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# Synthesis and structural characterisation of the palladium cluster compounds $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}PPh_2py)_2(PBz_3)_2]$ and $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CNR)(PBz_3)_4]$ (R = $^t$Bu, 2,6-dimethylphenyl and cyclohexyl)

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We have reported previously that the reaction of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) with $PBz_3$ in the presence of $SO_2$ yields $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}dba)(PBz_3)_2]$ (**1**) and $[Pd_3(\mu\text{-}SO_2)_3(PBz_3)_3]$ (**2**) (which can be prepared selectively by varying the concentration of $SO_2$). Here the reactions of **1** and **2** with $PPh_2py$ (diphenylpyridine phosphine) to yield $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}PPh_2py)(PBz_3)_2]$ (**4**) and $[Pd_3(\mu\text{-}PPh_2py)_2(\mu\text{-}SO_2)_2(PBz_3)_2]$ (**5**), respectively, are reported. Structural characterisation of **5** shows it to be an unusual trimetallic compound. The reaction between the tetrahedral cluster $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CO)(PBz_3)_4]$ (**3**) (which is prepared by reacting dimer **1** with COS) and CNR has also been studied. The isostructural clusters $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4]$ (R = $^t$Bu, **6**; CNCy, **7**; CNXyl, **8**; CNMe, **9**) have been prepared and the structures of three of them are described here.

Low-oxidation-state palladium complexes are used extensively as catalysts in a wide range of organometallic transformations.[1] In many of these reactions, the palladium source of choice is $[Pd_2(dba)_3]\cdot$Solvent (dba = dibenzylideneacetone, Solvent = $CHCl_3$, $C_6H_6$) which, in the presence of phosphines, generates catalytically active Pd(0) species.[2] Besides its implications in catalysis, the reaction of $Pd_2(dba)_3$ with phosphines in the presence of bridging molecules such as $SO_2$ and CO has been used for the synthesis of cluster compounds.[3] One of the advantages of using $Pd_2(dba)_3$ is that, in spite of being a very stable compound which can be stored for long periods of time, it reacts readily with a wide range of ligands. In most of these reactions, all the dba molecules from the starting material are displaced to yield dba-free compounds.

We have reported recently that the reaction between $Pd_2(dba)_3$, $PBz_3$ and $SO_2$ leads to the formation of the dba-containing dimer $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}dba)(PBz_3)_2]$ (**1**) which is in equilibrium with the trimeric species $[Pd_3(\mu\text{-}SO_2)_3(PBz_3)_3]$ (**2**).[4] Under an atmosphere of $SO_2$ the equilibrium is shifted towards **2** which can then be easily isolated as a stable compound (see Scheme 1). Dimer **1** is a synthetically attractive species since it has a labile dba molecule which can be easily displaced to generate the unsaturated fragment "$Pd_2(\mu\text{-}SO_2)(PBz_3)_2$". Consequently, the reaction of **1** with donor species can yield a wide range of simple substitution products, such as $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}dppm)(PBz_3)_2]$, or cluster compounds such as $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CO)(PBz_3)_4]$ (**3**).[4,5]

Herein we report the synthesis of the new dimer $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}PPh_2py)(PBz_3)_2]$ (**4**) from the reaction between **1** and the bidentate ligand $PPh_2py$. During this study, it was discovered that the palladium triangle **2** also reacts with $PPh_2py$ yielding the novel trimetallic species $[Pd_3(\mu\text{-}PPh_2py)_2(\mu\text{-}SO_2)_2(PBz_3)_2]$ (**5**). Furthermore, the reaction between the electron deficient cluster **3** (obtained by reacting **1** with COS) and four different isocyanides has also been investigated and found to give the new tetrapalladium clusters with general formula $Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4$ (R = $^t$Bu, **6**; CNCy, **7**; CNXyl, **8**; CNMe, **9**). The structural characterisation of three of these clusters and of the trimetallic complex **5** are also reported.

## Results and discussion

### Syntheses of $[Pd_2(\mu\text{-}PPh_2py)(\mu\text{-}SO_2)(PBz_3)_2]$ (4) and $[Pd_3(\mu\text{-}PPh_2py)_2(\mu\text{-}SO_2)_2(PBz_3)_2]$ (5)

Previous studies have shown that the dba molecule in $[Pd_2(\mu\text{-}dba)(\mu\text{-}SO_2)(PBz_3)_2]$ (**1**) can be easily displaced by ligands such as dppm.[4] To study further the reactivity of dimer **1**, it was decided to react it with the bidentate P–N ligand $PPh_2py$ expecting the formation of $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}PPh_2py)(PBz_3)_2]$. One equivalent of $PPh_2py$ was added to a solution of **1** in toluene and the course of this reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After approximately 30 min, the signals corresponding to the starting materials disappeared and a new set of three signals in a 1 : 1 : 1 ratio appeared (besides two small multiplets at 5.8 and 19.8 – see below). Addition of diethyl ether to this solution precipitated a small amount of a yellow–orange solid (corresponding to the small multiplets observed in the $^{31}P\{^1H\}$ NMR spectrum) which was filtered off. The remaining solution was evaporated to dryness and washed with diethyl ether to yield a yellow solid which was characterised as $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}PPh_2py)(PBz_3)_2]$ (**4**) (see Scheme 1) on the basis of $^{31}P\{^1H\}$ NMR and IR spectroscopy and FAB(+) mass spectrometry. The $^{31}P\{^1H\}$ NMR spectrum of this solid showed three signals at 32.0, 9.5 and 5.1 ppm in a 1 : 1 : 1 ratio. The signal at 32.0 (a doublet of doublets $^2J$ = 24 Hz and $^3J$ = 15 Hz) can be assigned to the phosphorus atom of the bridging $PPh_2py$. The signal at 9.5 (a doublet of doublets with $^3J$ = 87 Hz and $^3J$ = 15 Hz) has been assigned to the $PBz_3$ ligand further away from the phosphorus atom of the bridging $PPh_2py$. Finally, the signal at 5.1 (a doublet of doublets with $^2J$ = 24 Hz and $^3J$ = 87 Hz) corresponds to the second $PBz_3$ ligand (bonded to the same palladium atom as the phosphorus atom of the $PPh_2py$ ligand). The IR spectrum of the new dimer **4** showed strong $\nu(SO_2)$ stretching modes at 1092, 1070 and 1028 $cm^{-1}$ suggesting that the dimer has retained the $SO_2$ group present in the starting material; no stretching modes corresponding to bridging dba were observed. Further evidence for the formulation of **4** came from elemental analyses and from the FAB(+) mass spectrum which showed the molecular peak

