Synthesis, Structure and Reactions of a Palladium Cluster Compound containing Bound Acetonitrile, $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$‡

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The cluster compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ **1a** reacts with acetonitrile to give a tetranuclear compound $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$ **2a**. Compound **2a** has been characterised by a single-crystal X-ray analysis, and shown to have a butterfly arrangement of palladium atoms with Pd–Pd bond distances between 2.754(1) and 2.969(1) Å. Comparison of the solid-state cross-polarisation magic angle spinning $^{31}P\text{-}\{^1H\}$ NMR spectrum with the low-temperature solution $^{31}P\text{-}\{^1H\}$ spectrum indicates that this structure is maintained in solution. However, at room temperature, solutions of **2a** revert back to **1a**. Like the *triangulo*-osmium clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$, it has proved possible to replace the labile acetonitrile ligand, and $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PMePh_2)_5]$ **1b** can be converted into $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(PMePh_2)_5]$ **3** *via* the compound $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PMePh_2)_4]$ **2b**.

The synthesis of carbonyl phosphine cluster compounds of palladium and platinum has attracted much attention.[1–5] Although the majority of work has concentrated on platinum, there has been considerable research into the synthesis of palladium carbonyl phosphine clusters. These compounds have been synthesised either from the reduction of palladium(II) compounds, for example the conversion of palladium(II) acetate into $[Pd_{10}(CO)_{12}(PBu_3)_6]$,[3] or from palladium(0) monomers, including $[Pd(\sigma,\eta^3\text{-}C_8H_{12})(PMe_3)]$ in the synthesis of $[Pd_7(CO)_7(PMe_3)_7]$[6] and $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone) in the synthesis of $[Pd_8(CO)_8(PMe_3)_7]$.[7] Far less research has been reported for phosphine palladium clusters containing ligands other than CO. Recently, we reported the synthesis of a series of pentapalladium cluster compounds with bridging sulfur dioxide ligands. Reaction of $[Pd_2(dba)_3]\cdot CHCl_3$ with L (L = phosphine or arsine) under an atmosphere of SO_2 gives $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2L_5]$.[8] The related compound with L = PMe_3 has also been synthesised in the reaction of $[Pd_8(CO)_8(PMe_3)_7]$ with SO_2.[9] The chemistry of this series of compounds has been studied and the research described in this paper demonstrates the reaction with acetonitrile, and the subsequent replacement of the bound acetonitrile ligand with a phosphine.

Results and Discussion

The compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ **1a** is soluble in dichloromethane, tetrahydrofuran (thf) and toluene to give red-green dichroic solutions, but attempts to dissolve it in acetonitrile led to a change in colour of the solid from dark green to orange-red. The IR spectrum of the red solid showed bands due to the ν(SO_2) stretching modes at 1212m, 1174s, 1062m and 1051s cm^{-1}. These are shifted from those associated with **1a** which were observed at 1214m, 1194m and 1064s cm^{-1}. The presence of a co-ordinated acetonitrile molecule was inferred from the observation of the ν(CH_3) stretching mode at 2925m cm^{-1} and the ν(CN) stretching mode at 2275w cm^{-1}.

Initial attempts to analyse the compound using $^{31}P\text{-}\{^1H\}$ NMR spectroscopy proved inconclusive, and spectra obtained in dichloromethane showed the presence of the starting material **1a**, and an additional broad singlet at δ 14.5. The colour of the CH_2Cl_2 solution changed slowly on standing from red to red-green dichroic and was associated with the reversion of the compound to **1a**. This was demonstrated by a time-dependent solution IR study, the results of which are shown in Fig. 1. A

