Substitution and Fragmentation Reactions of Pentapalladium Cluster Compounds†

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The reactions of the pentapalladium cluster compounds $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$ [L = PPh_3, $P(C_6H_4OMe\text{-}p)_3$ or PMe_2Ph] with carbon monoxide and xylyl isocyanide are discussed. In the reaction with CO the structure of the reaction product is dependent on the nature of the phosphine. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PR_3)_5]$ reacts to give $[Pd_5(SO_2)_2(CO)_2(PR_3)_5]$ (R = Ph **1a** or $C_6H_4OMe\text{-}p$ **1b**) whereas $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ reacts to give $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2**. The molecular structure of **2** has been determined by a single-crystal X-ray diffraction study. It consists of an edge-bridged tetrahedron of palladium atoms with three edges bridged by sulfur dioxide ligands and two faces capped by carbon monoxide ligands. Both capping CO ligands are asymmetric, one so much so that it is best regarded as an edge-bridging carbonyl. Each palladium atom also carries a terminal phosphine ligand. The identities of **1a** and **1b** were confirmed by $^{31}P\text{-}\{^1H\}$-NMR spectroscopy and fast atom bombardment mass spectrometry. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ reacts with xylyl isocyanide to give the *triangulo*-palladium compound $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**. The molecular structure of **3** has been determined by a single-crystal X-ray diffraction study. It is based on a triangle of palladium atoms with Pd–Pd distances between 2.7369(4) and 2.7947(4) Å, within the previously observed range for 44-electron tripalladium cluster compounds.

The reaction of cluster compounds with molecules such as carbon monoxide or xylyl isocyanide (2,6-dimethylphenyl isocyanide, CNC_8H_9) can lead to substitution of some or all of the ligands. For example, the *triangulo*-platinum cluster compound $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ reacts with 1 equivalent of carbon monoxide to give $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}CO)\{P(C_6H_{11})_3\}_3]$ and with an excess of carbon monoxide to give $[Pt_3(\mu\text{-}SO_2)(\mu\text{-}CO)_2\{P(C_6H_{11})_3\}_3]$.[1] Trimethylamine *N*-oxide needs to be added to facilitate the removal of the final sulfur dioxide ligand and give the compound $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$.[2] Reaction of $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_3]$ with CNC_8H_9 gives the 44-electron *triangulo* cluster $[Pt_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2\{P(C_6H_{11})_3\}_3]$ with 2 equivalents of isocyanide and the dimer $[Pt_2(\mu\text{-}SO_2)(CNC_8H_9)_2\{P(C_6H_{11})_3\}_2]$ with 3 equivalents of isocyanide.[3] This is in contrast to the reaction of xylyl isocyanide with $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ which gives two 42-electron *triangulo*-cluster compounds with phosphine replacement: $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)\{P(C_6H_{11})_3\}_2]$ with 3 equivalents of CNC_8H_9 and $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_2\{P(C_6H_{11})_3\}]$ with 5 equivalents of CNC_8H_9.[4]

In palladium cluster chemistry reactions with carbon monoxide have been shown in some cases to lead to a reversible addition which can occur with a change in the metal geometry. The 58-electron compound $[Pd_4(\mu\text{-}CO)_5(PBu_3)_4]$ has a butterfly geometry and adds CO to give the tetrahedral cluster $[Pd_4(\mu\text{-}CO)_6(PBu_3)_4]$.[5] A similar change has been postulated in the conversion of $[Pd_4(\mu\text{-}CO)_2(\mu\text{-}I)_2(PPh_3)_4]$ into $[Pd_4(\mu\text{-}CO)_3(\mu\text{-}I)_2(PPh_3)_4]$.[6]

Recently, we reported the synthesis of a series of compounds of the general type $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$ (L = phosphine or arsine).[7] This paper investigates the reaction of these compounds with carbon monoxide and xylyl isocyanide.

Results and Discussion

Reactions with CO.—When CO was bubbled through a dichloromethane solution of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PR_3)_5]$ (R = Ph or $C_6H_4OMe\text{-}p$) the colour of the solution changed from green-red dichroic to red. Removal of the solvent under reduced pressure followed by recrystallisation from dichloromethane–diethyl ether gave dark red crystals that analysed correctly for $[Pd_5(SO_2)_2(CO)_2(PR_3)_5]$ (R = Ph **1a** or $C_6H_4OMe\text{-}p$ **1b**). Confirmation of this formulation was obtained by IR and $^{31}P\{^1H\}$ NMR spectroscopy and fast atom bombardment (FAB) mass spectrometry. In contrast to this, when CO was bubbled through a dichloromethane solution of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ the colour of the solution rapidly lightened to orange. Removal of the solvent under reduced pressure, followed by recrystallisation from dichloromethane–diethyl ether, gave a good yield of red crystals which analysed for $[Pd_5(SO_2)_3(CO)_2(PMe_2Ph)_5]$ **2**. This formulation was confirmed by IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, FAB mass spectrometry and an X-ray single-crystal analysis.

The IR spectra of compounds **1a** and **1b** showed the presence of both bridging carbonyl and sulfur dioxide ligands. For **1a** ν(CO) was observed at 1828(br) cm^{-1} and $\nu(SO_2)$ at 1190m and 1054s cm^{-1}; for compound **1b** ν(CO) was observed at 1824(br) cm^{-1} and $\nu(SO_2)$ at 1050s cm^{-1}. The location of the second band due to the $\nu(SO_2)$ stretching mode in the latter case was prevented by the strong absorption associated with the phosphine ligands. The carbonyl absorptions in both cases were consistent with μ-CO ligands.

The FAB mass spectra have been obtained for both compounds **1a** (Fig. 1) and **1b** (Fig. 2) and the results are summarised in Tables 1 and 2 respectively. Both compounds had weak but well defined peaks due to $[M]^+$. They showed similar decomposition pathways, with rapid loss of SO_2 and CO, followed by loss of fragments of phosphine ligands, then complete phosphine ligands. Series of peaks, spaced by approximately 77 and 107 *m/z* units, correspond to consecutive loss of phenyl and *p*-methoxyphenyl fragments respectively. The ionic species observed in the mass spectra are similar to those observed in the spectrum of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ suggesting the compounds have related molecular structures.[7]

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

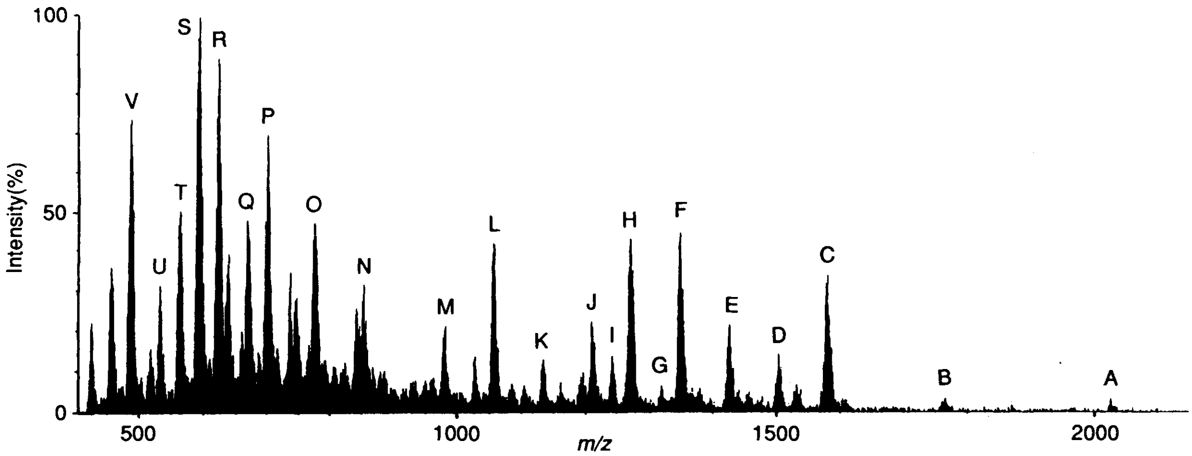


Fig. 1 The FAB mass spectrum of $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5]$ **1a**

