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Metallacyclic platinum(II) bis(sulfonamides)

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Abstract

A series of metallacyclic platinum(II) bis(sulfonamido) complexes have been synthesised by reaction of *cis*-[PtCl₂L₂] [L = PPh₃ or L₂ = 1,5-*cyclo*-octadiene (cod)] with the sulfonamides [RSO₂NHCH₂CH₂NHSO₂R, RSO₂NHCH₂CHMeNHSO₂R or RSO₂NHC₆H₄NHSO₂R; R = Ph or *p*-C₆H₄Me] and Ag₂O. The products have been characterised by NMR spectroscopy, electrospray mass spectrometry, elemental analysis, and for the complexes [Pt{N(SO₂Ph)CH₂CH₂N(SO₂Ph)}(PPh₃)₂] and [Pt{N(SO₂Ph)C₆H₄N(SO₂Ph)}(cod)], by single-crystal X-ray structure determinations. In both of these complexes, one of the amido nitrogen atoms has the expected approximately planar geometry, but the other nitrogen atom is surprisingly distorted towards a tetrahedral geometry. The more pyramidal nitrogen has a higher *trans*-influence in the solid state, reflected by a shorter Pt–N bond, and longer *cyclo*-octadiene Pt–C bond length *trans* to this nitrogen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum(II) complexes; Metallacyclic bis(sulfonamide) complexes; X-ray crystal structure

1. Introduction

Silver(I) oxide has been shown to be a useful reagent for the synthesis of a wide range of complexes (especially metallacyclic complexes) of platinum(II) and palladium(II) [1,2], gold(III) [3], as well as other metals such as ruthenium(II) [2] and rhodium(I) and (III) [4], where it acts as both a halide-abstracting reagent and a strong base. In this paper, we report the synthesis of some five-membered ring metallacyclic bis(sulfonamide) complexes of platinum(II) using silver(I) oxide. Gagné and co-workers have recently reported some closely related complexes 1, formed by reaction of the carbonato complex [Pt(CO₃)(Ph₂PCH₂CH₂PPh₂)] with the chisulfonamides RSO₂-NH-CH(Ph)CH(Ph)-NHral SO_2R [R = CF₃ or *p*-Bu^tC₆H₄] [5]. These appear to be the only other examples of five-membered ring platinum bis(sulfonamide) complexes. However, there is interest in five-membered ring sulfonamide complexes of other metals [6,8], especially as they are useful chiral auxiliaries for various reactions [9]. Related chelating

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carboxamide ligands and their metal complexes have also been widely investigated [10] as have platinum and palladium complexes of other sulfonamide ligands [11].

2. Results and discussion

2.1. Syntheses

The reactions of cis-[PtCl₂(PPh₃)₂] or [PtCl₂(cod)] (cod = 1,5-cyclo-octadiene) with bis(sulfonamides) of the general formula RSO₂-NH-(X)-NH-SO₂R [where R = Ph or $p-CH_3C_6H_4$ (Tol) and $X = CH_2CH_2$, CHMeCH₂ or C₆H₄] in the presence of excess Ag₂O in refluxing dichloromethane results in the formation of metallacyclic platinum(II) bis(sulfonamido) complexes, 2-6. The products are isolated as air- and water-stable white to pale yellow powders. This synthetic route is complementary to the one described by Gagné et al for the synthesis of complex 1 [5], and should allow access to a potentially wide range of derivatives by displacement of the labile cod ligand. The attempted synthesis of the triphenylphosphine and *p*-toluenesulfonyl analogues of 6 gave materials which had the expected spectroscopic properties, but which were red in colour, and did not give good elemental microanalytical data.

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This may be due to oxidation of the ligand occurring, since complexes containing oxidised *o*-phenylenediamine-derived ligands have been isolated [7,12], and silver(I) ions have oxidising characteristics. No further studies were carried out with these red materials.