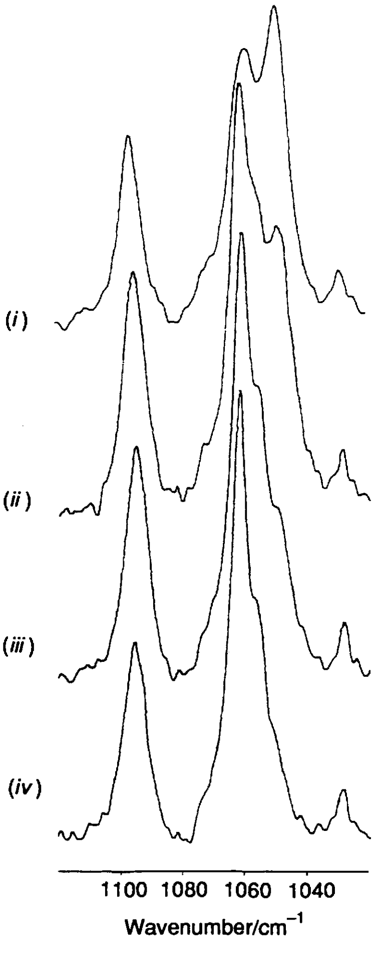

Fig. 1 Time-dependent infrared study of compound **2a** in dichloromethane (*i*) 5, (*ii*) 15, (*iii*) 25 and (*iv*) 40 min

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

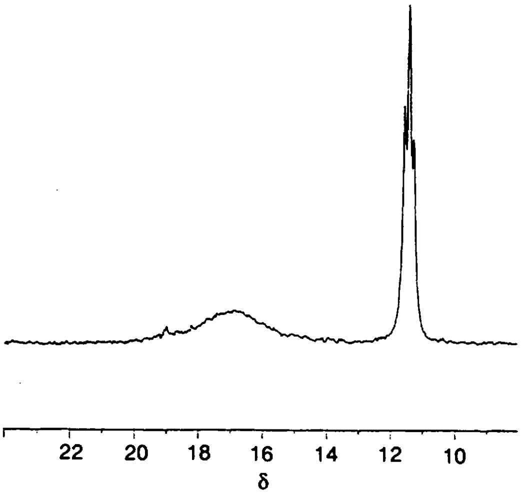

Fig. 2 Low-temperature $^{31}P-\{^1H\}$ NMR spectrum of compound **2a**

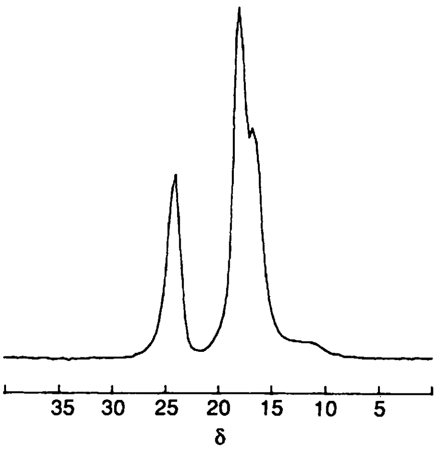

Fig. 3 CP MAS solid-state $^{31}P-\{^1H\}$ NMR spectrum of compound **2a**

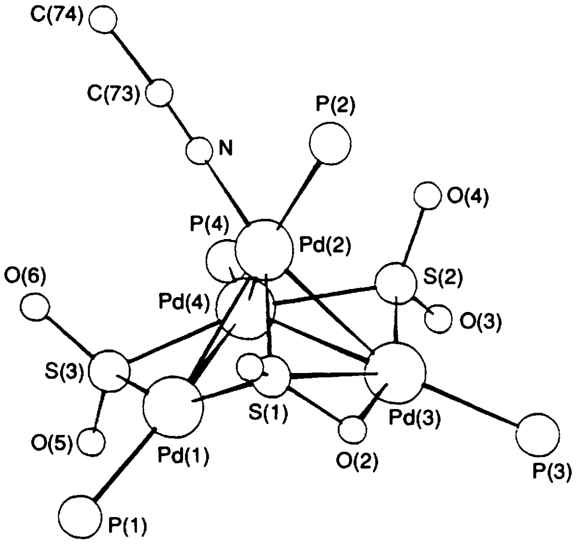

Fig. 4 Molecular structure of compound **2a** with phenyl groups omitted for clarity

