Synthesis and Characterisation of Tetra- and Penta-palladium Clusters with Sulfur Dioxide as a Ligand†

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Several pentanuclear palladium clusters, $[Pd_5(SO_2)_4L_5]$ [L = PPh_3 **1**, $PMePh_2$ **2**, PMe_2Ph **3**, $P(C_6H_4OMe\text{-}p)_3$ **4**, $P(C_6H_4OMe\text{-}m)_3$ **5** or $AsPh_3$ **6**], have been synthesised from the reaction of $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone, PhCH=CHCOCH=CHPh) with L under an atmosphere of SO_2. Compounds **1**–**3** have also been synthesised from the reduction of palladium(II) acetate by $NaBH_4$ in the presence of L and SO_2. The molecular structure of **6** has been determined by a single-crystal X-ray study. The palladium cluster core has a distorted trigonal-bipyramidal geometry with two of the equatorial–apical edges bridged by $\mu\text{-}SO_2$ ligands, and two triangular faces capped by $\mu_3\text{-}SO_2$ ligands. Each metal atom is also co-ordinated to a terminal $AsPh_3$ ligand. Compounds **1**–**5** have also been characterised on the basis of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and fast atom bombardment (FAB) mass spectrometry. The reaction of $[Pd_2(dba)_3]\cdot CHCl_3$ with PMe_3 under a SO_2 atmosphere does not, surprisingly, give $[Pd_5(SO_2)_4(PMe_3)_5]$ **7** but the tetranuclear cluster $[Pd_4(SO_2)_3(PMe_3)_5]$ **8**. This compound has been characterised by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and FAB mass spectrometry. The reaction of $[Pd_2(dba)_3]\cdot CHCl_3$ with $PMePh_2$ and SO_2 gives a related compound, $[Pd_4(SO_2)_3(PMePh_2)_5]$ **9**, as a minor product, which has been characterised by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

In recent years the synthesis of carbonyl phosphine clusters of palladium and platinum has attracted much attention.[1–4] In palladium chemistry, clusters with up to 38 metal atoms have been synthesised and characterised by X-ray diffraction methods.[5] The π-acid character of CO, combined with its small size and ability to undergo a range of reactions leading to cluster formation, has been important in the development of this area. Palladium(0) clusters have been synthesised from palladium-(II) and -(0) monomers. Examples include palladium(II) acetate in the synthesis of $[Pd_{10}(CO)_{12}(PBu_3)_6]$[6] and the palladium(0) compound $[Pd(\sigma,\eta^3\text{-}C_8H_{12})(PMe_3)]$ in the synthesis of $[Pd_7(CO)_7(PMe_3)_7]$.[7]

The sulfur oxides have been shown to be a flexible group of ligands in both mononuclear and cluster chemistry, and interest in this area has increased due to environmental considerations. Sulfur monoxide can act as a bridging ligand between two[8] or three[9] metal atoms, and compounds containing S_2O_2,[10] S_2O_3[11] and S_2O_4[12] ligands have also been characterised. Sulfur dioxide forms a large number of metal complexes,[13] and the stereochemical and electronic control of the $M\text{-}SO_2$ bonding geometry have been studied. Linkage isomerisation σ to η^2 has been observed in $[Mo(CO)_2(SO_2)(PPh_3)_2(CNC_6H_{11})]$.[14] McAuliffe and co-workers have shown that the nature of the reaction with SO_2 depends on the substituents on the metal: $[Mn(OPPh_3)_4I_2]$ gives $[Mn(OPPh_3)_4(O_2SI)_2]$[15] whereas $[Mn(OPPh_3)_4(NCS)_2]$ gives $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$, in which the SO_2 can undergo aerial oxidation to derivatives of sulfuric acid.[16] Sulfur dioxide can also insert into M–H bonds with disproportionation to give co-ordinated SO_3H.[17] It has proved to be a useful π-acid ligand in cluster chemistry, and a flexible alternative to CO.[18–21] Recently, it has been shown that the palladium carbonyl phosphine cluster $[Pd_8(CO)_8(PMe_3)_7]$ reacts with SO_2 to give the pentanuclear cluster $[Pd_5(SO_2)_4(PMe_3)_5]$.[22] The research described in this paper provides a general route into related palladium clusters based either on palladium(II) acetate or the palladium(0) complex of PhCH=CHCOCH=CHPh (dba).

Results and Discussion

The compound $[Pd_2(dba)_3]\cdot CHCl_3$ has proved to be a convenient and effective palladium(0) starting material for cluster syntheses, and has been utilised in the synthesis of $[Pd_8(CO)_8(PMe_3)_7]$.[23] The reaction between $[Pd_2(dba)_3]\cdot CHCl_3$ and tertiary phosphines and arsines (L) in the presence of SO_2 gives rise to the pentanuclear clusters $[Pd_5(SO_2)_4L_5]$ [L = PPh_3 **1**, $PMePh_2$ **2**, PMe_2Ph **3**, $P(C_6H_4OMe\text{-}p)_3$ **4**, $P(C_6H_4OMe\text{-}m)_3$ **5** or $AsPh_3$ **6**]. It proceeds rapidly, and the clusters are obtained in good yield. A SO_2-saturated toluene or dichloromethane solution of the phosphine or arsine is added to a solution of $[Pd_2(dba)_3]\cdot CHCl_3$ in the same solvent, and then SO_2 is bubbled through the solution for 10–15 min. After removal of the solvent under reduced pressure, washing with diethyl ether to remove dba, and recrystallisation from dichloromethane–ether, the clusters **1**–**6** were obtained as either dark green or red crystals.

Compounds **1**–**3** have also been synthesised from the sodium tetrahydroborate reduction of palladium(II) acetate in the presence of L and SO_2. When an ethanolic solution of $NaBH_4$ is added to a SO_2-saturated solution of palladium acetate and phosphine in toluene an immediate darkening of colour is observed. The compounds $[Pd_5(SO_2)_4L_5]$ have been obtained in reasonable yields after washing with ethanol and recrystallisation from dichloromethane with either ether or hexane as the co-solvent.

When a SO_2-saturated toluene solution of PMe_3 is added to a toluene solution of $[Pd_2(dba)_3]\cdot CHCl_3$ using the same procedure as above, recrystallisation gives red microcrystals. These have been shown to consist primarily of $[Pd_4(SO_2)_3(PMe_3)_5]$ **8**, with $[Pd_5(SO_2)_4(PMe_3)_5]$ **7** present only as a minor product. Further recrystallisation gives pure **8**. This is in contrast to the reaction of $[Pd_8(CO)_8(PMe_3)_7]$ with SO_2, which gives only compound **7**.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