10, $R = p - Bu^{t}C_{6}H_{4}$

The NMR spectra of the complexes are as expected. The phosphine complex **2** shows a single ³¹P NMR resonance, with ${}^{1}J(\text{PtP}) = 3552$ Hz. This is very com-



Fig. 1. PLUTO diagram of the structure of $[Pt\{N(SO_2Ph)CH_2CH_2N(SO_2Ph)\}(PPh_3)_2]$ (2) showing the atom numbering scheme. The minor component of the disordered portion of the structure has been omitted for clarity.

parable with the values of 3614 and 3520 Hz observed for complexes la and 1b [5], and is higher than those in other platinum(II) bis(amide) complexes such as in the β-propiolactam complex cis-[Pt{NC(O)CH₂CH₂)₂- $(PPh_3)_2$ (7) (3054 Hz) [13], cis-[Pt(isat)_2(PPh_3)_2] (8) (Hisat = isatin, 2,3-dihydroindole-2,3-dione) (3284 Hz) [14] and the ureylene complex $[Pt(NPhCONPh)(PPh_3)_2]$ (3337 Hz) [15], and is more comparable to the value for PPh₃ ligand *trans* to the sulfonamide saccharinate (sac) in cis-[PtCl(sac)(PPh₃)₂] (9) (3483 Hz) [16]. This indicates that the sulfonamide ligand has a relatively low trans-influence compared to other amidate ligands. The cod CH groups give characteristic resonances in the ¹H and ¹³C-{¹H} NMR spectra, showing the expected coupling to ¹⁹⁵Pt, e.g. in complex 4 ${}^{2}J(PtH) = 64$ and ${}^{1}J(\text{PtC}) = 145$ Hz respectively. The symmetrical complexes 2, 4 and 6 give a single CH resonance, but in 5 there is no plane of symmetry, and four separate CH resonances are observed as overlapping peaks. In addition, in complex 5 the asymmetric carbon results in splitting of the H-2', H-3' and C-2' signals (Scheme 1), but the 5' signals were not split, presumably because the site of asymmetry is too far removed. The H-3' signals were split in the ¹H NMR spectrum, but splitting of the C-3' signals was not resolved in the ¹³C spectrum.

The only significant bands in the IR spectra of complexes 2-6 are those associated with the sulfonyl groups, which show both symmetric (ca. 1350 cm⁻¹) and antisymmetric (ca. 1140 cm⁻¹) modes, similar to the free sulfonamide ligands. The complexes all give strong $[M + H]^+$ ions in their positive ion electrospray (ES) mass spectra.

2.2. X-ray crystal structure determinations of $[Pt \{N(SO_2Ph)CH_2CH_2N(SO_2Ph)\}(PPh_3)_2]$ (2) and $[Pt \{N(SO_2Ph)C_6H_4N(SO_2Ph)\}(cod)]$ (6)

The structures confirm the complexes as bis(sulfonamide) metallacycles, containing five-membered Pt-N-C-C-N rings. Complex 2 crystallises with one molecule of dichloromethane in the lattice, and disorder was observed, both in the dichloromethane, and in one half of the metallacyclic ligand. The phenyl ring, C(71)to C(76), its associated sulforyl group [S(1), O(1), O(2)], the nitrogen atom [N(1)], and the metallacyclic carbon atom [C(1)] adopt two sites in the lattice (in an approximate 60:40 ratio). The non-disordered portion and the major component of the disordered fraction of the structure is shown in Fig. 1, together with the atom numbering scheme. Selected bond lengths and angles are given in Table 1. Discussion on the structural features associated with the disordered portion of the structure is unwarranted due to the large errors involved with the associated bond lengths and angles. However, the non-disordered fragment of the structure is well defined.

