

# Reactivity of the palladium dimer $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$ . Syntheses and structural characterisation of $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$ , $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dppm})(\text{PBz}_3)_2]$ , $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$ , $[\text{Pd}_3(\mu\text{-CO})_2\text{-}$ $(\mu\text{-SO}_2)(\text{PBz}_3)_3]$ and $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_2(\text{PBz}_3)_3]$ (Bz = benzyl)†

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The reaction between  $[\text{Pd}_2(\text{dba})_3]\cdot\text{solvent}$  (dba = dibenzylideneacetone, solvent =  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$ ) and  $\text{PBz}_3$  (Bz = benzyl) in the presence of  $\text{SO}_2$  led to either  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  **1** or  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$  **2** depending on the absence or presence of an excess of  $\text{SO}_2$  in solution or in the recrystallisation. The crystal structure of **2** shows it to be a regular *triangulo*-cluster with Pd–Pd bond distances 2.7225(9) Å. Complex **1** reacted with dppm with displacement of dba to give  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dppm})(\text{PBz}_3)_2]$  **3**. The crystal structure of **3** shows it to have a much shorter Pd–Pd bond length than **1** [2.670(2) Å for **3** cf. 2.885(2) Å for **1**], which can be rationalised on the basis of the palladium atoms having been formally oxidised to  $\text{Pd}^{\text{I}}$  and the  $\text{SO}_2$  reduced to  $\text{SO}_2^{2-}$ . Complex **1** reacted with  $\text{PBz}_3$  to give two mononuclear complexes, the previously characterised  $[\text{Pd}(\text{dba})(\text{PBz}_3)_2]$  and the new complex  $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$  **4** which was characterised by a single crystal X-ray analysis. Complex **4** forms a distorted T-shaped structure with the P–Pd–P angle 163.67(14)°. It contains a  $\eta^1$ -pyramidal  $\text{SO}_2$  ligand, and is the first mononuclear palladium  $\text{SO}_2$  complex to be crystallographically characterised. Complex **1** reacts with CO to give a mixture of the *triangulo*-clusters  $[\text{Pd}_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(\text{PBz}_3)_3]$  **5** and  $[\text{Pd}_3(\mu\text{-CO})(\mu\text{-SO}_2)_2(\text{PBz}_3)_3]$  **6**. Reaction with an excess of CO converted **6** into **5**, and the crystal structure of **5** reveals relatively short Pd–Pd bond lengths consistent with a 42-electron cluster. Complex **1** reacted with  $\text{CNBu}^t$  to give  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_2(\text{PBz}_3)_3]$  which has also been crystallographically characterised.

The reactions between zero oxidation state palladium complexes and small molecules such as CO,  $\text{H}_2$ , CNR and  $\text{SO}_2$  have been implicated in a number of catalytic processes.<sup>1</sup> One of the most versatile palladium(0) sources is the dimer  $[\text{Pd}_2(\text{dba})_3]\cdot\text{solvent}$  (dba = dibenzylideneacetone, solvent =  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$ ).<sup>2</sup> When this complex is treated with strongly co-ordinating ligands such as phosphines the dba molecules are usually displaced and the *in situ* formation of palladium(0) phosphine complexes is observed. Initially, it was assumed that dba was an “innocent” ligand which would easily be substituted and not be involved in further reactions. However, during the last few years there has been an increasing amount of structural and kinetic evidence which shows that dba is much more involved in the reaction mechanisms than was originally thought. It has been demonstrated that it is not uncommon to keep dba in the co-ordination sphere and not only have compounds such as  $[\text{Pd}(\text{dba})\text{L}_2]$  (L =  $\text{PBz}_3$  or  $\text{PPh}_2(\text{C}_{10}\text{H}_7)$ ;  $\text{L}_2 = \text{dppe}$ ; Bz =  $\text{CH}_2\text{Ph}$ ) been characterised structurally, but in some cases addition of an excess of phosphine is unable to displace dba from the palladium co-ordination sphere.<sup>2b,3,4</sup> In addition, Amatore and co-workers<sup>5</sup> have shown that the presence of dba has a strong influence on the kinetics of substitution and oxidative-addition reactions of palladium complexes.

We have recently reported the synthesis and structural characterisation of the dimer  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  **1**.<sup>6a</sup> This dimer is readily obtained in high yields when  $[\text{Pd}_2(\text{dba})_3]\cdot\text{sol}$

vent is treated with two molar equivalents of  $\text{PBz}_3$  under an  $\text{SO}_2$  atmosphere. Complex **1** has a unique bridging dba molecule which remains labile to substitution reactions, thus allowing **1** to act as a potential convenient source of “ $[\text{Pd}_2(\mu\text{-SO}_2)(\text{PBz}_3)_2]$ ” fragments for cluster aggregation reactions. This has been shown by the reaction between **1** and COS which gives the tetrametallic cluster  $[\text{Pd}_4(\mu_3\text{-S})(\mu\text{-SO}_2)(\text{CO})(\text{PBz}_3)_4]$ .<sup>6b</sup> In this paper the reactions between **1** and carbon monoxide, *tert*-butyl isocyanide, bis(diphenylphosphino)methane (dppm) and tribenzylphosphine are discussed. We also report the isolation of a *triangulo*-palladium compound which seems to be an intermediate in the reaction between  $[\text{Pd}_2(\text{dba})_3]$ ,  $\text{PBz}_3$  and  $\text{SO}_2$  to give the isolated dimer **1**.

## Results and discussion

### Synthesis of $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$ **1** and $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$ **2**

We have recently reported that the reaction between  $[\text{Pd}_2(\text{dba})_3]\cdot\text{solvent}$ , 2  $\text{PBz}_3$  and  $\text{SO}_2$  gives the orange-yellow dimer  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  **1**.<sup>6a</sup> This compound has been structurally and spectroscopically characterised, and its  $^1\text{P}\{-^1\text{H}\}$  NMR spectrum shows a singlet at  $\delta$  2.8. When monitoring this reaction as a function of time *via*  $^1\text{P}\{-^1\text{H}\}$  NMR spectroscopy we found evidence that prior to the formation of dimer **1** a different species was present in solution. The spectrum of the initial red solution under an  $\text{SO}_2$  atmosphere showed only a single sharp peak at  $\delta$  19.3. After removing the solvent under reduced pressure followed by redissolving the residues under an

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3981/>

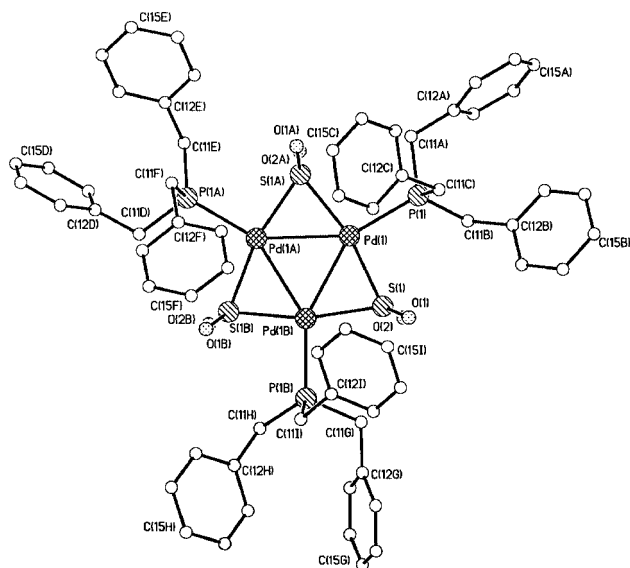


Fig. 1 Molecular structure of  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$ .