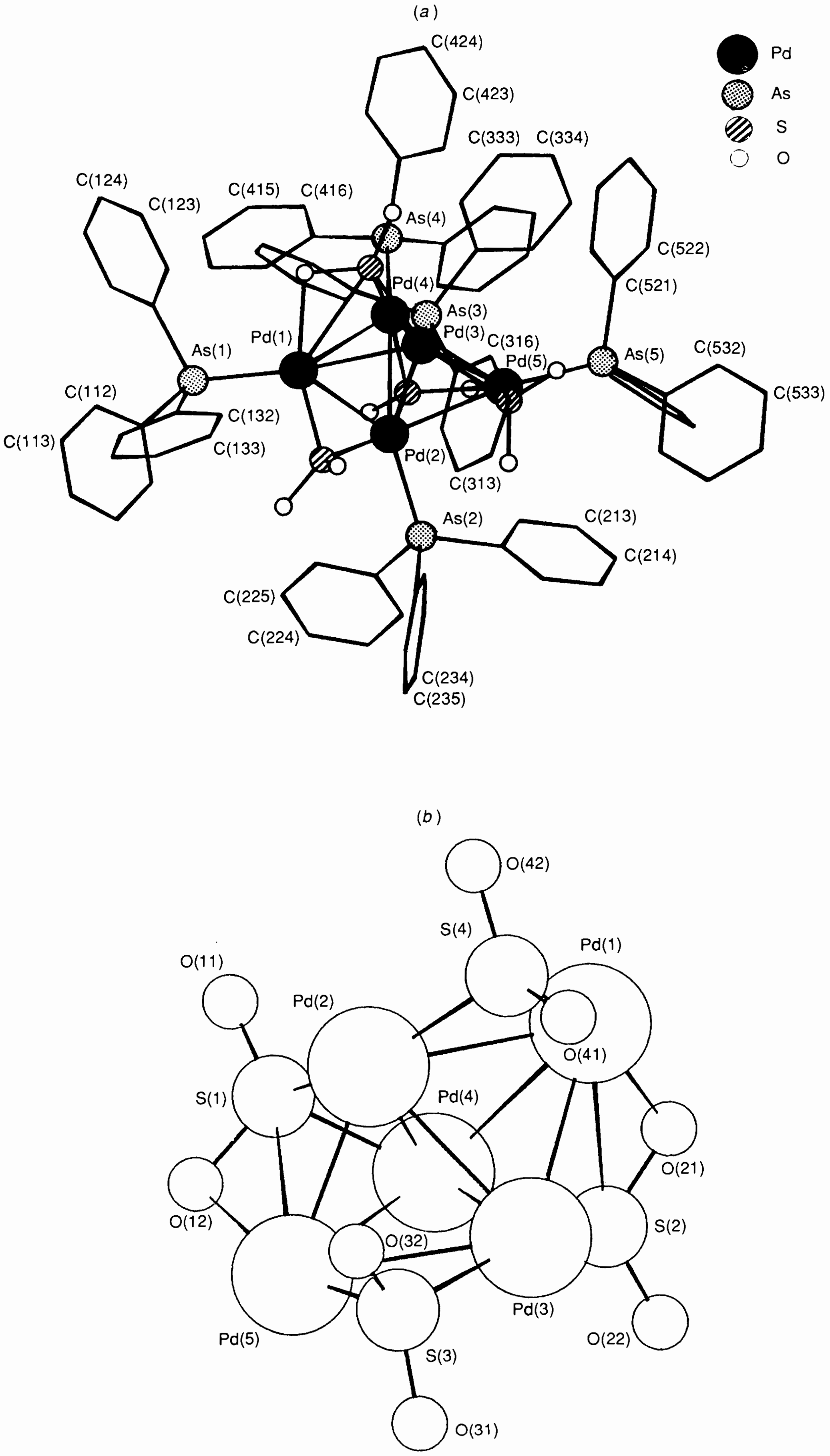


Fig. 1 The molecular geometry of compound **6**: (*a*) showing all non-hydrogen atoms; (*b*) with triphenylarsine ligands omitted for clarity

Table 1 Crystal data for compound **6***

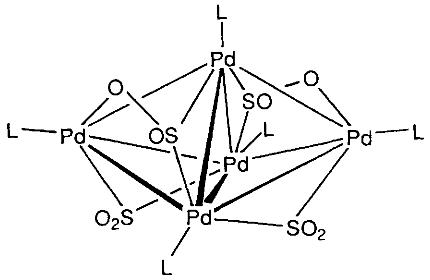
Formula	$C_{90}H_{75}As_5O_8Pd_5S_4 \cdot 0.5C_6H_6 \cdot C_4H_{10}O$
M	2319.42 (2432.60 including 0.5 benzene and ether)
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	20.845(5)
b/Å	16.217(4)
c/Å	14.610(2)
α/°	97.4(2)
β/°	99.7(2)
γ/°	86.6(2)
U/Å^3	4823.5
Z	2
D_c/g cm^{-3}	1.702
F(000)	2402
μ/cm^{-1}	27.388
Crystal colour	Dark green
Data collection	
X-radiation	Mo-Kα, λ = 0.710 69 Å
$\theta_{min}, \theta_{max}$/°	0, 24
Minimum, maximum, *h,k,l*	−23, 23; −18, 18; 0, 16
ω-scan width/°	0.6 + 0.35tanθ
horizontal aperture/mm	2.5
total data collected	19 264
total unique data	15 131
total observed data [$I > 3\sigma(I)$]	8181
merging *R* factor	0.0366
Absorption correction	ψ-scan profile; minimum/maximum corrections, 1.00, 1.35
Final *R*	0.0411
Final *R′*	0.0472

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \{\Sigma[w(|F_o| - |F_w|)^2]/\Sigma(w|F_o|^2)\}^{\frac{1}{2}}$.

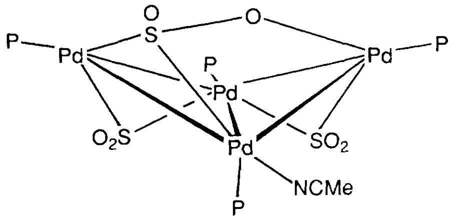
X-Ray Crystallographic Analysis.—The structure of compound **6** was confirmed by a single-crystal X-ray crystallographic investigation (details of which are summarised in Table 1). The relevant atomic coordinates and bond lengths and angles are summarised in Tables 2 and 3. The cluster is illustrated in Fig. 1(*a*) and the important structural features are emphasised in Fig. 1(*b*). The five palladium atoms form a distorted trigonal bipyramid. Distances within the equatorial triangle are Pd(2)–Pd(3) 2.929(1), Pd(2)–Pd(4) 2.832(1) and Pd(3)–Pd(4) 2.825(1) Å. The longest distance is associated with the metal–metal bond which is not bridged by a SO_2 ligand. Palladium–palladium distances between equatorial and apical atoms show a much greater range, and demonstrate some distortion from a regular trigonal bipyramid towards a square-based pyramid. The distances between Pd(4) and the apical palladium atoms Pd(1) and Pd(5) are 3.177(1) and 3.096(1) Å respectively. These are considerably longer than the other equatorial–apical bonds which average 2.89 Å. However, they are very much shorter than the equivalent distances found in the related compound $[Pd_5(SO_2)_4(PMe_3)_5]$ which average 3.410(5) Å.[22] The non-bridged equatorial distance is also longer in this compound, at 3.026(5) Å. This difference in the structures is associated with the electronic nature of the terminal ligands. The ligand $AsPh_3$ is a better π acceptor than PMe_3, and consequently is better at stabilising the metal orbitals. This leads to $[Pd_5(SO_2)_4(AsPh_3)_5]$ having a more symmetrical structure, typical for nickel clusters, whereas in contrast $[Pd_5(SO_2)_4(PMe_3)_5]$ has a distorted structure, more typical of platinum cluster compounds.

The Pd–Pd bond lengths in structurally characterised palladium clusters vary from 2.576(1) to 3.026(5) Å, although contacts as long as 3.138(5)[23] and 3.178 Å[5] have been proposed to represent bonded distances. These are considerably longer than the Pd–Pd distance in palladium metal, which is 2.745 Å.[24] This suggests that these cases and the long Pd–Pd contacts in **6** involve relatively weak palladium–palladium interactions.

