{\text{max}}$ (°)	0, 21
$\omega$ -scan width parameters	$0.50 + 0.35$ , (width = $A + B \tan \theta$ )
Horizontal aperture parameters	$1.00 + 0$ , (APT = $A + B \tan \theta$ )
Min/max $h, k, l$	$-18/18, -1/21, -1/41$
Total data collected	20968
Total unique data	15330
Total observed data ( $I > 3\sigma$ )	5414
Sheldrick merging $R$ -factors	5.71

rings in each independent molecule are approximately parallel (interplanar angle 1.39° molecule A, 9.14° molecule B), stacked above one another in staggered conformations, with interplanar distances of 3.54 Å (A) and 3.59 Å (B). Selected molecular dimensions and the final fractional coordinates are given in Tables 5 and 6.

## Experimental

All reactions were performed by standard Schlenk-line techniques under pure dry nitrogen. The solvents used were dry and oxygen free. Microanalyses were carried out by Mr. M. Gascoyne and his staff at this laboratory. Infra red spectra were recorded as Nujol mulls on a Perkin-Elmer 1700FT spectrometer.

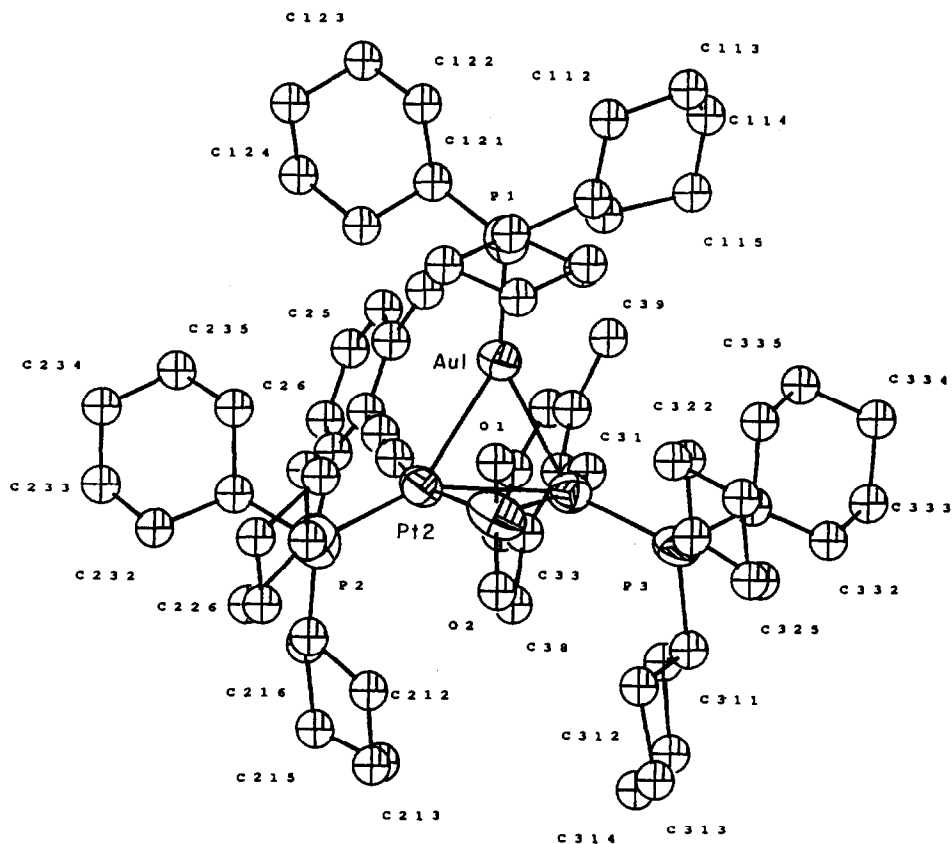


Fig. 5. Molecule A from above the plane of the metal core. The hydrogen atoms are omitted for clarity.

