Reactivity of the palladium dimer [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$]. Synthesis and structural characterisation of [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$], [Pd$_2$(μ-SO$_2$)(μ-dppm)(PBz$_3$)$_2$], [Pd(SO$_2$)(PBz$_3$)$_2$], [Pd$_3$(μ-CO)$_2$-(μ-SO$_2$)(PBz$_3$)$_3$] and [Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$] (Bz = benzyl) †

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The reaction between [Pd$_2$(dba)$_3$]·solvent (dba = dibenzylideneacetone, solvent = CHCl$_3$ or C$_6$H$_6$) and PBz$_3$ (Bz = benzyl) in the presence of SO$_2$ led to either [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] **1** or [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] **2** depending on the absence or presence of an excess of 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 [Pd$_2$(μ-SO$_2$)(μ-dppm)(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 Pd^I and the SO$_2$ reduced to SO$_2^{2-}$. Complex **1** reacted with PBz$_3$ to give two mononuclear complexes, the previously characterised [Pd(dba)(PBz$_3$)$_2$] and the new complex [Pd(SO$_2$)(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 η^1-pyramidal SO$_2$ ligand, and is the first mononuclear palladium SO$_2$ complex to be crystallographically characterised. Complex **1** reacts with CO to give a mixture of the *triangulo*-clusters [Pd$_3$(μ-CO)$_2$(μ-SO$_2$)(PBz$_3$)$_3$] **5** and [Pd$_3$(μ-CO)(μ-SO$_2$)$_2$(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 CNBu^t to give [Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$] which has also been crystallographically characterised.

The reactions between zero oxidation state palladium complexes and small molecules such as CO, H$_2$, CNR and SO$_2$ have been implicated in a number of catalytic processes.[1] One of the most versatile palladium(0) sources is the dimer [Pd$_2$(dba)$_3$]·solvent (dba = dibenzylideneacetone, solvent = CHCl$_3$ or C$_6$H$_6$).[2] 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 [Pd(dba)L$_2$] (L = PBz$_3$ or PPh$_2$(C$_{10}$H$_7$); L$_2$ = dppe; Bz = CH$_2$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.[2b,3,4] In addition, Amatore and co-workers[5] 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 [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] **1**.[6a] This dimer is readily obtained in high yields when [Pd$_2$(dba)$_3$]·sol-

vent is treated with two molar equivalents of PBz$_3$ under an 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 "[Pd$_2$-(μ-SO$_2$)(PBz$_3$)$_2$]" fragments for cluster aggregation reactions. This has been shown by the reaction between **1** and COS which gives the tetrametallic cluster [Pd$_4$(μ$_3$-S)(μ-SO$_2$)(CO)(PBz$_3$)$_4$].[6b] 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 [Pd$_2$(dba)$_3$], PBz$_3$ and SO$_2$ to give the isolated dimer **1**.

Results and discussion

Synthesis of [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] 1 and [Pd$_3$(μ-SO$_2$)$_3$-(PBz$_3$)$_3$] 2

We have recently reported that the reaction between [Pd$_2$-(dba)$_3$]·solvent, 2 PBz$_3$ and SO$_2$ gives the orange-yellow dimer [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] **1**.[6a] This compound has been structurally and spectroscopically characterised, and its ^{31}P-{^{1}H} NMR spectrum shows a singlet at δ 2.8. When monitoring this reaction as a function of time *via* ^{31}P-{^{1}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 SO$_2$ atmosphere showed only a single sharp peak at δ 19.3. After removing the solvent under reduced pressure followed by redissolving the residues under an

Fig. 1 Molecular structure of [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$].

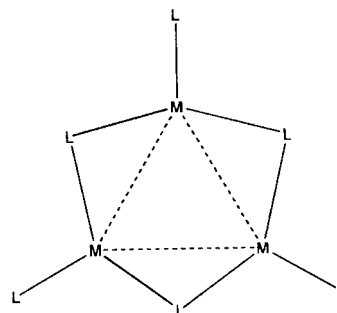|			
Pd(1)–S(1)	2.2641(19)	Pd(1)–S(1A)	2.2841(18)
Pd(1)–P(1)	2.3367(18)	Pd(1)–Pd(1A)	2.7225(9)
Pd(1)–Pd(1B)	2.7225(9)	S(1)–O(1)	1.438(6)
S(1)–O(2)	1.440(6)	S(1)–Pd(1B)	2.2841(18)
S(1)–Pd(1)–S(1A)	166.01(6)	S(1)–Pd(1)–P(1)	94.70(7)
S(1A)–Pd(1)–P(1)	99.02(7)	S(1)–Pd(1)–Pd(1A)	113.54(5)
S(1A)–Pd(1)–Pd(1A)	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 ML$_3$ fragments.

atmosphere of N$_2$ the peak at δ 2.8, corresponding to **1**, was observed in the ^{31}P-{^{1}H} NMR spectrum. This suggested that the compound with the resonance at δ 19.3 readily decomposes in the absence of an SO$_2$ atmosphere to yield **1**. In order to isolate this new compound a layer of SO$_2$-saturated ethanol was added directly to the reaction mixture under an atmosphere of SO$_2$. Upon slow diffusion of the ethanol layer into the toluene solution at −25 °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 SO$_2$ ligand with two intense peaks at 1244 and 1067 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 [Pd$_x$(SO$_2$)$_x$(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 [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] **2** (see Fig. 1). 42-Electron *triangulo*-clusters of formula [Pt$_3$(μ-SO$_2$)$_3$(PR$_3$)$_3$] are well known and have been crystallographically characterised for PR$_3$ = PPh$_3$ or PCy$_3$. However, the structure of **2** represents the first example of an analogous palladium triangle with the general formula [Pd$_3$(μ-SO$_2$)$_3$(PR$_3$)$_3$].