There are two μ-SO_2 and two μ_3-SO_2 ligands co-ordinated to the Pd_5 core. Two of the equatorial–apical edges are bridged by μ-SO_2 ligands. Both of these groups are unsymmetrical with S–Pd_{apical} distances shorter than S–$Pd_{equatorial}$ by 0.183 and 0.203 Å respectively. Two of the triangular metal faces are capped by μ_3-SO_2 ligands. These groups have short Pd–S contacts between two equatorial Pd atoms, and considerably longer contacts to the apical Pd atoms [2.834(3) and 2.866(3) Å]. Short contacts are made to the apical Pd atoms through a lone pair on an oxygen atom of the SO_2. These distances, Pd(1)–O(21) 2.245(8) and Pd(5)–O(12) 2.311(7) Å, are slightly but not significantly longer than those in $[Pd_5(SO_2)_4(PMe_3)_5]$ which are 2.18(3) and 2.22(3) Å respectively.



This mode of SO_2 co-ordination has previously been observed in the cluster compounds $[Rh_4(\mu\text{-}CO)_4(\mu\text{-}SO_2)(\mu_3\text{-}SO_2)_2\{P(OPh)_3\}_4]$[25] and $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$,[26] the structure of which is illustrated below, but has not been observed in platinum and iridium cluster compounds.



This suggests that this bridging mode is of considerable importance in the chemistry of SO_2 cluster compounds of palladium and rhodium. The μ_3-SO_2 ligands are acting as four-electron donors, so consequently the total number of valence electrons in this series of pentapalladium clusters is 72. This electron count is that predicted for trigonal-bipyramidal clusters by the polyhedral skeletal electron-pair theory.[27]

The research described in this paper has demonstrated that the $[Pd_5(SO_2)_4L_5]$ structure occurs for a large range of phosphines with differing sizes and electronic properties, from PMe_3 with a cone angle of 118° to PPh_3 with a cone angle of 145°.[28] The unusual stability of this cluster is probably connected to the μ_3-SO_2 co-ordination mode. There does, however, exist an upper limit to phosphine size, above which the Pd_5 structure becomes sterically disfavoured. The phosphine $P(C_6H_{11})_3$ has a cone angle of 170°, and has been shown to give only the tetranuclear product $[Pd_4(SO_2)_3\{P(C_6H_{11})_3\}_4]$.[22]

Spectroscopic Characterisation of the Compounds.—Compounds **1**–**5** were characterised on the basis of $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopic data; **1** was also characterised by FAB (fast atom bombardment) mass spectroscopy. The $^{31}P\text{-}\{^1H\}$ NMR data are summarised in Table 4.

All the pentapalladium phosphine cluster compounds have a $^{31}P\text{-}\{^1H\}$ NMR spectrum consisting of a singlet, a doublet and a triplet in the intensity ratio 2:2:1. Coupling is only observed between the phosphorus atoms on the unique equatorial

Table 2 Final fractional coordinates (× 10^4) for non-hydrogen atoms of compound **6** with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	1 467.3(4)	7 405.3(6)	4 238.3(6)	C(236)	2 781(4)	10 722(5)	3 344(6)
Pd(2)	2 806.1(4)	7 582.7(5)	4 069.1(6)	C(311)	971(4)	8 406(5)	728(6)
Pd(3)	1 857.4(4)	7 034.0(5)	2 415.2(6)	C(312)	1 235(5)	9 082(6)	1 281(5)
Pd(4)	2 430.0(4)	5 907.5(5)	3 666.4(6)	C(313)	1 238(5)	9 843(5)	968(8)
Pd(5)	3 297.8(4)	6 721.4(6)	2 537.3(6)	C(314)	985(6)	9 917(5)	54(9)
As(1)	1 002.7(6)	7 643.7(8)	5 676.2(8)	C(315)	760(5)	9 270(7)	−515(6)
As(2)	3 664.6(5)	8 600.5(7)	4 441.3(9)	C(316)	729(5)	8 480(6)	−202(6)
As(3)	931.0(5)	7 394.6(8)	1 247.9(8)	C(321)	62(5)	7 530(7)	1 583(8)
As(4)	2 576.3(5)	4 462.4(7)	3 919.1(8)	C(322)	−132(5)	7 089(6)	2 152(8)
As(5)	3 949.9(5)	6 034.9(8)	1 434.4(8)	C(323)	−761(6)	7 158(8)	2 373(8)
S(1)	3 383(1)	6 418(2)	4 422(2)	C(324)	−1 186(5)	7 669(9)	2 000(10)
S(2)	1 404(1)	5 969(2)	2 863(2)	C(325)	−998(6)	8 135(8)	1 450(10)
S(3)	2 666(1)	7 544(2)	1 692(2)	C(326)	−377(7)	8 063(8)	1 243(9)
S(4)	1 961(1)	8 549(2)	4 329(2)	C(331)	798(5)	6 568(6)	178(6)
O(7)	7 610(7)	8 686(8)	3 140(10)	C(332)	1 293(4)	6 291(8)	−268(7)
O(11)	3 630(4)	6 400(5)	5 400(5)	C(333)	1 236(6)	5 690(8)	−1 050(8)
O(12)	3 867(3)	6 133(5)	3 807(5)	C(334)	674(7)	5 345(6)	−1 339(7)
O(21)	1 009(3)	6 195(5)	3 625(6)	C(335)	187(6)	5 602(8)	−915(9)
O(22)	1 093(4)	5 385(5)	2 118(6)	C(336)	248(4)	6 199(8)	−147(8)
O(31)	2 555(4)	7 285(6)	690(6)	C(411)	2 463(4)	4 294(5)	5 171(4)
O(32)	2 907(4)	8 372(5)	1 961(7)	C(412)	2 161(4)	4 933(4)	5 680(5)
O(41)	1 597(4)	9 032(5)	3 633(7)	C(413)	2 051(4)	4 857(5)	6 590(5)
O(42)	2 146(4)	9 022(5)	5 248(6)	C(414)	2 248(4)	4 146(6)	6 963(4)
C(71)	6 960(10)	8 730(10)	1 940(10)	C(415)	2 556(4)	3 506(5)	6 471(6)
C(72)	7 330(10)	9 430(10)	2 680(10)	C(416)	2 667(4)	3 577(4)	5 573(6)
C(73)	7 840(8)	8 980(10)	4 060(10)	C(421)	2 025(4)	3 669(4)	3 077(5)
C(74)	8 265(9)	8 450(10)	4 540(10)	C(422)	1 929(4)	3 730(5)	2 138(6)
C(111)	539(6)	8 664(7)	6 062(7)	C(423)	1 557(5)	3 175(6)	1 517(5)
C(112)	−65(6)	8 718(7)	6 224(9)	C(424)	1 296(4)	2 533(5)	1 812(7)
C(113)	−363(5)	9 470(10)	6 494(9)	C(425)	1 395(4)	2 468(5)	2 766(7)
C(114)	−84(8)	10 143(7)	6 633(9)	C(426)	1 750(4)	3 034(5)	3 391(5)
C(115)	549(8)	10 121(7)	6 530(10)	C(431)	3 440(3)	3 972(5)	3 841(5)
C(116)	843(5)	9 368(9)	6 230(10)	C(432)	3 944(4)	4 205(4)	4 544(5)
C(121)	378(3)	6 815(5)	5 715(6)	C(433)	4 569(3)	3 863(5)	4 502(5)
C(122)	−81(4)	6 645(6)	4 924(5)	C(434)	4 687(3)	3 307(5)	3 736(6)
C(123)	−549(4)	6 086(6)	4 886(6)	C(435)	4 187(4)	3 079(5)	3 053(5)
C(124)	−568(4)	5 676(5)	5 625(8)	C(436)	3 563(3)	3 416(5)	3 082(5)
C(125)	−139(5)	5 825(6)	6 405(7)	C(511)	4 819(3)	5 647(5)	1 947(5)
C(126)	347(4)	6 391(6)	6 460(5)	C(512)	4 893(3)	5 168(5)	2 672(5)
C(131)	1 672(3)	7 531(6)	6 743(5)	C(513)	5 511(4)	4 906(5)	3 075(5)
C(132)	2 270(4)	7 166(6)	6 607(5)	C(514)	6 050(3)	5 130(5)	2 766(6)
C(133)	2 751(3)	7 063(6)	7 350(7)	C(515)	5 980(3)	5 614(5)	2 059(6)
C(134)	2 642(4)	7 318(8)	8 242(5)	C(516)	5 369(3)	5 874(5)	1 630(5)
C(135)	2 073(5)	7 703(9)	8 393(5)	C(521)	3 555(4)	5 044(4)	778(6)
C(136)	1 576(4)	7 807(8)	7 650(6)	C(522)	3 895(3)	4 305(5)	569(6)
C(211)	4 409(3)	8 373(5)	3 785(6)	C(523)	3 608(5)	3 605(4)	123(7)
C(212)	4 797(4)	7 648(4)	3 930(5)	C(524)	2 586(3)	4 318(7)	3(8)
C(213)	5 327(4)	7 473(5)	3 467(7)	C(525)	2 925(5)	3 626(5)	−181(7)
C(214)	5 483(4)	7 997(6)	2 899(7)	C(526)	2 902(4)	5 057(5)	469(7)
C(215)	5 116(5)	8 705(5)	2 760(6)	C(531)	4 145(4)	6 642(5)	475(5)
C(216)	4 575(4)	8 900(4)	3 219(6)	C(532)	4 202(4)	6 249(4)	−416(5)
C(221)	4 074(4)	8 739(5)	5 748(4)	C(533)	4 421(5)	6 681(6)	−1 046(5)
C(222)	4 734(4)	8 884(5)	6 001(6)	C(534)	4 572(5)	7 489(6)	−807(7)
C(223)	5 006(3)	9 027(6)	6 937(7)	C(535)	4 498(5)	7 887(4)	70(8)
C(224)	4 612(5)	9 016(6)	7 592(5)	C(536)	4 277(5)	7 464(5)	705(5)
C(225)	3 961(5)	8 843(7)	7 345(5)	C(601)	3 940(10)	1 030(20)	350(20)
C(226)	3 695(3)	8 683(6)	6 412(6)	C(602)	3 460(10)	1 470(10)	780(20)
C(231)	3 428(4)	9 747(3)	4 244(5)	C(603)	2 950(10)	1 050(20)	1 020(10)
C(232)	2 946(4)	9 902(4)	3 515(5)	C(604)	2 940(10)	190(20)	830(20)
C(233)	3 743(3)	10 403(5)	4 788(5)	C(605)	3 420(10)	−260(10)	400(20)
C(234)	3 133(5)	11 389(4)	3 896(7)	C(606)	3 920(10)	160(20)	160(10)
C(235)	3 591(4)	11 225(4)	4 601(6)				