atmosphere of  $\text{N}_2$  the peak at  $\delta$  2.8, corresponding to **1**, was observed in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum. This suggested that the compound with the resonance at  $\delta$  19.3 readily decomposes in the absence of an  $\text{SO}_2$  atmosphere to yield **1**. In order to isolate this new compound a layer of  $\text{SO}_2$ -saturated ethanol was added directly to the reaction mixture under an atmosphere of  $\text{SO}_2$ . Upon slow diffusion of the ethanol layer into the toluene solution at  $-25^\circ\text{C}$  red crystals were formed. IR spectroscopy of these crystals showed no peaks arising from the carbonyl group in the dba ligand and confirmed the presence of the  $\text{SO}_2$  ligand with two intense peaks at 1244 and  $1067\text{ cm}^{-1}$ . There were peaks in the FAB-MS with high  $m/z$ , indicating the possible presence of a cluster compound. The C and H elemental analyses suggested that the formulation of the new compound should be  $[\text{Pd}_x(\text{SO}_2)_x(\text{PBz}_3)_x]$ .

As these results were not conclusive a single crystal X-ray crystallographic analysis was completed, and this confirmed the compound to be the trimeric species  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$  **2** (see Fig. 1). 42-Electron *triangulo*-clusters of formula  $[\text{Pt}_3(\mu\text{-SO}_2)_3(\text{PR}_3)_3]$  are well known and have been crystallographically characterised for  $\text{PR}_3 = \text{PPh}_3$  or  $\text{PCy}_3$ . However, the structure of **2** represents the first example of an analogous palladium triangle with the general formula  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PR}_3)_3]$ .

The compound  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$  crystallises in the high symmetry space group  $R\bar{3}$ ; selected bond lengths and angles are given in Table 1. The molecular structure of **2** consists of three palladium atoms arranged in an equilateral triangle with a crystallographically imposed threefold axis and with Pd–Pd equal to  $2.7225(9)\text{ \AA}$ . These distances are slightly longer than the range  $2.576(1)$ – $2.719(6)\text{ \AA}$  previously reported for 42 electron *triangulo*-palladium clusters.<sup>7</sup> The range of Pt–Pt bond lengths previously reported for the analogous  $[\text{Pt}_3(\mu\text{-SO}_2)_3(\text{PR}_3)_3]$ <sup>8,9</sup> triangles are  $2.813(1)$ – $2.815(1)$  ( $\text{R} = \text{Cy}$ ) and  $2.695(1)$ – $2.712(1)\text{ \AA}$  ( $\text{R} = \text{Ph}$ ).

In compound **2** each metal atom is bound to two bridging sulfur dioxide ligands and one tribenzylphosphine group. There is a small but significant difference between the distances from each palladium atom to the two sulfur atoms bonded to it [Pd(1)–S(1)  $2.264(2)$  and Pd(1)–S(1A)  $2.284(2)\text{ \AA}$ ]. This difference is also reflected in the two S–Pd–Pd angles of each  $\text{SO}_2$ -bridged edge [S(1A)–Pd(1)–Pd(1A)  $52.90(5)^\circ$  and S(1)–Pd(1)–Pd(1B)  $53.57(5)^\circ$ ]. The palladium, phosphorus and sulfur atoms are situated in approximately planar arrangements, the three sulfur atoms lying  $-0.674\text{ \AA}$  below the  $\text{Pd}_3$  plane and the phosphorus atoms  $0.1196\text{ \AA}$  above it. Mingos and co-workers<sup>10</sup> have suggested that this virtually planar geometry, which is observed in 42 electron *triangulo*-platinum clusters such as  $[\text{Pt}_3(\mu\text{-CO})_3]$

Table 1 Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for compound **2**

Pd(1)–S(1)	2.2641(19)	Pd(1)–S(1A)	2.2841(18)
Pd(1)–P(1)	2.3367(18)	Pd(1)–Pd(1A)	2.7225(9)
Pd(1)–Pd(1B)	2.7225(9)	S(1)–O(1)	1.438(6)
S(1)–O(2)	1.440(6)	S(1)–Pd(1B)	2.2841(18)
S(1)–Pd(1)–S(1A)	166.01(6)	S(1)–Pd(1)–P(1)	94.70(7)
S(1A)–Pd(1)–P(1)	99.02(7)	S(1)–Pd(1)–Pd(1A)	113.54(5)
S(1A)–Pd(1)–Pd(1A)	52.90(5)	P(1)–Pd(1)–Pd(1A)	151.68(6)
S(1)–Pd(1)–Pd(1B)	53.57(5)	S(1A)–Pd(1)–Pd(1B)	112.87(5)
P(1)–Pd(1)–Pd(1B)	148.06(6)	Pd(1A)–Pd(1)–Pd(1B)	60.0
Pd(1)–S(1)–Pd(1B)	73.53(6)	O(1)–S(1)–O(2)	116.2(4)

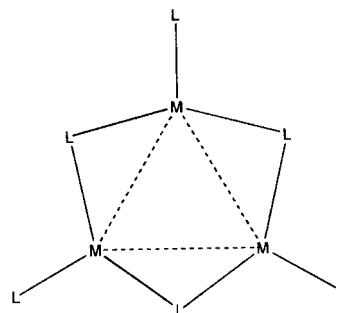
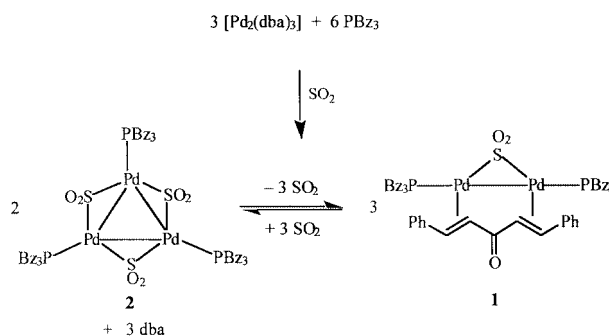


Fig. 2 Schematic representation of a metal triangle formed by three T-shaped  $\text{ML}_3$  fragments.

$(\text{PCy}_3)_3]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_3\text{L}_3]$ , can be viewed in terms of three T-shaped  $\text{ML}_3$  fragments sharing common bridging groups (ignoring the bridged metal–metal bonds), Fig. 2.

Consistent with this description the unique S–Pd–S bond angle in compound **2** is  $166.01(6)^\circ$  which is comparable to those observed in  $[\text{Pt}_3(\mu\text{-SO}_2)_3(\text{PR}_3)_3]$  (mean S–Pt–S  $167.4^\circ$ ). These values are typical of T-shaped molecules and may be compared with the P–M–P angle of  $159.3^\circ$  reported<sup>11</sup> for the  $d^8$  complex  $[\text{Rh}(\text{PPh}_3)_3]^+$  and that of  $163(1)^\circ$  observed in the present study for  $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$  **4** (see below).