The compound [Pd$_3$(μ-SO$_2$)$_3$(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) Å. These distances are slightly longer than the range 2.576(1)–2.719(6) Å previously reported for 42 electron *triangulo*-palladium clusters.[7] The range of Pt–Pt bond lengths previously reported for the analogous [Pt$_3$(μ-SO$_2$)$_3$(PR$_3$)$_3$] tri-angles are 2.813(1)–2.815(1) (R = Cy) and 2.695(1)–2.712(1) Å (R = 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) Å]. This difference is also reflected in the two S–Pd–Pd angles of each SO$_2$-bridged edge [S(1A)–Pd(1)–Pd(1A) 52.90(5)° and S(1)–Pd(1)–Pd(1B) 53.57(5)°]. The palladium, phosphorus and sulfur atoms are situated in approximately planar arrangements, the three sulfur atoms lying –0.674 Å below the Pd$_3$ plane and the phosphorus atoms 0.1196 Å above it. Mingos and co-workers[10] have suggested that this virtually planar geometry, which is observed in 42 electron *triangulo*-platinum clusters such as [Pt$_3$(μ-CO)$_3$-

(PCy$_3$)$_3$] and [Pt$_3$(μ-SO$_2$)$_3$L$_3$], can be viewed in terms of three T-shaped 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)° which is comparable to those observed in [Pt$_3$(μ-SO$_2$)$_3$(PR$_3$)$_3$] (mean S–Pt–S 167.4°). These values are typical of T-shaped molecules and may be compared with the P–M–P angle of 159.3° reported[11] for the d^8 complex [Rh(PPh$_3$)$_3$]$^+$ and that of 163(1)° observed in the present study for [Pd(SO$_2$)(PBz$_3$)$_2$] **4** (see below).
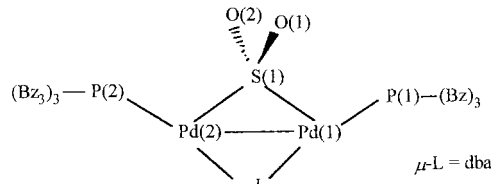
The reaction between [Pd$_2$(dba)$_3$]·solvent and PBz$_3$ under an atmosphere of SO$_2$ is summarised in Scheme 1. An equilibrium is established between [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] **2** and [Pd$_2$(μ-SO$_2$)-(μ-dba)(PBz$_3$)$_2$] **1** with the concentration of SO$_2$ in solution determining the relative amount of the two complexes. Removal of the solvent (and hence any excess of SO$_2$) results in the equilibrium shifting to the right hand side, favouring complex **1**. Under an SO$_2$ atmosphere the equilibrium is shifted to the left hand side, favouring **2**.
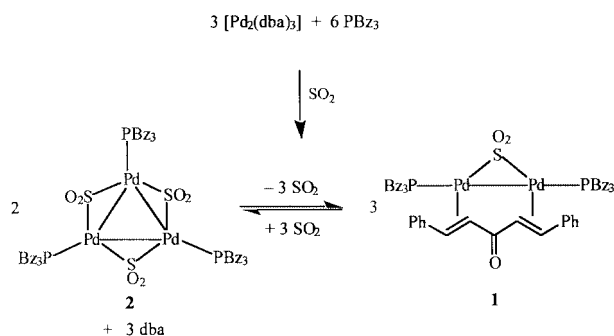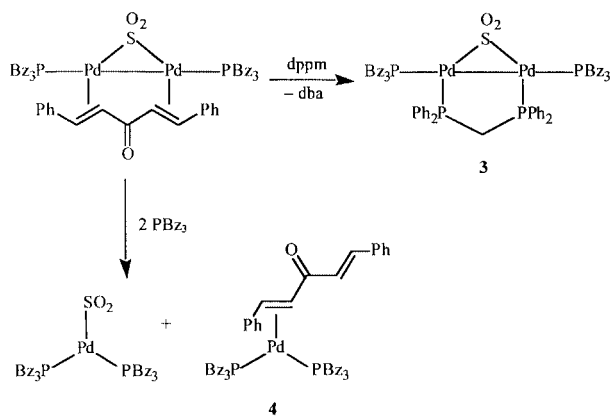

Scheme 1

Synthesis of [Pd$_2$(μ-SO$_2$)(μ-dppm)(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 (Ph$_2$PCH$_2$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$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] **1** and [Pd$_2$(μ-SO$_2$)(μ-dppm)(PBz$_3$)$_2$] **3**