palladium and those on the other equatorial palladium atoms. No coupling is observed between the unique phosphorus atom and those on the apical palladium atoms, probably due to the long Pd–Pd contacts (assuming the structure is the same as **6**), and also between the non-unique equatorial phosphorus atoms and those on the apical palladium atoms. This could arise because these Pd–P bonds are almost perpendicular. The low-temperature ^{31}P-{^{1}H} NMR spectrum of **7** also shows the singlet–doublet–triplet pattern. In all cases (*i.e.* **1**–**5** and **7**) ^{3}J(P^{3,4}–P^{5}) = 29 Hz, suggesting the compounds are isostructural in solution.

The room-temperature spectrum of complex **3** is broad and the sample needs to be cooled to 273 K to resolve the pattern and obtain the relevant coupling constant. The exchange process responsible for this broadening becomes faster on decreasing the size of the phosphine. The possibility of

Table 3 Selected bond lengths (Å) and angles (°) for compound **6**

Pd(1)–Pd(2)	2.877(1)	Pd(2)–Pd(5)	2.794(1)	Pd(4)–Pd(5)	3.096(1)	S(1)–O(11)	1.438(7)
Pd(1)–Pd(3)	2.894(1)	Pd(2)–As(2)	2.451(1)	Pd(4)–As(4)	2.413(1)	S(1)–O(12)	1.476(7)
Pd(1)–Pd(4)	3.177(1)	Pd(2)–S(1)	2.250(3)	Pd(4)–S(1)	2.251(3)	S(2)–O(21)	1.489(8)
Pd(1)–As(1)	2.435(1)	Pd(2)–S(4)	2.335(3)	Pd(4)–S(2)	2.262(3)	S(2)–O(22)	1.438(8)
Pd(1)–S(2)	2.866(3)	Pd(3)–Pd(4)	2.825(1)	Pd(5)–As(5)	2.404(1)	S(3)–O(31)	1.453(9)
Pd(1)–S(4)	2.152(3)	Pd(3)–Pd(5)	2.995(1)	Pd(5)–S(1)	2.834(3)	S(3)–O(32)	1.443(9)
Pd(1)–O(21)	2.245(8)	Pd(3)–As(3)	2.449(1)	Pd(5)–S(3)	2.171(3)	S(4)–O(41)	1.449(8)
Pd(2)–Pd(3)	2.929(1)	Pd(3)–S(2)	2.236(3)	Pd(5)–O(12)	2.311(7)	S(4)–O(42)	1.460(8)
Pd(2)–Pd(4)	2.832(1)	Pd(3)–S(3)	2.374(3)				
Pd(3)–Pd(1)–Pd(2)	61.00(3)	S(1)–Pd(2)–As(2)	100.55(8)	As(4)–Pd(4)–Pd(2)	151.38(5)	Pd(4)–S(1)–Pd(2)	77.98(8)
Pd(4)–Pd(1)–Pd(2)	55.51(3)	S(4)–Pd(2)–Pd(1)	47.37(8)	As(4)–Pd(4)–Pd(3)	145.22(5)	Pd(5)–S(1)–Pd(2)	65.49(7)
Pd(4)–Pd(1)–Pd(3)	55.22(3)	S(4)–Pd(2)–Pd(3)	81.37(8)	As(4)–Pd(4)–Pd(5)	122.08(4)	Pd(5)–S(1)–Pd(4)	74.02(8)
As(1)–Pd(1)–Pd(2)	126.41(5)	S(4)–Pd(2)–Pd(4)	114.70(8)	S(1)–Pd(4)–Pd(1)	99.79(7)	O(11)–S(1)–Pd(2)	115.0(3)
As(1)–Pd(1)–Pd(3)	172.51(5)	S(4)–Pd(2)–Pd(5)	137.55(9)	S(1)–Pd(4)–Pd(2)	50.99(7)	O(11)–S(1)–Pd(4)	125.3(4)
As(1)–Pd(1)–Pd(4)	126.45(5)	S(4)–Pd(2)–As(2)	95.11(8)	S(1)–Pd(4)–Pd(3)	107.91(7)	O(11)–S(1)–Pd(5)	160.7(4)
S(2)–Pd(1)–Pd(2)	89.88(6)	S(4)–Pd(2)–S(1)	149.3(1)	S(1)–Pd(4)–Pd(5)	61.64(7)	O(12)–S(1)–Pd(2)	114.6(3)
S(2)–Pd(1)–Pd(3)	45.67(6)	Pd(2)–Pd(3)–Pd(1)	59.22(3)	S(1)–Pd(4)–As(4)	101.33(8)	O(12)–S(1)–Pd(4)	105.7(3)
S(2)–Pd(1)–Pd(4)	43.59(6)	Pd(4)–Pd(3)–Pd(1)	67.49(3)	S(2)–Pd(4)–Pd(1)	60.87(8)	O(12)–S(1)–Pd(5)	54.4(3)
S(2)–Pd(1)–As(1)	129.19(7)	Pd(4)–Pd(3)–Pd(2)	58.93(3)	S(2)–Pd(4)–Pd(2)	105.01(8)	O(12)–S(1)–O(11)	113.7(4)
S(4)–Pd(1)–Pd(2)	52.96(8)	Pd(5)–Pd(3)–Pd(1)	112.41(3)	S(2)–Pd(4)–Pd(3)	50.67(7)	Pd(3)–S(2)–Pd(1)	67.82(8)
S(4)–Pd(1)–Pd(3)	85.26(9)	Pd(5)–Pd(3)–Pd(2)	56.26(3)	S(2)–Pd(4)–Pd(5)	106.33(8)	Pd(4)–S(2)–Pd(1)	75.54(8)
S(4)–Pd(1)–Pd(4)	108.20(8)	Pd(3)–Pd(3)–Pd(4)	64.20(3)	S(2)–Pd(4)–As(4)	102.60(8)	Pd(4)–S(2)–Pd(3)	77.81(9)
S(4)–Pd(1)–As(1)	100.32(9)	As(3)–Pd(3)–Pd(1)	107.68(4)	S(2)–Pd(4)–S(1)	156.0(1)	O(21)–S(2)–Pd(1)	50.8(3)
S(4)–Pd(1)–S(2)	130.5(1)	As(3)–Pd(3)–Pd(2)	148.03(5)	Pd(3)–Pd(5)–Pd(2)	60.68(3)	O(21)–S(2)–Pd(3)	115.3(3)