FAB mass spectrometry was carried out by the SERC mass spectrometry service, Swansea.  $^{31}\text{P}\{-^1\text{H}\}$  and  $^{195}\text{Pt}\{-^1\text{H}\}$  NMR spectra were recorded on a Bruker AM 300 spectrometer. Samples for  $^{31}\text{P}\{-^1\text{H}\}$  were referenced to  $\text{PO}(\text{OMe})_3$  in  $\text{D}_2\text{O}$  and  $^{195}\text{Pt}\{-^1\text{H}\}$  samples to  $\text{Na}_2\text{PtCl}_6$  in  $\text{D}_2\text{O}$ . All  $^{31}\text{P}$  NMR samples were run in  $\text{CH}_2\text{Cl}_2$  and all  $^{195}\text{Pt}$  samples in  $\text{CD}_2\text{Cl}_2$ . NMR computer simulations were carried out using the Oxford University Vax computer system, utilizing a program developed by Dr. R.K. Harris of the University of East Anglia and adapted for use at Oxford by Dr. A.E. Derome.

The complexes  $[\text{Pt}_2(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_2]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_2(\text{CNxylyl})_2(\text{PCy}_3)_3]$  were made by standard methods [4].

*Synthesis of  $[\text{Pt}_2\text{Au}(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_3]^+ \text{PF}_6^- \cdot \frac{1}{2}\text{THF}$  (I)*

$[\text{AuCl}(\text{PCy}_3)]$  (0.257 g, 0.50 mmol) was added to a stirred solution of  $[\text{Pt}_2(\mu\text{-SO}_2)(\text{CNxylyl})_2(\text{PCy}_3)_2]$ , (0.64 g, 0.50 mmol) in  $\text{CH}_2\text{Cl}_2$ . An excess of  $\text{TIPF}_6$  (0.70 g, 2.00 mmol) was then added, and the solution immediately became cloudy. Stirring was continued for 30 min, during which the solution lightened in colour from orange/yellow to pale yellow. The solution was filtered and the solvent removed under reduced pressure. The product was recrystallized from THF with a small portion of ether as cosolvent, to give I as a yellow, microcrystalline solid.



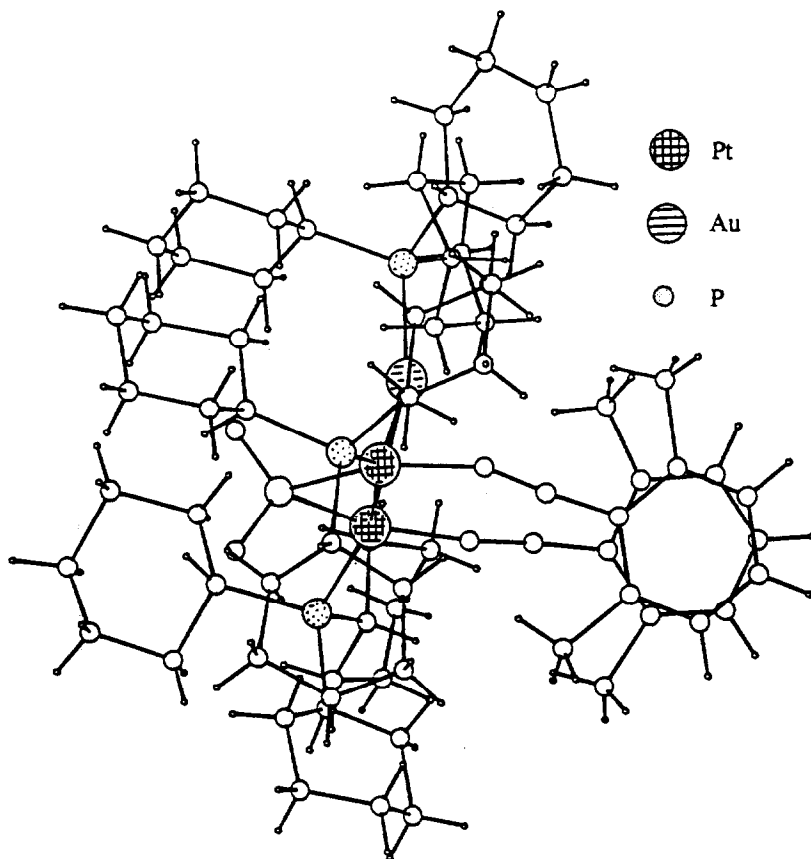


Fig. 6. Molecule A from the plane of the metal core, showing clearly the staggered conformation adopted by the isocyanide ligands. The hydrogen atoms are now included.