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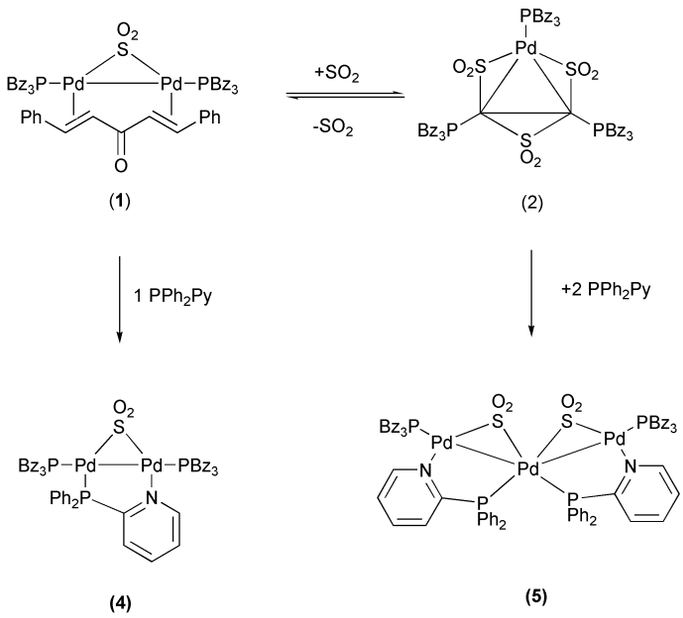



**Scheme 1**

at 1149 a.m.u. (which corresponds to $\{Pd_2(PPh_2py)(SO_2)(PBz_3)_2\}^+$).

As mentioned above the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture from which compound **4** was obtained showed the presence of a small quantity (approximately 10%) of a second compound with two sets of multiplets at 5.8 and 19.8 ppm (each of which is *dominated* by a doublet). This compound was isolated as a yellow/orange solid by addition of a small amount of diethyl ether to the reaction mixture (at −30 °C). The IR spectrum of the isolated solid showed characteristic bands for coordinated $SO_2$ and no bands associated with dba. The mass spectrum of the compound showed the molecular peak at 1580 a.m.u which is consistent with the formulation $[Pd_3(Ph_2Ppy)_2(PBz_3)_2(SO_2)_2]$, suggesting the presence of a trinuclear species. We have established previously that dimer **1** and trimer **2** are in equilibrium (depending on the concentration of $SO_2$).[4] Consequently, the formation of the second product in the reaction between **1** and $PPh_2py$ could be the result of the presence of traces of **2** in the original mixture. To explore this possibility, it was then decided to react the tri-palladium triangle **2** with two equivalents of $PPh_2py$. The course of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy which showed the complete conversion of the starting material to the same product obtained in low amounts in the previous reaction (*i.e.* the product with the two sets of multiplets at 5.8 and 19.8 ppm). A yellow–orange crystalline product was obtained by addition of diethyl ether and characterised spectroscopically and structurally as the novel trinuclear complex $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}PPh_2py)_2(PBz_3)_2]$ (**5**).

The complicated (and poorly resolved) splitting pattern observed in the $^{31}P\{^1H\}$ NMR spectrum of **5** suggested the presence of a system with second-order couplings. Only when a single crystal X-ray crystallographic study was carried out (*vide infra*) did it become evident that this was due to an AA′BB′ type system (where the two $PBz_3$ and the two $PPh_2py$ ligands are chemically but not magnetically equivalent). The IR spectrum of the new product showed strong $\nu(SO_2)$ stretches at 1140, 1090 and 1071 $cm^{-1}$ and an absence of the characteristic stretches associated with dba. The FAB(+) mass spectrum showed the molecular peak at 1582 a.m.u. which corresponds to a species with formula $\{Pd_3(PPh_2py)_2(PBz_3)_2(SO_2)_2\}^+$. The formulation of **5** was further confirmed by elemental analyses.

In order to unambiguously characterise the new product, single crystals of this species were grown and an X-ray crystallographic analysis was undertaken. The molecule (Fig. 1) has