Table I						
Selected	bond	lengths	(Å) and angles	(°) for		
$\left[Pt\{N(SO_2Ph)CH_2CH_2N(SO_2Ph)\}(PPh_3)_2\right] (2)$						
Pt-P(1)		2.270(2)	Pt-P(2)	2.292(2)		
Pt-N(1)		2.24(1) ^a	Pt-N(2)	2.090(6)		
N(2)-C(2)		1.49(1)	N(2)–S(2)	1.615(6)		
S(2)–O(3)		1.443(5)	S(2)-O(4)	1.440(6)		
P(2)-Pt-P(1)	97.98(7)	N(2)-Pt-N(1)	74.8(3) ^a		
P(1)-Pt-N((2)	170.1(2)	P(2)-Pt-N(2)	91.1(2)		
Pt-N(2)-C	(2)	110.2(5)	Pt-N(2)-S(2)	114.1(3)		
N(2)-S(2)-	O(3)	107.2(3)	N(2)-S(2)-O(4)	114.6(3)		
O(3)–S(2)–	O(4)	115.9(3)				

^a The disorder in this portion of the structure casts doubt on the accuracy of these values.



Fig. 2. View of **2** bisecting N(1)–Pt–N(2), illustrating the lack of planarity of the five-membered metallacycle, the pyramidalisation of nitrogen N(2), and the different orientations of the phenyl rings.

The platinum coordination plane shows a slightly distorted square-planar geometry. Deviations from planarity [where the plane is defined by Pt(1), P(1), P(2) and N(2)] are observed for both sites of N(1), [below the plane by 0.64(2) Å for N(1) and 1.41(2) Å for N(1A)]. The other atoms within the platinum coordination sphere are within 0.046 Å of the least-squares plane. The distortion from square-planar geometry, prompted by the steric bulk of the PPh₃ ligands and the bite of the metallacycle, is reflected in the P(1)–Pt–P(2) and N(1)–Pt–N(2) bond angles of 97.98 (7) and 74.8(3)° respectively, though the disorder casts doubt on the accuracy of the latter angle.

The P(1)–Pt and P(2)–Pt bond lengths are 2.270(2) and 2.292(2) Å. A similar difference in Pt–P bond lengths was observed in the bis(amide) complex $[Pt{NC(O)CH_2CH_2}_2(PPh_3)_2]$ (7) [2.291(3) and 2.266(3) Å] [13], but not in the complex *cis*-[Pt(isat)_2(PPh_3)_2] (8) [2.2959(7) and 2.2956 Å] [14]. The (non-disordered) Pt–N(2) bond length of 2.090(6) Å is similar to that

observed in many platinum(II) amide systems, e.g. 2.050(2) and 2.060(2) Å observed in cis-[P(isat)₂(PPh₃)₂] (8), [14] 2.064(6) Å in cis-[PtCl(sac)(PPh₃)₂] (9) [16] and 2.09 Å observed for cis-[Pt(NPh₂)Cl(PEt₃)₂] [17]. In the closely related complex **la**, Pt–N bond lengths of 2.119(2) and 2.125(2) Å are observed, while in the derivative **10**, the Pt–N bond length is 2.062(6) Å, indicating poorer donor properties of the CF₃-substituted ligand [5].

Considering the plane defined by Pt(1), N(2), S(2)and C(2), the nitrogen atom N(2) occupies a position 0.337 Å above the plane. All other atoms lie below the plane [Pt(1) 0.09, S(2) 0.12, C(2) 0.13 Å]. Such geometry indicates a significant degree of tetrahedral character in the geometry of the N(2) atom. The deviation from planarity expected for a sp^2 hybridised nitrogen atom is also apparent in the sum of the angles surrounding N(2). The calculated value of 339.3° is intermediate between the expected 360° for trigonal planar and 328.5° for tetrahedral geometry, and is very different to the closely related complex la, where the sums of the nitrogen bond angles around the (essentially planar) nitrogens are 358.1 and 358.4° [5]. The geometry about N(1) appears more planar than N(2) but the disordered site does not warrant extensive study of its geometry. However the Pt–N bond associated with the pyramidal nitrogen appears substantially shorter [Pt-N(2) 2.090(6) Å] than the Pt–N bond to the trigonal planar nitrogen [Pt-N(1) 2.24 Å]. As a result of the pyramidal geometry about N(2), the orientation of the phenyl rings with respect to the metallacyclic plane is also affected, as shown in Fig. 2. One phenyl ring [bonded to S(1)-N(1)] is approximately perpendicular to the P(1), P(2), Pt(1), N(1), N(2) plane, while the other is almost parallel.