Table 5

Important bond lengths (Å) and angles (°) for molecule A of I

Au(1)–Pt(2)	2.705(7)	Pt(3)–Au(1)–Pt(2)	59.8(2)
Au(1)–Pt(3)	2.717(7)	P(1)–Au(1)–Pt(2)	147.1(10)
Au(1)–P(1)	2.27(4)	P(1)–Au(1)–Pt(3)	145.5(9)
Pt(2)–Pt(3)	2.704(8)	Pt(3)–Pt(2)–Au(1)	60.3(2)
Pt(2)–P(2)	2.25(4)	P(2)–Pt(2)–Au(1)	145.8(11)
Pt(2)–S(1)	2.25(4)	P(2)–Pt(2)–Pt(3)	146.9(10)
Pt(2)–C(21)	1.94(6)	S(1)–Pt(2)–Pt(3)	51.9(9)
Pt(3)–P(3)	2.28(4)	Pt(2)–Pt(3)–Au(1)	59.9(2)
Pt(3)–S(1)	2.21(3)	P(3)–Pt(3)–Au(1)	140.7(8)
Pt(3)–C(31)	1.93(5)	P(3)–Pt(3)–Pt(2)	151.3(9)
S(1)–O(1)	1.42(7)	S(1)–Pt(3)–Pt(2)	53.5(10)
S(1)–O(2)	1.47(8)	O(2)–S(1)–O(1)	113.3(50)
N(21)–C(21)	1.20983(8)	C(22)–N(21)–C(21)	175.19(1)
N(21)–C(22)	1.4012(3)	C(32)–N(31)–C(31)	168.41(2)
N(31)–C(31)	1.19	N(21)–C(21)–Pt(2)	173.2(33)
N(31)–C(32)	1.4052(2)	N(31)–C(31)–Pt(3)	157.7(27)

Table 6

Final fractional atomic coordinates for I. Estimated standard deviations are in parentheses