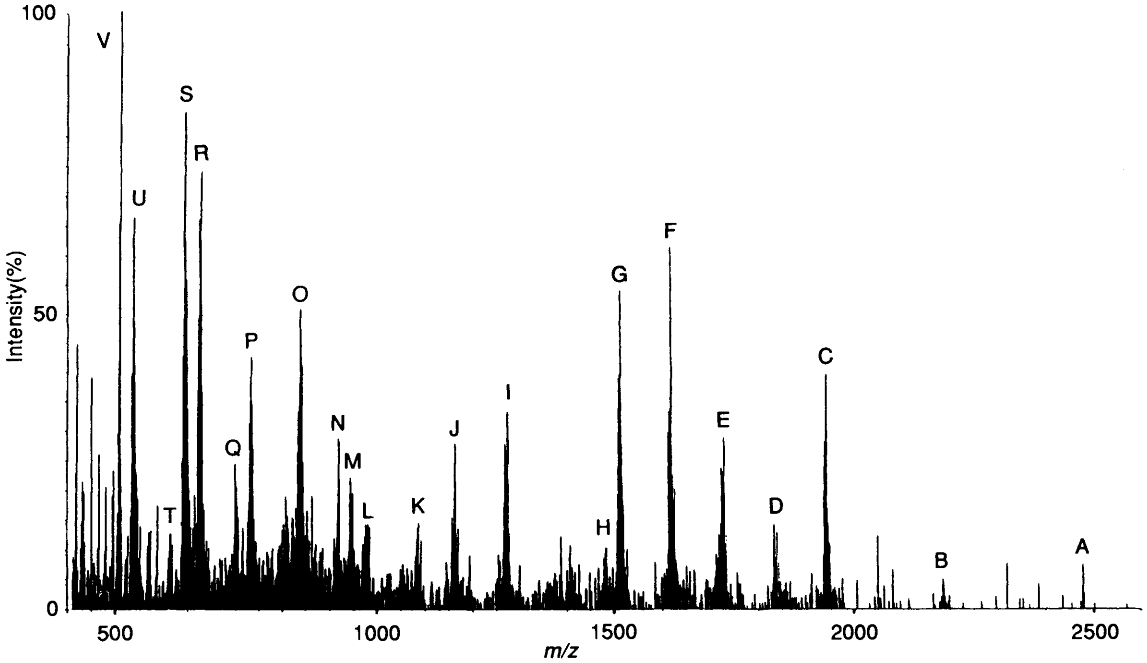


Fig. 2 The FAB mass spectrum of $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2\{P(C_6H_4OMe\text{-}p)_3\}_5]$ **1b**

The $^{31}P\text{-}\{^1H\}$ NMR spectra of the compounds were very broad and uninformative at room temperature, and the samples needed to be cooled to 220 K to resolve the spectra. Both compounds showed similar patterns, which are illustrated for compound **1b** in Fig. 3 together with a simulation of the low-temperature spectrum based on the spin system A_2BCD. The results for both **1a** and **1b** are summarised in Table 3. The low-temperature spectra showed the presence of four different phosphine environments in the ratio of 2:1:1:1 with three doublets and a doublet of doublet of triplets. Hence the structure of the compound must be one in which only two of the five phosphine environments are equivalent. This rules out a structure in which the two $\mu\text{-}SO_2$ ligands in $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PR_3)_5]$ have simply been substituted by μ-CO ligands, as this species has a C_2 axis with only one phosphorus atom on the axis and would give a similar $^{31}P\text{-}\{^1H\}$ NMR spectrum to $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PR_3)_5]$. In order to give the observed spectrum, the compound must have either a σ_v mirror of symmetry with three phosphorus atoms lying on the plane of the mirror or a C_2 axis with three phosphorus atoms on the axis, though no reasonable structures are based on the latter arrangement. There are two possible structures **A** and **B** containing a mirror plane of symmetry, and both are based on the formula $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PR_3)_5]$, with a trigonal bipyramidal metal core. Both structures have 72 valence electrons, as does the starting compound $[Pd_5(SO_2)_4(PR_3)_5]$. This is the number predicted for a trigonal-bipyramidal transition-metal cluster compound by the electron-counting rules.[8] In both cases the structures are labelled so that the observed couplings occur between P^1 and P^2, P^2 and P^3 and P^2 and P^4. Structure **A** is more likely, as in this case the largest coupling constant, 53 or 56 Hz, results from coupling between two phosphorus atoms which have an angle between the P–Pd bonds of around 180°, across an unbridged Pd–Pd bond. For structure **B**, the large coupling would be associated with a smaller angle between P–Pd bonds and a larger Pd–Pd distance. So far it has been impossible to confirm the proposed structure by an X-ray diffraction study, as single crystals of sufficiently high quality have not been grown.

The IR spectrum of compound **2** indicated the presence of bridging SO_2 groups, with $\nu(SO_2)$ observed at 1201s, 1067m and 1047vs cm^{-1}. Only one peak was observed in the carbonyl stretching mode region, with $\nu(CO)$ at 1908s cm^{-1}. This is at a higher frequency than would normally be expected for a bridging carbonyl ligand, but at a lower frequency than expected for a terminal carbonyl. The wavenumber of the absorption did not shift significantly on changing the phase from a Nujol mull to a dichloromethane solution. The ^{31}P-

Table 1 Important peaks in the FAB mass spectrum of $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5]$ **1a**

	m/z	Relative intensity	Assignment
A	2027	4	$[M]^+$
B	1766	4	$[M - 2SO_2 - 2CO - Ph]^+$
C	1582	34	$[M - 2SO_2 - 2CO - PPh_3]^+$
D	1504	15	$[M - 2SO_2 - 2CO - PPh_3 - Ph]^+$
E	1426	22	$[M - 2SO_2 - 2CO - PPh_3 - 2Ph]^+$
F	1349	45	$[M - 2SO_2 - 2CO - PPh_3 - 3Ph]^+$
G	1318	7	$[M - 2SO_2 - 2CO - 2PPh_3]^+$
H	1271	43	$[M - 2SO_2 - 2CO - PPh_3 - 4Ph]^+$
I	1242	15	$[M - 2SO_2 - 2CO - 2PPh_3 - Ph]^+$
J	1209	23	$[M - Pd - 2SO_2 - 2CO - 2PPh_3]^+$
K	1134	14	$[M - Pd - 2SO_2 - 2CO - 2PPh_3 - Ph]^+$
L	1057	42	$[M - 2SO_2 - 2CO - 3PPh_3]^+$
M	982	22	$[M - 2SO_2 - 2CO - 3PPh_3 - Ph]^+$
N	854	33	$[M - 2SO_2 - 2CO - 2PPh_3 - 6Ph]^+$
O	777	48	$[M - 2SO_2 - 2CO - 2PPh_3 - 7Ph]^+$
P	701	71	$[M - 2SO_2 - 2CO - 2PPh_3 - 8Ph]^+$
Q	669	48	$[M - 2SO_2 - 2CO - 3PPh_3 - 5Ph]^+$
R	624	90	$[M - 2SO_2 - 2CO - 2PPh_3 - 9Ph]^+$
S	594	100	$[M - 2SO_2 - 2CO - 3PPh_3 - 6Ph]^+$
T	564	51	$[M - 2SO_2 - 2CO - 4PPh_3 - 3Ph]^+$
U	532	32	$[M - 2SO_2 - 2CO - 5PPh_3]^+$
V	487	45	$[M - Pd - 2SO_2 - 2CO - 3PPh_3 - 6Ph]^+$

$[M] = [Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5]$.

Table 2 Important peaks in the FAB mass spectrum of $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2\{P(C_6H_4OMe\text{-}p)_3\}_5]$ **1b**

	m/z	Relative intensity	Assignment
A	2478	8	$[M]^+$
B	2185	5	$[M - 2SO_2 - 2CO - R]^+$
C	1942	39	$[M - 2SO_2 - 2CO - PR_3]^+$
D	1833	15	$[M - 2SO_2 - 2CO - PR_3 - R]^+$
E	1730	29	$[M - 2SO_2 - 2CO - PR_3 - 2R]^+$
F	1620	61	$[M - 2SO_2 - 2CO - PR_3 - 3R]^+$
G	1514	54	$[M - 2SO_2 - 2CO - PR_3 - 4R]^+$
H	1481	11	$[M - 2SO_2 - 2CO - 2PR_3 - R]^+$
I	1271	33	$[M - 2SO_2 - 2CO - 2PR_3 - 3R]^+$
J	1162	28	$[M - 2SO_2 - 2CO - 2PR_3 - 4R]^+$
K	1086	15	$[M - 2SO_2 - 2CO - PR_3 - 8R]^+$
L	979	15	$[M - 2SO_2 - 2CO - PR_3 - 9R]^+$
M	943	23	$[M - 2SO_2 - 2CO - 2PR_3 - 6R]^+$
N	917	29	$[M - 2SO_2 - 2CO - 3PR_3 - 3R]^+$
O	838	51	$[M - 2SO_2 - 2CO - 2PR_3 - 7R]^+$
P	731	43	$[M - 2SO_2 - 2CO - 2PR_3 - 8R]^+$
Q	698	25	$[M - 2SO_2 - 2CO - 3PR_3 - 5R]^+$
R	626	74	$[M - 2SO_2 - 2CO - 2PR_3 - 9R]^+$
S	594	84	$[M - 2SO_2 - 2CO - 3PR_3 - 6R]^+$
T	563	13	$[M - 2SO_2 - 2CO - 4PR_3 - 3R]^+$
U	488	66	$[M - Pd - 2SO_2 - 2CO - 3PR_3 - 6R]^+$
V	459	100	$[M - Pd - 2SO_2 - 2CO - 4PR_3 - 3R]^+$

$[M] = [Pd_5(\mu\text{-}SO_2)_2(\mu\text{-}CO)_2\{P(C_6H_4OMe\text{-}p)_3\}_5]$; R = C_6H_4OMe-*p*.