In order to see if the amide pyramidalisation was a general feature in this type of complex, and to try and obtain a non-disordered structure for more accurate comparisons, the molecular structure of $[Pt\{N(SO_2Ph)C_6H_4SO_2Ph)\}(cod)]$ (6) was determined; the molecular structure and atom numbering scheme are shown in Fig. 3, with selected bond lengths and angles in Table 2.

The overall geometry of **6** is similar to that of **2**; one of the nitrogen atoms [N(1)] is more pyramidal in nature, while the other [N(2)] is more planar, as shown by the sum of the bond angles about N(1) (343.35°) and N(2) (355.6°). Both phenyl substituents are positioned above the metallacyclic plane, whereas the *o*-phenylene ring, which forms part of the metallacycle is positioned slightly below the plane, as shown in Fig. 4. The angle between the least-squares plane of the phenylene ring of the ligand [defined by atoms C(1) to C(6)] and the platinum least-squares coordination plane [defined by Pt(1), N(1), N(2) and the midpoints of the C(35)–C(36) and C(31)–C(32) bonds respectively] is 36.75°. As with the structure of **2**, the bond length between platinum and the pyramidal nitrogen [Pt–N(1) 2.058(3) Å] is shorter than that to the more planar nitrogen [Pt–N(2) 2.081(3) Å]. Concomitantly, the Pt–C(35) and Pt–C(36) bond lengths [*trans* to N(1)], at 2.201(3) and 2.217(3) Å, are longer than the Pt–C(31) and Pt–C(32) bond lengths [*trans* to N(2)], which are 2.152(3) and 2.182(3) Å. This suggests that the more pyramidal N(1) nitrogen of **6** has a higher *trans* influence than the more planar nitrogen; it is noteworthy that the ¹H and ¹³C NMR spectra show only a single cod CH resonance.



Fig. 3. Molecular structure of $[Pt{N(SO_2Ph)C_6H_4N(SO_2Ph)}(cod)]$ (6) showing the atom numbering scheme.

Table 2Selectedbo $Pt{N(SO_2Ph)C_6}$	nd lengths H ₄ N(SO ₂ Ph)}(co	(Å) and od)] (6)	angles for
Pt(1)-N(1)	2.058(3)	Pt(1)–N(2)	2.081(3)
Pt(1)-C(31)	2.152(3)	Pt(1)–C(32)	2.182(3)
Pt(1)-C(35)	2.201(3)	Pt(1)-C(36)	2.217(3)
S(1)–O(1)	1.443(2)	S(1)–O(2)	1.444(2)
S(1)–N(1)	1.626(3)	S(1) - C(11)	1.777(3)
S(2)–O(4)	1.438(3)	S(2)–O(3)	1.438(3)
S(2)–N(2)	1.617(3)	S(2)-C(21)	1.776(3)
N(1)–C(1)	1.441(4)	N(2)–C(2)	1.432(4)
C(1)–C(2)	1.407(5)	C(31)-C(32)	1.394(5)
C(35)-C(36)	1.386(5)		
N(1)-Pt(1)-N(2)	79.49(10)	N(1)-Pt(1)-C(31)	91.87(12)
N(1)-Pt(1)-C(32	2) 94.73(12)	N(2)-Pt(1)-C(35)	103.98(12)
N(2)-Pt(1)-C(36	6) 99.07(12)	O(1)-S(1)-O(2)	118.02(15)
O(1)–S(1)–N(1)	108.68(15)	O(2)-S(1)-N(1)	107.47(14)
N(1)-S(1)-C(11)	110.42(15)	O(4)–S(2)–O(3)	116.33(17)
O(4)–S(2)–N(2)	107.13(15)	O(3)-S(2)-N(2)	112.13(15)
C(1)-N(1)-S(1)	115.7(2)	C(1)-N(1)-Pt(1)	108.86(19)
S(1)-N(1)-Pt(1)	118.79(15)	C(2)-N(2)-S(2)	118.9(2)
C(2)-N(2)-Pt(1)	109.6(2)	S(2)-N(2)-Pt(1)	127.13(15)