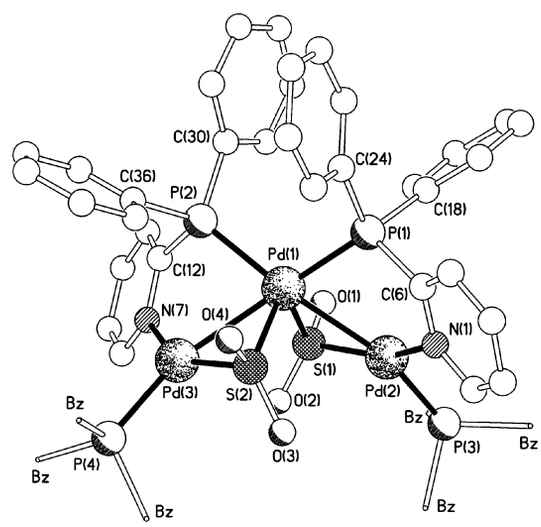



**Fig. 1** The molecular structure of **5**.

non-crystallographic $C_2$ symmetry about an axis passing through Pd(1) and bisecting the P(1)–Pd(1)–P(2) angle. Pd(1) is six-coordinate, being bonded to two *cis* $PPh_2py$ phosphines, two $\mu\text{-}SO_2$ units, and two four-coordinate palladium centres. The geometrical arrangement of the three palladium centres is unusual[6] in that in virtually all other comparable examples of trinuclear metal–metal compounds an essentially triangular three-bond arrangement is observed. Here the bonded Pd(1)–Pd(2) and Pd(1)–Pd(3) distances are 2.671(1) and 2.655(1) Å, respectively (Table 1), distances directly comparable with that observed in, for example, $[Pd_2(\mu\text{-}SO_2)(\mu\text{-dppm})(PBz_3)_2]$,[4] whilst the non-bonded Pd(2) ··· Pd(3) distance is 4.43 Å. It is worth noting that the Pd–Pd bonding distances observed in this trimer are relatively short. These distances are significantly shorter than in dimer **1** and also shorter than the values reported previously for $SO_2$-containing palladium cluster compounds. As has been discussed before for $[Pd_2(\mu\text{-}SO_2)(\mu\text{-dppm})(PBz_3)_2]$,[4a] such short Pd–Pd distances are not consistent with a system containing palladium centres in zero oxidation state (as could be formally assigned for this trinuclear compound). The values are more typical of $Pd^I$–$Pd^I$ bonds or bonds where the palladium centres have fractional positive charge. Hence, the $SO_2$ molecules in **5** are best considered not as neutral ligands but should be formally described as negatively charged species. The

**Table 1** Selected bond lengths (Å) and angles (°) for **5**

| | | | |
|---|---|---|---|
| Pd(1)–Pd(2) | 2.6708(6) | Pd(1)–Pd(3) | 2.6552(6) |
| Pd(1)–S(1) | 2.425(2) | Pd(1)–S(2) | 2.416(2) |
| Pd(1)–P(1) | 2.301(2) | Pd(1)–P(2) | 2.322(2) |
| Pd(2)–S(1) | 2.191(2) | Pd(2)–P(3) | 2.275(2) |
| Pd(2)–N(1) | 2.197(5) | Pd(3)–S(2) | 2.206(2) |
| Pd(3)–P(4) | 2.271(2) | Pd(3)–N(7) | 2.191(5) |
| P(1)–Pd(1)–P(2) | 112.91(6) | P(1)–Pd(1)–S(2) | 102.73(6) |
| P(2)–Pd(1)–S(2) | 112.58(6) | P(1)–Pd(1)–S(1) | 116.04(6) |
| P(2)–Pd(1)–S(1) | 102.88(6) | S(2)–Pd(1)–S(1) | 110.02(6) |
| P(1)–Pd(1)–Pd(3) | 151.51(5) | P(2)–Pd(1)–Pd(3) | 74.37(4) |
| S(2)–Pd(1)–Pd(3) | 51.31(4) | S(1)–Pd(1)–Pd(3) | 87.26(4) |
| P(1)–Pd(1)–Pd(2) | 75.62(4) | P(2)–Pd(1)–Pd(2) | 150.19(5) |
| S(2)–Pd(1)–Pd(2) | 91.91(4) | S(1)–Pd(1)–Pd(2) | 50.65(4) |
| Pd(3)–Pd(1)–Pd(2) | 112.43(2) | S(1)–Pd(2)–N(1) | 152.7(2) |
| S(1)–Pd(2)–P(3) | 97.31(6) | N(1)–Pd(2)–P(3) | 109.8(2) |
| S(1)–Pd(2)–Pd(1) | 58.86(4) | N(1)–Pd(2)–Pd(1) | 93.9(2) |
| P(3)–Pd(2)–Pd(1) | 155.79(4) | N(7)–Pd(3)–S(2) | 149.9(2) |
| N(7)–Pd(3)–P(4) | 113.6(2) | S(2)–Pd(3)–P(4) | 96.45(6) |
| N(7)–Pd(3)–Pd(1) | 91.19(14) | S(2)–Pd(3)–Pd(1) | 58.73(4) |
| P(4)–Pd(3)–Pd(1) | 155.13(5) | | |

mean S–O distance of 1.469(5) Å in **5** is longer than those reported for other palladium–$SO_2$ complexes where the metal centre is considered to be in lower oxidation states (*e.g.* 1.447(13) Å in $Pd(PBz_3)_2(SO_2)$, 1.449(4) Å in $Pd_3(\mu\text{-}CO)_2(\mu\text{-}SO_2)(PBz_3)_3$ and 1.439(6) Å in $Pd_3(\mu\text{-}SO_2)_3(PBz_3)_3$).[4] This suggests that the $SO_2$ ligands in **5** are more strongly electron-accepting which could account for the relatively short Pd–Pd distances observed in **5** (consistent with the palladium centres being in higher oxidation states).

Within the two three-membered rings the Pd–S bonding is asymmetric with, in each case, the bond to Pd(1) being *ca.* 0.2 Å longer than those to Pd(2) and Pd(3), reflecting the higher coordination number of Pd(1) *cf.* Pd(2) and Pd(3). The bite of the two five-membered chelate rings results in a contraction of the P(1)–Pd(1)–Pd(2) and P(2)–Pd(1)–Pd(3) angles to *ca.* 75° and an expansion of the P(1)–Pd(1)–P(2) angle to 112.9(1)°; the planes of the two $Pd_2S$ three-membered rings subtend an angle of *ca.* 102°. Both five-membered chelate rings have sharply folded geometries, with out of plane fold angles about their P ··· Pd vectors of *ca.* 50°. The geometries at Pd(2) and Pd(3) are essentially planar (deviations from planarity of 0.05 and 0.02 Å respectively), the distortion in the *cis* angles being large as a consequence of the different bridging ligands. The Pd–P and Pd–N distances throughout are unexceptional. The exterior of the complex (which is dominated by the phenyl rings and benzyl groups) coupled with the inclusion of disordered dichloromethane molecules, precludes any significant intermolecular interactions.