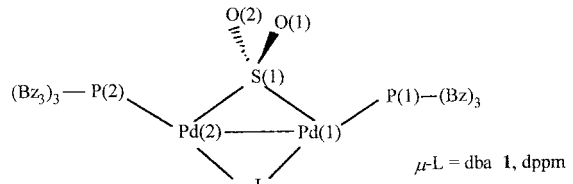
The reaction between  $[\text{Pd}_2(\text{dba})_3]$ ·solvent and  $\text{PBz}_3$  under an atmosphere of  $\text{SO}_2$  is summarised in Scheme 1. An equilibrium is established between  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$  **2** and  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  **1** with the concentration of  $\text{SO}_2$  in solution determining the relative amount of the two complexes. Removal of the solvent (and hence any excess of  $\text{SO}_2$ ) results in the equilibrium shifting to the right hand side, favouring complex **1**. Under an  $\text{SO}_2$  atmosphere the equilibrium is shifted to the left hand side, favouring **2**.



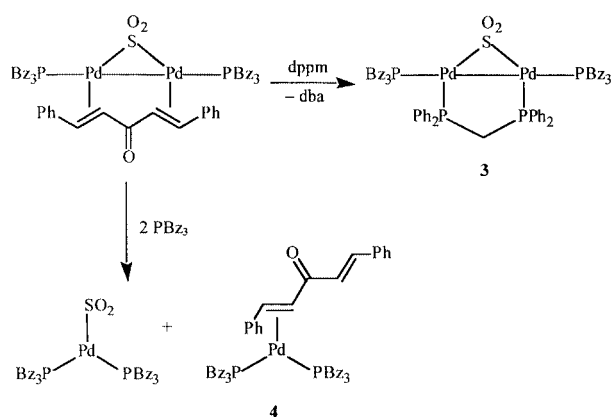
Scheme 1

### Synthesis of $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dppm})(\text{PBz}_3)_2]$ **3**

The possibility of replacing the dba ligand from compound **1** by another bridging ligand was explored by treating **1** with dppm ( $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ). Although dppm can chelate to a single metal atom the bite angle associated with dppm is also appropriate for it to form bridged binuclear complexes in which the two metal centres are held together and may form a metal–

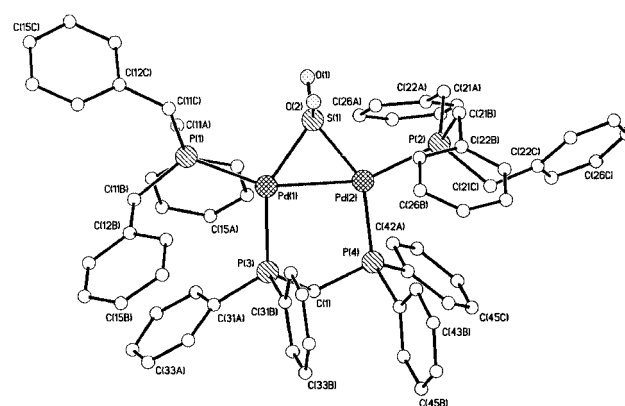
**Table 2** Selected bond lengths (Å) and angles (°) for [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] **1** and [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dppm)(PBz<sub>3</sub>)<sub>2</sub>] **3**


	<b>1</b>	<b>3</b>		<b>1</b>	<b>3</b>
Pd(1)–Pd(2)	2.885(2)	2.6703(14)	S(1)–Pd(1)–P(1)	93.64(14)	104.30(12)
Pd(1)–P(1)	2.325(4)	2.326(2)	S(1)–Pd(2)–P(2)	91.21(14)	104.76(12)
Pd(1)–P(3)	—	2.322(2)	S(1)–Pd(2)–Pd(1)	50.01(9)	53.09(9)
Pd(2)–P(2)	2.335(4)	2.326(2)	S(1)–Pd(1)–Pd(2)	50.19(10)	53.75(8)
Pd(2)–P(4)	—	2.324(2)	O(1)–S(1)–O(2)	113.9(6)	109.8(5)
Pd(1)–S(1)	2.246(4)	2.239(2)	P(1)–Pd(1)–Pd(2)	139.10(11)	154.59(8)
Pd(2)–S(1)	2.252(4)	2.241(3)	P(2)–Pd(2)–Pd(1)	140.25(11)	157.45(8)
S(1)–O(1)	1.473(10)	1.496(8)			
S(1)–O(2)	1.458(11)	1.498(8)			

**Scheme 2**

metal bond. The addition of a benzene solution containing one molar equivalent of dppm to a benzene solution of **1** immediately gave rise to a change from orange-yellow to yellow. The solid, which was obtained by the removal of the solvent under reduced pressure, followed by washing with methanol, analysed correctly for [Pd<sub>2</sub>(SO<sub>2</sub>)(dppm)(PBz<sub>3</sub>)<sub>2</sub>]·2MeOH. The isolated product gave rise to two peaks in the <sup>31</sup>P-{<sup>1</sup>H} NMR at δ 22.2 and 7.7 (C<sub>6</sub>D<sub>6</sub>) which are observed as triplets with a small coupling constant of 10 Hz. These suggest the presence of an AA'XX' system of phosphorus nuclei and are consistent with the replacement of dba by a bridging dppm ligand and the retention of the PBz<sub>3</sub> ligands. The SO<sub>2</sub> stretching vibrations in the IR spectrum at 1025 and 1147 cm<sup>-1</sup> are lower than those found in [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>], indicating stronger Pd–SO<sub>2</sub> back donation interactions. This could be a consequence of stronger electron donation from the phosphine to the metal. No peaks corresponding to the carbonyl stretching vibration were observed in the IR spectrum, indicating that the dba ligand had been displaced in the reaction. The FAB mass spectrum contains the parent molecular ion, [Pd<sub>2</sub>(SO<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, with *m/z* 1272. The formulation of the compound **3** as [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dppm)(PBz<sub>3</sub>)<sub>2</sub>] was confirmed by a single crystal X-ray crystal diffraction study (see Fig. 3).

This dimer crystallises with four molecules of methanol and half a molecule of benzene per molecule. Some of the structural features of **3** are compared with equivalent data for the starting material [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] in Table 2. One of the most notable features of complex **3** is the relatively short distance between the two palladium atoms [2.6703(14) Å]. This distance is significantly shorter than in complex **1** and also shorter than has been previously observed in SO<sub>2</sub>-containing palladium(0) cluster compounds.<sup>7</sup> If the SO<sub>2</sub> ligand is con-



and can be kept in air for many months. This is probably due to the sulfur atom being co-ordinatively saturated since it is utilising both the HOMO and LUMO in its bonding to the two metal atoms. Similar complexes of palladium(I) dimers,  $[(\text{Ph}_3\text{P})\text{Pd}(\mu\text{-SC}_6\text{F}_5)(\mu\text{-dppm})\text{Pd}(\text{SC}_6\text{F}_5)] \cdot 1.4\text{CH}_2\text{Cl}_2$  and  $[(\text{Ph}_3\text{P})\text{Pd}(\mu\text{-SC}_6\text{F}_5)(\mu\text{-dppm})\text{Pd}(\text{PPh}_3)][\text{SO}_3\text{CF}_3] \cdot 2\text{CH}_2\text{Cl}_2$ , have recently been synthesized.<sup>15</sup> These complexes also have bicyclic structures formed through the simultaneous bridging of the palladium(I) centres by a dppm and a sulfur ligand.