Table 1 Crystal data for compound **2a**

Formula	$C_{74}H_{63}NO_6P_4Pd_4S_3 \cdot 0.25CH_2Cl_2$
M	1707.98 (1729.21 including solvent)
Crystal system	Orthorhombic
Space group	*Pbca* (no. 61)
a/Å	17.976(8)
b/Å	25.316(3)
c/Å	32.703(6)
U/Å^3	14 883
Z	8
D_c/g cm^{-3}	1.55
F(000)	6920
μ/cm^{-1}	11.71
Crystal colour	Red
Data collection	
X-radiation	Mo-Kα, λ = 0.710 69 Å
$\theta_{max,min}$/°	1, 22.5
ω-scan width/°	0.85 + 0.35 tanθ
total data collected	12 130
total unique and observed data [$I > 3\sigma(I)$]	4588
merging *R* factor	0.0163
Absorption correction	DIFABS[10]
Refinement	
no. of parameters	481
ratio data:parameters	9.54
weighting scheme	Chebyshev (coefficients 5.954, −0.481, 4.330)
final *R*	0.0492
final *R′*	0.0575

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

dichloromethane solution of the complex was made up, and the IR spectrum of this was recorded after 5, 15, 25 and 40 min. The peak at 1050 cm^{-1} that disappears with time is associated with the acetonitrile-containing compound **2a**, whereas the peak at 1063 cm^{-1} that increases in intensity with time is due to $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ **1a**.[8]

It has proved possible to get $^{31}P-\{^1H\}$ NMR spectra of compound **2a** by dissolving it in dichloromethane at −20 °C. Spectra can be recorded at this temperature and lower with no evidence of any decomposition to **1a**. The low-temperature spectrum in CD_2Cl_2 is shown in Fig. 2. Even at 180 K the static no-exchange limit was not reached. At this temperature the spectrum showed two main features in a 3:1 intensity ratio. The more intense resembles a triplet, but since there is no complementary multiplet in the spectrum it is more accurately represented as three singlets with similar chemical shifts. Thus **2a** contains four types of phosphorus atoms all in different chemical environments.

A cross-polarisation magic angle spinning (CP MAS) solid-state $^{31}P-\{^1H\}$ NMR spectrum for compound **2a** was also recorded (Fig. 3). The spectrum shows one signal, at δ 24.1, in a very different phosphorus environment from the other three, which are centred at δ 18.1. A shoulder on this peak at δ 16.8 may be attributed to one of these three environments, with the other two not resolved. This spectrum is very similar in appearance to the low-temperature solution $^{31}P-\{^1H\}$ NMR spectrum, which suggests that the solid-state and solution structures of the compound are similar. Although some information has been obtained from spectroscopic methods it has not been possible to characterise the compound completely using these techniques and therefore a single-crystal X-ray diffraction study was undertaken.

Crystal and Molecular Structure of $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$ **2a**.—Single crystals of compound **2a** were grown from the slow diffusion of acetonitrile into a dichloromethane solution of compound **1a**. The details of the data collection and structure solution are given in Table 1, the fractional atomic coordinates in Table 2 and important bond lengths and angles in Table 3. The cluster compound is illustrated in Fig. 4. The compound crystallises in the space group *Pbca* and no disorder was apparent in the structure. The structure consists of well separated molecules of $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$ together with occluded solvent