$\{^1H\}$ NMR spectrum showed a singlet at δ −22.4, a doublet at −14.7 and a triplet at −18.9 in an intensity ratio of 2:2:1 with the coupling constant in the doublet and triplet equal to 26 Hz. These features are also observed in the spectrum of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$. However, in all of the spectra observed for $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$ the singlet and doublet have very similar chemical shifts, with the triplet 8 or 9 ppm upfield.[7] In this case the order of the chemical shifts is different, suggesting that although the product has the same symmetry as $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ it is not based on the same structure. The $^{31}P\text{-}\{^1H\}$ NMR spectrum is consistent with the solid-state structure being retained in solution.

The FAB mass spectrum was not particularly informative about the ligand sphere as the highest m/z peak observed was for the ion $[Pd_5(PMe_2Ph)_5]^+$ at $m/z = 1220$ (M'). The only other discernible peaks in the spectrum were for the ions $[M' - Ph]^+$ at $m/z = 1143$, $[M' - PMe_2Ph]^+$ at $m/z = 1083$ and $[M' - 5Ph]^+$ at $m/z = 837$. This decomposition pattern suggests that phenyl groups are lost more readily from the PMe_2Ph ligands than are the methyl groups. The lack of resolution in the spectrum made it impossible to characterise the product fully on the basis of spectroscopic techniques alone. A single-crystal X-ray analysis was undertaken to confirm its formulation and establish the co-ordination modes of the carbonyl and sulfur dioxide ligands around the metal core.

Crystals of compound **2** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a tetrahydrofuran (thf) solution. Details of the data collection and structure solution are given in Table 4, the final fractional atomic coordinates are given in Table 5 and important bond lengths and angles are summarised in Table 6. The cluster compound is illustrated in Fig. 4(*a*), with the core shown in Fig. 4(*b*) to emphasise the co-ordination geometries of the carbonyl ligands. Compound **2** crystallises in the space group $P2_1/n$. The

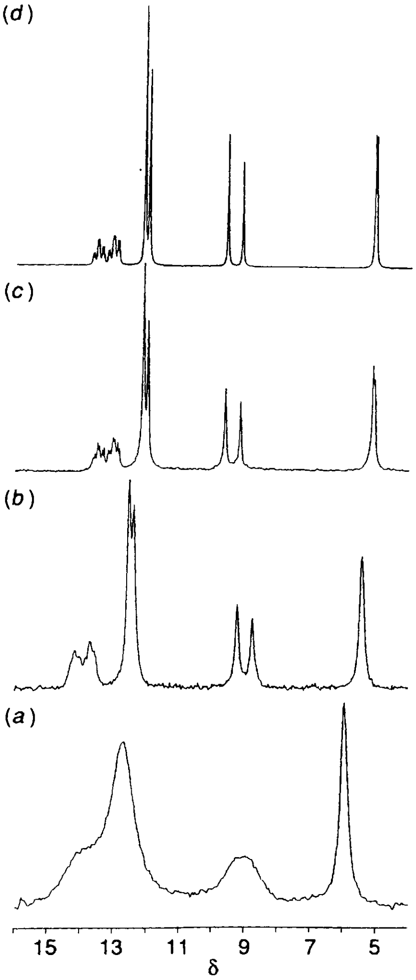
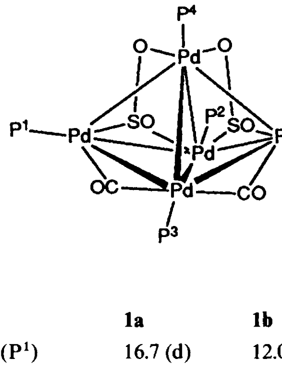
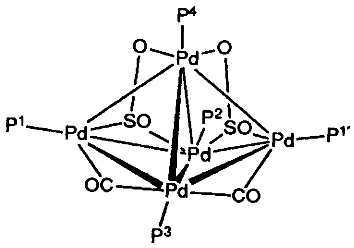


Fig. 3 The $^{31}P-\{^1H\}$ NMR spectra of compound **1b**; (*a*) at room temperature, (*b*) at 270 K, (*c*) at 220 K, and (*d*) simulated

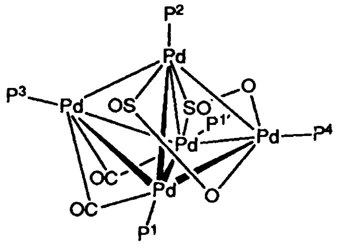
Table 3 $^{31}P-\{^1H\}$ NMR data for compounds **1a** and **1b** at 220 K in CD_2Cl_2. Coupling constants in Hz



	1a	**1b**
$\delta(P^1)$	16.7 (d)	12.0 (d)
$\delta(P^2)$	12.0 (d)	9.3 (d)
$\delta(P^3)$	16.1 (ddt)	13.2 (ddt)
$\delta(P^4)$	10.1 (d)	5.1 (d)
$^3J(P^1-P^2)$	15	16
$^3J(P^2-P^3)$	53	56
$^3J(P^2-P^4)$	6	6



A



B

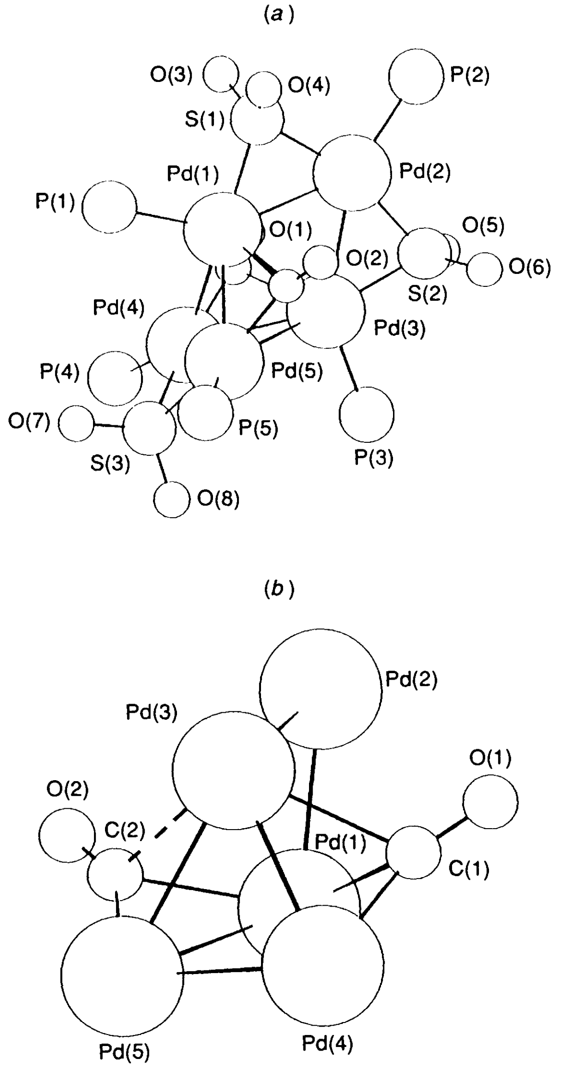


Fig. 4 Molecular structure of $[Pd_5(\mu-SO_2)_3(\mu-CO)(\mu_3-CO)(PMe_2Ph)_5]$ **2**; (*a*) with methyl and phenyl groups omitted for clarity; (*b*) with only palladium atoms and carbonyl groups shown

structure consists of well separated molecules of the cluster with no occluded solvent. The metal core has a geometry based on an edge-bridged tetrahedron, with the Pd–Pd bond distances lying between 2.7357(9) and 2.9680(9) Å. There is some distortion from an idealised edge-bridged tetrahedron with a compression towards the axis of symmetry running through the bridging

Table 4 Crystal data* for $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2** and $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**