### Syntheses of $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4]$ (R = $CN^tBu$, 6; CNCy, 7; CNXyl, 8; CNMe, 9)

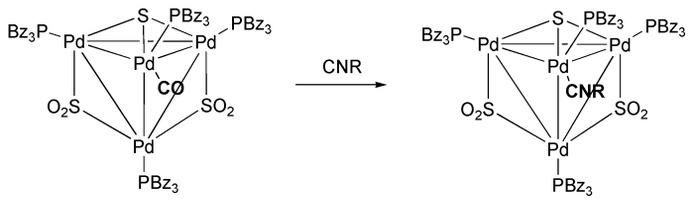
In a previous communication we reported that the reaction between $[Pd_2(\mu\text{-dba})(SO_2)(PBz_3)_2]$ (**1**) and COS produces the novel tetrahedral cluster compound $[Pd_4(\mu\text{-}S)(\mu\text{-}SO_2)_2(CO)(PBz_3)_4]$ (**3**).[5] The crystallographic analysis of this cluster revealed that each palladium atom is bonded to a terminal phosphine ligand. There are also two edge-bridging $SO_2$ ligands, a terminal CO and one face-capping S atom. In this reaction the COS molecule reacts dissociatively with **1**, releasing CO and S which act as independent ligands in **3**. An interesting feature of this cluster is its polyhedral electron count of 58, which is not consistent with PSEPT (which predicts an electron count of 60 for tetrahedral clusters).[7] Consequently this compound can be considered an electron-poor or unsaturated cluster which should react readily with two-electron donor ligands thereby increasing its electron count. In order to explore this possibility it was decided to react **3** with one equivalent of the isocyanide $CN^tBu$. As soon as these species were mixed an immediate darkening of the solution (to very dark red) was observed. After approximately 2 h the reaction mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy which showed the presence of three non-equivalent phosphorus environments in a 2 : 1 : 1 ratio. In comparison to the starting material, the signals of the new compound had shifted, although the coupling pattern observed was the same as that of **3** (*i.e.* a doublet of doublets for the signal integrating to two and a doublet of doublets and a doublet of triplets for the remaining two signals). This pattern suggested that, although a change had occurred, the metal core of the starting material and the number of distinct phosphine environments was unchanged. Upon addition of diethyl ether to the reaction mixture, a dark red–purple crystalline solid was obtained. The IR spectrum of this solid showed a strong stretching frequency at 2156 $cm^{-1}$, characteristic of terminally coordinated $CN^tBu$, and $\nu(SO_2)$ vibrations at 1093, 1070 and 1024 $cm^{-1}$. The characteristic stretch at 2030 $cm^{-1}$ associated with the CO ligand of the starting material was not present in this spectrum suggesting that a simple substitution reaction of the CO by $CN^tBu$ had occurred. Further evidence that the new compound was the result of a simple substitution reaction came from the FAB(+) mass spectrum which showed the molecular peak at 1883 a.m.u. (corresponding to the formulation $\{Pd_4(S)(SO_2)_2(CN^tBu)(PBz_3)_4\}^+$). This spectroscopic evidence together with the elemental analyses, suggested the formula $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CN^tBu)(PBz_3)_4]$ (**6**) for the new cluster, which was later confirmed by an X-ray crystallographic analysis (*vide infra*).

These results indicate that by reacting **3** with $CN^tBu$ a simple substitution reaction of the CO ligand takes place instead of the expected addition of the isocyanide. Consequently, the skeletal electron count of the new cluster **6** is still 58 indicating that this particular geometry and combination of ligands favours the formation of electron poor tetrahedral palladium clusters (instead of a butterfly arrangement which would be consistent with the electron counting rules).

To explore the generality of this reaction, **3** was reacted with a series of isocyanides with different electronic and steric properties (*i.e.* CNCy, CNXyl and CNMe). The reactions were carried out in an analogous manner to the synthesis of **6** and the products obtained were characterised by $^{31}P\{^1H\}$ NMR and IR spectroscopy, FAB(+) mass spectrometry and elemental analyses. In all three cases the products obtained were analogous to **6**, *i.e.* the clusters $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4]$ (R = CNCy, **7**; CNXyl, **8**; CNMe, **9**) resulting from the simple substitution of CO by CNR (see Scheme 2). In spite of having full characterisation of the four new tetra-palladium clusters (and the starting material **3**), their $^{31}P\{^1H\}$ NMR spectra showed some unusual coupling patterns (see below for discussion). Consequently it was of interest to compare their structural parameters, and thus X-ray crystallographic studies of **6**, **7** and **8** were carried out.

### Structural characterisation of $[Pd_4(\mu_3\text{-}S)(\mu\text{-}SO_2)_2(CNR)(PBz_3)_4]$ (R = $CN^tBu$, 6; CNCy, 7; CNXyl, 8)

All three clusters **6**–**8** have a nucleus isostructural[8] with that of **3**,[5] but with the terminal carbonyl replaced by $CN^tBu$ (**6**), CNCy (**7**) or CNXyl (**8**). Each of these complexes exhibit molecular $C_s$ symmetry about a plane including Pd(1), Pd(2), S(1) and P(2), and have a tetrahedral tetrapalladium core with a capping $\mu_3$-sulfide and a pair of bridging sulfur dioxides (Fig. 2). The Pd–Pd bonds lie between 2.706(1) and 3.100(2) Å (Table 2) and are in the range observed previously in $SO_2$-containing clusters.[9] However, in each of **3** and **6**–**8**, one of the Pd–Pd bonds, that between Pd(3) and Pd(4), is appreciably longer than the others (Table 2). Asymmetry in $Pd_4$ clusters is well established, and in some cases the "sixth" bond is so long that a "butterfly" designation[10] is more appropriate (*vide infra*). There is also asymmetry in the bond distances to the capping sulfide