μ-L = dba **1**, dppm **3**

	1	3		1	3
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
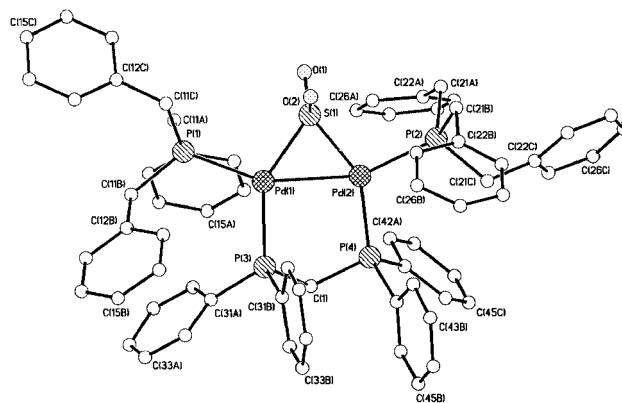
Fig. 3 Molecular structure of [Pd$_2$(μ-SO$_2$)(μ-dppm)(PBz$_3$)$_2$].

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$_2$(SO$_2$)(dppm)(PBz$_3$)$_2$]·2MeOH. The isolated product gave rise to two peaks in the ^{31}P-{^{1}H} NMR at δ 22.2 and 7.7 (C$_6$D$_6$) 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$_3$ ligands. The SO$_2$ stretching vibrations in the IR spectrum at 1025 and 1147 cm^{-1} are lower than those found in [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$], indicating stronger Pd–SO$_2$ 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$_2$(SO$_2$)(Ph$_2$PCH$_2$PPh$_2$)-(PBz$_3$)$_2$]$^+$, with m/z 1272. The formulation of the compound **3** as [Pd$_2$(μ-SO$_2$)(μ-dppm)(PBz$_3$)$_2$] 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$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] 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$_2$-containing palladium(0) cluster compounds.[7] If the SO$_2$ ligand is con-

sidered to be neutral, the dimer formally contains palladium(0) centres but the metal–metal distance is in fact more characteristic of the Pd–Pd bond lengths observed in palladium(I) dimers.[12] For example similar Pd–Pd bond lengths have been observed for palladium(I) dimers containing dppm and dpmMe (dpmMe = 1,1-bis(diphenylphosphino)ethane) {e.g. 2.699(5) Å in [Pd$_2$(μ-dppm)$_2$Br$_2$][13a] and 2.6639(7) in [Pd$_2$(μ-dpmMe)$_2$-Cl$_2$]^{13b}}. It is not the small bite angle of the dppm ligand that is responsible for the short Pd–Pd distance in **3** because in the palladium(0) dimer [Pd$_2$(μ-dppm)$_3$] the Pd–Pd bond length is 2.959(2) Å.[14]

The mean Pd–S distance in complex **3** of 2.240(3) Å is not significantly shorter than that of 2.249(4) Å in **1**, but the mean S–O distance of 1.496(8) Å in **3** is longer than that of 1.466(10) Å in **1**, and correspondingly **3** has the lower ν(SO$_2$) stretching vibrations in the IR spectrum. This indicates that the SO$_2$ ligand in **3** is more strongly electron-accepting and could account for the fact that Pd–Pd distance indicates a formal palladium oxidation state of +1 and hence a Pd–Pd bond order of 1, if the SO$_2$ ligand is formally considered as an (SO$_2$)$^{2-}$ species.

The other major difference between complexes **1** and **3** is the larger angles in **3**, for example S(1)–Pd(1)–P(1) and S(1)–Pd(2)–P(2) have a mean value of 104.55(9)° in **3** compared to 92.43(14)° in **1**. This can be attributed to the greater flexibility of the dppm ligand compared to the dba ligand which leads to less steric crowding. The phenyl rings of dppm are more able to orientate themselves into the most sterically favourable position whereas the dba ligand is more rigid due to the conjugation between the unsaturated groups across the ligand. The tribenzylphosphine ligands are of approximately equal distance from the palladium atoms in both dimers.

The compound [Pd$_2$(μ-SO$_2$)(μ-dppm)(PBz$_3$)$_2$] is very stable

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, [(Ph₃P)-Pd(μ-SC₆F₅)(μ-dppm)Pd(SC₆F₅)]·1.4CH₂Cl₂ and [(Ph₃P)Pd-(μ-SC₆F₅)(μ-dppm)Pd(PPh₃)][SO₃CF₃]·2CH₂Cl₂, have recently been synthesized.[15] 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 [Pd₂(μ-SO₂)(μ-dba)(PBz₃)₂] with PBz₃

Since the addition of dppm to [Pd₂(μ-SO₂)(μ-dba)(PBz₃)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 ³¹P-{¹H} NMR spectrum of this solution contained two signals of equal intensity, one at δ 20.5 and the other at δ 7.8. The signal at δ 7.8 consists of one sharp intense peak surrounded by two small and broad peaks at δ 9.2 and 6.4. This signal has been previously assigned to the presence of [Pd(dba)(PBz₃)₂] in solution.[6a] 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 δ 20.5 in the ³¹P-{¹H} 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 ³¹P-{¹H} NMR spectrum of the resultant solution consisted of just one single sharp peak at δ 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 SO₂ vibrations were observed at 1033 and 1182 cm⁻¹. Crystals of **4** analysed correctly for [Pd(SO₂)(PBz₃)₂]·CH₂Cl₂ 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-co-ordinate palladium complex with two PBz₃ ligands and an η¹-SO₂ 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 P(1)–Pd–P(2) angle of 163.67(14)° considerably greater than that of 107.2(3)° in the related three-co-ordinate [Pd(dba)(PBz₃)₂], a difference that may be attributed to the greater bulk of the dba ligand compared to SO₂. The SO₂ ligand is co-ordinated in a pyramidal mode (mean Pd–S–O 105.8(5)°), with the two oxygen atoms lying on opposite sides of the mean co-ordination plane (deviations O(1) −1.365 and O(2) 0.956 Å).