Table 2 Fractional atomic coordinates for compound **2a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	0.359 29(5)	0.023 02(4)	0.339 99(3)	C(29)	0.061 9(8)	−0.185 2(6)	0.306 3(4)
Pd(2)	0.291 90(5)	−0.070 64(4)	0.318 51(3)	C(30)	0.138 8(8)	−0.179 5(5)	0.308 9(4)
Pd(3)	0.373 88(5)	−0.096 53(4)	0.390 92(3)	C(31)	0.317 0(7)	−0.207 6(5)	0.296 9(4)
Pd(4)	0.248 97(5)	−0.019 83(4)	0.392 81(3)	C(32)	0.389 4(7)	−0.206 5(5)	0.310 6(4)
S(1)	0.410 1(2)	−0.051 7(1)	0.311 9(1)	C(33)	0.428 1(9)	−0.250 9(7)	0.319 2(5)
S(2)	0.266 0(2)	−0.104 3(1)	0.419 5(1)	C(34)	0.393 3(9)	−0.299 3(6)	0.314 0(5)
S(3)	0.264 8(2)	0.064 7(1)	0.370 9(1)	C(35)	0.324 6(10)	−0.302 9(7)	0.303 1(6)
P(1)	0.436 7(2)	0.090 3(1)	0.317 0(1)	C(36)	0.284 5(9)	−0.255 8(7)	0.293 3(5)
P(2)	0.276 1(2)	−0.146 7(1)	0.279 2(1)	C(37)	0.474 1(8)	−0.115 6(6)	0.481 1(4)
P(3)	0.439 6(2)	−0.149 8(1)	0.435 5(1)	C(38)	0.542 0(9)	−0.131 0(6)	0.500 3(5)
P(4)	0.150 2(2)	−0.001 7(1)	0.436 7(1)	C(39)	0.564 8(10)	−0.102 3(7)	0.535 2(5)
O(1)	0.439 2(5)	−0.056 0(4)	0.270 5(3)	C(40)	0.526 5(11)	−0.063 3(8)	0.549 2(6)
O(2)	0.458 4(5)	−0.078 8(3)	0.342 5(3)	C(41)	0.461 0(12)	−0.047 0(9)	0.531 7(7)
O(3)	0.264 5(5)	−0.105 2(4)	0.463 6(3)	C(42)	0.436 9(11)	−0.073 9(8)	0.496 3(6)
O(4)	0.226 4(5)	−0.147 2(4)	0.400 6(3)	C(43)	0.386 4(7)	−0.205 5(5)	0.454 2(4)
O(5)	0.279 2(5)	0.101 8(4)	0.404 3(3)	C(44)	0.381 0(9)	−0.218 2(7)	0.494 8(5)
O(6)	0.212 3(5)	0.082 5(4)	0.340 8(3)	C(45)	0.340 2(12)	−0.263 6(8)	0.507 0(7)
C(73)	0.115 8(9)	−0.042 1(6)	0.313 2(4)	C(46)	0.304 3(11)	−0.292 4(8)	0.477 1(6)
C(74)	0.037 3(9)	−0.027 4(9)	0.304 7(6)	C(47)	0.305 4(9)	−0.278 9(7)	0.438 2(5)
N	0.176 1(6)	−0.051 5(4)	0.319 6(3)	C(48)	0.348 1(8)	−0.236 2(6)	0.426 3(5)
C(1)	0.529 6(8)	0.065 5(6)	0.301 9(4)	C(49)	0.523 6(8)	−0.179 8(6)	0.414 5(4)
C(2)	0.564 5(10)	0.085 1(7)	0.267 3(6)	C(50)	0.571 8(9)	−0.148 9(7)	0.391 3(5)
C(3)	0.636 0(13)	0.063 6(9)	0.257 2(7)	C(51)	0.638 5(11)	−0.172 8(8)	0.376 6(6)
C(4)	0.664 4(11)	0.024 1(8)	0.279 1(6)	C(52)	0.656 3(11)	−0.222 1(8)	0.386 8(6)
C(5)	0.631 0(11)	0.005 9(8)	0.313 5(6)	C(53)	0.612 6(12)	−0.252 7(9)	0.411 2(7)
C(6)	0.561 3(9)	0.027 7(7)	0.325 9(5)	C(54)	0.543 7(10)	−0.230 4(7)	0.424 7(6)
C(7)	0.399 2(7)	0.121 6(5)	0.272 0(4)	C(55)	0.099 8(7)	−0.060 6(5)	0.451 8(4)
C(8)	0.355 2(10)	0.093 1(7)	0.246 7(6)	C(56)	0.077 4(7)	−0.095 1(5)	0.421 6(4)
C(9)	0.325 3(11)	0.115 9(8)	0.211 0(6)	C(57)	0.037 1(9)	−0.140 3(7)	0.431 4(5)
C(10)	0.339 5(11)	0.167 3(8)	0.202 8(6)	C(58)	0.024 5(11)	−0.152 1(8)	0.471 9(6)
C(11)	0.380 7(10)	0.195 8(7)	0.225 5(6)	C(59)	0.049 7(10)	−0.120 3(7)	0.502 1(5)
C(12)	0.414 1(9)	0.147 6(7)	0.261 7(5)	C(60)	0.085 4(8)	−0.073 4(6)	0.492 7(5)
C(13)	0.457 3(9)	0.145 1(7)	0.351 7(5)	C(61)	0.180 4(7)	0.029 7(5)	0.483 5(4)
C(14)	0.527 6(10)	0.154 2(7)	0.366 8(6)	C(62)	0.253 9(8)	0.031 3(6)	0.491 9(4)
C(15)	0.543 7(11)	0.194 1(8)	0.395 3(6)	C(63)	0.278 4(10)	0.057 4(7)	0.528 0(6)
C(16)	0.485 4(13)	0.221 0(9)	0.406 4(6)	C(64)	0.229 7(11)	0.079 4(8)	0.553 7(6)
C(17)	0.417 9(12)	0.215 4(8)	0.395 9(7)	C(65)	0.156 5(11)	0.080 1(8)	0.544 5(6)
C(18)	0.400 8(10)	0.147 6(7)	0.365 7(6)	C(66)	0.130 8(9)	0.054 5(6)	0.509 8(5)
C(19)	0.308 6(7)	−0.144 2(5)	0.225 6(4)	C(67)	0.073 5(7)	0.041 6(5)	0.417 8(4)
C(20)	0.320 6(9)	−0.098 2(7)	0.206 8(5)	C(68)	0.090 0(9)	0.094 2(7)	0.412 0(5)
C(21)	0.349 5(12)	−0.099 2(9)	0.164 2(6)	C(69)	0.036 9(10)	0.129 4(7)	0.397 7(5)
C(22)	0.357 0(11)	−0.144 8(9)	0.148 5(6)	C(70)	−0.028 3(10)	0.109 7(7)	0.385 7(5)
C(23)	0.344 6(12)	−0.191 3(9)	0.164 5(7)	C(71)	−0.047 1(10)	0.058 5(8)	0.390 7(6)
C(24)	0.319 6(9)	−0.191 3(7)	0.205 6(5)	C(72)	0.005 0(8)	0.023 4(6)	0.407 4(5)
C(25)	0.176 6(7)	−0.161 5(5)	0.274 3(4)	C(75)	0.239 3(41)	0.110 2(30)	0.067 1(23)
C(26)	0.138 5(8)	−0.148 7(5)	0.238 6(4)	Cl(1)	0.232 2(16)	0.154 5(11)	0.098 7(9)
C(27)	0.063 2(9)	−0.154 2(6)	0.237 1(5)	Cl(2)	0.236 9(26)	0.053 6(11)	0.085 1(14)
C(28)	0.024 5(9)	−0.174 3(6)	0.271 1(5)				