**Scheme 2** Synthesis of **6**–**9**.

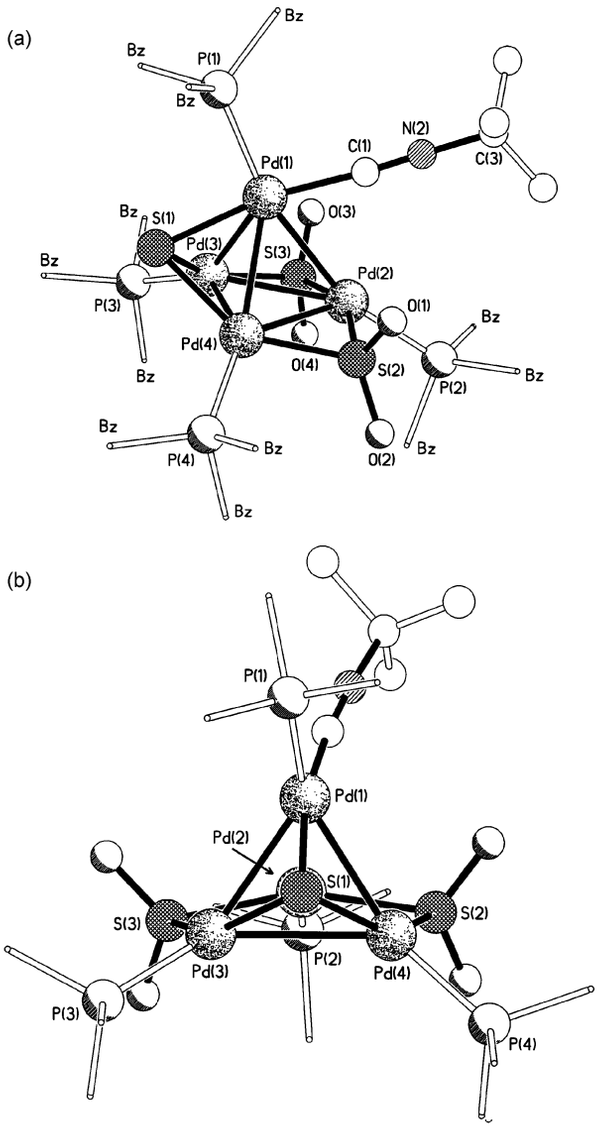



**Fig. 2** (a) Perspective view of the molecular structure of **6**, and (b) as viewed down the S(1) ··· Pd(2) vector showing the pseudo $C_s$ symmetry of the nucleus.

S(1), with the link to the apical palladium Pd(1) being shorter than those to the two basal palladiums Pd(3) and Pd(4). As was seen in **5** the sulfur dioxide bridges are asymmetric, though here the difference is only 0.1 Å for the Pd–S distances. The Pd–P distances are also comparable to those seen in **5**. Inspection of space-filling models reveals that despite the presence of a large number of bulky peripheral benzyl substituents there still exist pronounced unhindered "windows" to both the sulfide and $SO_2$ ligands (see Fig. 3). These "windows" offer the prospect for further coordination at these sites. There are no packing interactions of note.

In spite of the complete and consistent characterisation of clusters **3** and **6**–**9**, a closer inspection of their $^{31}P\{^1H\}$ NMR spectra in solution revealed some interesting features. In the five clusters, there are four phosphine ligands two of which are equivalent (*i.e.* there are three non-equivalent phosphorus environments). This suggests that the $^{31}P\{^1H\}$ NMR spectra of the clusters should show $A_2BX$ patterns with the signal for the two equivalent phosphines split into a doublet of doublets and the other two phosphines into doublets of triplets. However, this is not the pattern observed in the $^{31}P\{^1H\}$ NMR spectra of any of these clusters. Although at different chemical shifts, the five clusters have the same pattern of signals consistent with three different phosphorus environments in a 2 : 1 : 1 ratio. The signal integrating to 2 (phosphine **a** in Scheme 3) is split into a doublet (and not into a doublet of doublets as suggested by the structure).

**Table 2** Selected comparative bond lengths (Å) for **3** and **6**–**8**

| | **3**[a] | **6** | **7** | **8** |
|---|---|---|---|---|
| Pd(1)–Pd(2) | 2.7851(6) | 2.8184(7) | 2.8165(14) | 2.752(2) |
| Pd(1)–Pd(3) | 2.7416(6) | 2.7715(7) | 2.724(2) | 2.762(2) |
| Pd(1)–Pd(4) | 2.7735(6) | 2.7056(8) | 2.7766(13) | 2.766(2) |
| Pd(2)–Pd(3) | 2.8614(6) | 2.8946(7) | 2.854(2) | 2.908(2) |
| Pd(2)–Pd(4) | 2.8741(6) | 2.8514(7) | 2.912(2) | 2.847(3) |
| Pd(3)–Pd(4) | 2.9404(6) | 3.0397(8) | 3.052(2) | 3.100(2) |
| Pd(1)–S(1) | 2.2865(14) | 2.292(2) | 2.304(4) | 2.306(7) |
| Pd(1)–P(1) | 2.3089(14) | 2.274(2) | 2.289(3) | 2.264(6) |
| Pd(1)–C(1) | 1.938(6) | 1.972(9) | 1.94(2) | 2.05(3) |
| Pd(2)–S(2) | 2.3475(14) | 2.300(2) | 2.332(3) | 2.321(7) |
| Pd(2)–S(3) | 2.3019(14) | 2.330(2) | 2.306(3) | 2.324(5) |
| Pd(2)–P(2) | 2.3267(14) | 2.337(2) | 2.348(4) | 2.303(7) |
| Pd(3)–S(1) | 2.3759(14) | 2.377(2) | 2.400(4) | 2.372(5) |
| Pd(3)–S(3) | 2.2276(14) | 2.192(2) | 2.210(4) | 2.169(5) |
| Pd(3)–P(3) | 2.2791(14) | 2.271(2) | 2.298(4) | 2.289(5) |
| Pd(4)–S(1) | 2.4179(14) | 2.396(2) | 2.397(3) | 2.313(7) |
| Pd(4)–S(2) | 2.2147(14) | 2.214(2) | 2.197(4) | 2.152(7) |
| Pd(4)–P(4) | 2.2805(14) | 2.290(2) | 2.276(3) | 2.293(7) |

[a] Complex **3** has been renumbered with respect to the original report in ref. 5 for consistency with the other three structures.

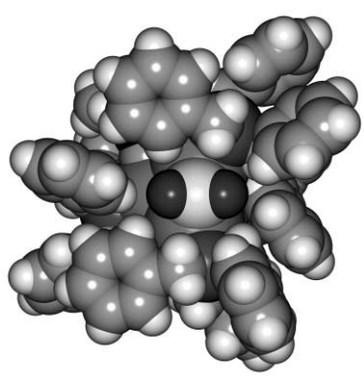
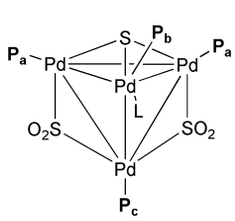


**Fig. 3** Space-filling representation of the molecular structure of **6** showing one of the exposed $SO_2$ units (centre).