#### Reaction of $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$ with $\text{PBz}_3$

Since the addition of dppm to  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  resulted in the simple substitution of the dba ligand, the reaction of the dimer with tribenzylphosphine was also studied. The addition of two molar equivalents of tribenzylphosphine to a benzene solution containing complex **1** gave rise to a ruby-red solution within a few seconds. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of this solution contained two signals of equal intensity, one at  $\delta$  20.5 and the other at  $\delta$  7.8. The signal at  $\delta$  7.8 consists of one sharp intense peak surrounded by two small and broad peaks at  $\delta$  9.2 and 6.4. This signal has been previously assigned to the presence of  $[\text{Pd}(\text{dba})(\text{PBz}_3)_2]$  in solution.<sup>6a</sup> Half of the dimer, therefore, is converted into this complex and the other half into a new product **4** which appears as a singlet at  $\delta$  20.5 in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum. In order to convert all of the reaction mixture into the new product **4**, sulfur dioxide gas was bubbled through the solution for 5 min. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of the resultant solution consisted of just one single sharp peak at  $\delta$  20.5. The solvent was removed under reduced pressure and the residual solids were washed with several portions of methanol to remove the excess of dba; orange crystals of **4** were grown by redissolving the product in dichloromethane and adding a methanol layer above the solution. The IR spectrum of the crystals obtained confirmed that there was no dba in compound **4** and sharp bands for  $\text{SO}_2$  vibrations were observed at 1033 and 1182  $\text{cm}^{-1}$ . Crystals of **4** analysed correctly for  $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2] \cdot \text{CH}_2\text{Cl}_2$  and this formulation was corroborated by a single crystal X-ray crystallographic determination.

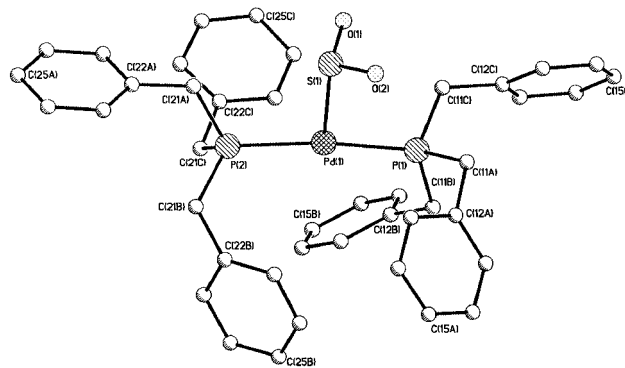
The X-ray crystal analysis shows that complex **4** is a three-coordinate palladium complex with two  $\text{PBz}_3$  ligands and an  $\eta^1\text{-SO}_2$  molecule as illustrated in Fig. 4. The Pd, S, and the two P atoms are approximately coplanar, the palladium atom being 0.157 Å out of the plane of the three donor atoms. The co-ordination of the palladium atom may be described as T-shaped with a  $\text{P}(1)\text{-Pd-P}(2)$  angle of  $163.67(14)^\circ$  considerably greater than that of  $107.2(3)^\circ$  in the related three-coordinate  $[\text{Pd}(\text{dba})(\text{PBz}_3)_2]$ , a difference that may be attributed to the greater bulk of the dba ligand compared to  $\text{SO}_2$ . The  $\text{SO}_2$  ligand is co-ordinated in a pyramidal mode (mean  $\text{Pd-S-O}$   $105.8(5)^\circ$ ), with the two oxygen atoms lying on opposite sides of the mean co-ordination plane (deviations  $\text{O}(1) -1.365$  and  $\text{O}(2) 0.956$  Å).

For platinum the first structurally characterised three-coordinate bis(phosphine) sulfur dioxide complex,  $[\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2]$ , was reported in 1983<sup>16</sup> but to our knowledge **4** is the first example of a mononuclear three-coordinate palladium phosphine  $\text{SO}_2$  complex that has been crystallographically characterised, though complexes of the general formulae  $[\text{Pd}(\text{SO}_2)(\text{PR}_3)_2]$  and  $[\text{Pd}(\text{SO}_2)(\text{PR}_3)_3]$  have been reported and characterised by IR spectroscopy.<sup>17</sup> Three-coordinate nickel(0)-sulfur dioxide complexes of similar formulation have also been reported with the bulky organophosphines  $\text{PCy}_3$ ,  $\text{PCy}_2\text{Ph}$  and  $\text{PBz}_2\text{Ph}$ . Crystal structure studies of the nickel(0) complex  $[\text{Ni}(\text{SO}_2)(\text{PCy}_3)_2]$  shows large differences in the three-coordinate structure from those of the related palladium and platinum complexes, **4** and  $[\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2]$ . Selected bond lengths and angles for these three compounds are listed in Table 3 for ease of comparison. The main difference lies in the

**Table 3** Selected bond lengths (Å) and angles ( $^\circ$ ) for  $[\text{M}(\text{SO}_2)\text{L}_2]$

	$[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$ <b>4</b>	$[\text{Ni}(\text{SO}_2)(\text{PCy}_3)_2]$ <sup>19</sup>	$[\text{Pt}(\text{SO}_2)(\text{PCy}_3)_2]$ <sup>16</sup>
M-S	2.282(4)	2.150 <sup>a</sup>	2.299(1)
M-P(1)	2.312(3)	2.211	2.304(1)
M-P(2)	2.328(3)	2.211	2.309(1)
S-O(1)	1.428(13)	1.540 <sup>a</sup>	1.465(3)
S-O(2)	1.467(13)	1.560 <sup>a</sup>	1.461(3)
P(1)-M-P(2)	163.67(14)	118.5	165.72(4)
S-M-P(1)	96.52(14)	114.3 <sup>a</sup>	95.03(4)
S-M-P(2)	97.27(14)	127.0 <sup>a</sup>	97.39(4)
M-S-O(1)	104.8(5)	116.0 <sup>a</sup>	104.8(1)
M-S-O(2)	106.8(5)	103.0 <sup>a</sup>	104.1(1)
O(1)-S-O(2)	112.4(9)	130.0 <sup>a</sup>	113.1(2)

<sup>a</sup> Denotes averaged atomic positions.