molecules, best modelled as dichloromethane with a partial occupancy.

The metal geometry of the cluster may be described as a 'butterfly', based on two edge-sharing metal triangles. The palladium–palladium bond lengths lie between 2.754(1) and 2.969(1) Å, which are all within the previously observed limits for Pd–Pd bonds. The distance between Pd(1) and Pd(3) is 3.465(1) Å, too long to represent any significant bonding interaction. Each metal atom is bonded to a terminal triphenylphosphine ligand. Of the three SO_2 ligands, two bridge two metal atoms in the conventional manner and the third bridges three metal atoms in the same fashion as observed for $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(AsPh_3)_5]$,[8] with the sulfur atom bridging two palladium atoms and an oxygen atom acting as a two-electron donor to a third. An acetonitrile ligand bound terminally to one of the palladium atoms completes the ligand co-ordination sphere.

Compound **2a** is the first example of a palladium or platinum cluster compound to contain the acetonitrile ligand. Examples of mono- and di-meric palladium compounds containing bonded acetonitrile ligands are given in Table 4. The Pd–N bond length in $[Pd_4(SO_2)_3(MeCN)(PPh_3)_4]$ is 2.14(1) Å, and this therefore represents the longest bond thus far observed between palladium and acetonitrile. The ion $[Pd(MeCN)_4]^{2+}$ has been reported,[15] but not structurally characterised.