The reason why one amide nitrogen should undergo a tetrahedral distortion in both structures is not clear, especially as there was no indication of tetrahedral distortion in the closely related complex la. The vast majority of reported structures of amido complexes show trigonal planar geometry about the nitrogen atom. The amide nitrogen of $[(\eta^5-C_5H_5)Re(NO)(PPh_3)-$ (NHPh)] has a tetrahedrally-substituted arrangement [18]. The cause of the distortion in the case of complexes 2 and 6 is not known, and pyramidal nitrogen atoms would be more likely to be associated with alkyl/aryl-substituted amides rather than sulfonamides (or carboxamides). Protonation of one of the amido nitrogen atoms was considered, but can be ruled out on the basis that (i) no counterion has been located in either structure and satisfactory elemental microanalytical data were obtained; (ii) the bond between platinum and a 'protonated' N would be longer than the other Pt-N bond, but the opposite is observed; (iii) the nitrogen of a protonated sulfonamide RSO₂NHR' is extremely weakly basic, and would be expected to coordinate weakly, if at all, to platinum.

3. Experimental

3.1. General

All reactions were carried out in air. The compounds silver(I) oxide [19], and the range of bis(sulfonamide) starting materials used were synthesised using modified literature procedures, starting from the diamine and either benzene- or *p*-toluene-sulfonyl chlorides [7,20]. Dichloromethane and light petroleum (b.p. 40–60°C) were distilled from calcium hydride, while tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl. *cis*-[PtCl₂(PPh₃)₂] was prepared by ligand displacement [21] of 1,5-*cyclo*-octadiene (cod) from [PtCl₂(cod)] [22].

¹H, ¹³C-{¹H} and ³¹P-{¹H} NMR spectra were recorded on a Bruker AC300P instrument at 300.13, 75.47 and 121.5 MHz, respectively, in CDCl₃. Assignment of individual resonances was achieved by standard two-dimensional (COSY, C-H correlation, NOE) and DEPT135 NMR experiments, acquired either on this instrument or on a Bruker DRX 400 instrument. ¹H and ³¹C NMR spectra are referenced relative to CHCl₃ and ³¹P NMR spectra are referenced relative to an external standard of 85% H₃PO₄. Scheme 1 shows the atom numbering scheme used for the sulfonamide ligands; A, B and C refer to the labelling used for the ethylenediamine-, 1,2-propanediamine- and ophenylenediamine-derived ligands respectively. For the benzenesulfonyl derivatives, no 5' signal occurs, and for the 1,2-propanediamine ligand the inequivalent aryl resonances were not distinguished.



Fig. 4. View of 6 bisecting N(1)-Pt(1)-N(2). C(1A) and C(2A) are dummy atoms representing the midpoints of the C(35)-C(36) and C(31)-C(32) bonds respectively.

IR spectra were recorded as KBr disks on a Perkin– Elmer 1600 series instrument. Melting points were recorded on a Reichert Thermopan instrument, and are uncorrected. Elemental analyses were provided by the Campbell Microanalytical Laboratory, University of Otago. Electrospray mass spectra were recorded on a VG Platform II instrument in positive ion mode, using MeCN-H₂O (1:1 v/v) as the mobile phase. Observed isotope patterns recorded under high resolution conditions were compared with those theoretically calculated by the isotope program [23]. Stated m/z values correspond to that of the most intense peak in the isotope pattern.