**Scheme 3** NMR labelling scheme.

For the remaining two signals, one of them (phosphine **c**) is split into a doublet of triplets, as would be expected from the molecular structure, but the other (phosphine **b**) is split into a doublet – and not a doublet of triplets. This pattern suggests that for the five clusters the $P_a$–$P_c$ and $P_b$–$P_c$ couplings are observed but the one between $P_a$ and $P_b$ is not. Coupling constants are angularly dependant and coupling is at a minimum between atoms having a torsional relationship of about 90°.[11] Although this could be a potential explanation for the observed behaviour, close inspection of the structural parameters from the X-ray structures does not indicate this to be the case. It is possible however, that the coupling constant *via* the $P_a$–Pd–Pd–$P_b$ bonds is equal but opposite in sign to the coupling constant *via* $P_a$–Pd–($SO_2$)–Pd–$P_b$. An analogous observation has been made by Grim[12] who demonstrated that the overall phosphorus–phosphorus coupling constants in coordinated bisphosphine ligands can be separated into two components: transmission *via* the σ ligands in the backbone and *via* the σ bonds through the metal centres. This seems the most plausible explanation for the consistent lack of $P_a$–$P_b$ coupling constants observed in our systems.

## Conclusion

In this paper we have shown the wide range of multi-metallic compounds that can be prepared using [$Pd_2$(μ-$SO_2$)(μ-dba)-($PBz_3$)$_2$] (**1**) as a starting material. The reaction of this compound with $PPh_2$py yields the new asymmetric dimer [$Pd_2$(μ-$SO_2$)(μ-$PPh_2$py)($PBz_3$)$_2$]. On the other hand, the triangular cluster [$Pd_3$(μ-$SO_2$)$_3$($PBz_3$)$_3$] (which can be prepared from dimer **1** and $SO_2$) reacts readily with $PPh_2$py to form the novel trimetallic compound [$Pd_3$(μ-$SO_2$)$_2$(μ-$PPh_2$py)$_2$($PBz_3$)$_2$]. This compound has an unusual and unprecedented geometry for palladium.

The reaction of dimer **1** with COS leads to the formation of cluster [$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CO)($PBz_3$)$_4$].[5] We have demonstrated that, although this cluster is unsaturated (having an electron count of 58) the addition of the two-electron-donor isocyanides does not lead to a simple addition reaction to the cluster core (and consequent increase in the electron count); instead, a substitution takes place and the new unsaturated clusters [$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CNR)($PBz_3$)$_4$] are formed (still with an electron count of 58).

## Experimental

### General

Reactions were routinely carried-out using Schlenk-line techniques under an atmosphere of pure nitrogen. The solvents used were dry and free of oxygen. Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer between 4000 and 250 $cm^{-1}$ as KBr pellets. $^{31}P\{^1H\}$ NMR spectra were performed on a JEOL JNM-EX270 spectrometer operating at a frequency of 109.4 MHz with chemical shifts reported relative to $H_3PO_4$. Mass spectra were recorded on a VG AutoSpec-Q as FAB using 3-nitrobenzyl alcohol as matrix. The compounds [$Pd_2$(μ-dba)(μ-$SO_2$)($PBz_3$)$_2$], [$Pd_3$-(μ-$SO_2$)$_3$($PBz_3$)$_3$] and [$Pd_4$(μ-$SO_2$)$_2$($\mu_3$-S)(CO)($PBz_3$)$_4$] were prepared according to reported procedures.

### Syntheses

**[$Pd_2$(μ-$Ph_2$Ppy)(μ-$SO_2$)($PBz_3$)$_2$] (4).** To a solution of [$Pd_2$-(μ-$SO_2$)(μ-dba)($PBz_3$)$_2$] (100 mg, 0.089 mmol) in toluene (10 ml) was added one equivalent of $PPh_2$py (23 mg, 0.089 mmol) dissolved in toluene (5 ml). Upon stirring, the solution changed from yellow to orange. Diethyl ether was added to the mixture and kept at −30 °C overnight. A small quantity of precipitate was obtained, isolated by filtration and identified as compound **4** (see below). The solvent from the remaining solution was removed under reduced pressure and to the remaining brown residue diethyl ether was added to remove any remaining dba and stirred rapidly for 10 min. The remaining dark yellow solid was formulated as $Pd_2$(μ-$SO_2$)(μ-$PPh_2$py)($PBz_3$)$_2$. Yield 70 mg (68%). Found: C, 56.37; H, 4.18, N, 1.38. $C_{59}H_{56}NO_2P_3Pd_2S\cdot CHCl_3$ requires: C, 56.89; H, 4.50; N, 1.11% (NOTE: the analyses were repeated four times giving the same values consistently, which are in agreement with an inclusion of one molecule of chloroform per molecule of dimer – the presence of chloroform is associated with the starting material). $\nu_{max}$/$cm^{-1}$ 1598, 1580 (CN from pyridine), 1092, 1070 and 1028 ($SO_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 5.1 (dd, 1P, $^3J_{P_aP_b}$ = 87 Hz, $^2J_{P_aP_c}$ = 24 Hz) 9.5 (dd, 1P, $^3J_{P_aP_b}$ = 87 Hz, $^3J_{P_bP_c}$ = 15 Hz) and 32.0 (dd, 1P, $^3J_{P_bP_c}$ = 15 Hz, $^2J_{P_aP_c}$ = 24 Hz). FAB-$MS^+$: *m*/*z* 1148 {[$Pd_2$($PPh_2$py)($PBz_3$)$_2$($SO_2$)]$^+$}, 1057 {[$Pd_2$($PPh_2$py)($PBz_3$)-($PBz_2$)($SO_2$)]$^+$}, 781 {[$Pd_2$($PPh_2$py)($PBz_3$)]$^+$}.