For platinum the first structurally characterised three co-ordinate bis(phosphine) sulfur dioxide complex, [Pt(SO₂)-(PCy₃)₂], was reported in 1983[16] but to our knowledge **4** is the first example of a mononuclear three-co-ordinate palladium phosphine SO₂ complex that has been crystallographically characterised, though complexes of the general formulae [Pd(SO₂)(PR₃)₂] and [Pd(SO₂)(PR₃)₃] have been reported and characterised by IR spectroscopy.[17] Three-co-ordinate nickel(0)–sulfur dioxide complexes of similar formulation have also been reported with the bulky organophosphines PCy₃, PCy₂Ph and PBz₂Ph. Crystal structure studies of the nickel(0) complex [Ni(SO₂)(PCy₃)₂] shows large differences in the three-co-ordinate structure from those of the related palladium and platinum complexes, **4** and [Pt(SO₂)(PCy₃)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 (°) for [M(SO₂)L₂]

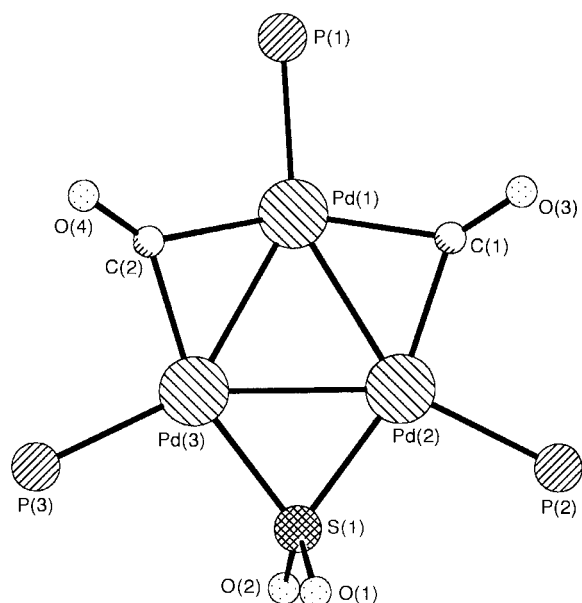|	[Pd(SO₂)-(PBz₃)₂] 4	[Ni(SO₂)-(PCy₃)₂][19]	[Pt(SO₂)-(PCy₃)₂][16]
M–S	2.282(4)	2.150ᵃ	2.299(1)
M–P(1)	2.312(3)	2.211	2.304(1)
M–P(2)	2.328(3)	2.211	2.309(1)
S–O(1)	1.428(13)	1.540ᵃ	1.465(3)
S–O(2)	1.467(13)	1.560ᵃ	1.461(3)
P(1)–M–P(2)	163.67(14)	118.5	165.72(4)
S–M–P(1)	96.52(14)	114.3ᵃ	95.03(4)
S–M–P(2)	97.27(14)	127.0ᵃ	97.39(4)
M–S–O(1)	104.8(5)	116.0ᵃ	104.8(1)
M–S–O(2)	106.8(5)	103.0ᵃ	104.1(1)
O(1)–S–O(2)	112.4(9)	130.0ᵃ	113.1(2)

ᵃ Denotes averaged atomic positions.
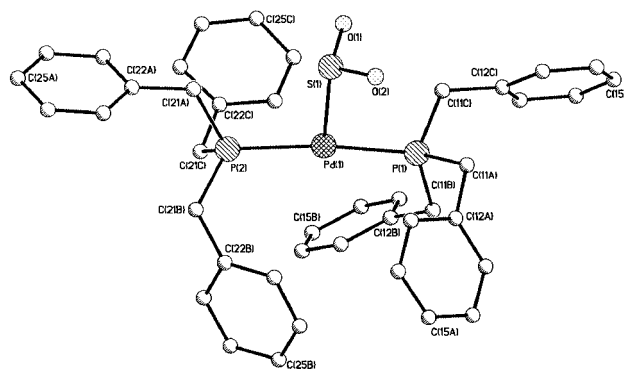
Fig. 4 Molecular structure of [Pd(SO₂)(PBz₃)₂].