	2	**3**
Formula	$C_{42}H_{55}O_8P_5Pd_5S_3$	$C_{72}H_{63}N_2O_4P_3Pd_3S_2\cdot 0.75C_6H_6$
M	1470.94	1496.54 (1555.12 including solvent)
a/Å	17.737(3)	24.958(9)
b/Å	22.315(2)	19.95(1)
c/Å	13.702(3)	14.82(1)
β/°	100.21(2)	90.19(5)
U/Å³	5337.2	7378
D_c/g cm⁻³	1.830	1.40
F(000)	2596	3148
μ	19.379	8.78
Crystal size/mm	0.25 × 0.2 × 0.1	0.5 × 0.3 × 0.2
Data collection		
θ_{min}, θ_{max}/°	0, 24	1, 25
ω-Scan width/°	0.75 + 0.35 tan θ	0.80 + 0.35 tan θ
Total data collected	12 560	14 946
Total observed data [$I > 3\sigma(I)$]	4836	10 532
Merging *R* factor	0.0263	0.0242
Refinement		
No. of parameters	569	526
Ratio data:parameters	8.50	20.02
Weighting scheme	Unit weights	Chebyshev (coefficients 6.842, −1.525, 4.900)
Final *R*	0.0314	0.0388
Final *R'*	0.0351	0.0434

* Details in common: crystal system, monoclinic; space group $P2_1/n$ (no. 14); $Z = 4$; crystal colour, red; Mo-Kα radiation (λ = 0.710 69 Å); absorption correction, DIFABS; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \{\Sigma[w(|F_o| - F_c|)^2]/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

Table 5 Fractional atomic coordinates for $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.180 33(4)	0.130 52(3)	0.128 57(5)	C(22)	0.264 0(6)	0.209 0(5)	−0.281 2(7)
Pd(2)	0.220 10(4)	0.168 31(3)	−0.051 46(5)	C(23)	0.273 6(5)	0.084 0(4)	−0.228 9(6)
Pd(3)	0.288 07(4)	0.218 60(3)	0.131 14(4)	C(24)	0.238 8(6)	0.027 6(5)	−0.245 7(9)
Pd(4)	0.306 02(4)	0.138 56(3)	0.293 54(5)	C(25)	0.282 1(8)	−0.021 8(5)	−0.252(1)
Pd(5)	0.185 77(4)	0.216 66(3)	0.280 66(5)	C(26)	0.358 9(7)	−0.019 3(5)	−0.240 2(9)
P(1)	0.107 9(1)	0.062 1(1)	0.203 1(2)	C(27)	0.393 7(7)	0.032 9(6)	−0.222(1)
P(2)	0.219 9(1)	0.151 3(1)	−0.216 2(2)	C(28)	0.351 4(6)	0.084 8(6)	−0.217(1)
P(3)	0.384 8(1)	0.280 6(1)	0.211 8(2)	C(31)	0.410 8(5)	0.341 4(4)	0.136 0(7)
P(4)	0.396 7(1)	0.080 7(1)	0.393 1(2)	C(32)	0.484 6(6)	0.071 4(6)	0.342(1)
P(5)	0.096 9(1)	0.266 7(1)	0.356 1(2)	C(33)	0.475 9(4)	0.241 3(4)	0.245 0(6)
S(1)	0.136 4(1)	0.096 3(1)	−0.028 1(2)	C(34)	0.501 6(5)	0.206 7(4)	0.172 5(7)
S(2)	0.307 4(1)	0.241 9(1)	−0.023 6(1)	C(35)	0.571 8(5)	0.178 9(4)	0.190 3(7)
S(3)	0.261 0(1)	0.182 0(1)	0.420 4(2)	C(36)	0.617 5(5)	0.185 1(4)	0.282 2(7)
O(1)	0.357 4(4)	0.088 6(4)	0.109 0(5)	C(37)	0.592 7(5)	0.216 4(5)	0.353 4(7)
O(2)	0.092 8(5)	0.249 2(4)	0.081 7(5)	C(38)	0.522 5(5)	0.246 1(4)	0.338 4(7)
O(3)	0.157 8(5)	0.036 0(3)	−0.045 4(5)	C(41)	0.430 3(7)	0.106 0(5)	0.518 9(8)
O(4)	0.056 1(4)	0.109 9(3)	−0.065 1(5)	C(42)	0.370 7(6)	0.319 1(5)	0.325 1(8)
O(5)	0.383 5(3)	0.226 2(3)	−0.043 1(4)	C(43)	0.363 4(5)	0.004 8(4)	0.404 7(6)
O(6)	0.283 5(4)	0.302 2(3)	−0.057 1(5)	C(44)	0.366 2(6)	−0.036 5(5)	0.331 1(8)
O(7)	0.224 3(4)	0.141 1(4)	0.479 9(5)	C(45)	0.338 9(7)	−0.093 5(6)	0.337(1)
O(8)	0.311 3(4)	0.225 2(3)	0.479 0(5)	C(46)	0.305 8(6)	−0.110 1(5)	0.415 7(9)
C(1)	0.324 7(6)	0.113 8(5)	0.161 7(7)	C(47)	0.300 6(6)	−0.070 5(6)	0.488 1(9)
C(2)	0.135 9(6)	0.226 6(5)	0.139 1(7)	C(48)	0.329 3(6)	−0.013 1(5)	0.483 2(7)
C(11)	0.077 7(7)	−0.004 5(5)	0.132 2(8)	C(51)	0.005 9(5)	0.280 1(6)	0.274 6(8)
C(12)	0.152 0(7)	0.030 3(6)	0.320 9(8)	C(52)	0.069 2(6)	0.226 1(5)	0.457 8(8)
C(13)	0.016 0(7)	0.092 9(5)	0.224 2(9)	C(53)	0.123 6(5)	0.340 9(5)	0.408 8(7)
C(14)	−0.028 6(7)	0.121 7(7)	0.143(1)	C(54)	0.197 7(7)	0.354 6(5)	0.440 6(9)
C(15)	−0.100 7(8)	0.145 8(7)	0.157(2)	C(55)	0.221 3(8)	0.409 7(6)	0.482(1)
C(16)	−0.124(1)	0.140 7(8)	0.249(2)	C(56)	0.168 9(8)	0.452 0(6)	0.487 2(9)
C(17)	−0.078(1)	0.111 6(9)	0.326(2)	C(57)	0.094 9(9)	0.439 5(6)	0.458(1)
C(18)	−0.010 3(9)	0.089 9(7)	0.310(1)	C(58)	0.070 0(7)	0.383 7(6)	0.419 8(9)
C(21)	0.127 6(5)	0.139 4(5)	−0.293 4(7)				

metal and the centre of the tetrahedron, and hence the two shortest M–M distances are those between the palladium atoms bridged by the metal, Pd(1)–Pd(3) 2.7373(9) Å, and between those furthest from the metal bridge, Pd(4)–Pd(5) 2.7357(9) Å.

Each metal atom is co-ordinated to a terminal PMe_2Ph ligand, and the cluster also contains three bridging sulfur dioxide and two bridging carbonyl ligands. Two of the three SO_2 ligands themselves bridge the Pd–Pd bonds between the bridging metal atom, Pd(2) and the two nearest metal atoms, Pd(1) and Pd(3), and the third bridges the opposite edge of the

Table 6 Selected bond lengths (Å) and angles (°) for $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2**

Pd(1)–Pd(2)	2.812 4(9)	Pd(2)–Pd(3)	2.811 2(9)	Pd(3)–C(1)	2.44(1)	S(1)–O(3)	1.429(7)
Pd(1)–Pd(3)	2.737 3(9)	Pd(2)–P(2)	2.288(2)	Pd(4)–Pd(5)	2.735 7(9)	S(1)–O(4)	1.456(7)
Pd(1)–Pd(4)	2.885 4(9)	Pd(2)–S(1)	2.249(2)	Pd(4)–P(4)	2.310(2)	S(2)–O(5)	1.465(6)
Pd(1)–Pd(5)	2.824 1(9)	Pd(2)–S(2)	2.242(2)	Pd(4)–S(3)	2.257(2)	S(2)–O(6)	1.461(7)
Pd(1)–P(1)	2.343(3)	Pd(3)–Pd(4)	2.827 0(9)	Pd(4)–C(1)	1.97(1)	S(3)–O(7)	1.453(7)
Pd(1)–S(1)	2.281(2)	Pd(3)–Pd(5)	2.968 0(9)	Pd(5)–P(5)	2.319(2)	S(3)–O(8)	1.456(7)
Pd(1)–C(1)	2.55(1)	Pd(3)–P(3)	2.325(2)	Pd(5)–S(3)	2.267(2)	O(1)–C(1)	1.15(1)
Pd(1)–C(2)	2.30(1)	Pd(3)–S(2)	2.266(2)	Pd(5)–C(2)	2.00(1)	O(2)–C(2)	1.12(1)