O(21)–Pd(1)–Pd(2)	117.6(2)	As(3)–Pd(3)–Pd(4)	147.73(5)	Pd(4)–Pd(5)–Pd(2)	57.20(3)	O(21)–S(2)–Pd(4)	102.3(3)
O(21)–Pd(1)–Pd(3)	75.0(2)	As(3)–Pd(3)–Pd(5)	137.92(5)	Pd(4)–Pd(5)–Pd(3)	55.23(3)	O(22)–S(2)–Pd(1)	155.6(4)
O(21)–Pd(1)–Pd(4)	63.5(2)	S(2)–Pd(3)–Pd(1)	66.50(8)	As(5)–Pd(5)–Pd(2)	167.32(5)	O(22)–S(2)–Pd(3)	115.6(4)
O(21)–Pd(1)–As(1)	99.0(2)	S(2)–Pd(3)–Pd(2)	102.70(8)	As(5)–Pd(5)–Pd(3)	132.00(5)	O(22)–S(2)–Pd(4)	128.7(4)
O(21)–Pd(1)–S(2)	30.9(2)	S(2)–Pd(3)–Pd(4)	51.52(7)	As(5)–Pd(5)–Pd(4)	127.60(5)	O(22)–S(2)–O(21)	112.9(5)
O(21)–Pd(1)–S(4)	159.9(2)	S(2)–Pd(3)–Pd(5)	110.44(8)	S(1)–Pd(5)–Pd(2)	47.12(6)	Pd(5)–S(3)–Pd(3)	82.3(1)
Pd(3)–Pd(2)–Pd(1)	59.78(3)	S(2)–Pd(3)–As(3)	96.62(8)	S(1)–Pd(5)–Pd(3)	89.85(6)	O(31)–S(3)–Pd(3)	110.9(4)
Pd(4)–Pd(2)–Pd(1)	67.63(3)	S(3)–Pd(3)–Pd(1)	133.99(8)	S(1)–Pd(5)–Pd(4)	44.34(6)	O(31)–S(3)–Pd(5)	115.9(4)
Pd(4)–Pd(2)–Pd(3)	58.70(3)	S(3)–Pd(3)–Pd(2)	79.80(8)	S(1)–Pd(5)–As(5)	125.78(7)	O(32)–S(3)–Pd(3)	122.1(4)
Pd(5)–Pd(2)–Pd(1)	119.32(4)	S(3)–Pd(3)–Pd(4)	110.11(8)	S(3)–Pd(5)–Pd(2)	86.39(8)	O(32)–S(3)–Pd(5)	107.1(4)
Pd(5)–Pd(2)–Pd(3)	63.06(3)	S(3)–Pd(3)–Pd(5)	45.91(7)	S(3)–Pd(5)–Pd(3)	51.77(8)	O(32)–S(3)–O(31)	114.5(6)
Pd(5)–Pd(2)–Pd(4)	66.76(3)	S(3)–Pd(3)–As(3)	95.95(8)	S(3)–Pd(t)–Pd(4)	107.00(8)	Pd(2)–S(4)–Pd(1)	79.7(1)
As(2)–Pd(2)–Pd(1)	141.07(5)	S(3)–Pd(3)–S(2)	149.9(1)	S(3)–Pd(5)–As(5)	101.81(9)	O(41)–S(4)–Pd(1)	107.3(4)
As(2)–Pd(2)–Pd(3)	135.45(5)	Pd(2)–Pd(4)–Pd(1)	56.87(3)	S(3)–Pd(5)–S(1)	132.4(1)	O(41)–S(4)–Pd(2)	125.1(4)
As(2)–Pd(2)–Pd(4)	149.82(4)	Pd(3)–Pd(4)–Pd(1)	57.29(3)	O(12)–Pd(5)–Pd(2)	75.9(2)	O(42)–S(4)–Pd(1)	118.7(4)
As(2)–Pd(2)–Pd(5)	94.83(4)	Pd(3)–Pd(4)–Pd(2)	62.36(3)	O(12)–Pd(5)–Pd(3)	118.9(2)	O(42)–S(4)–Pd(2)	108.0(4)
S(1)–Pd(2)–Pd(1)	109.18(7)	Pd(5)–Pd(4)–Pd(1)	102.54(3)	O(12)–Pd(5)–Pd(4)	65.7(2)	O(42)–S(4)–O(41)	114.3(6)
S(1)–Pd(2)–Pd(3)	104.59(7)	Pd(5)–Pd(4)–Pd(2)	56.02(3)	O(12)–Pd(5)–As(5)	95.2(2)	S(1)–O(12)–Pd(5)	94.3(3)
S(1)–Pd(2)–Pd(4)	51.03(7)	Pd(5)–Pd(4)–Pd(3)	60.56(3)	O(12)–Pd(5)–S(1)	31.3(2)	S(2)–O(21)–Pd(1)	98.2(4)
S(1)–Pd(2)–Pd(5)	67.39(7)	As(4)–Pd(4)–Pd(1)	135.38(5)	O(12)–Pd(5)–S(3)	162.1(2)		

Table 4 ^{31}P-$\{^1H\}$ NMR data for compounds **1**–**5***

	$\delta(^{31}P)$		
Compound	$P^{1,2}$	$P^{3,4}$	P^5
1	19.0	19.3	10.7
2	3.0	4.5	−6.5
3	−11.7	−11.5	−21.3
4	16.3	16.2	6.6
5	16.3	16.2	6.6

* All δ values referenced against trimethyl phosphate in D_2O; $^3J(P^{3,4}$–$P^5)$ = 29 Hz in each case. Samples run in CD_2Cl_2 and spectra recorded at room temperature except for complex **3** which was recorded at 273 K

establishing whether it involved phosphine dissociation could not be established directly because the clusters react with free phosphine. In order to determine whether the fluxionality is inter- or intra-molecular an equimolar mixture of **1** and **3** was stirred for 1 h. The ^{31}P-$\{^1H\}$ NMR spectrum after this time showed the presence of additional peaks as well as those for **1** and **3**, showing that phosphine exchange had occurred. Similarly, a mixture of **1** and **6** shows more complex signals at δ 19 and 11 than the simple singlet, doublet and triplet pattern of **1**, again demonstrating that exchange has occurred between the phosphine and arsine ligands, even though **1** is not fluxional on the NMR time-scale. These experiments provide good evidence for the intermolecular exchange process involving phosphine dissociation.