3.1.1. $[Pt \{N(SO_2Ph)CH_2CH_2N(SO_2Ph)\}(PPh_3)_2]$ (2)

A mixture of cis-[PtCl₂(PPh₃)₂] (50 mg, 0.063 mmol), Ag₂O (100 mg, 0.431 mmol) and N,N'-bis(benzenesulfonyl)ethylenediamide (22 mg, 0.063 mmol) in dichloromethane (20 ml) was refluxed for 16 h. The mixture was filtered to remove silver salts, the filtrate evaporated to dryness under reduced pressure, and the product recrystallised from dichloromethane-diethyl ether to give a white microcrystalline solid (55 mg, 83%). Found: С, 52.8; Н, 4.1; N, 2.7. C₅₀H₄₄N₂O₄S₂P₂Pt·CH₂Cl₂ requires C, 53.6; H, 4.1; N, 2.5%. M.p. 126-130°C (dec.). IR: v(SO₂) 1384(s) and 1142(s) cm⁻¹. NMR: ¹H, δ 7.1–7.8 (m, Ph), 2.95 (m, H-1"); ${}^{31}P-{}^{1}H$, δ 3.6 [s, ${}^{1}J$ (PtP) 3552]; ${}^{13}C-{}^{1}H$, δ 127-135 (m, Ph), 59.2 (s, C-1"). ESMS (cone voltage 20 V) $[M + H]^+$ (1059, 100%), $[M + NH_4]^+$ (1076, 20%).

X-ray quality colourless crystals were grown by vapour diffusion of diethyl ether into a dichloromethane solution at 4°C.

3.1.2. $[Pt \{N(SO_2Ph)CH_2CH_2N(SO_2Ph)\}(cod)]$ (3)

A mixture of [PtCl₂(cod)] (30 mg, 0.080 mmol), Ag₂O (50 mg, 0.216 mmol) and N,N'-bis(benzenesulfonyl)ethylenediamide (27 mg, 0.080 mmol) in dichloromethane (20 ml) was refluxed for 18 h. The mixture was filtered to remove silver salts, the filtrate evaporated to dryness under reduced pressure, and the product recrystallised from dichloromethane-diethyl ether to give a white microcrystalline solid (37 mg, 72%). Found: C, 41.4; H, 4.1; N, 4.5. C₂₂H₂₆N₂O₄S₂Pt requires C, 41.2; H, 4.1; N, 4.4%. M.p. 167-171°C (dec.). IR: $v(SO_2)$ 1301(s) and 1146(s) cm⁻¹. NMR: ¹H, δ 7.78 [d, 4H, H-2', ³J(HH) 9], 7.39–7.50 [m, 6H, H-3' and H-4'], 6.26 [t, 4H, cod CH, ²J(PtH) 63], 2.93 [m, 4H, H-1"], 2.35–2.6 [m, 8H, cod CH₂]; ${}^{13}C-{}^{1}H$ }, δ 143.2 (s, C-1'), 131.5 (s, C-4'), 128.9 (s, C-3'), 126.4 (s, C-2'), 99.1 [t, cod CH, ¹J(PtC) 144], 54.9 (s, C-1"), 30.3



Scheme 1.

(s, cod CH₂). ESMS (cone voltage 50 V) $[M + H]^+$ (642, 100%).

3.1.3. $[Pt{N(SO_{2}Tol)CH_{2}CH_{2}N(SO_{2}Tol)}(cod)]$ (4)