**Fig. 4** Molecular structure of  $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$ .

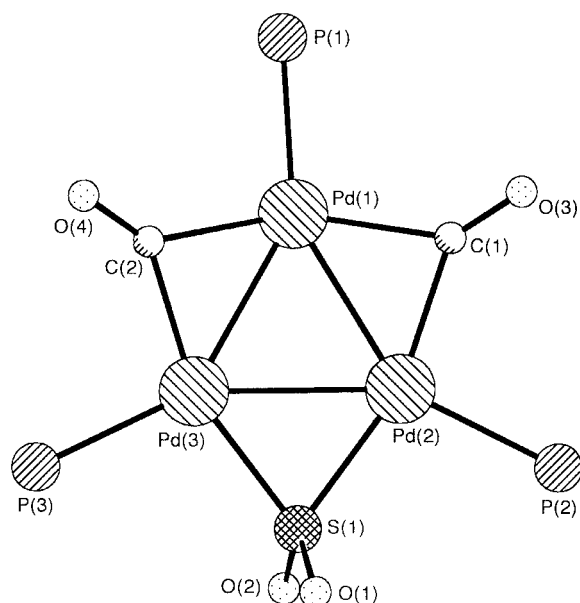
fact that whereas the palladium and platinum complexes have definite T-shaped co-ordination geometry at the metal centre [ $\text{P-Pd-P}$   $163.6(1)^\circ$  and  $\text{P-Pt-P}$   $165.72(4)^\circ$ ], the nickel compound is more appropriately described as trigonal planar ( $\text{P-Ni-P}$   $118.5$ , mean  $\text{S-Ni-P}$   $120.9^\circ$ ). Similarly the palladium and platinum compounds both exhibit pyramidal  $\text{M-SO}_2$  co-ordination with approximately tetrahedral angles at S (mean  $\text{S-M-P}$   $96.9(1)$  and  $96.18(4)^\circ$ ,  $\text{O-S-O}$   $113.2(8)$  and  $113.1^\circ$  respectively), whereas the nickel complex has a virtually planar  $\text{Ni-SO}_2$  arrangement (mean  $\text{S-Ni-O}$   $109.5^\circ$  and  $\text{O-S-O}$   $130.0^\circ$ ). The  $\eta^1$ -pyramidal co-ordination of  $\text{SO}_2$  in the palladium and platinum compounds means that the  $\text{ML}_2$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ) fragment makes use of its  $\sigma$ -donating ability to co-ordinate to  $\text{SO}_2$ .<sup>18</sup> In the nickel complexes the  $\text{SO}_2$  is co-ordinated in a  $\eta^1$ -planar mode consistent with the lower basicity of the first row transition metal.

The reactions of the dimer  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  with other phosphines were also studied. However, these investigations proved to be inconclusive since mixtures of products were obtained, and further work is required to separate the range of products formed.

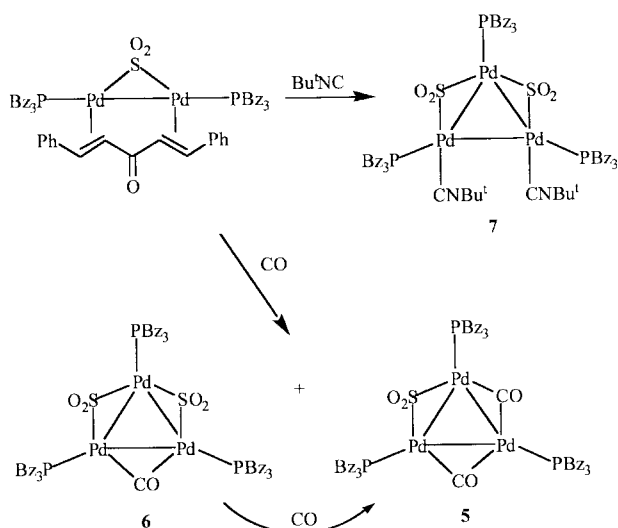
#### Reaction of $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$ with CO

In order to study the possible aggregation of compound **1** into higher nuclearity clusters its reactions with CO and  $\text{CNBu}^t$  were studied. On bubbling CO gas through a THF solution of **1** a rapid change to dark red occurred. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of this solution showed the presence of two products, both characterised as unsymmetrical *triangulo*-clusters by the presence of a doublet and triplet in 2:1 intensity ratio. The major compound (**5**) showed a triplet at  $\delta$  15.5 and a doublet at  $\delta$  9.6, with a coupling constant of 41 Hz. The minor compound (**6**) gave a doublet at  $\delta$  16.5 and a triplet at  $\delta$  8.8, with a coupling constant of 52 Hz. Further bubbling of CO gas through the solution led to the disappearance of the peaks associated with **6**, demonstrating that **6** can be converted into **5** by addition of





**Fig. 5** Molecular structure of  $[\text{Pd}_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(\text{PBz}_3)_3]$ . The benzyl groups have been omitted for clarity.



**Scheme 3**

CO (Scheme 3). The IR spectrum of **5** confirmed the presence of both CO and  $\text{SO}_2$  with  $\nu(\text{CO})$  at 1911 and 1857  $\text{cm}^{-1}$ , and  $\nu(\text{SO}_2)$  at 1056 and 1187  $\text{cm}^{-1}$  respectively. Crystals of this product were grown from a THF–hexane mixture and, upon X-ray analysis, were found to be a palladium cluster of formula  $[\text{Pd}_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(\text{PBz}_3)_3]$  **5** which is consistent with the  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR data.

Compound **5** is a 42-electron *triangulo*-cluster complex with Pd–Pd bond distances of 2.6850(6), 2.6942(6) and 2.7192(6) Å, the longest bond length being that bridged by  $\text{SO}_2$  (see Fig. 5). These distances are all shorter than the Pd–Pd bond lengths previously reported for other Pd– $\text{SO}_2$  triangles which cover a range from 2.7225(9) (complex **2**) to 2.994(1) Å.<sup>7</sup> Two of the Pd–Pd edges in **5** are bridged by carbon monoxide ligands and the third edge is bridged by a sulfur dioxide ligand, creating a pseudo- $C_{2v}$  symmetry axis along the vector which runs through the unique palladium atom (bonded to both CO ligands) and bisects the  $\text{SO}_2$ -bridged Pd–Pd edge. The palladium triangle, carbon monoxide ligands, phosphorus and sulfur atoms all lie in approximately the same plane. This geometry is typical of 42-electron *triangulo*-cluster compounds of platinum and palladium. Selected bond lengths and angles for **5** are given in Table 4.

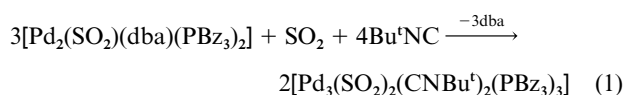
**Table 4** Selected bond lengths (Å) and angles (°) for compound **5**

Pd(1)–Pd(2)	2.6850(6)	Pd(2)–C(1)	2.086(6)
Pd(1)–Pd(3)	2.6942(6)	Pd(3)–P(3)	2.322(1)
Pd(1)–P(1)	2.332(1)	Pd(3)–S(1)	2.264(1)
Pd(1)–C(1)	2.068(6)	Pd(3)–C(2)	2.068(6)
Pd(1)–C(2)	2.048(6)	S(1)–O(1)	1.446(4)
Pd(2)–Pd(3)	2.7192(6)	S(1)–O(2)	1.453(4)
Pd(2)–P(2)	2.312(1)	C(1)–O(3)	1.138(7)
Pd(2)–S(1)	2.270(1)	C(2)–O(4)	1.139(7)
Pd(3)–Pd(1)–Pd(2)	60.73(1)	O(3)–C(1)–Pd(1)	137.7(5)
C(1)–Pd(1)–C(2)	147.9(2)	O(3)–C(1)–Pd(2)	140.1(5)
Pd(1)–Pd(2)–Pd(3)	59.80(1)	Pd(1)–C(2)–Pd(3)	81.8(2)
C(1)–Pd(2)–S(1)	159.9(2)	O(4)–C(2)–Pd(1)	137.8(5)
Pd(1)–Pd(3)–Pd(2)	59.47(1)	O(4)–C(2)–Pd(3)	140.2(5)
S(1)–Pd(3)–C(2)	159.9(2)	Pd(2)–S(1)–Pd(3)	73.70(4)
Pd(2)–C(1)–Pd(1)	80.5(2)	O(1)–S(1)–O(2)	113.1(2)

Although compound **6** was not isolated, it is reasonable to assign its identity to the other mixed CO/ $\text{SO}_2$  *triangulo*-cluster,  $[\text{Pd}_3(\mu\text{-CO})(\mu\text{-SO}_2)_2(\text{PBz}_3)_3]$ .