The IR spectra of complexes **1**–**6** show the presence of three or four bands that can be assigned to the SO_2 ligands. The strongest band is between 1059 and 1066 cm⁻¹, and in the case of **2** and **3** this is split into two bands. There are also two bands at around 1200 cm⁻¹, separated by 20 cm⁻¹. In the case of **4** and **5** the lower-wavenumber band appears only as a shoulder on the phosphine absorption.

A FAB mass spectrum has also been recorded for compound **1**. It is shown in Fig. 2, and the major peak assignments are given in Table 5. The spectrum shows that **1** readily loses SO_2 under FAB conditions. Although the M^+ peak is observed at m/z = 2100, it is low in intensity with respect to $[M - 2SO_2]^+$ at m/z = 1972. The highest-intensity peak is that at m/z = 1581, due to the $[M - 4SO_2 - PPh_3]^+$ ion. After loss of the SO_2 ligands, first phenyl groups, then whole triphenylphosphine ligands are lost from the Pd_5 core, and indeed the bare Pd_5^+ cluster is observed at m/z = 533. Similar results have been observed for gold phosphine clusters such as $[Au_6Pt(PPh_3)_7]^{2+}$ and $[Au_6(PPh_3)_6]^{2+}$.[29] Concurrent with the loss of PPh_3 is decomposition to smaller clusters by loss of Pd. For instance, the peaks at m/z = 1212 and 1137 are consistent with the

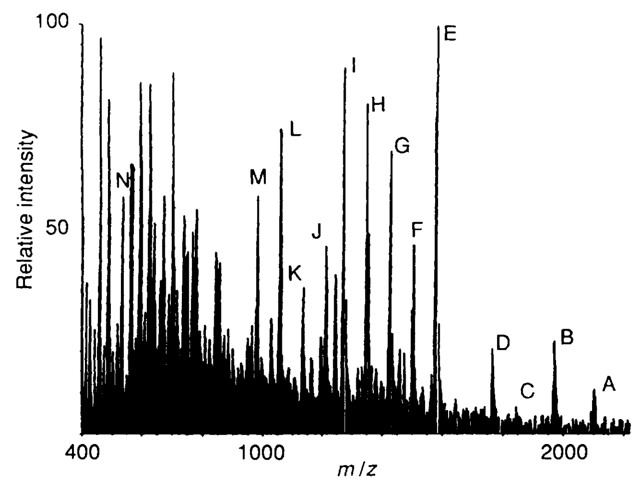


Fig. 2 The FAB mass spectrum of compound **1**

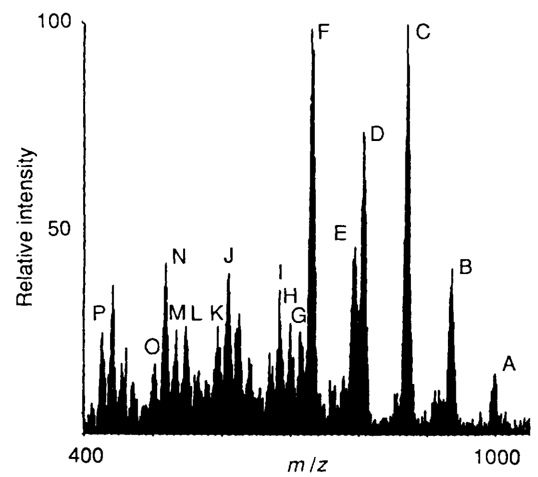


Fig. 3 The FAB mass spectrum of compound **8**

Table 5 Selected peaks in the FAB mass spectrum of [$Pd_5(SO_2)_4(PPh_3)_5$] **1**

Peak	*m/z*	Relative intensity	Assignment *
A	2100	10	M^+
B	1972	21	$[M - 2SO_2]^+$
C	1843	7	$[M - 4SO_2]^+$
D	1767	20	$[M - 4SO_2 - Ph]^+$
E	1581	100	$[M - 4SO_2 - PPh_3]^+$
F	1504	46	$[M - 4SO_2 - PPh_3 - Ph]^+$
G	1428	70	$[M - 4SO_2 - PPh_3 - 2Ph]^+$
H	1348	82	$[M - 4SO_2 - PPh_3 - 3Ph]^+$
I	1272	90	$[M - 4SO_2 - PPh_3 - 4Ph]^+$
J	1212	47	$[M - Pd - 4SO_2 - 2PPh_3]^+$
K	1137	36	$[M - Pd - 4SO_2 - 2PPh_3 - Ph]^+$
L	1058	75	$[M - 4SO_2 - 3PPh_3]^+$
M	981	59	$[M - 4SO_2 - 3PPh_3 - Ph]^+$
N	533	58	$[M - 4SO_2 - 5PPh_3]^+$

* $M = Pd_5(SO_2)_4(PPh_3)_5$.

Table 6 Selected peaks in the FAB mass spectrum of [$Pd_4(SO_2)_3(PMe_3)_5$] **8**

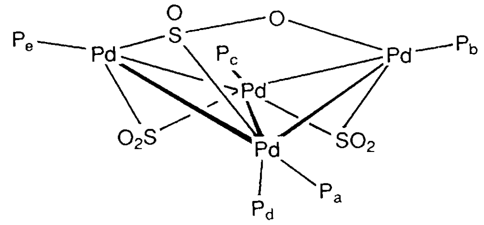
Peak	*m/z*	Relative intensity	Assignment *
A	999	15	M^+
B	936	42	$[M - SO_2]^+$
C	869	100	$[M - 2SO_2]^+$
D	805	74	$[M - 3SO_2]^+$
E	791	46	$[M - 3SO_2 - Me]^+$
F	728	98	$[M - 3SO_2 - PMe_3]^+$
G	713	25	$[M - 3SO_2 - PMe_3 - Me]^+$
H	699	27	$[M - 3SO_2 - PMe_3 - 2Me]^+$
I	683	35	$[M - 3SO_2 - PMe_3 - 3Me]^+$
J	609	40	$[M - 3SO_2 - 2PMe_3 - 3Me]^+$
K	593	26	$[M - 3SO_2 - 2PMe_3 - 4Me]^+$
L	547	26	$[M - 3SO_2 - 3PMe_3 - 2Me]^+$
M	533	25	$[M - 3SO_2 - 3PMe_3 - 3Me]^+$
N	517	42	$[M - 3SO_2 - 3PMe_3 - 4Me]^+$
O	502	17	$[M - 3SO_2 - 4PMe_3]^+$
P	426	25	$[M - 3SO_2 - 5PMe_3]^+$

* $M = Pd_4(SO_2)_3(PMe_3)_5$.

Pd_4 clusters $[Pd_4(PPh_3)_3]^+$ and $[Pd_4(PPh_3)_2(PPh_2)]^+$ respectively.