A mixture of PtCl₂(cod)] (40 mg, 0.107 mmol), Ag₂O N,N'-bis(toluene-(50 mg, 0.216 mmol) and sulfonyl)ethylenediamide (39 mg, 0.107 mmol) in dichloromethane (20 ml) was refluxed for 18 h. The mixture was filtered to remove silver salts, the filtrate evaporated to dryness under reduced pressure, and the product recrystallised from dichloromethane-diethyl ether to give a white microcrystalline solid (49 mg, 69%). Found: C, 43.0; H, 4.4; N, 4.4. C₂₄H₃₀N₂O₄S₂Pt requires C, 43.0; H, 4.5; N, 4.2%. M.p. 168-172°C (dec.). IR: v(SO₂) 1333(s) and 1142(s) cm⁻¹. NMR: ¹H, δ 7.65 [d, 4H, H-2', ³J(HH) 8], 7.20 [d, 4H, H-3', ${}^{3}J(\text{HH})$ 8], 6.25 [t, 4H, cod CH, ${}^{2}J(\text{PtH})$ 64], 2.90 (m, 4H, H-1"), 2.32-2.57 (m, 8H, cod CH₂), 2.41 (s, 6H, H-5'); ${}^{13}C-{}^{1}H$, δ 142.0 (s, C-4'), 140.2 (s, C-1'), 129.5 (s, C-3'), 126.5 (s, C-2'), 98.9 [t, cod CH, ¹J(PtC) 145], 55.0 (s, C-1"), 30.3 (s, cod CH₂), 21.5 (s, C-5'). ESMS (cone voltage 50 V) $[M + H]^+$ (670, 100%).

3.1.4. $[Pt \{N(SO_2Tol)CHMeCH_2N(SO_2Tol)\}(cod)]$ (5)

A mixture of [PtCl₂(cod)] (30 mg, 0.080 mmol), Ag₂O (50 mg, 0.216 mmol) and N,N'-bis(p-toluenesulfonyl)-1,2-diamidopropane (31 mg, 0.080 mmol) in dichloromethane (20 ml) was refluxed for 6 h. The mixture was filtered to remove silver salts, the filtrate evaporated to dryness under reduced pressure, and the product recrystallised from dichloromethane-diethyl ether to give a white microcrystalline solid (34 mg, 62%). Found: C, 43.6; H, 4.6; N, 4.3. C₂₅H₃₂N₂O₄S₂Pt requires C, 43.9; H, 4.7; N, 4.1%. M.p. 190-196°C (dec.). IR: $v(SO_2)$ 1305(5) and 1146(s) cm⁻¹. NMR: ¹H, δ 7.68 [d, 2H, H-2', ³J(HH) 8], 7.58 [d, 2H, H-2', ³J(HH) 8], 7.20 [d, 2H, H-3', ³J(HH) 8], 7.16 [d, 2H, H-3', ³J(HH) 8], 6.4 and 6.2 (overlap, 4H, cod CH), 3.5 (m, 1H, H-1"), 2.6/2.7 (overlap, 10H, cod CH₂ and H-2"), 2.40 (s, 6H, H-5'), 1.20 [d, 3H, H-3"), ${}^{3}J(HH)$ 6]; ¹³C-{¹H}, δ 141.9 (s, C-4'), 141.7 (s, C-4'), 141.4 (s, C-1'), 139.4 (s, C-1'), 129.3 (m, C-3'), 126.5/127.2 (m, C-2'), 96.8-101.1 (m, cod CH), 60.3 (s, C-1"), 59.5 (s, C-2"), 32.7 (s, cod CH₂), 32.3 (s, cod CH₂), 28.3 (s, cod CH₂), 27.9 (s, cod CH₂), 22.6 (s, C-3"), 21.5 (s, C-5'). ESMS (cone voltage 50 V) $[M + H]^+$ (684, 100%).