Pd(3)–Pd(1)–Pd(2)	60.85(2)	C(2)–Pd(1)–S(1)	107.9(3)	S(2)–Pd(3)–P(3)	95.01(8)	P(5)–Pd(5)–Pd(3)	147.94(7)
Pd(4)–Pd(1)–Pd(2)	112.91(3)	C(2)–Pd(1)–C(1)	118.1(4)	C(1)–Pd(3)–Pd(1)	58.6(3)	P(5)–Pd(5)–Pd(4)	149.53(7)
Pd(4)–Pd(1)–Pd(3)	60.30(2)	Pd(3)–Pd(2)–Pd(1)	58.26(2)	C(1)–Pd(3)–Pd(2)	80.2(2)	S(3)–Pd(5)–Pd(1)	109.22(7)
Pd(5)–Pd(1)–Pd(2)	117.51(3)	P(2)–Pd(2)–Pd(1)	149.14(7)	C(1)–Pd(3)–Pd(4)	43.2(2)	S(3)–Pd(5)–Pd(3)	104.36(7)
Pd(5)–Pd(1)–Pd(3)	64.49(2)	P(2)–Pd(2)–Pd(3)	150.42(7)	C(1)–Pd(3)–Pd(5)	92.5(2)	S(3)–Pd(5)–Pd(4)	52.62(6)
Pd(5)–Pd(1)–Pd(4)	57.25(2)	S(1)–Pd(2)–Pd(1)	52.14(6)	C(1)–Pd(3)–P(3)	109.7(3)	S(3)–Pd(5)–P(5)	97.62(9)
P(1)–Pd(1)–Pd(2)	145.07(7)	S(1)–Pd(2)–Pd(3)	110.38(6)	C(1)–Pd(3)–S(2)	107.5(2)	C(2)–Pd(5)–Pd(1)	53.6(3)
P(1)–Pd(1)–Pd(3)	153.87(7)	S(1)–Pd(2)–P(2)	97.82(9)	Pd(3)–Pd(4)–Pd(1)	57.25(2)	C(2)–Pd(5)–Pd(3)	63.1(3)
P(1)–Pd(1)–Pd(4)	96.09(7)	S(2)–Pd(2)–Pd(1)	110.06(6)	Pd(5)–Pd(4)–Pd(1)	60.25(2)	C(2)–Pd(5)–Pd(4)	109.8(3)
P(1)–Pd(1)–Pd(5)	94.11(7)	S(2)–Pd(2)–Pd(3)	51.82(5)	Pd(5)–Pd(4)–Pd(3)	64.47(2)	C(2)–Pd(5)–P(5)	99.2(3)
S(1)–Pd(1)–Pd(2)	51.10(6)	S(2)–Pd(2)–P(2)	99.80(9)	P(4)–Pd(4)–Pd(1)	142.04(7)	C(2)–Pd(5)–S(3)	162.1(3)
S(1)–Pd(1)–Pd(3)	111.94(7)	S(2)–Pd(2)–S(1)	162.20(8)	P(4)–Pd(4)–Pd(3)	141.94(7)	Pd(2)–S(1)–Pd(1)	76.76(7)
S(1)–Pd(1)–Pd(4)	147.74(7)	Pd(2)–Pd(3)–Pd(1)	60.89(2)	P(4)–Pd(4)–Pd(5)	147.91(7)	O(4)–S(1)–O(3)	114.2(5)
S(1)–Pd(1)–Pd(5)	152.03(7)	Pd(4)–Pd(3)–Pd(1)	62.45(2)	S(3)–Pd(4)–Pd(1)	107.47(6)	Pd(3)–S(2)–Pd(2)	77.15(7)
S(1)–Pd(1)–P(1)	94.01(9)	Pd(4)–Pd(3)–Pd(2)	114.77(3)	S(3)–Pd(4)–Pd(3)	109.21(7)	O(6)–S(2)–O(5)	112.8(4)
C(1)–Pd(1)–Pd(2)	78.5(2)	Pd(5)–Pd(3)–Pd(1)	59.17(2)	S(3)–Pd(4)–Pd(5)	52.95(6)	Pd(5)–S(3)–Pd(4)	74.43(7)
C(1)–Pd(1)–Pd(3)	54.9(2)	Pd(5)–Pd(3)–Pd(2)	112.97(3)	S(3)–Pd(4)–P(4)	95.14(9)	O(8)–S(3)–O(7)	113.5(4)
C(1)–Pd(1)–Pd(4)	42.0(2)	Pd(5)–Pd(3)–Pd(4)	56.28(2)	C(1)–Pd(4)–Pd(1)	59.8(3)	Pd(3)–C(1)–Pd(1)	66.5(3)
C(1)–Pd(1)–Pd(5)	93.8(2)	P(3)–Pd(3)–Pd(1)	152.62(6)	C(1)–Pd(4)–Pd(3)	58.0(3)	Pd(4)–C(1)–Pd(1)	78.2(3)
C(1)–Pd(1)–P(1)	116.0(2)	P(3)–Pd(3)–Pd(2)	145.54(6)	C(1)–Pd(4)–Pd(5)	112.0(3)	Pd(4)–C(1)–Pd(3)	78.8(4)
C(1)–Pd(1)–S(1)	106.5(2)	P(3)–Pd(3)–Pd(4)	91.79(6)	C(1)–Pd(4)–P(4)	99.9(3)	O(1)–C(1)–Pd(1)	124.2(8)
C(2)–Pd(1)–Pd(2)	85.3(3)	P(3)–Pd(3)–Pd(5)	99.80(6)	C(1)–Pd(4)–S(3)	165.0(3)	O(1)–C(1)–Pd(3)	120.5(8)
C(2)–Pd(1)–Pd(3)	64.9(3)	S(2)–Pd(3)–Pd(1)	111.91(6)	Pd(3)–Pd(5)–Pd(1)	56.34(2)	O(1)–C(1)–Pd(4)	153.9(9)
C(2)–Pd(1)–Pd(4)	96.8(3)	S(2)–Pd(3)–Pd(2)	51.03(6)	Pd(4)–Pd(5)–Pd(1)	62.50(2)	Pd(5)–C(2)–Pd(1)	81.9(3)
C(2)–Pd(1)–Pd(5)	44.4(2)	S(2)–Pd(3)–Pd(4)	150.03(7)	Pd(4)–Pd(5)–Pd(3)	59.26(2)	O(2)–C(2)–Pd(1)	125.3(8)
C(2)–Pd(1)–P(1)	111.1(3)	S(2)–Pd(3)–Pd(5)	149.42(6)	P(5)–Pd(5)–Pd(1)	136.02(7)	O(2)–C(2)–Pd(5)	149.9(9)

tetrahedron between Pd(4) and Pd(5). The average Pd–S bond length is 2.26(1) Å which is similar to that in other cluster compounds containing $\mu\text{-}SO_2$ ligands. The two SO_2 ligands bridging to Pd(2) are somewhat asymmetric, with the shorter bond to the palladium atom in the tetrahedron. The two carbonyl groups both show incipient μ-, μ_3-CO character, bridging two opposite faces of the tetrahedron. Both are, however, highly asymmetric, with one short Pd–C contact and two considerably longer. One of the carbonyls tends towards an edge-bridging location, with the longest contact, Pd(3)–C(2) at 2.73(1) Å, rather long to be considered bonding and the other tends towards μ_3-CO. Both carbonyl ligands have their shortest contacts to palladium atoms on the edge of the tetrahedron away from the metal bridge, with C(2)–Pd(5) 2.00(1) Å and C(1)–Pd(4) 1.97(1) Å. In solution the carbonyls take up equivalent positions on the NMR time-scale.

Asymmetric μ_3-CO ligands are quite common in palladium cluster chemistry, and examples are listed in Table 7. Similar distortions, with two long and one short Pd–C bond lengths, have been observed in $[Pd_8(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(PMe_3)_7]$[13] and $[Pd_{10}(\mu\text{-}CO)_8(\mu_3\text{-}CO)_4(PBu_3)_6]$.[5] However, the carbonyl ligands in $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ are the most asymmetric that have been observed to date, and it is this asymmetry that accounts for the unusual value for the ν(CO) stretching mode that was observed in the IR spectrum and noted above.