The compound [$Pd_4(SO_2)_3(PMe_3)_5$] **8** has been obtained pure from the reaction of [$Pd_2(dba)_3$]·$CHCl_3$ and PMe_3 under a SO_2 atmosphere. It has been characterised on the basis of FAB mass and ^{31}P-{^1H} NMR spectroscopy. The FAB mass spectrum is shown in Fig. 3, and the major peaks are given, together with their interpretations, in Table 6. The highest peak, at $m/z = 999$, corresponds to the molecular ion peak. The two most intense peaks are those at $m/z = 869$, corresponding to loss of two SO_2 ligands and $m/z = 728$, due to loss of all three SO_2 and one PMe_3 ligand. As with compound **1**, the peak caused by loss of all SO_2 ligands and one phosphine is very intense. Again, as with **1**, the SO_2 ligands are lost from the cluster first, then methyl fragments followed by complete phosphine ligands.

The room-temperature ^{31}P-{^1H} NMR spectrum of compound **8** shows the presence of five broad resonances, all of equal intensity. When the sample is cooled to 250 K these sharpen to a singlet, a doublet, two pairs of doublet of doublets and a doublet of doublet of doublets. The chemical shifts and coupling constants are given in Table 7, and the spectrum is shown in Fig. 4 together with a computer simulation. This spectrum shows that **8** has five phosphine groups, all in unique environments. One structure for [$Pd_4(SO_2)_3(PMe_3)_5$] consistent with the data is shown below. It is analogous to that described for [$Pd_4(SO_2)_3(MeCN)(PPh_3)_4$].[26] It is not possible, with the current information, to assign the resonances unambiguously. Comparison with the spectrum for [$Pd_5(SO_2)_4L_5$] suggests that the coupling constant will be low or unobserved between P_b and P_c, P_b and P_d, P_b and P_e and also P_c and P_e. This leads to the interpretation given in Table 7, although it is possible that the assignments for P_c and P_d should be reversed. Although all other coupling constants were set at zero for the simulation there is some evidence that this is an oversimplification. Some additional small couplings are observed on the peaks assigned to P_c and P_d. However, it was not possible to assign these coupling constants as the splittings were not resolved on all the peaks. They are all less than 5 Hz.



Compounds **1** and **3**–**6** are the only cluster products formed from the reaction between [$Pd_2(dba)_3$]·$CHCl_3$, L and SO_2. With $PMePh_2$, however, the reaction is more complex. In toluene a red product is formed which has been shown by ^{31}P-{^1H} NMR spectroscopy to be a mixture of compounds

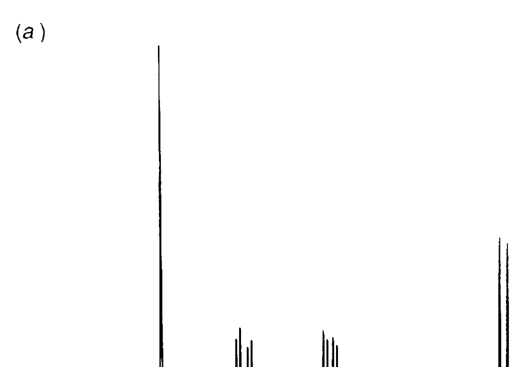


Fig. 4 Observed (*b*) and simulated (*a*) $^{31}P-\{^1H\}$ NMR spectra of compound **8**

Table 7 $^{31}P-\{^1H\}$ NMR data (J in Hz) for compounds **8** and **9**

	8	**9**
$\delta(P_a)$	−18.7 (ddd)	5.4 (ddd)
$\delta(P_b)$	−24.0 (s)	−2.5 (d)
$\delta(P_c)$	−27.4 (dd)	−3.2 (dd)
$\delta(P_d)$	−31.0 (dd)	−6.8 (dd)
$\delta(P_e)$	−38.9 (d)	−7.8 (dd)
$J(P_a-P_c)$	58	48
$J(P_a-P_e)$	39	28
$J(P_c-P_d)$	20	19
$J(P_a-P_d)$	49	47
$J(P_b-P_e)$	0	6

2 and **9**. Compound **9** is fluxional in solution at room temperature. If the sample is cooled to 253 K the spectrum sharpens to give five resonances, all of equal intensity. The chemical shifts and coupling constants are given in Table 7. This spectrum is very similar to that of **8**, and suggests that **9** is $[Pd_4(SO_2)_3(PMePh_2)_5]$. Compound **9** is not formed in the reaction between palladium acetate, SO_2, $PMePh_2$ and $NaBH_4$, so this is a better method for preparing pure samples of **2**, although the yield is considerably lower.

The reactions of these tetra- and penta-palladium cluster compounds are currently being investigated and will be described in subsequent papers.

Experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen, with dry dioxygen-free solvents. Microanalyses (C, H and N) were carried out by Mr. M. Gascoyne and his staff at this laboratory. The FAB mass spectra were recorded by Dr. J. Ballantine and staff at the SERC Mass Spectrometry Service Centre at the University of Swansea. Infrared spectra were recorded on a Perkin-Elmer FT1710 spectrometer as Nujol mulls between KBr discs, $^{31}P-\{^1H\}$ NMR spectra using a Bruker AM-300 spectrometer operating at 121.497 MHz with trimethyl phosphate in D_2O as reference. The NMR computer simulations were carried out using the Oxford University VAX computer system with a program developed by Professor R. K. Harris, then of the University of East Anglia, and adapted for use at Oxford by Dr. A. E. Derome.

The compound $[Pd_2(dba)_3]\cdot CHCl_3$ was synthesised using the method of Ukai *et al.*[30]

Syntheses.—$[Pd_5(SO_2)_4(PPh_3)_5]$ **1**. (*i*) The compound $[Pd_2(dba)_3]\cdot CHCl_3$ (0.80 g, 0.77 mmol) was dissolved in toluene (30 cm^3), and a sulfur dioxide-saturated solution of PPh_3 (0.406 g, 1.55 mmol) in toluene (10 cm^3) added. Sulfur dioxide was bubbled through the solution for 15 min. The solvent was then removed under reduced pressure and the green solid obtained washed several times with diethyl ether to remove dba. Recrystallisation from dichloromethane–ether gave dark green crystals of **1**. Yield 0.58 g (89%).

(*ii*) The compound $[Pd(MeCO_2)_2]$ (0.40 g, 1.78 mmol) and PPh_3 (0.466 g, 1.78 mmol) were dissolved in toluene (40 cm^3) and the solution saturated with SO_2. Sodium tetrahydroborate (0.034 g, 0.99 mmol) in ethanol (5 cm^3) was added with stirring, giving an immediate darkening of colour. The solution was stirred for 30 min and the solvent removed under reduced pressure. The crude product was washed with ethanol, and recrystallised from dichloromethane–hexane giving dark green crystals of compound **1**. Yield 0.36 g (48%) (Found: C, 51.8; H, 3.8. $C_{90}H_{75}O_8P_5Pd_5S_4$ requires C, 51.5; H, 3.6%); $\nu/cm^{-1}(SO_2)$ 1214m, 1194m and 1064s.

$[Pd_5(SO_2)_4(PMePh_2)_5]$ **2**. (*i*) The compound $[Pd_2(dba)_3]\cdot CHCl_3$ (0.36 g, 0.35 mmol) was dissolved in dichloromethane (50 cm^3), and a SO_2-saturated solution of $PMePh_2$ (0.139 g, 0.70 mmol) in dichloromethane (10 cm^3) added. Sulfur dioxide was bubbled through the solution for 10 min after which time the solvent was removed under reduced pressure and the red solid obtained washed several times with ether. Careful recrystallisation from dichloromethane–ether gave dark red crystals of compound **2**.