3.1.5. $[Pt\{N(SO_2Ph)C_6H_4N(SO_2Ph)\}(cod)]$ (6)

A mixture of $PtCl_2(cod)$] (40 mg, 0.107 mmol), Ag_2O (50 mg, 0.216 mmol) and N,N'-bis(benzenesulfonyl)-*o*-phenylenediamide (42 mg, 0.107 mmol) in dichloromethane (20 ml) was refluxed for 22 h. The mixture was filtered to remove silver salts, the filtrate evaporated to dryness under reduced pressure, and the product recrystallised from dichloromethane–diethyl ether to give a yellow microcrystalline solid (57 mg,

77%). Found: C, 45.5; H, 3.6; N, 4.3. C₂₆H₂₆N₂O₄S₂Pt requires C, 45.3; H, 3.8; N, 4.1%. M.p. 200-205°C (dec.). IR: $v(SO_2)$ 1301(s) and 1146(s) cm⁻¹. NMR: ¹H, δ 7.62 [m, 4H, H-2', ³J(HH) 8], 7.47 (m, 2H, H-4'), 7.35 [m, 4H, H-3', ³J(HH) 8], 7.27 (m, 2H, H-2"), 6.65 (m, 2H, H-3"), 6.36 [t, 4H, cod CH, ²J(PtH) 61], 2.6 and 2.3 (m, 8H, cod CH₂); ${}^{13}C-\{{}^{1}H\}$, δ 143.2 (s, C-1'), 142.5 (s, C-1"), 131.7 (s, C-4'), 128.9 (s, C-3'), 126.8 (s, C-2'), 122.8 (s, C-3"), 121.4 (s, C-2"), 101.5 [t, cod CH, $^{1}J(PtC)$ 143], 30.2 (s, cod CH₂). ESMS (cone voltage 20 V): $[M + H]^+$ (690, 58%), $[M + NH_4]^+$ (707, 100%), $[M + K]^+$ (728, 11%), $[2L + NH_4]^+$ (794, 14%), [M + $L + NH_4]^+$ where L = N, N'-(1096. 19%), bis(benzenesulfonyl)-o-phenylenediamide.

X-ray quality straw-yellow crystals were grown by vapour diffusion of diethyl ether into a dichloromethane solution at 4°C.

3.2. X-ray crystal structure determinations

3.2.1. $[Pt \{N(SO_2Ph)C_2H_2N(SO_2Ph)\}(PPh_3)_2] \cdot CH_2Cl_2$ (2 · CH_2Cl_2)

Crystal data: $C_{50}H_{44}N_2O_4P_2PtS_2$ ·CH₂Cl₂, $M_r = 1142.95$, monoclinic, space group $P2_1/n$, a = 12.2981(2), b = 22.7569(4), c = 17.0806(3) Å, $\beta = 97.422(1)^\circ$, V = 4740.2(1) Å³, Z = 4, $D_{calc} = 1.602$ g cm⁻³, μ (Mo K α) = 3.276 mm⁻¹, T = 203(2) K, 28593 reflections measured, 10720 unique ($R_{int} = 0.0373$), 8337 to $\theta = 25^\circ$ used in calculations. Final $wR_2 = 0.1127$, $R_1 = 0.0650$ (all data).

The PhSO₂N group associated with N(1) was disordered over two sites. The disorder was modelled as a major component (60%), and a minor component (40%) for which only the C(1), N(1), S(1), O(1), O(2) and C(71) sites could be included since the remainder of the C(71)–C(76) ring could not be resolved from the major component.

3.2.2. $[Pt\{N(SO_2Ph)C_6H_4N(SO_2Ph)\}(cod)]$ (6)

Crystal data: $C_{26}H_{26}N_2O_4PtS_2$, $M_r = 689.70$, monoclinic, space group $P2_1/n$, a = 9.4752(2), b = 16.0938(3), c = 15.4245(3) Å, $\beta = 91.654(1)^\circ$, V = 2351.13(8) Å³, Z = 4, $D_{calc} = 1.948$ g cm⁻³, μ (Mo K α) = 6.184 mm⁻¹, T = 170(2) K, 14456 reflections measured, 5097 unique ($R_{int} = 0.0285$) used in calculations. Final $wR_2 = 0.0667$, $R_1 = 0.0276$ (all data).

4. Supplementary material

Tables of atomic coordinates, thermal parameters, bond lengths and bond angles for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC), Nos. 151 750 (for 2) and 151 749 (for 6). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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