Atom	x	y	z	Atom	x	y	z
Au(1)	-0.0138(3)	0.1847(2)	0.3993(1)	C(221)	0.147(5)	0.410(4)	0.353(2)
Au(4)	-0.4927(3)	0.3090(2)	0.0961(1)	C(212)	0.089(5)	0.461(5)	0.363(2)
Pt(2)	0.0517(3)	0.2880(2)	0.3785(1)	C(213)	0.077(6)	0.510(4)	0.339(3)
Pt(3)	-0.0930(3)	0.2870(2)	0.3845(1)	C(214)	0.060(5)	0.485(5)	0.306(2)
Pt(5)	-0.5567(3)	0.2665(2)	0.1496(1)	C(215)	0.123(6)	0.452(5)	0.294(2)
Pt(6)	-0.4109(3)	0.2733(2)	0.1486(1)	C(216)	0.142(5)	0.395(4)	0.318(2)
P(1)	-0.005(2)	0.099(2)	0.4305(9)	C(221)	0.174(5)	0.370(4)	0.423(2)
P(2)	0.153(2)	0.344(2)	0.380(1)	C(222)	0.185(5)	0.325(3)	0.447(2)
P(3)	-0.198(2)	0.334(2)	0.3971(9)	C(223)	0.181(6)	0.352(3)	0.484(2)
P(4)	-0.500(2)	0.372(2)	0.052(1)	C(224)	0.241(6)	0.409(5)	0.482(2)
P(5)	-0.660(2)	0.274(2)	0.1766(8)	C(225)	0.225(6)	0.452(3)	0.458(3)
P(6)	-0.305(2)	0.288(2)	0.1760(9)	C(226)	0.229(6)	0.430(4)	0.421(2)
P(8)	-0.520(4)	0.197(3)	-0.049(2)	C(231)	0.231(4)	0.298(4)	0.364(2)
P(9)	0.023(4)	0.396(3)	0.174(3)	C(232)	0.306(5)	0.333(3)	0.364(3)
S(1)	-0.013(2)	0.333(2)	0.4172(9)	C(233)	0.356(4)	0.289(5)	0.348(2)
S(2)	-0.484(2)	0.333(2)	0.1748(9)	C(234)	0.363(4)	0.229(5)	0.362(3)
F(81)	-0.432(8)	0.199(7)	-0.045(3)	C(235)	0.292(6)	0.192(3)	0.361(3)
F(82)	-0.520(6)	0.231(5)	-0.013(3)	C(236)	0.241(5)	0.235(4)	0.384(2)
F(83)	-0.603(8)	0.202(6)	-0.047(3)	C(311)	-0.221(5)	0.411(4)	0.377(2)
F(84)	-0.517(6)	0.136(5)	-0.030(3)	C(312)	-0.171(5)	0.455(5)	0.390(2)
F(85)	-0.521(7)	0.258(7)	-0.066(3)	C(313)	-0.195(6)	0.525(3)	0.374(3)
F(86)	-0.528(7)	0.166(6)	-0.082(3)	C(314)	-0.186(6)	0.511(4)	0.338(2)
F(91)	0.068(8)	0.358(7)	0.198(3)	C(315)	-0.223(6)	0.464(5)	0.381(2)
F(92)	-0.023(8)	0.414(6)	0.207(3)	C(316)	-0.207(6)	0.399(4)	0.340(2)
F(93)	0.059(8)	0.457(8)	0.180(4)	C(321)	-0.199(5)	0.353(4)	0.442(2)
F(94)	-0.012(7)	0.337(7)	0.170(3)	C(322)	-0.183(5)	0.299(4)	0.463(2)