#### Reaction of $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$ with CNBu<sup>t</sup>

On adding two molar equivalents of *tert*-butyl isocyanide to a toluene solution of  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dba})(\text{PBz}_3)_2]$  the solution changed to light yellow. After removing the solvent under reduced pressure and washing with methanol to remove the dba the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) contained a doublet at  $\delta$  11.7 and a triplet at  $\delta$  2.3 in a ratio of 2:1 with a coupling constant  $^3J_{\text{PP}} = 34$  Hz. This spectrum suggested that a *triangulo*-palladium cluster compound with two phosphorus environments in a 2:1 ratio had been formed. Together with the other spectroscopic data this enabled us to formulate it as  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_2(\text{PBz}_3)_3]$  **7**. For a balanced equation, (1),



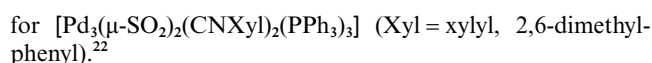
between **1** and **7**, additional sulfur dioxide needs to be present. In accordance with this equation, when the synthesis of **7** was carried out under an atmosphere of  $\text{SO}_2$  the yield was greatly improved and the product more readily isolated.

The isocyanide ligands of this product showed  $\nu(\text{CN})$  bands at 2175 and 2148  $\text{cm}^{-1}$  which are higher than that of free *tert*-butyl isocyanide which appears at 2136  $\text{cm}^{-1}$ . The analogous *tert*-butyl isocyanide *triangulo*-palladium cluster  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_3]$  also shows an increase in  $\nu(\text{CN})$  from free CNBu<sup>t</sup> with peaks observed in the IR spectrum at 2170 and 2155  $\text{cm}^{-1}$ .<sup>20</sup> A decrease in  $\nu(\text{CN})$  from that of free CNBu<sup>t</sup> might have been expected as isocyanides, like carbon monoxide, are  $\pi$ -acceptor ligands. An increase in  $\nu(\text{CN})$  indicates that little, if any, electron density is being donated from the metal centre into the  $\pi^*$  antibonding orbital of the isocyanide ligand. Complex **7** also shows an intense and sharp  $\text{SO}_2$  peak at 1012  $\text{cm}^{-1}$  and no peaks due to dba could be identified. The FAB-MS showed the expected fragmentation pattern for a compound of formula  $[\text{Pd}_3(\text{SO}_2)_2(\text{CNBu}^t)_2(\text{PBz}_3)_3]$ . The peak with the highest  $m/z$  was observed at 1527 and assigned as  $[\text{M}]^+$ . The assignments of the fragments are shown in Table 5.

Crystals suitable for a single crystal structural analysis were obtained from a benzene–methanol solution (see Fig. 6). This analysis confirmed that **7** is the *triangulo*-cluster compound  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_2(\text{PBz}_3)_3]$  which contains two edge-bridging  $\text{SO}_2$  ligands and two terminal isocyanide ligands. The compound crystallises with half a molecule of  $\text{H}_2\text{O}$  which presumably was incorporated from the atmosphere during the process of recrystallisation. The calculated elemental analyses based on this formulation were more consistent with the

**Table 6** Selected bond lengths (Å) and angles (°) for complex **7**

Pd(1)–Pd(3)	2.722(2)	Pd(1)–Pd(2)	2.764(2)
Pd(2)–Pd(3)	2.801(2)	Pd(1)–S(2)	2.272(4)
Pd(1)–S(1)	2.272(4)	Pd(1)–P(1)	2.296(5)
Pd(2)–C(2)	2.006(14)	Pd(2)–S(1)	2.240(4)
Pd(2)–P(2)	2.309(4)	Pd(3)–C(4)	2.005(14)
Pd(3)–S(2)	2.240(4)	Pd(3)–P(3)	2.309(4)
S(1)–Pd(1)–S(2)	149.00(19)	S(1)–Pd(1)–P(1)	101.36(18)
S(2)–Pd(1)–P(1)	109.24(18)	S(1)–Pd(1)–Pd(3)	100.81(13)
S(2)–Pd(1)–Pd(3)	52.36(9)	P(1)–Pd(1)–Pd(3)	151.57(15)
S(1)–Pd(1)–Pd(2)	51.69(10)	S(2)–Pd(1)–Pd(2)	97.84(13)
P(1)–Pd(1)–Pd(2)	146.89(15)	Pd(3)–Pd(1)–Pd(2)	61.39(5)
C(2)–Pd(2)–S(1)	160.5(6)	C(2)–Pd(2)–P(2)	102.5(5)
S(1)–Pd(2)–Pd(1)	52.76(9)	P(2)–Pd(2)–Pd(1)	137.88(14)
C(2)–Pd(2)–Pd(3)	69.5(5)	S(1)–Pd(2)–Pd(3)	99.33(13)
P(2)–Pd(2)–Pd(3)	163.02(13)	Pd(1)–Pd(2)–Pd(3)	58.57(5)
C(4)–Pd(3)–Pd(1)	100.4(6)	C(4)–Pd(3)–Pd(2)	71.7(5)
S(2)–Pd(3)–Pd(2)	97.57(13)	Pd(1)–Pd(3)–Pd(2)	60.04(5)



It is interesting that the compounds  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNXyl})_2(\text{PCy}_3)_3]$  and  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNXyl})_2(\text{PPh}_3)_3]$  were prepared from the reaction of higher nuclearity clusters with 2,6-dimethylphenyl isocyanide. The other known compound of this type,  $[\text{Pd}_3(\mu\text{-SO}_2)_2(\text{CNBu}^t)_3]$ , does not contain any phosphine ligands and was prepared from  $[\text{Pd}_3(\mu\text{-CNBu}^t)_3(\text{CNBu}^t)_3]$  and an excess of  $\text{SO}_2$ . The synthetic route to complex **7** is therefore unusual for this type of trinuclear cluster compound.

The dimer  $[\text{Pd}_2(\mu\text{-dba})(\mu\text{-SO}_2)(\text{PBz}_3)_2]$  has proved to be a good starting material for the formation of novel dimeric and *triangulo*-palladium compounds. The formation of  $[\text{Pd}(\text{SO}_2)(\text{PBz}_3)_2]$  when treating **1** with  $\text{PBz}_3$  and of  $[\text{Pd}_2(\mu\text{-SO}_2)(\mu\text{-dppm})(\text{PBz}_3)_2]$  when using  $\text{dppm}$ , together with the evidence of different reactions between **1** and a range of phosphines, suggest that this is a fruitful area for the synthesis of novel  $\text{Pd}/\text{SO}_2/\text{PR}_3$  complexes. During the synthesis of **1** the novel *triangulo*-cluster  $[\text{Pd}_3(\mu\text{-SO}_2)_3(\text{PBz}_3)_3]$  **2** has been isolated and crystallographically characterised. The selective formation of **1** or **2** strongly depends on the concentration of  $\text{SO}_2$ .