fact that whereas the palladium and platinum complexes have definite T-shaped co-ordination geometry at the metal centre [P–Pd–P 163.6(1) and P–Pt–P 165.72(4)°], the nickel compound is more appropriately described as trigonal planar (P–Ni–P 118.5, mean S–Ni–P 120.9°). Similarly the palladium and platinum compounds both exhibit pyramidal M–SO₂ co-ordination with approximately tetrahedral angles at S (mean S–M–P 96.9(1) and 96.18(4)°, O–S–O 113.2(8) and 113.1° respectively), whereas the nickel complex has a virtually planar Ni–SO₂ arrangement (mean S–Ni–O 109.5° and O–S–O 130.0°). The η¹-pyramidal co-ordination of SO₂ in the palladium and platinum compounds means that the ML₂ (M = Pd or Pt) fragment makes use of its σ-donating ability to co-ordinate to SO₂.[18] In the nickel complexes the SO₂ is co-ordinated in a η¹-planar mode consistent with the lower basicity of the first row transition metal.
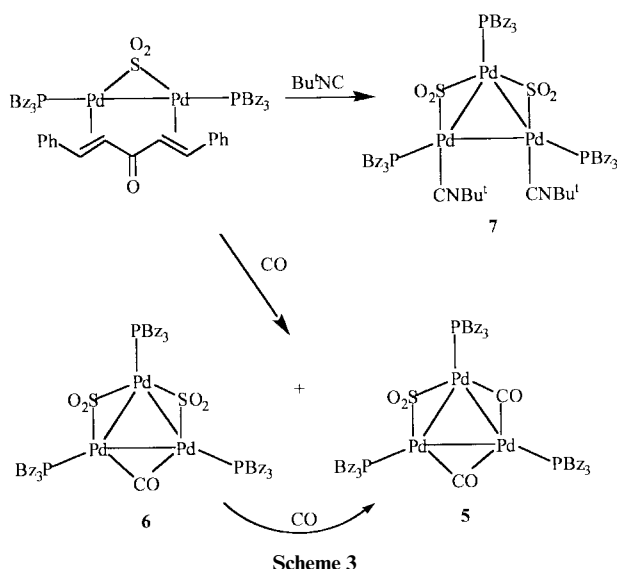
The reactions of the dimer [Pd₂(μ-SO₂)(μ-dba)(PBz₃)₂] with other phosphines were also studied. However, these investigations proved to be inconclusive since mixtures of products were obtained, and further work is required to separate the range of products formed.

Reaction of [Pd₂(μ-SO₂)(μ-dba)(PBz₃)₂] with CO

In order to study the possible aggregation of compound **1** into higher nuclearity clusters its reactions with CO and CNBuᵗ were studied. On bubbling CO gas through a THF solution of **1** a rapid change to dark red occurred. The ³¹P-{¹H} 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 δ 15.5 and a doublet at δ 9.6, with a coupling constant of 41 Hz. The minor compound (**6**) gave a doublet at δ 16.5 and a triplet at δ 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 $[Pd_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(PBz_3)_3]$. The benzyl groups have been omitted for clarity.

Scheme 3

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/SO₂ *triangulo*-cluster, $[Pd_3(\mu\text{-CO})(\mu\text{-SO}_2)_2(PBz_3)_3]$.

Reaction of $[Pd_2(\mu\text{-SO}_2)(\mu\text{-dba})(PBz_3)_2]$ with CNBu^t

On adding two molar equivalents of *tert*-butyl isocyanide to a toluene solution of $[Pd_2(\mu\text{-SO}_2)(\mu\text{-dba})(PBz_3)_2]$ the solution changed to light yellow. After removing the solvent under reduced pressure and washing with methanol to remove the dba the $^{31}P\text{-}\{^1H\}$ NMR spectrum (C_6D_6) contained a doublet at δ 11.7 and a triplet at δ 2.3 in a ratio of 2:1 with a coupling constant $^3J_{P,P} = 34$ 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 $[Pd_3(\mu\text{-SO}_2)_2(CNBu^t)_2(PBz_3)_3]$ **7**. For a balanced equation, (1),

$$3[Pd_2(SO_2)(dba)(PBz_3)_2] + SO_2 + 4Bu^tNC \xrightarrow{-3dba}$$

$$2[Pd_3(SO_2)_2(CNBu^t)_2(PBz_3)_3] \quad (1)$$
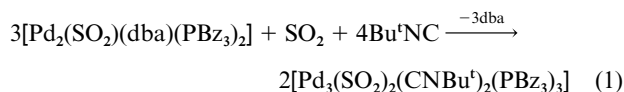
between **1** and **7**, additional sulfur dioxide needs to be present. In accordance with this equation, when the synthesis of **7** was carried out under an atmosphere of SO₂ the yield was greatly improved and the product more readily isolated.

The isocyanide ligands of this product showed $v(CN)$ bands at 2175 and 2148 cm^{-1} which are higher than that of free *tert*-butyl isocyanide which appears at 2136 cm^{-1}. The analogous *tert*-butyl isocyanide *triangulo*-palladium cluster $[Pd_3(\mu\text{-SO}_2)_2(CNBu^t)_5]$ also shows an increase in $v(CN)$ from free CNBu^t with peaks observed in the IR spectrum at 2170 and 2155 cm^{-1}.[20] A decrease in $v(CN)$ from that of free CNBu^t might have been expected as isocyanides, like carbon monoxide, are π-acceptor ligands. An increase in $v(CN)$ indicates that little, if any, electron density is being donated from the metal centre into the π* antibonding orbital of the isocyanide ligand. Complex **7** also shows an intense and sharp SO₂ peak at 1012 cm^{-1} and no peaks due to dba could be identified. The FAB-MS showed the expected fragmentation pattern for a compound of formula $[Pd_3(SO_2)_2(CNBu^t)_2(PBz_3)_3]$. The peak with the highest m/z was observed at 1527 and assigned as $[M]^+$. 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 $[Pd_3(\mu\text{-SO}_2)_2(CNBu^t)_2(PBz_3)_3]$ which contains two edge-bridging SO₂ ligands and two terminal isocyanide ligands. The compound crystallises with half a molecule of H₂O 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