The compound $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ has the 70 valence electrons predicted by the electron-counting rules for an edge-bridged tetrahedral pentanuclear cluster compound of palladium or platinum.[8] It is isoelectronic with $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)_5]$ **4**[14] and also the platinum cluster compounds $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$[15] and $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$ **5**.[16] In both **4** and **5** the $\mu\text{-}SO_2$ ligands occupy identical positions on the edge-bridged tetrahedral metal framework to those of the $\mu\text{-}SO_2$ ligands in **2**. Reaction of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ with CO occurs with rearrangement of the pentapalladium core. This is in contrast to the reaction of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ with CO which gives the 72-electron compound $[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5]$. This difference in product formulation could have a steric origin, since no penta-palladium or -platinum cluster containing five triphenylphosphine ligands has been observed with the edge-bridged tetrahedral structure. Both compounds **1a** and **2** reacted with SO_2 to regenerate the $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$ cluster compounds [equations (1) and (2)].

$$[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5] \underset{SO_2}{\overset{CO}{\rightleftharpoons}} [Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5] \quad (1)$$

$$[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5] \underset{SO_2}{\overset{CO}{\rightleftharpoons}} [Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5] \quad (2)$$

Reaction with Xylyl Isocyanide.—When a dichloromethane solution containing 3 equivalents of xylyl isocyanide was added to a dichloromethane solution of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ a rapid colour change occurred from green-red dichroic to orange. On removal of the solvent under reduced pressure and recrystallisation from toluene–hexane red crystals were obtained. These were characterised as $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3** on the basis of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, and a single-crystal X-ray analysis.

The IR spectrum showed peaks at 1203s, 1055s and 1044vs cm^{-1} indicative of the $\nu(SO_2)$ stretching modes of bridging SO_2 ligands, and peaks at 2119s and 2092s cm^{-1} characteristic of the ν(CN) stretching modes of terminal isocyanide ligands. The ^{31}P-

Table 7 Bond lengths Pd–C in palladium clusters containing μ_3-CO ligands

Compound *	Pd–C/Å	Ref.
$[Pd_3(\mu_3\text{-}O_2CCF_3)(\mu_3\text{-}CO)(dppm)_3]^+$	2.175(11), 2.141(12), 2.080(10)	9, 10
$[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(dppm)_3]^+$	2.14(2), 2.25(2), 2.17(2)	11
$[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(dppm)_3]^+$	2.137(8), 2.192(8), 2.160(8)	10
$[Pd_3(C_5Me_5)_3(\mu_3\text{-}CO)_2]^+$	2.171(4), 2.033(4), 2.061(3)	12
$[Pd_8(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(PMe_3)_7]$	2.420(25), 2.198(25), 2.036(24)	13
$[Pd_{10}(\mu\text{-}CO)_8(\mu_3\text{-}CO)_4(PBu_3)_6]$	2.255(9), 2.332(9), 2.043(8)	5
	2.310(9), 2.301(9), 2.042(8)	
	2.263(8), 2.288(8), 2.050(8)	
	2.259(10), 2.256(10), 2.037(8)	
$[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$	2.00(1), 2.30(1), 2.73(1)	This work
	1.97(1), 2.44(1), 2.55(1)	

* dppm = $Ph_2PCH_2PPh_2$.

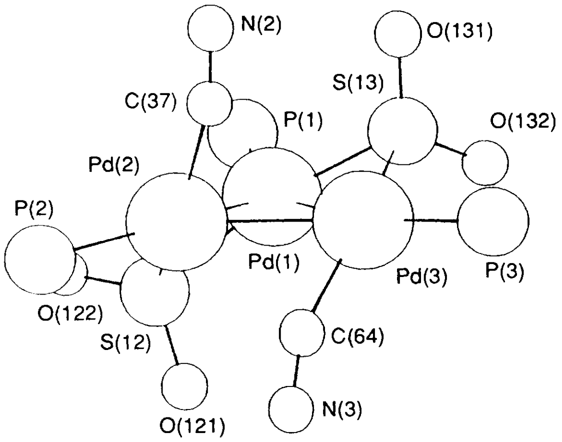


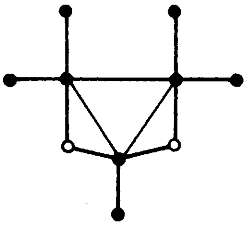
Fig. 5 Molecular structure of $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3** with phenyl and xylyl groups omitted for clarity

{^1H} NMR spectrum showed the presence of a doublet at δ 20.0 and a triplet at 13.7 in the intensity ratio of 2:1. The coupling constant within the two signals was 43 Hz. This spectrum indicated that the product was a *triangulo*-cluster compound with two phosphine ligands in equivalent environments, and the third in a different environment. The most likely structure for **3** is $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ as the cluster compounds $[M_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2\{P(C_6H_{11})_3\}_3]$ (M = Pd[17] or Pt[3]) are both known. These have $^3J_{PP}$ coupling constants of 29 Hz for the tripalladium compound and 38 Hz for the triplatinum compound. The identity of **3** was confirmed by a single-crystal X-ray analysis.

Single crystals of X-ray quality were grown by the slow diffusion of hexane into a benzene solution of the compound. Details of the data collection and structure solution are given in Table 4, the final fractional atomic coordinates are given in Table 8 and the important bond lengths and angles are summarised in Table 9. The molecule is illustrated in Fig. 5. The compound crystallises in the space group $P2_1/n$ without disorder. The structure consists of well separated molecules of $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ with occluded solvent molecules, best modelled as two benzene molecules with partial occupancies, one of which lies across the crystallographic centre of inversion.

As anticipated from the spectroscopic data, the molecule is based on a *triangulo*-palladium core. The triangle is bridged along two edges by sulfur dioxide ligands, with the third edge unbridged. The two palladium atoms which form this edge are co-ordinated to both a phosphine ligand and a terminal isocyanide ligand, whereas the third palladium atom is co-ordinated to only a phosphine ligand. The three sides of the triangle have different lengths, with the two bridged edges shorter, at 2.7663(4) and 2.7369(4) Å, than the unbridged edge at 2.7947(4) Å.

In previously characterised *triangulo*-palladium clusters the Pd–Pd bond lengths of those with 42 valence electrons lie between 2.576(1) and 2.651(2) Å, whereas for those with 44 valence electrons they lie between 2.734(4) and 3.000(5) Å. The bond lengths for $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$, which has 44 valence electrons, fall within the latter range. The palladium and phosphorus atoms in **3** and related compounds are all essentially coplanar. However, the isocyanide carbon atoms and SO_2 sulfur atoms are found significantly out of the plane in a transoid arrangement with each other. This is in contrast to palladium and platinum *triangulo* clusters with three bridged edges, in which all of the ligand atoms co-ordinated to the metals are roughly in the plane defined by the metal triangle. This distortion from the planar arrangement can be explained by describing the 44-electron triangle as being built up from two square-planar 16-electron ML_4 fragments and one T-shaped ML_3 fragment as shown below.[3] Given this analysis the Pd–Pd–S angles should be close to 90°, and in order to facilitate this the sulfur atoms move out of the plane of the metal triangle. Similar reasoning has been used to rationalise a related distortion of the sulfur atoms out of the metal plane in $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_2\{Ph_2P(CH_2)_3PPh_2\}]$.[18] It would, however, be an oversimplification to regard this as the complete reason for the distortion from planarity. The steric demand of the SO_2 groups is likely to be another factor since in 44-electron cluster compounds such as $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_4]$ the carbonyl ligands are coplanar with the metal atoms.[19] The sulfur dioxide ligands in $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ are somewhat distorted, with bonds to the palladium atoms carrying the isocyanide ligands shorter than those to the unique palladium atom. This may be due to the π-acid properties of the isocyanide ligands. The isocyanides themselves are essentially linear, with C–N–C angles of 175.6(4) and 174.0(4)°.



Experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen, with dry, dioxygen-free solvents. Microanalyses (C, H, N) were carried out by Mr. M. Gascoyne and his staff at this laboratory. Infrared spectra were recorded on a Perkin-Elmer FT-1710 spectrometer as Nujol mulls between KBr discs or as solutions in KBr cells, ^{31}P-{^1H}

Table 8 Fractional atomic coordinates for $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.188 95(1)	0.135 40(1)	0.559 74(2)
Pd(2)	0.249 25(1)	0.026 50(1)	0.615 18(2)
Pd(3)	0.152 49(1)	0.058 28(1)	0.699 40(2)
P(1)	0.181 92(4)	0.197 15(5)	0.429 24(6)
P(2)	0.331 36(4)	−0.028 12(5)	0.616 54(7)
P(3)	0.088 84(4)	0.025 24(5)	0.803 63(6)
S(12)	0.279 14(4)	0.131 19(5)	0.588 76(7)
S(13)	0.102 32(4)	0.108 54(5)	0.592 34(6)
O(121)	0.292 3(1)	0.175 4(1)	0.663 5(2)
O(122)	0.318 2(1)	0.132 9(2)	0.516 4(2)
O(131)	0.075 2(1)	0.068 0(2)	0.525 1(2)
O(132)	0.069 3(1)	0.162 0(2)	0.630 4(2)
N(2)	0.173 9(1)	−0.085 5(2)	0.529 7(2)
N(3)	0.248 4(2)	0.062 1(2)	0.839 8(2)
C(1)	0.210 3(2)	0.146 7(2)	0.338 1(3)
C(2)	0.233 1(3)	0.174 8(3)	0.262 3(4)
C(3)	0.253 3(4)	0.134 1(3)	0.193 6(4)
C(4)	0.251 9(3)	0.066 8(3)	0.201 5(4)
C(5)	0.228 4(3)	0.037 8(3)	0.276 1(4)
C(6)	0.208 5(2)	0.077 9(2)	0.344 6(3)
C(7)	0.114 1(2)	0.214 9(2)	0.390 2(3)
C(8)	0.093 3(2)	0.187 4(3)	0.311 7(4)
C(9)	0.040 4(3)	0.200 1(4)	0.288 0(5)
C(10)	0.008 1(3)	0.239 3(4)	0.341 8(6)
C(11)	0.027 9(3)	0.265 1(4)	0.419 3(5)
C(12)	0.080 2(2)	0.252 1(3)	0.445 5(4)
C(13)	0.217 3(2)	0.276 8(2)	0.415 4(3)
C(14)	0.197 6(2)	0.327 8(2)	0.363 1(3)
C(15)	0.228 9(3)	0.384 3(3)	0.345 8(4)
C(16)	0.278 4(2)	0.390 7(3)	0.383 6(4)
C(17)	0.297 9(2)	0.340 5(3)	0.436 7(4)
C(18)	0.267 6(2)	0.284 1(2)	0.452 7(4)
C(19)	0.389 1(2)	0.023 0(2)	0.648 8(3)
C(20)	0.383 6(2)	0.066 9(3)	0.719 5(3)
C(21)	0.425 1(2)	0.108 0(3)	0.744 8(4)
C(22)	0.471 7(2)	0.107 0(4)	0.700 0(5)
C(23)	0.478 7(3)	0.060 8(5)	0.634 0(6)
C(24)	0.437 3(2)	0.019 8(4)	0.606 1(5)
C(25)	0.334 9(2)	−0.101 2(2)	0.690 9(3)
C(26)	0.380 7(2)	−0.119 3(4)	0.736 1(5)
C(27)	0.381 7(3)	−0.176 6(4)	0.790 8(6)
C(28)	0.338 0(3)	−0.213 9(3)	0.800 8(5)
C(29)	0.292 8(3)	−0.197 0(3)	0.756 2(4)
C(30)	0.290 7(2)	−0.140 7(2)	0.701 6(4)
C(31)	0.350 9(2)	−0.061 7(2)	0.506 5(3)
C(32)	0.374 1(2)	−0.123 9(2)	0.495 5(4)
C(33)	0.389 2(2)	−0.145 6(3)	0.410 0(4)
C(34)	0.381 2(2)	−0.105 3(4)	0.336 3(4)
C(35)	0.358 8(2)	−0.042 9(3)	0.346 9(3)
C(36)	0.342 8(2)	−0.021 4(3)	0.431 2(3)
C(37)	0.197 0(2)	−0.045 9(2)	0.571 9(3)
C(38)	0.148 1(2)	−0.131 1(2)	0.473 1(3)
C(39)	0.179 0(2)	−0.166 7(2)	0.410 6(3)
C(40)	0.239 6(2)	−0.159 6(3)	0.409 8(4)
C(41)	0.152 1(3)	−0.209 3(3)	0.352 9(4)
C(42)	0.098 1(3)	−0.216 9(3)	0.356 3(4)
C(43)	0.068 3(2)	−0.181 5(3)	0.417 3(4)
C(44)	0.092 7(2)	−0.137 9(2)	0.479 0(3)
C(45)	0.060 9(2)	−0.098 8(3)	0.545 7(4)
C(46)	0.017 0(2)	0.037 6(2)	0.783 4(2)
C(47)	−0.005 5(2)	0.009 2(3)	0.707 0(3)
C(48)	−0.059 5(2)	0.014 6(3)	0.689 8(4)
C(49)	−0.091 2(2)	0.050 9(3)	0.745 5(4)
C(50)	−0.069 7(2)	0.080 8(4)	0.819 4(5)
C(51)	−0.015 7(2)	0.073 6(3)	0.839 9(4)
C(52)	0.091 8(2)	−0.063 2(2)	0.835 4(3)
C(53)	0.051 6(2)	−0.093 7(3)	0.885 6(3)
C(54)	0.054 8(3)	−0.162 0(3)	0.906 8(4)
C(55)	0.097 7(3)	−0.199 3(3)	0.878 3(4)
C(56)	0.136 6(3)	−0.169 4(3)	0.828 8(4)
C(57)	0.134 6(2)	−0.101 1(3)	0.807 6(3)
C(58)	0.102 1(2)	0.073 0(2)	0.906 6(3)
C(59)	0.112 6(3)	0.140 3(3)	0.896 6(4)
C(60)	0.123 9(4)	0.180 1(3)	0.970 5(5)
C(61)	0.124 8(4)	0.152 4(4)	1.055 0(5)
C(62)	0.114 3(4)	0.087 2(4)	1.066 0(4)
C(63)	0.103 3(3)	0.045 8(3)	0.992 2(3)
C(64)	0.219 5(2)	0.053 4(2)	0.779 5(3)
C(65)	0.287 7(2)	0.070 2(3)	0.906 9(3)
C(66)	0.308 0(3)	0.010 6(5)	0.944 1(3)
C(67)	0.285 5(4)	−0.055 6(5)	0.919 5(6)
C(68)	0.346 6(4)	0.015 9(5)	1.011 6(6)
C(69)	0.364 4(4)	0.071 3(5)	1.027 9(6)
C(70)	0.349 4(4)	0.134 3(6)	0.997 3(5)
C(71)	0.305 1(3)	0.133 3(4)	0.929 8(4)
C(72)	0.282 7(4)	0.192 7(4)	0.886 6(5)
C(73)	0.510 6(6)	0.008 0(7)	0.085 5(7)
C(74)	0.489 0(6)	−0.045 9(7)	0.061 5(9)
C(75)	0.522 4(5)	0.055 1(6)	0.027 5(10)
C(76)	0.473 5(8)	0.222 9(10)	0.385 0(12)
C(77)	0.422 1(9)	0.196 3(11)	0.398 9(13)
C(78)	0.409 6(10)	0.145 4(13)	0.359 4(16)
C(79)	0.442 7(8)	0.121 3(10)	0.289 1(13)
C(80)	0.480 7(6)	0.156 9(7)	0.265 4(9)
C(81)	0.498 5(7)	0.210 1(9)	0.318 6(11)

NMR spectra on a Brüker AM-300 spectrometer operating at 121.49 MHz and referenced to $P(OMe)_3O$ in D_2O. The NMR computer simulations were carried out using the Oxford University VAX computer system and a program developed by Professor R. K. Harris, then of the University of East Anglia, and adapted for use in Oxford by Dr. A. E. Derome. The FAB mass spectra were recorded by Dr. J. Ballantine and his staff at the SERC Mass Spectrometry Service Centre at the University of Swansea. Experiments were carried out using a VG ZAB-E high-resolution double-focusing mass spectrometer. Samples were suspended in a matrix of 3-nitrobenzyl alcohol and bombarded with a high-energy beam of xenon atoms to generate ions.

The compounds $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$, $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2\{P(C_6H_4OMe\text{-}p)_3\}_5]$ and $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ were synthesised as described previously.[7]

Syntheses.—$[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2(PPh_3)_5]$ **1a**. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ (0.30 g, 0.14 mmol) was dissolved in dichloromethane (40 cm^3), and CO bubbled through the solution for 60 min. The solvent was then removed under reduced pressure, and the crude solid recrystallised from dichloromethane–diethyl ether to give dark red crystals of compound **1a**. Yield 0.26 g (90%) (Found: C, 54.8; H, 3.7. $C_{92}H_{75}O_6P_5Pd_5S_2$ requires C, 54.5; H, 3.7%); ν(CO) at 1828br cm^{-1}; $\nu(SO_2)$ at 1190m and 1054s cm^{-1}; $\delta(^{31}P)$ (CD_2Cl_2, 220 K) 16.7 (2 P, d, *J* = 15), 16.1 (1 P, ddt, *J* = 53, 6, 15), 12.0 (1 P, d, *J* = 53) and 10.1 (1 P, d, *J* = 6 Hz).