## Experimental

## General

All the reactions were routinely carried out using standard Schlenk-line techniques under an atmosphere of pure nitrogen. The solvents were used dry and free of oxygen. Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer between 4000 and 250  $\text{cm}^{-1}$  as KBr pellets,  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra on a JEOL JNM-EX270 Fourier-transform spectrometer operating at a frequency of 109.4 MHz with chemical shifts reported relative to  $\text{H}_3\text{PO}_4$  and mass spectra by Mr J. Barton at Imperial College on a VG AutoApec-Q as FAB using 3-nitrobenzyl alcohol as matrix. The compound  $[\text{Pd}_2(\text{dba})_3]_3$ -solvent was prepared according to literature procedures.<sup>23</sup> Other reagents were used as obtained from commercial sources.

**[Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] 1.** The compound PBz<sub>3</sub> (184 mg, 0.60 mmol) was dissolved in 15 cm<sup>3</sup> toluene and SO<sub>2</sub> gas was bubbled through for 1 min. This solution was then added to a solution of [Pd<sub>2</sub>(dba)<sub>3</sub>]<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (300 mg, 0.30 mmol) in 25 cm<sup>3</sup> toluene, followed by the further addition of SO<sub>2</sub> gas (*ca.* 10 min) whereupon the solution changed from deep purple to red. The mixture was stirred under an atmosphere of SO<sub>2</sub> for 30 min to ensure completion of the reaction. The solvent was removed

**Table 7** Crystallographic details for complexes **2**, **3**, **4**, **5** and **7**

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>7</b>
Chemical formula	C <sub>63</sub> H <sub>63</sub> O <sub>6</sub> P <sub>3</sub> Pd <sub>3</sub> S <sub>3</sub>	C <sub>74</sub> H <sub>83</sub> O <sub>6</sub> P <sub>4</sub> Pd <sub>2</sub> S	C <sub>43</sub> H <sub>44</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>2</sub> PdS	C <sub>65</sub> H <sub>63</sub> O <sub>4</sub> P <sub>3</sub> Pd <sub>3</sub> S	C <sub>73</sub> H <sub>82</sub> N <sub>2</sub> O <sub>4.5</sub> P <sub>3</sub> Pd <sub>3</sub> S <sub>2</sub>
Formula weight	1424.42	1437.1	864.08	1352.4	1535.34
<i>T</i> /K	223(2)	173(2)	293(2)	293(2)	299(2)
System, space group	Trigonal, <i>R</i> $\bar{3}$	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$	Trigonal, <i>R</i> $\bar{3}$	Orthorhombic, <i>Pbca</i>
<i>a</i> /Å	24.985(2)	22.498(7)	9.931(3)	44.09(4)	22.985(9)
<i>b</i> /Å	24.985(2)	14.064(3)	11.331(2)	44.09(4)	24.213(10)
<i>c</i> /Å	16.219(3)	23.376(13)	19.275(4)	16.22(1)	26.93(2)
$\alpha$ /°			84.427(12)		
$\beta$ /°		112.47(3)	87.31(2)		
$\gamma$ /°			64.216(14)		
<i>U</i> /Å <sup>3</sup>	8768.0(19)	6835(4)	1943.9(8)	27306(2)	14985(13)
<i>Z</i>	6	4	2	18	8
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	1.154	0.70	0.788	1.02	0.878
Reflections collected	4121	11348	5108	12417	10814
Independent reflections	3354 [ <i>R</i> (int) = 0.0471]	9505 [ <i>R</i> (int) = 0.1248]	4178 [ <i>R</i> (int) = 0.0314]	6500 [ <i>R</i> (int) = 0.017]	9186 [ <i>R</i> (int) = 0.0959]
Final <i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0491, 0.1105	0.0738, 0.1637	0.0870, 0.2234	0.027, 0.035	0.0750, 0.1715

under reduced pressure and the yellow-red residue washed with two successive 30 cm<sup>3</sup> portions of ethanol to remove the free dba. The remaining yellow powder was recrystallised from a toluene-diethyl ether mixture at 4 °C. Yield 302 mg (89%). Found: C, 63.0; H, 5.3. C<sub>59</sub>H<sub>56</sub>O<sub>3</sub>P<sub>2</sub>Pd<sub>2</sub>S requires C, 63.2; H, 5.0%.  $\tilde{\nu}_{\max}$ /cm<sup>-1</sup> 1606 (C=O), 1195 (SO<sub>2</sub>) and 1054 (SO<sub>2</sub>).  $\delta_P$  [(CD<sub>3</sub>)<sub>2</sub>CO] 2.8 (s). FAB-MS<sup>+</sup>: *m/z* 1120 {[M]<sup>+</sup>}, 822 {[Pd<sub>2</sub>(PBz<sub>3</sub>)<sub>2</sub>]<sup>+</sup>} and 731 {[Pd<sub>2</sub>(PBz<sub>3</sub>)(PBz<sub>2</sub>)]<sup>+</sup>}.

**[Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PBz<sub>3</sub>)<sub>3</sub>] 2.** A mixture of [Pd<sub>2</sub>(dba)<sub>3</sub>]·C<sub>6</sub>H<sub>6</sub> (300 mg, 0.30 mmol) and PBz<sub>3</sub> (184 mg, 0.60 mmol) in 20 cm<sup>3</sup> toluene was stirred for 30 min followed by the addition of SO<sub>2</sub> gas (*ca.* 10 min) whereupon the solution changed from deep purple to red. The mixture was stirred under an atmosphere of SO<sub>2</sub> for 30 min to ensure completion of the reaction, then was filtered under an atmosphere of SO<sub>2</sub> and an SO<sub>2</sub>-degassed ethanol (30 cm<sup>3</sup>) layer was added. The mixture was kept under SO<sub>2</sub> and cooled slowly to -25 °C, whereupon dark red-purple crystals of [Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(PBz<sub>3</sub>)<sub>3</sub>] separated. Yield 240 mg (84%). Crystals suitable for a single crystal X-ray analysis were grown from a toluene-ethanol mixture under an atmosphere of SO<sub>2</sub>. Found: C, 52.6; H, 4.3. C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>PdS requires C, 53.1; H, 4.5%.  $\tilde{\nu}_{\max}$ /cm<sup>-1</sup> 1244 (SO<sub>2</sub>) and 1067 (SO<sub>2</sub>).  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 19.3 (s).

**[Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)<sub>2</sub>] 3.** To a benzene (20 cm<sup>3</sup>) solution of [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] (100 mg, 0.09 mmol) a benzene solution (20 cm<sup>3</sup>) containing bis(diphenylphosphino)methane (34 mg, 0.09 mmol) was added. The orange-yellow solution immediately changed to a brighter yellow. After 1 h the solvent was removed under reduced pressure and the residue washed with five 20 cm<sup>3</sup> portions of methanol to remove the dba. Yellow crystals suitable for a single-crystal X-ray analysis were obtained on recrystallisation from a benzene-methanol mixture and cooling slowly to 4 °C. Yield 103 mg (86%). Found: C, 61.5; H, 5.0 for the solid obtained before recrystallisation. C<sub>67</sub>H<sub>64</sub>O<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>S·2MeOH requires C, 62.1; H, 5.4%.  $\tilde{\nu}_{\max}$ (SO<sub>2</sub>)/cm<sup>-1</sup> 1147 and 1025.  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 22.2 (t, *J* = 10, 2P) and 7.7 (t, *J* = 10 Hz, 2P). FAB-MS<sup>+</sup>: *m/z* 1272 {[Pd<sub>2</sub>(SO<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)<sub>2</sub>]<sup>+</sup>}, 1207 {[Pd<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)<sub>2</sub>]<sup>+</sup>}, 1113 {[Pd<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)(PBz<sub>2</sub>)]<sup>+</sup>} and 902 {[Pd<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)(PBz<sub>3</sub>)]<sup>+</sup>}.