**[$Pd_3$($PPh_2$py)$_2$($PBz_3$)$_2$(μ-$SO_2$)$_2$] (5).** To a solution of [$Pd_3$-(μ-$SO_2$)$_3$($PBz_3$)$_3$], (160 mg, 0.098 mmol) in toluene (20 $cm^3$) was added two equivalents of $PPh_2$py (50 mg, 0.190 mmol) under nitrogen, to give a yellow–orange coloured solution. After 2 h the solvent was removed under reduced pressure and the remaining orange solid washed several times with diethyl ether. This solid was recrystallised from a dichloromethane–diethyl ether mixture to give [$Pd_3$(μ-$SO_2$)$_2$($Ph_2$Ppy)$_2$($PBz_3$)$_2$] as a crystalline sample. Yield 0.14 g (61%). Found: C, 58.60; H, 4.57; N, 1.61. $C_{76}H_{70}N_2P_4O_4S_2Pd_3\cdot 0.5C_7H_8$ requires: C, 58.63; H, 4.58; N, 1.72%. $\nu_{max}$/$cm^{-1}$ 1598, 1582 (CN), 1140 1090 and 1071 ($SO_2$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ 5.8 (m, $PPh_2$py) 19.8 (m, $PBz_3$). FAB-$MS^+$: *m*/*z* 1580 {[$Pd_3$($PPh_2$py)$_2$($PBz_3$)$_2$($SO_2$)$_2$]$^+$}, 1517 {[$Pd_3$($PPh_2$py)$_2$($PBz_3$)$_2$$SO_2$]$^+$}, 1453 {[$Pd_3$($PPh_2$py)$_2$-($PBz_3$)$_2$]$^+$}, 1149 {[$Pd_3$($PPh_2$py)$_2$($PBz_3$)]$^+$}, 780 {[$Pd_2$($PPh_2$py)-($PBz_3$)]$^+$}. Crystals suitable for X-ray crystallography were grown from a mixture of dichloromethane and diethyl ether.

**[$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CN$^t$Bu)($PBz_3$)$_4$] (6).** To a solution of [$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CO)($PBz_3$)$_4$] (80 mg, 0.044 mmol) in toluene (20 $cm^3$) one equivalent of CN$^t$Bu, (3.5 mg, 0.044 mmol) in toluene (5 $cm^3$), was added *via* syringe and the solution left stirring under nitrogen for 2 h. The solvent was removed under reduced pressure and the remianing solid recrystallised from a dichloromethane–methanol mixture. Yield 30 mg, (30%). Found: C, 56.75; H, 4.94; N, 0.71. $C_{89}H_{93}NO_4P_4Pd_4S_3$ requires: C, 56.72; H, 4.97; N, 0.74%. $\nu_{max}$/$cm^{-1}$ 2156 (CN), 1099, 1070 and 1032 ($SO_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 17.8 (d, 2P, $^3J_{PP}$ = 62 Hz) 15.3 (d, 1P, $^3J_{PP}$ = 107 Hz) and 6.9 (dt, 1P, $^3J_{PP}$ = 62 Hz and $^3J_{PP}$ = 107 Hz). FAB-$MS^+$: *m*/*z* 1883 {[$Pd_4$($SO_2$)$_2$(S)(CN$^t$-Bu)($PBz_3$)$_4$]$^+$}, 1737 {[$Pd_4$($SO_2$)(S)($PBz_3$)$_4$]$^+$}, 1370 {[$Pd_4$(S)-($PBz_3$)$_3$]$^+$}. Crystals suitable for a single-crystal X-ray analyses were obtained from a dichloromethane–methanol mixture.

**[$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CNCy)($PBz_3$)$_4$] (7).** To a solution of [$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CO)($PBz_3$)$_4$] (80 mg, 0.044 mmol) in toluene (20 $cm^3$) one equivalent of CNCy (4.00 × $10^{-3}$ $cm^3$, 0.044 mmol) in toluene (5 $cm^3$) was added. The solution was left to stir under nitrogen for 2 h, after which the solvent was removed under reduced pressure. The resulting red solid was recrystallised from a dichloromethane–methanol mixture. Yield 20 mg (24%). Found: C, 57.37; H, 4.94; N, 0.59. $C_{91}H_{95}NO_4P_4Pd_4S_3$ requires C, 57.20; H, 4.98; N, 0.73%. $\nu_{max}$/$cm^{-1}$ 2161 (CN), 1095, 1072 and 1024 ($SO_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 17.3 (d, 2P, $^3J_{PP}$ = 60 Hz), 13.8 (d, 1P, $^3J_{PP}$ = 101 Hz) and 6.9 (dt, 1P, $^3J_{PP}$ = 60 Hz and $^3J_{PP}$ = 101 Hz). FAB-$MS^+$: *m*/*z* 1801 {[$Pd_4$-($SO_2$)$_2$(S)($PBz_3$)$_4$]$^+$}, 1673 {[$Pd_4$(S)($PBz_3$)$_4$]$^+$}, 1370 {[$Pd_4$(S)-($PBz_3$)$_3$]$^+$}. Crystals suitable for a single-crystal X-ray analysis were obtained from a dichloromethane–methanol mixture.

**[$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CNXyl)($PBz_3$)$_4$] (8).** To a solution of [$Pd_4$(μ-$SO_2$)$_2$(μ-S)(CO)($PBz_3$)$_4$] (80 mg, 0.044 mmol) in toluene (20 $cm^3$) one equivalent of CNXyl, (6 mg, 0.044 mmol) in