(*ii*) The compound $[Pd(MeCO_2)_2]$ (0.36 g, 1.60 mmol) and $PMePh_2$ (0.321 g, 1.60 mmol) were dissolved in toluene (40 cm^3) and the solution saturated with SO_2. Sodium tetrahydroborate (0.030 g, 0.79 mmol) in ethanol (5 cm^3) was added with stirring, giving an immediate darkening of colour. The solution was stirred for 30 min, and the solvent removed under reduced pressure. The crude product was washed with ethanol, and recrystallised from dichloromethane–hexane giving dark red crystals of compound **2**. Yield 0.20 g (35%) (Found: C, 43.6; H, 4.0. $C_{65}H_{65}O_8P_5Pd_5S_4$ requires C, 43.6; H, 3.7%); $\nu/cm^{-1}(SO_2)$ 1195m, 1179m, 1059s and 1050m. FAB mass spectrum: m/z 1790, $[M]^+$; 1454, $[M - 4SO_2 - Ph]^+$; 1332, $[M - 4SO_2 - PMePh_2]^+$.

$[Pd_5(SO_2)_4(PMe_2Ph)_5]$ **3**. (*i*) This was synthesised by the same method as for compound **1** using $[Pd_2(dba)_3]\cdot CHCl_3$ (0.40 g, 0.39 mmol) and PMe_2Ph (0.107 g, 0.77 mmol). Recrystallisation from dichloromethane–ether gave dark red crystals of compound **3**. Yield 0.17 g, (74%).

(*ii*) The compound $[Pd(MeCO_2)_2]$ (0.25 g, 1.11 mmol) and PMe_2Ph (0.15 g, 1.11 mmol) were dissolved in toluene (40 cm^3) and the solution saturated with SO_2. Sodium tetrahydroborate (0.022 g, 0.58 mmol) in ethanol (5 cm^3) was added with stirring, giving an immediate darkening in colour. The solution was stirred for 30 min, and the solvent removed under reduced pressure. The crude product was washed with cold ethanol, and recrystallised from dichloromethane–ether giving red crystals of compound **3**. Yield 0.15 g (46%) (Found: C, 32.5; H, 3.6. $C_{40}H_{55}O_8P_5Pd_5S_4$ requires C, 32.5; H, 3.7%); ν/cm^{-1}(SO_2) 1202m, 1166m, 1064s and 1055m.

$[Pd_5(SO_2)_4\{P(C_6H_4OMe\text{-}p)_3\}_5]$ **4**. This was synthesised by the same method as for compound **1** using $[Pd_2(dba)_3]\cdot CHCl_3$ (0.40 g, 0.39 mmol) and $P(C_6H_4OMe\text{-}p)_3$ (0.272 g, 0.77 mmol). Recrystallisation from dichloromethene–ether gave dark green crystals of compound **4**. Yield 0.26 g (66%) (Found: C, 48.5; H, 4.1. $C_{105}H_{105}O_8P_5Pd_5S_4\cdot CH_2Cl_2$ requires C, 48.3; H, 4.1%); ν/cm^{-1}(SO_2) 1206m and 1061s.

$[Pd_5(SO_2)_4\{P(C_6H_4OMe\text{-}m)_3\}_5]$ **5**. This was synthesised by the same method as for compound **1** using $[Pd_2(dba)_3]\cdot CHCl_3$ (0.40 g, 0.39 mmol) and $P(C_6H_4OMe\text{-}m)_3$ (0.272 g, 0.77 mmol). Recrystallisation from dichloromethane–ether gave dark green crystals of compound **5**. Yield 0.25 g (63%) (Found: C, 48.5; H, 4.2. $C_{105}H_{105}O_8P_5Pd_5S_4\cdot CH_2Cl_2$ requires C, 48.3; H, 4.1%); ν/cm^{-1}(SO_2) 1207m and 1063s.

$[Pd_5(SO_2)_4(AsPh_3)_5]$ **6**. This was prepared by the same method as for compound **1** using $[Pd_2(dba)_3]\cdot CHCl_3$ (0.50 g, 0.48 mmol) and $AsPh_3$ (0.295 g, 0.96 mmol). Recrystallisation from dichloromethene–ether gave dark green crystals of **6**. Yield 0.36 g (80%) (Found: C, 45.9; H, 3.4. $C_{90}H_{75}As_5O_8Pd_5S_4\cdot 0.5CH_2Cl_2$ requires C, 46.0; H, 3.2%); ν/cm^{-1}(SO_2) 1216m, 1196m and 1066s. FAB mass spectrum: m/z 2066, $[M - 4SO_2]^+$.

$[Pd_4(SO_2)_3(PMe_3)_5]$ **8**. The compound $[Pd_2(dba)_3]\cdot CHCl_3$ (0.40 g, 0.39 mmol) was dissolved in toluene (30 cm^3), and a sulfur dioxide-saturated solution of PMe_3 (0.059 g, 0.77 mmol) added. Sulfur dioxide was bubbled through the solution for 5 min then the mixture was stirred for 2 h. The solvent was removed under reduced pressure and the red solid obtained washed several times with ether to remove dba. Recrystallisation from tetrahydrofuran–ether gave dark red crystals of compound **8**. Yield 0.15 g (76%) (Found: C, 17.8; H, 4.4. $C_{15}H_{45}O_6P_5Pd_4S_3$ requires C, 18.0; H, 4.5%); ν/cm^{-1}(SO_2) 1177m, 1144m, 1052s and 1037s.

$[Pd_4(SO_2)_3(PMePh_2)_5]$ **9**. The compound $[Pd_2(dba)_3]\cdot CHCl_3$ (0.20 g, 0.19 mmol) was dissolved in benzene (40 cm^3) and $PMePh_2$ (0.038 g, 0.19 mmol) added. One equivalent of SO_2 gas was added, and the mixture was stirred for 8 h. Further equivalents of $PMePh_2$ (0.038 g) and SO_2 were added and the mixture stirred for 3 h. The solvent was removed under reduced pressure and the red solid obtained was washed several times with ether, and recrystallised from benzene–ether. The $^{31}P-\{^1H\}$ NMR spectrum showed this to contain 90% compound **9** and only 10% **2** (Found: C, 49.6; H, 4.1. $C_{65}H_{65}O_6P_5Pd_4S_3\cdot 0.5C_6H_6$ requires C, 49.3; H, 4.1%); ν/cm^{-1}(SO_2) 1204m, 1180m, 1055s and 1043s.

Crystal Structure Determination of $[Pd_5(SO_2)_4(AsPh_3)_5]$ **6**.—Crystals of compound **6** used in the analysis were grown by slow diffusion of ether into a benzene solution. A single crystal of dimensions 0.36 × 0.28 × 0.30 mm was mounted on a glass fibre and transferred to the goniometer head of an Enraf–Nonius CAD-4 diffractometer. The experimental details associated with the crystallographic determination are summarised in Table 1. An absorption correction based on azimuthal scans of the crystal was applied to the data (minimum/maximum corrections 1.00, 1.35).

The positions of the five palladium atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located in subsequent Fourier difference syntheses.[31,32] The hydrogen atoms were included in idealised positions. All non-hydrogen atoms except the badly disordered diethyl ether and the half-occupancy benzene solvate molecules were assigned anisotropic thermal parameters in the final cycles of least-squares refinement which converged at R 0.0411 and R' 0.0472 (unit weights).

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