$[Pd_5(\mu_3\text{-}SO_2)_2(\mu\text{-}CO)_2\{P(C_6H_4OMe\text{-}p)_3\}_5]$ **1b**. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2\{P(C_6H_4OMe\text{-}p)\}_5]$ (0.20 g, 0.078 mmol) was dissolved in dichloromethane (40 cm^3), and CO bubbled through the solution for 60 min. The solvent was then removed under reduced pressure, and the crude solid recrystallised from dichloromethane–diethyl ether to give dark red crystals of compound **1b**. Yield 0.17 g (87%) (Found: C, 51.9; H, 4.4. $C_{107}H_{105}O_{11}P_5Pd_5S_2$ requires C, 51.9; H, 4.3%); ν(CO) at 1824br cm^{-1}; $\nu(SO_2)$ at 1050s cm^{-1}; $\delta(^{31}P)$ (CD_2Cl_2, 220 K) 13.2 (1 P, ddt, *J* = 56, 6, 16), 12.0 (2 P, d, *J* = 16), 9.3 (1 P, d, *J* = 56) and 5.1 (1 P, d, *J* = 6 Hz).

$[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2**. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMe_2Ph)_5]$ (0.30 g, 0.20 mmol) was dissolved in dichloromethane (30 cm^3), and CO bubbled

Table 9 Selected bond lengths (Å) and angles (°) for $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**

Pd(1)–Pd(2)	2.766 3(4)	Pd(3)–S(13)	2.253 1(9)
Pd(1)–Pd(3)	2.736 9(4)	Pd(3)–C(64)	2.050(4)
Pd(1)–S(12)	2.292(1)	S(12)–O(121)	1.452(3)
Pd(1)–S(13)	2.281(1)	S(12)–O(122)	1.451(3)
Pd(1)–P(1)	2.299 0(9)	S(13)–O(131)	1.450(3)
Pd(2)–Pd(3)	2.794 7(4)	S(13)–O(132)	1.461(3)
Pd(2)–P(2)	2.321(1)	C(37)–N(2)	1.160(5)
Pd(2)–S(12)	2.252 8(9)	C(38)–N(2)	1.394(5)
Pd(2)–C(37)	2.048(4)	C(64)–N(3)	1.159(5)
Pd(3)–P(3)	2.315(1)	C(65)–N(3)	1.404(5)
Pd(3)–Pd(1)–Pd(2)	61.04(1)	C(37)–Pd(2)–S(12)	144.2(1)
S(12)–Pd(1)–Pd(2)	51.86(2)	Pd(2)–Pd(3)–Pd(1)	60.001(9)
S(12)–Pd(1)–Pd(3)	99.57(3)	P(3)–Pd(3)–Pd(1)	153.52(3)
S(13)–Pd(1)–Pd(2)	105.53(3)	P(3)–Pd(3)–Pd(2)	146.01(3)
S(13)–Pd(1)–Pd(3)	52.41(2)	S(13)–Pd(3)–Pd(1)	53.33(2)
S(13)–Pd(1)–S(12)	151.98(3)	S(13)–Pd(3)–Pd(2)	105.40(3)
P(1)–Pd(1)–Pd(2)	135.28(3)	S(13)–Pd(3)–P(3)	102.44(4)
P(1)–Pd(1)–Pd(3)	155.87(3)	C(64)–Pd(3)–Pd(1)	101.0(1)
P(1)–Pd(1)–S(12)	104.45(4)	C(64)–Pd(3)–Pd(2)	62.8(1)
P(1)–Pd(1)–S(13)	103.55(4)	C(64)–Pd(3)–P(3)	99.3(1)
Pd(3)–Pd(2)–Pd(1)	58.962(9)	C(64)–Pd(3)–S(13)	151.5(1)
P(2)–Pd(2)–Pd(1)	148.29(3)	Pd(2)–S(12)–Pd(1)	74.98(3)
P(2)–Pd(2)–Pd(3)	150.09(3)	O(122)–S(12)–O(121)	113.5(2)
S(12)–Pd(2)–Pd(1)	53.15(2)	Pd(3)–S(13)–Pd(1)	74.26(3)
S(12)–Pd(2)–Pd(3)	98.88(3)	O(132)–S(13)–O(131)	114.2(2)
S(12)–Pd(2)–P(2)	98.27(3)	N(2)–C(37)–Pd(2)	164.6(3)
C(37)–Pd(2)–Pd(1)	96.7(1)	N(3)–C(64)–Pd(3)	160.6(4)
C(37)–Pd(2)–Pd(3)	75.5(1)	C(38)–N(2)–C(37)	175.6(4)
C(37)–Pd(2)–P(2)	103.4(1)	C(65)–N(3)–C(64)	174.0(4)

through the solution for 5 min. This led to rapid lightening of the colour to orange. After stirring for 60 min under a carbon monoxide atmosphere, the solvent was removed under reduced pressure, and the solid obtained recrystallised from dichloromethane–diethyl ether to give red crystals of compound **2**. Yield 0.26 g (87%) (Found: C, 33.9; H, 3.7. $C_{42}H_{55}O_8P_5Pd_5S_3$ requires C, 34.3; H, 3.8%); ν(CO) at 1908s cm^{-1}; $\nu(SO_2)$ at 1201s, 1067m and 1047vs cm^{-1}; $\delta(^{31}P)$ (CD_2Cl_2) −14.7 (2 P, d), −18.9 (1 P, t) and −22.4 (2 P, s), $^3J_{PP}$ = 26 Hz.

$[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**. The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ (0.20 g, 0.095 mmol) was dissolved in dichloromethane (20 cm^3), and a solution of C_8H_9NC (0.037 g, 0.29 mmol) in dichloromethane (10 cm^3) added. A rapid colour change to orange occurred. The mixture was stirred for 4 h, and the solvent was removed under reduced pressure. The crude solid was recrystallised from toluene–hexane to give red crystals of compound **3**. Yield 0.16 g (68%) (Found: C, 58.2; H, 4.5; N, 1.8. $C_{72}H_{63}N_2O_4P_3Pd_3S_2$ requires C, 57.8; H, 4.2; N, 1.9%). $\nu(SO_2)$ at 1203s, 1055s and 1044vs cm^{-1}; ν(NC) at 2119s and 2092s cm^{-1}; $\delta(^{31}P)$ 20.0 (2 P, d) and 13.7 (1 P, t), $^3J_{PP}$ = 43 Hz.

Crystal Structure Determination of $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(PMe_2Ph)_5]$ **2**.—Crystals of compound **2** used in the analysis were grown by a slow diffusion of hexane into a thf solution. A single crystal 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 4. The positions of the five palladium atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were located in subsequent Fourier difference syntheses. The hydrogen atoms were included in idealised positions. After initial refinement with isotropic thermal parameters an empirical absorption correction was applied to the data. All non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of least-squares refinement which converged at *R* 0.0314 and *R′* 0.0351. The methyl carbon atoms are numbered such that C(*n*1) and C(*n*2) are bonded to P(*n*) (*n* = 1–5) with the exception that C(42) is bonded to C(3) and C(32) bonded to C(4); C(*n*3) is also bonded to P(*n*) with the other phenyl carbon atoms in each ring C(*n*4) to C(*n*8).

Crystal Structure Determination of $[Pd_3(\mu\text{-}SO_2)_2(CNC_8H_9)_2(PPh_3)_3]$ **3**.—Crystals of compound **3** used in the analysis were grown by slow diffusion of hexane into a benzene solution. A single crystal 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 4. The structure was solved by direct methods, with all atoms except for three hydrogen atoms located in subsequent Fourier difference syntheses. All of the atoms were given anisotropic thermal parameters, except those of one of the solvent molecules and three of the carbon atoms in one isocyanide ligand. On application of a Chebyshev weighting scheme the model converged at *R* 0.0388 and *R′* 0.0434. The carbon atoms are numbered such that C(1), C(7) and C(13) are bound to P(1); C(19), C(25) and C(31) are bound to P(2) and C(46), C(52) and C(58) are bound to P(3). For the isocyanide ligands C(37) is bound to Pd(2) and the xylyl group contains C(38) to C(45) with C(40) and C(45) the methyl groups; C(64) is bound to Pd(3) and the xylyl group contains C(65) to C(72) with C(68) and C(72) the methyl groups. The solvated benzene molecules contain C(73)–C(75) and C(76)–C(81) with the former on the crystallographic centre of inversion. The programs and sources of scattering factors used are given in refs. 20–22.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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