**Table 3** Crystal data, data collection and refinement parameters for compounds **5**–**8**[a]

| | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| Formula | $C_{76}H_{70}N_2O_4P_4S_2Pd_3$ | $C_{89}H_{93}NO_4P_4S_3Pd_4$ | $C_{91}H_{95}NO_4P_4S_3Pd_4$ | $C_{93}H_{93}NO_4P_4S_3Pd_4$ |
| Solvent | $3CH_2Cl_2$ | 3MeOH·0.25$CHCl_3$ | 1.5MeOH | MeOH |
| $M_w$ | 1837.3 | 2012.3 | 1960.4 | 1966.4 |
| Colour, habit | Yellow prisms | Orange–red prisms | Orange–red rhombs | Deep red rhombs |
| Crystal size/mm | 0.16 × 0.13 × 0.07 | 0.13 × 0.13 × 0.05 | 0.40 × 0.23 × 0.23 | 0.19 × 0.14 × 0.09 |
| $T$/K | 203 | 203 | 293 | 193 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$/Å | 13.958(1) | 13.747(1) | 13.822(3) | 15.855(1) |
| $b$/Å | 14.475(1) | 15.258(1) | 15.464(4) | 16.749(1) |
| $c$/Å | 20.157(2) | 23.473(3) | 23.567(7) | 18.981(1) |
| $\alpha$/° | 95.19(1) | 72.39(1) | 71.32(2) | 83.38(1) |
| $\beta$/° | 100.05(1) | 85.51(1) | 85.57(2) | 67.89(1) |
| $\gamma$/° | 97.31(1) | 86.12(1) | 87.92(1) | 72.74(1) |
| $V$/Å$^3$ | 3950.9(5) | 4673.4(7) | 4757(2) | 4459.5(4) |
| $Z$ | 2 | 2 | 2 | 2 |
| $D_c$/g cm$^{-3}$ | 1.544 | 1.430 | 1.369 | 1.464 |
| Radiation used | Cu-K$\alpha$[b] | Cu-K$\alpha$[b] | Cu-K$\alpha$ | Cu-K$\alpha$[b] |
| $\mu$/mm$^{-1}$ | 8.97 | 7.98 | 7.63 | 8.14 |
| $\theta$ range/° | 2.2–60.0 | 2.0–60.0 | 2.0–60.0 | 2.5–60.0 |
| Unique reflections measured | 11712 | 13762 | 13957 | 13214 |
| Observed, $\|F_o\| > 4\sigma(\|F_o\|)$ | 9349 | 10552 | 8535 | 9944 |
| Absorption correction | Ellipsoidal | Empirical | Empirical | Empirical |
| Max., min. transmission | 0.44, 0.32 | 0.70, 0.25 | 0.46, 0.05 | 0.48, 0.06 |
| No. of variables | 798 | 922 | 901 | 1049 |
| $R_1$, $wR_2$[c] | 0.053, 0.124 | 0.054, 0.121 | 0.089, 0.216 | 0.133, 0.303 |

[a] *Details in common*: graphite-monochromated radiation, refinement based on $F^2$. [b] Rotating anode source. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

toluene (5 cm$^3$) was added. The reaction mixture was left stirring under nitrogen for 2 h. The solvent was removed under reduced pressure and the remaining dark solid recrystallised from dichloromethane–methanol. Yield 20 mg (24%). Found: C, 57.96; H, 5.10; N, 0.52. $C_{93}H_{93}NO_4P_4Pd_4S_3$ requires C, 57.79; H, 4.82; N, 0.72%. $\nu_{max}$/cm$^{-1}$ 2144 (CN), 1093, 1070 and 1024 ($SO_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): $\delta$ 17.5 (d, 2P, $^3J_{PP}$ = 57 Hz) 6.6 (d, 1P, $^3J_{PP}$ = 104 Hz) and 4.5 (dt, 1P, $^3J_{PP}$ = 57 Hz and $^3J_{PP}$ = 104 Hz). FAB-MS$^+$: *m*/*z* 1932, $\{[Pd_4(SO_2)_2(S)(CNXyl)(PBz_3)_4]^+\}$, 1802 $\{[Pd_4(SO_2)_2(S)(PBz_3)_4]^+\}$, 1371 $\{[Pd_4(S)(PBz_3)_3]^+\}$. Crystals suitable for a single-crystal X-ray analysis were obtained from a dichloromethane–methanol mixture.

**$[Pd_4(\mu\text{-}SO_2)_2(\mu\text{-}S)(CNMe)(PBz_3)_4]$ (9).** To a solution of $[Pd_4(\mu\text{-}SO_2)_2(\mu\text{-}S)(CO)(PBz_3)_4]$ (80 mg, 0.044 mmol) in toluene (20 cm$^3$) one equivalent of CNMe (1.00 × 10$^{-3}$ cm$^3$, 0.044 mmol) in toluene (5 cm$^3$) was added *via* a syringe. After leaving the solution stirring for 2 h under nitrogen, the solvent was removed under reduced pressure and the remaining red solid redissolved in methanol. A red crystalline material precipitated out of solution. Yield 30 mg (35%). Found: C, 57.12; H, 4.85; N, 0.80. $C_{86}H_{87}NO_4P_4Pd_4S_3$·0.5$C_7H_8$ requires C, 56.92; H, 4.82; N, 0.74%. $\nu_{max}$/cm$^{-1}$ 2183 (CN), 1099, 1070 and 1032 ($SO_2$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): 17.7 (d, 2P, $^3J_{PP}$ = 57 Hz), 13.9 (d, 1P, $^3J_{PP}$ = 97 Hz) and 9.7 (dt, 1P, $^3J_{PP}$ = 57 Hz and $^3J_{PP}$ = 97 Hz). FAB-MS$^+$: *m*/*z* 1843 $\{[Pd_4(SO_2)_2(S)(CNMe)(PBz_3)_4]^+\}$, 1738 $\{[Pd_4(SO_2)(S)(PBz_3)_4]^+\}$, 1370 $\{[Pd_4(S)(PBz_3)_3]^+\}$.

### Crystallography

Table 3 provides a summary of the crystallographic data for compounds **5**–**8**. Data were collected on Siemens P4 diffractometers using $\omega$-scans. The structures were solved by direct methods and refined based on $F^2$ using the SHELXTL program system.[13] The high final residual electron density (located around the metal centres) and *R*-factor for **8** (and the consequent large e.s.d.s for the bond lengths) are due to poor crystal quality and the presence of substantial disorder (primarily in the pendant aromatic rings) in the structure. Similar disorder is seen in each of the other three complexes (though to a lesser extent than in **8**), and in all four structures there is disorder in the included solvent molecules.

CCDC reference numbers 204856–204859.

See http://www.rsc.org/suppdata/dt/b3/b302034g/ for crystallographic data in CIF or other electronic format.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