**[Pd(SO<sub>2</sub>)(PBz<sub>3</sub>)] 4.** The compound PBz<sub>3</sub> (54 mg, 0.18 mmol) was added directly to a solution of 100 mg (0.09 mmol) [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] in 20 cm<sup>3</sup> THF with stirring. The phosphine dissolved and reacted in a few seconds to give a ruby-red solution. Sulfur dioxide gas was then bubbled through the solution for 10 min upon which it changed to orange and the

mixture was stirred under an atmosphere of SO<sub>2</sub> for 30 min. After reducing the volume of THF to approximately 5 cm<sup>3</sup>, diethyl ether was added to precipitate the orange solid, followed by filtration. Orange crystals of [Pd(SO<sub>2</sub>)(PBz<sub>3</sub>)<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub> were obtained by redissolving the compound in CH<sub>2</sub>Cl<sub>2</sub> followed by the addition of a methanol layer and cooling to -25 °C. Yield 119 mg (77%). Found: C, 61.6; H, 5.0. C<sub>43</sub>H<sub>44</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>PdS requires C, 59.8; H, 5.1%.  $\tilde{\nu}_{\max}$ (SO<sub>2</sub>)/cm<sup>-1</sup> 1182 and 1033.  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 20.5 (s). FAB-MS<sup>+</sup>: *m/z* 1240, 881, 811, 713 {[Pd(PBz<sub>3</sub>)<sub>2</sub>]<sup>+</sup>}, 501, 409 {[Pd(PBz<sub>3</sub>)]<sup>+</sup>} and 321.

**[Pd<sub>3</sub>(μ-CO)<sub>2</sub>(μ-SO<sub>2</sub>)(PBz<sub>3</sub>)<sub>3</sub>] 5.** Carbon monoxide was bubbled through a solution of [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] (150 mg, 0.13 mmol) in THF (20 cm<sup>3</sup>) with stirring, and an immediate change to red was observed. After 5 min the solvent was removed under reduced pressure and the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum recorded, showing a mixture of compounds **5** and **6**. The crude solid was dissolved in toluene and CO passed through the solution at 50 °C for 30 min. The solvent was removed under reduced pressure and the crude solid recrystallised from THF-hexane. Yield 93 mg (77%). Found: C, 58.4; H, 4.88. C<sub>65</sub>H<sub>63</sub>O<sub>4</sub>P<sub>3</sub>Pd<sub>3</sub>S·C<sub>4</sub>H<sub>8</sub>O requires C, 58.2; H, 5.02%.  $\tilde{\nu}_{\max}$ /cm<sup>-1</sup> 1911s (CO), 1857vs (CO), 1187s (SO<sub>2</sub>) and 1056vs (SO<sub>2</sub>).  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 15.5 (t, 1P, <sup>3</sup>*J*<sub>PP</sub> = 41) and 9.6 (d, 2P, <sup>3</sup>*J*<sub>PP</sub> = 41 Hz). For **6**:  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 16.5 (d, 2P, <sup>3</sup>*J*<sub>PP</sub> = 52) and 8.8 (t, 1P, <sup>3</sup>*J*<sub>PP</sub> = 52 Hz).

**[Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>2</sub>(CNBu<sup>t</sup>)<sub>2</sub>(PBz<sub>3</sub>)<sub>3</sub>] 7.** *tert*-Butyl isocyanide (30 mg, 0.36 mmol) in toluene (15 cm<sup>3</sup>) was added to a SO<sub>2</sub> saturated solution of [Pd<sub>2</sub>(μ-SO<sub>2</sub>)(μ-dba)(PBz<sub>3</sub>)<sub>2</sub>] (200 mg, 0.18 mmol) in toluene (40 cm<sup>3</sup>). An instant change to yellow was observed. After stirring the mixture for 30 min under an atmosphere of SO<sub>2</sub>, all of the solvent was removed under reduced pressure and diethyl ether added to the remaining oil to obtain a solid. The diethyl ether was removed by filtration and several washings with cold methanol portions were needed to remove the free dba. Crystals of [Pd<sub>3</sub>(μ-SO<sub>2</sub>)<sub>2</sub>(CNBu<sup>t</sup>)<sub>2</sub>(PBz<sub>3</sub>)<sub>3</sub>]·0.5H<sub>2</sub>O were obtained by dissolving the complex in benzene and adding an equal quantity of methanol, followed by slow evaporation of benzene under an air atmosphere at room temperature. Yield 149 mg (79%). Found: C, 55.7; H, 4.7. C<sub>73</sub>H<sub>81</sub>N<sub>2</sub>O<sub>4.5</sub>P<sub>3</sub>Pd<sub>3</sub>S<sub>2</sub>·2H<sub>2</sub>O requires C, 56.1; H, 5.5%.  $\tilde{\nu}_{\max}$ /cm<sup>-1</sup> 2175 (NC), 2148 (NC), 1160 (SO<sub>2</sub>) and 1012 (SO<sub>2</sub>).  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 11.7 (d, 2P, <sup>3</sup>*J*<sub>PP</sub> = 34) and 2.3 (t, 1P, <sup>3</sup>*J*<sub>PP</sub> = 34 Hz).

### Crystallography

X-Ray data were collected on a Siemens P4 four-circle diffractometer for compounds **2**, **3**, **4** and **7** and on an Enraf-Nonius

CAD4 diffractometer for **5**. Details of data collection, refinement and crystal data are listed in Table 7. Lorentz-polarisation and absorption corrections were applied to the data of all compounds.

**Structure solution and refinement.** For all compounds the positions of the metals and most of the non-hydrogen atoms were located using direct methods. The remaining non-hydrogen atoms, in all cases, were revealed from subsequent Fourier-difference syntheses. Refinement was based on  $F^2$ .<sup>23</sup> The carbon atom on one methanol solvate in **3** was disordered and resolved into two components of 0.75:0.25 site occupancy. Chemically equivalent bonds within the ligands in compounds **2**, **3**, **4** and **7** were constrained to be equal within e.s.d.s of 0.01–0.05 in the refinement. The phenyl rings in **7** were refined as rigid hexagons and for, all compounds, hydrogen atoms (except those on the methanol oxygen atom in **3**) were placed in calculated positions with displacement parameters equal to  $1.2U_{eq}$  and  $1.5U_{eq}$  of the parent carbon atoms for phenyl and methyl hydrogen atoms respectively. Semi-empirical absorption correction using  $\psi$  scans were applied to the data of **3** and, after initial refinement with isotropic displacement parameters, empirical absorption corrections<sup>24</sup> were applied to the data of **2**, **4** and **7**. All non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

For crystal **4** relatively high anisotropy in the displacement parameters indicates some rotation disorder of the phenyl rings but it was not possible to resolve this; the crystal diffracted relatively poorly at high angle and data in the limited  $\theta$  range 1.06 to 21° were used in the refinement.

CCDC reference number 186/1655.

See <http://www.rsc.org/suppdata/dt/1999/3981/> for crystallographic files in .cif format.

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