F(95)	0.08(1)	0.381(8)	0.153(4)	C(323)	-0.159(5)	0.325(5)	0.499(2)
F(96)	-0.034(9)	0.428(8)	0.159(4)	C(324)	-0.225(6)	0.360(5)	0.510(2)
N(21)	0.077(3)	0.207(3)	0.317(1)	C(325)	-0.244(6)	0.416(4)	0.486(2)
N(31)	-0.121(2)	0.230(2)	0.317(1)	C(326)	-0.265(5)	0.393(5)	0.453(2)
N(51)	-0.588(2)	0.146(2)	0.112(1)	C(331)	-0.273(4)	0.286(4)	0.384(2)
N(61)	-0.382(3)	0.153(3)	0.107(1)	C(332)	-0.351(5)	0.308(3)	0.379(2)
O(1)	0.001(4)	0.306(3)	0.448(2)	C(333)	-0.394(5)	0.259(5)	0.359(2)
O(2)	-0.017(4)	0.400(4)	0.418(2)	C(334)	-0.392(5)	0.197(4)	0.377(3)
O(3)	-0.480(4)	0.334(3)	0.210(2)	C(335)	-0.315(6)	0.175(3)	0.382(3)
O(4)	-0.489(4)	0.398(4)	0.164(2)	C(336)	-0.271(5)	0.223(5)	0.402(2)
O(965)	0.05(2)	0.06(2)	0.034(9)	C(411)	-0.424(4)	0.362(4)	0.027(2)
O(966)	0.07(2)	0.09(2)	0.06(1)	C(412)	-0.357(5)	0.339(4)	0.041(2)
O(967)	0.01(2)	0.09(2)	0.079(9)	C(413)	-0.297(5)	0.319(4)	0.017(3)
O(968)	-0.04(2)	0.07(2)	0.06(1)	C(414)	-0.281(4)	0.369(5)	-0.006(3)
O(969)	-0.01(2)	0.05(2)	0.035(9)	C(415)	-0.344(6)	0.394(5)	-0.020(2)
C(21)	0.069(4)	0.241(3)	0.340(2)	C(416)	-0.410(5)	0.420(4)	0.004(3)
C(22)	0.084(2)	0.170(2)	0.289(1)	C(421)	-0.577(4)	0.352(4)	0.024(2)
C(23)	0.064(3)	0.110(2)	0.295(2)	C(422)	-0.600(5)	0.409(4)	0.001(2)
C(24)	0.066(4)	0.066(3)	0.270(2)	C(423)	-0.664(6)	0.382(5)	-0.024(2)
C(25)	0.087(4)	0.084(4)	0.240(2)	C(424)	-0.721(4)	0.351(5)	0.010(2)
C(26)	0.107(4)	0.145(4)	0.234(2)	C(425)	-0.395(5)	0.299(4)	0.015(3)
C(27)	0.105(3)	0.188(3)	0.259(1)	C(426)	-0.642(5)	0.333(5)	0.042(2)
C(28)	0.042(5)	0.082(3)	0.325(2)	C(431)	-0.505(5)	0.451(4)	0.067(2)
C(29)	0.120(5)	0.259(3)	0.257(2)	C(432)	-0.571(4)	0.463(5)	0.087(3)
C(31)	-0.120(3)	0.243(3)	0.345(1)	C(433)	-0.561(5)	0.532(4)	0.103(3)
C(32)	-0.112(2)	0.207(2)	0.286(1)	C(434)	-0.492(6)	0.539(4)	0.120(2)
C(33)	-0.87(3)	0.249(3)	0.249(3)	C(435)	-0.423(5)	0.533(5)	0.102(3)