CO (Scheme 3). The IR spectrum of **5** confirmed the presence of both CO and SO₂ with $v(CO)$ at 1911 and 1857 cm^{-1}, and $v(SO_2)$ at 1056 and 1187 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 $[Pd_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(PBz_3)_3]$ **5** which is consistent with the $^{31}P\text{-}\{^1H\}$ 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 SO₂ (see Fig. 5). These distances are all shorter than the Pd–Pd bond lengths previously reported for other Pd–SO₂ triangles which cover a range from 2.7225(9) (complex **2**) to 2.994(1) Å.[7] 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 SO₂-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.
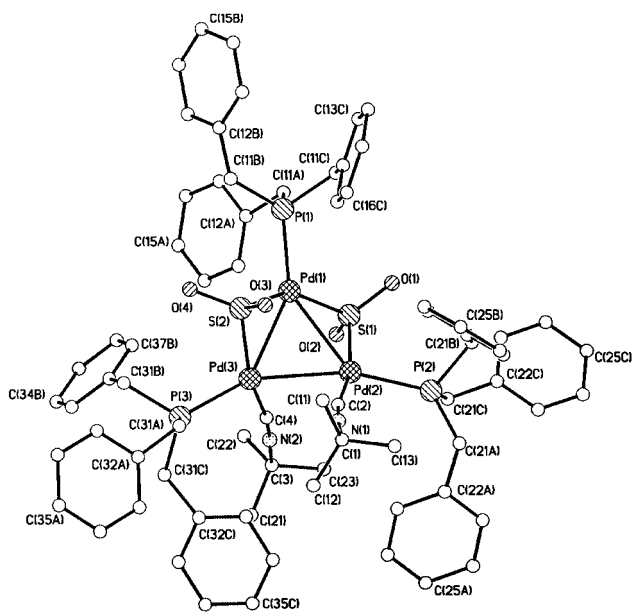
Table 5 Details for the positive ion FAB mass spectrum of compound **7**

m/z	Intensity (%)	Fragment
1527	18	[M]$^+$
1223	24	[M − PBz$_3$]$^+$
1140	50	[M − Bu^{t}NC − PBz$_3$]$^+$
1050	10	[M − Bu^{t}NC − PBz$_3$ − Bz]$^+$
1002	14	[M − 2PBz$_3$]$^+$
919	52	[M − Bu^{t}NC − 2PBz$_3$]$^+$
836	22	[M − 2Bu^{t}NC − 2PBz$_3$]$^+$
821	58	[M − Pd − 2Bu^{t}NC − 2SO$_2$ − PBz$_3$]$^+$
745	12	[M − 2Bu^{t}NC − 2PBz$_3$ − Bz]$^+$
729	54	[M − Pd − 2Bu^{t}NC − 2SO$_2$ − PBz$_3$ − Bz]$^+$

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)

Fig. 6 Molecular structure of [Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$].

observed elemental analyses than the unhydrated complex, but are still not completely satisfactory.

Complex **7** consists of a palladium triangle with two Pd–Pd edges bridged by a sulfur dioxide ligand. The two palladium atoms of the unbridged edge are each terminally bonded to an isocyanide ligand. Each palladium atom is also terminally bonded to a phosphine ligand in the plane of the palladium triangle {maximum deviations from [Pd(1), Pd(2), Pd(3), P(1), P(2), P(3)] mean plane: Pd(1) 0.0325, Pd(2) 0.0519, Pd(3) −0.0587, P(1) −0.0167, P(2) −0.0260, P(3) 0.0169 Å}. The C_2 rotational symmetry axis observed in [Pd$_3$(μ-CO)$_2$(μ-SO$_2$)-(PBz$_3$)$_3$] is also present, with this axis bisecting the Pd(2)–Pd(3) bond and passing through Pd(1). However the vertical plane of symmetry observed in [Pd$_3$(μ-CO)$_2$(μ-SO$_2$)(PBz$_3$)$_3$] is not present due to the isocyanide and sulfur dioxide ligands being greatly displaced from the plane of the palladium triangle. Selected bond lengths and angles for **7** are given in Table 6.