Table 6 (continued)

Atom	x	y	z	Atom	x	y	z
C(34)	-0.073(4)	0.229(4)	0.233(1)	C(436)	-0.428(4)	0.466(4)	0.084(3)
C(35)	-0.085(4)	0.168(4)	0.224(1)	C(511)	-0.736(4)	0.253(4)	0.151(2)
C(36)	-0.110(4)	0.126(3)	0.246(2)	C(512)	-0.742(5)	0.292(4)	0.119(2)
C(37)	-0.123(3)	0.146(2)	0.277(2)	C(513)	-0.806(6)	0.261(5)	0.095(2)
C(38)	-0.075(5)	0.319(3)	0.274(2)	C(514)	-0.866(4)	0.242(5)	0.110(2)
C(39)	-0.149(5)	0.097(2)	0.303(2)	C(515)	-0.874(4)	0.218(5)	0.144(3)
C(51)	-0.584(3)	0.198(2)	0.121(1)	C(516)	-0.808(5)	0.245(5)	0.167(2)
C(52)	-0.596(2)	0.092(2)	0.093(1)	C(521)	-0.666(5)	0.221(4)	0.212(2)
C(53)	-0.581(3)	0.037(2)	0.109(1)	C(522)	-0.653(5)	0.151(4)	0.200(2)
C(54)	-0.580(4)	-0.018(2)	0.091(2)	C(523)	-0.658(6)	0.110(3)	0.231(3)
C(55)	-0.595(4)	-0.017(3)	0.058(2)	C(524)	-0.589(5)	0.130(4)	0.257(2)
C(56)	-0.610(4)	0.039(3)	0.042(1)	C(525)	-0.605(6)	0.191(5)	0.269(2)
C(57)	-0.611(3)	0.094(3)	0.060(1)	C(526)	-0.597(5)	0.233(4)	0.236(2)
C(58)	-0.629(5)	0.152(3)	0.043(1)	C(531)	-0.669(5)	0.351(3)	0.196(2)
C(59)	-0.555(5)	0.033(3)	0.148(1)	C(532)	-0.682(6)	0.404(5)	0.169(2)
C(61)	-0.392(4)	0.198(3)	0.120(2)	C(533)	-0.667(6)	0.468(4)	0.189(3)
C(62)	-0.386(2)	0.099(3)	0.091(1)	C(534)	-0.726(6)	0.466(4)	0.214(3)
C(63)	-0.377(3)	0.043(3)	0.106(2)	C(535)	-0.718(6)	0.422(5)	0.243(2)
C(64)	-0.390(4)	-0.012(3)	0.090(2)	C(536)	-0.734(5)	0.356(4)	0.221(2)
C(65)	-0.413(4)	-0.010(3)	0.057(2)	C(611)	-0.221(5)	0.275(4)	0.153(2)
C(66)	-0.422(4)	0.046(4)	0.041(2)	C(612)	-0.233(5)	0.300(4)	0.116(2)
C(67)	-0.409(3)	0.101(3)	0.058(1)	C(613)	-0.159(5)	0.289(5)	0.099(2)
C(68)	-0.357(5)	0.039(4)	0.144(2)	C(614)	-0.135(5)	0.226(5)	0.100(2)
C(69)	-0.420(5)	0.169(4)	0.040(1)	C(615)	-0.124(5)	0.201(4)	0.135(3)
C(111)	-0.091(4)	0.055(4)	0.427(2)	C(616)	-0.200(5)	0.207(4)	0.151(2)
C(112)	-0.097(5)	-0.000(5)	0.449(2)	C(621)	-0.295(5)	0.368(3)	0.191(2)
C(113)	-0.174(6)	-0.034(4)	0.444(2)	C(622)	-0.309(5)	0.418(5)	0.165(2)
C(114)	-0.201(5)	-0.033(4)	0.414(3)	C(623)	-0.312(5)	0.481(4)	0.180(3)
C(115)	-0.198(5)	0.017(5)	0.388(2)	C(624)	-0.241(6)	0.495(3)	0.201(3)
C(116)	-0.111(5)	0.047(4)	0.395(2)	C(625)	-0.226(6)	0.449(5)	0.226(2)
C(121)	0.065(4)	0.046(4)	0.417(2)	C(626)	-0.216(5)	0.379(4)	0.210(2)
C(122)	0.088(5)	0.000(5)	0.451(2)	C(631)	-0.295(5)	0.238(4)	0.213(2)
C(123)	0.143(6)	-0.044(3)	0.434(3)	C(632)	-0.335(5)	0.177(4)	0.206(2)
C(124)	0.210(4)	-0.011(5)	0.421(3)	C(633)	-0.326(6)	0.127(3)	0.234(3)
C(125)	0.191(5)	0.032(5)	0.394(2)	C(634)	-0.363(6)	0.164(5)	0.263(2)
C(126)	0.132(5)	0.082(3)	0.408(2)	C(635)	-0.331(6)	0.222(5)	0.272(2)
C(131)	0.004(5)	0.121(4)	0.474(2)	C(636)	-0.331(6)	0.274(3)	0.242(2)
C(132)	-0.066(4)	0.153(5)	0.484(2)	C(965)	0.05(2)	0.06(2)	0.034(9)
C(133)	-0.061(5)	0.172(5)	0.519(2)	C(966)	0.07(2)	0.09(2)	0.06(1)
C(134)	0.008(6)	0.209(4)	0.524(2)	C(967)	0.01(2)	0.09(2)	0.079(9)
C(135)	0.079(4)	0.180(5)	0.515(2)	C(968)	-0.04(2)	0.07(2)	0.06(1)
C(136)	0.070(4)	0.138(5)	0.480(2)	C(969)	-0.01(2)	0.05(2)	0.035(9)

(Found: C, 45.4; H, 6.3; N, 1.5.  $C_{72}H_{117}AuF_6N_2O_2P_4Pt_2S$  calcd.: C, 45.5; H, 6.2; N, 1.5%). IR (Nujol):  $\nu(CN)$  at  $2137\text{ cm}^{-1}$  (vs) and  $\nu(SO_2)$  at  $1174\text{ cm}^{-1}$  (m) and  $1056\text{ cm}^{-1}$  (m). Details of the  $^{31}P\{-^1H\}$  and  $^{195}Pt\{-^1H\}$  NMR studies are summarised in Table 1.

*Synthesis of  $[Pt_3Au(\mu-SO_2)_2(\mu-CNxylyl)(PCy_3)_4]^+PF_6^- \cdot \frac{3}{2}C_7H_8$  (II)*

$[AuCl(PCy_3)]$  (0.154 g, 0.30 mmol) was added to a stirred solution of  $TIPF_6$  (0.11 g, 0.31 mmol) in THF. After 30 min the mixture was filtered into a stirred solution

of  $[\text{Pt}_3(\mu\text{-SO}_2)_2(\text{CNxylyl})_2(\text{PCy}_3)_3]$  (0.55 g, 0.30 mmol) in THF. A colour change from bright orange to red occurred immediately, and this was accompanied by slow precipitation of a fine white solid during the reaction period. Stirring was continued for 30 min and the solvent was then removed under reduced pressure to leave an impure orange/red product. Successive recrystallizations from toluene produced **II** as pure, orange microcrystals. (Found: C, 44.7; H, 6.2; N, 0.6.  $\text{C}_{93}\text{H}_{151.5}\text{AuF}_6\text{NO}_4\text{P}_5\text{Pt}_3\text{S}_2$  calcd.: C, 44.9; H, 6.3; N, 0.6%). IR (Nujol):  $\nu(\text{CN})$  at  $1980\text{ cm}^{-1}$  (m) and  $\nu(\text{SO}_2)$  at  $1176\text{ cm}^{-1}$  (m) and  $1078\text{ cm}^{-1}$  (m). Details of  $^{31}\text{P}\{-^1\text{H}\}$  NMR and  $^{195}\text{Pt}\{-^1\text{H}\}$  NMR studies are summarised in Table 2 and FAB mass spectrometry data in Table 3.

#### *Crystal structure determination of compound I*

Crystals of compound **I** were grown as yellow parallelipeds by layer diffusion of  $\text{Et}_2\text{O}$  into a THF solution of the compound at room temperature. A crystal of approximate dimensions  $0.3 \times 0.1 \times 0.1$  mm was mounted on a glass fibre and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Details of the data collection and refinement are summarised in Table 4. 20968 reflections were collected in five shells by  $\omega/2\theta$  scans (scanwidth  $0.5 + 0.35 \tan \theta$ ) using graphite monochromated  $\text{Mo-K}_\alpha$  radiation, of which 15330 were unique ( $R_{\text{merg}} = 0.0571$ ) and 5414 had  $I > 3\sigma I$ . These were corrected for Lorentz and polarization effects, and an empirical absorption correction using azimuthal scan data was applied (min/max correction = 1.00/1.24). Systematic absences ( $h0l$   $l \neq 2n$  absent,  $0k0$   $k \neq 2n$  absent) unambiguously determined the space group as  $\text{P2}_1/c$  (number 14).

Direct methods (SHELXS-86) revealed two crystallographically independent triangular groups of metal atoms and the remaining non-hydrogen atoms were located by successive difference Fourier syntheses. The two independent molecules were essentially identical. The hydrogen atoms were fixed in geometrically idealised positions. The metal, phosphorus and sulphur atoms were assigned anisotropic displacement parameters. The carbon atoms of the cyclohexyl groups were assigned isotropic thermal parameters according to their position in the rings, and those of the phenyl rings were allowed to vary independently, as were those of the fluorine atoms of the counterions, and the oxygen atoms of the sulphur dioxide ligands. The THF solvent molecule was considered to be five-fold disordered; each ring atom was treated as 80% C, 20% O and present as only half a molecule per asymmetric unit. The non-hydrogen atoms of this group were refined with a common thermal parameter. All hydrogen atoms were given an isotropic thermal parameter of  $0.14\text{ \AA}^2$  which was not refined. All the cyclohexyl and phenyl rings were refined as rigid groups. Programs and sources of scattering factor data are given in references [7] and [8].

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