Unlike [Pd$_3$(μ-CO)$_2$(μ-SO$_2$)(PBz$_3$)$_3$], which has a cluster valence electron count of 42, [Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$] is a 44-electron complex with Pd–Pd bond lengths between 2.722(2) and 2.801(2) Å. The Pd–Pd bond lengths in other crystallographically characterised 44-electron complexes range between 2.734(4) and 3.000(5) Å.[21] The Pd(1)–Pd(3) distance in complex **7** is therefore the shortest observed Pd–Pd bond length in all of these complexes. The longest Pd–Pd bond in complex **7** is the non-bridged bond [Pd(2)–Pd(3)] but this is longer than Pd(1)–Pd(2) by the same amount that Pd(1)–Pd(2) is to Pd(1)–Pd(3). In other words, although the Pd(2)–Pd(3) distance is the longest bond, the palladium triangle does not exhibit a regular isosceles geometry. A similar geometry has been noted previously

for [Pd$_3$(μ-SO$_2$)$_2$(CNXyl)$_2$(PPh$_3$)$_3$] (Xyl = xylyl, 2,6-dimethylphenyl).[22]

It is interesting that the compounds [Pd$_3$(μ-SO$_2$)$_2$(CNXyl)$_2$-(PCy$_3$)$_3$] and [Pd$_3$(μ-SO$_2$)$_2$(CNXyl)$_2$(PPh$_3$)$_3$] were prepared from the reaction of higher nuclearity clusters with 2,6-dimethylphenyl isocyanide. The other known compound of this type, [Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_5$], does not contain any phosphine ligands and was prepared from [Pd$_3$(μ-CNBu^t)$_3$(CNBu^t)$_3$] and an excess of SO$_2$. The synthetic route to complex **7** is therefore unusual for this type of trinuclear cluster compound.

Conclusion

The dimer [Pd$_2$(μ-dba)(μ-SO$_2$)(PBz$_3$)$_2$] has proved to be a good starting material for the formation of novel dimeric and *triangulo*-palladium compounds. The formation of [Pd(SO$_2$)-(PBz$_3$)$_2$] when treating **1** with PBz$_3$ and of [Pd$_2$(μ-SO$_2$)(μ-dppm)-(PBz$_3$)$_2$] when using 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 Pd/SO$_2$/PR$_3$ complexes. During the synthesis of **1** the novel *triangulo*-cluster [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] **2** has been isolated and crystallographically characterised. The selective formation of **1** or **2** strongly depends on the concentration of SO$_2$.

Experimental

General

Syntheses

[Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] 1. The compound PBz$_3$ (184 mg, 0.60 mmol) was dissolved in 15 cm^3 toluene and SO$_2$ gas was bubbled through for 1 min. This solution was then added to a solution of [Pd$_2$(dba)$_3$]·C$_6$H$_6$ (300 mg, 0.30 mmol) in 25 cm^3 toluene, followed by the further addition of SO$_2$ gas (*ca.* 10 min) whereupon the solution changed from deep purple to red. The mixture was stirred under an atmosphere of SO$_2$ 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**

	2	3	4	5	7
Chemical formula	$C_{63}H_{63}O_6P_3Pd_3S_3$	$C_{74}H_{83}O_6P_4Pd_2S$	$C_{43}H_{44}Cl_2O_2P_2PdS$	$C_{65}H_{63}O_4P_3Pd_3S$	$C_{73}H_{82}N_2O_{4.5}P_3Pd_3S_2$
Formula weight	1424.42	1437.1	864.08	1352.4	1535.34
T/K	223(2)	173(2)	293(2)	293(2)	299(2)
System, space group	Trigonal, $R\bar{3}$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Trigonal, $R\bar{3}$	Orthorhombic, $Pbca$
a/Å	24.985(2)	22.498(7)	9.931(3)	44.09(4)	22.985(9)
b/Å	24.985(2)	14.064(3)	11.331(2)	44.09(4)	24.213(10)
c/Å	16.219(3)	23.376(13)	19.275(4)	16.22(1)	26.93(2)
α/°			84.427(12)		
β/°		112.47(3)	87.31(2)		
γ/°			64.216(14)		
U/Å^3	8768.0(19)	6835(4)	1943.9(8)	27306(2)	14985(13)
Z	6	4	2	18	8
μ(Mo-Kα)/mm^{-1}	1.154	0.70	0.788	1.02	0.878
Reflections collected	4121	11348	5108	12417	10814
Independent reflections	3354 [R(int) = 0.0471]	9505 [R(int) = 0.1248]	4178 [R(int) = 0.0314]	6500 [R(int) = 0.017]	9186 [R(int) = 0.0959]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	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^3 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. $C_{59}H_{56}O_3P_2Pd_2S$ requires C, 63.2; H, 5.0%. $\tilde{v}_{max}$/cm^{-1} 1606 (C=O), 1195 (SO$_2$) and 1054 (SO$_2$). δ_P [(CD$_3$)$_2$CO] 2.8 (s). FAB-MS$^+$: m/z 1120 {[M]$^+$}, 822 {[Pd$_2$(PBz$_3$)$_2$]$^+$} and 731 {[Pd$_2$(PBz$_3$)(PBz$_2$)]$^+$}.

[Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] 2. A mixture of [Pd$_2$(dba)$_3$]·C$_6$H$_6$ (300 mg, 0.30 mmol) and PBz$_3$ (184 mg, 0.60 mmol) in 20 cm^3 toluene was stirred for 30 min followed by the addition of SO$_2$ gas (ca. 10 min) whereupon the solution changed from deep purple to red. The mixture was stirred under an atmosphere of SO$_2$ for 30 min to ensure completion of the reaction, then was filtered under an atmosphere of SO$_2$ and an SO$_2$-degassed ethanol (30 cm^3) layer was added. The mixture was kept under SO$_2$ and cooled slowly to –25 °C, whereupon dark red-purple crystals of [Pd$_3$(μ-SO$_2$)$_3$(PBz$_3$)$_3$] 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$_2$. Found: C, 52.6; H, 4.3. $C_{21}H_{21}O_2PPdS$ requires C, 53.1; H, 4.5%). $\tilde{v}_{max}$/cm^{-1} 1244 (SO$_2$) and 1067 (SO$_2$). δ_P (C$_6$D$_6$) 19.3 (s).

[Pd$_2$(μ-SO$_2$)(μ-Ph$_2$PCH$_2$PPh$_2$)(PBz$_3$)$_2$] 3. To a benzene (20 cm^3) solution of [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] (100 mg, 0.09 mmol) a benzene solution (20 cm^3) 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^3 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. $C_{67}H_{64}O_2P_4Pd_2S$·2MeOH requires C, 62.1; H, 5.4%. $\tilde{v}_{max}$(SO$_2$)/cm^{-1} 1147 and 1025. δ_P (C$_6$D$_6$) 22.2 (t, $J = 10$, 2P) and 7.7 (t, $J = 10$ Hz, 2P). FAB-MS$^+$: m/z 1272 {[Pd$_2$(SO$_2$)(Ph$_2$PCH$_2$PPh$_2$)(PBz$_3$)$_2$]$^+$}, 1207 {[Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)(PBz$_3$)$_2$]$^+$}, 1113 {[Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)(PBz$_3$)(PBz$_2$)]$^+$} and 902 {[Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)(PBz$_3$)]$^+$}.

[Pd(SO$_2$)(PBz$_3$)$_2$] 4. The compound PBz$_3$ (54 mg, 0.18 mmol) was added directly to a solution of 100 mg (0.09 mmol) [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] in 20 cm^3 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$_2$ for 30 min. After reducing the volume of THF to approximately 5 cm^3, diethyl ether was added to precipitate the orange solid, followed by filtration. Orange crystals of [Pd(SO$_2$)(PBz$_3$)$_2$]·CH$_2$Cl$_2$ were obtained by redissolving the compound in CH$_2$Cl$_2$ followed by the addition of a methanol layer and cooling to −25 °C. Yield 119 mg (77%). Found: C, 61.6; H, 5.0. $C_{43}H_{44}Cl_2O_2P_2PdS$ requires C, 59.8; H, 5.1%). $\tilde{v}_{max}$(SO$_2$)/cm^{-1} 1182 and 1033. δ_P (C$_6$D$_6$) 20.5 (s). FAB-MS$^+$: m/z 1240, 881, 811, 713 {[Pd-(PBz$_3$)$_2$]$^+$}, 501, 409 {[Pd(PBz$_3$)]$^+$} and 321.

[Pd$_3$(μ-CO)$_2$(μ-SO$_2$)(PBz$_3$)$_3$] 5. Carbon monoxide was bubbled through a solution of [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] (150 mg, 0.13 mmol) in THF (20 cm^3) with stirring, and an immediate change to red was observed. After 5 min the solvent was removed under reduced pressure and the ^{31}P-{^{1}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. $C_{65}H_{63}O_4P_3Pd_3S$·C_4H_8O requires C, 58.2; H, 5.02%. $\tilde{v}_{max}$/cm^{-1} 1911s (CO), 1857vs (CO), 1187s (SO$_2$) and 1056vs (SO$_2$). δ_P (C$_6$D$_6$) 15.5 (t, 1P, $^3J_{PP} = 41$) and 9.6 (d, 2P, $^3J_{PP} = 41$ Hz). For **6**: δ_P (C$_6$D$_6$) 16.5 (d, 2P, $^3J_{PP} = 52$) and 8.8 (t, 1P, $^3J_{PP} = 52$ Hz).

[Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$] 7. tert-Butyl isocyanide (30 mg, 0.36 mmol) in toluene (15 cm^3) was added to a SO$_2$ saturated solution of [Pd$_2$(μ-SO$_2$)(μ-dba)(PBz$_3$)$_2$] (200 mg, 0.18 mmol) in toluene (40 cm^3). An instant change to yellow was observed. After stirring the mixture for 30 min under an atmosphere of SO$_2$, 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$_3$(μ-SO$_2$)$_2$(CNBu^t)$_2$(PBz$_3$)$_3$]·0.5H$_2$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. $C_{73}H_{81}N_2O_4P_3Pd_3S_2$·2H$_2$O requires C, 56.1; H, 5.5%). $\tilde{v}_{max}$/cm^{-1} 2175 (NC), 2148 (NC), 1160 (SO$_2$) and 1012 (SO$_2$). δ_P (C$_6$D$_6$) 11.7 (d, 2P, $^3J_{PP} = 34$) and 2.3 (t, 1P, $^3J_{PP} = 34$ 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.[23] 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 ψ scans were applied to the data of **3** and, after initial refinement with isotropic displacement parameters, empirical absorption corrections[24] 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 θ range 1.06 to 21° were used in the refinement.

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

Acknowledgements

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