Compound **2a** has 58 valence electrons, and is therefore isoelectronic with the other previously characterised tetrapalladium cluster compounds, $[Pd_4(CO)_5L_4]$ (L = $PMePh_2$ or PBu_3),[16,17] with 'butterfly' arrangements of palladium atoms. The Pd–Pd bond lengths are greater in $[Pd_4(SO_2)_3(MeCN)(PPh_3)_4]$ presumably as a result of the larger bite angles associated with SO_2 ligands. The butterfly array is also more open, with a non-bonded Pd ··· Pd distance of 3.465(1) Å compared with 3.209(1) Å for $[Pd_4(CO)_5(PBu_3)_4]$. A related structure has been postulated for the compound $[Pd_4(SO_2)_3(PMe_3)_5]$[8] in which the tetrapalladium butterfly core and the SO_2 ligand co-ordination is the same as in **2a** but the PPh_3 and MeCN ligands are all replaced by PMe_3 ligands.

The osmium cluster compounds $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ are both known,[18] and are synthesised from the reaction of $[Os_3(CO)_{12}]$ with acetonitrile in the presence of Me_3NO. Although neither has been characterised

Table 3 Selected bond lengths (Å) and angles (°) for compound **2a**

Pd(1)–Pd(2)	2.754(1)	Pd(2)–S(1)	2.189(3)	Pd(3)–P(3)	2.310(4)	S(2)–O(3)	1.441(9)
Pd(1)–Pd(4)	2.845(1)	Pd(2)–P(2)	2.332(3)	Pd(3)–O(2)	2.241(9)	S(2)–O(4)	1.44(1)
Pd(1)–S(1)	2.292(3)	Pd(2)–N	2.14(1)	Pd(4)–S(2)	2.330(3)	S(3)–O(5)	1.462(9)
Pd(1)–S(3)	2.241(3)	Pd(3)–Pd(4)	2.969(1)	Pd(4)–S(3)	2.275(3)	S(3)–O(6)	1.44(1)
Pd(1)–P(1)	2.324(3)	Pd(3)–S(1)	2.897(3)	Pd(4)–P(4)	2.328(3)	C(73)–C(74)	1.48(2)
Pd(2)–Pd(3)	2.865(1)	Pd(3)–S(2)	2.162(3)	S(1)–O(1)	1.454(9)	C(73)–N	1.13(2)
Pd(2)–Pd(4)	2.855(1)			S(1)–O(2)	1.492(9)		
Pd(4)–Pd(1)–Pd(2)	61.31(3)	N–Pd(2)–Pd(1)	103.2(3)	Pd(2)–Pd(4)–Pd(1)	57.77(3)	O(1)–S(1)–Pd(3)	151.7(4)
S(1)–Pd(1)–Pd(2)	50.41(8)	N–Pd(2)–Pd(3)	122.7(3)	Pd(3)–Pd(4)–Pd(1)	73.11(3)	O(2)–S(1)–Pd(1)	110.0(4)
S(1)–Pd(1)–Pd(4)	101.93(8)	N–Pd(2)–Pd(4)	67.7(3)	Pd(3)–Pd(4)–Pd(2)	58.89(3)	O(2)–S(1)–Pd(2)	113.4(4)
S(3)–Pd(1)–Pd(2)	100.79(9)	N–Pd(2)–S(1)	153.7(3)	S(2)–Pd(4)–Pd(1)	119.07(9)	O(2)–S(1)–Pd(3)	49.6(3)
S(3)–Pd(1)–Pd(4)	51.49(8)	N–Pd(2)–P(2)	94.5(3)	S(2)–Pd(4)–Pd(2)	82.54(9)	O(2)–S(1)–O(1)	112.3(5)
S(3)–Pd(1)–S(1)	150.6(1)	Pd(4)–Pd(3)–Pd(2)	58.57(3)	S(2)–Pd(4)–Pd(3)	46.23(8)	Pd(4)–S(2)–Pd(3)	82.7(1)
P(1)–Pd(1)–Pd(2)	144.3(1)	S(1)–Pd(3)–Pd(2)	44.65(7)	S(3)–Pd(4)–Pd(1)	50.42(8)	O(3)–S(2)–Pd(3)	116.8(4)
P(1)–Pd(1)–Pd(4)	153.2(1)	S(1)–Pd(3)–Pd(4)	86.11(7)	S(3)–Pd(4)–Pd(2)	97.01(8)	O(3)–S(2)–Pd(4)	112.7(4)
P(1)–Pd(1)–S(1)	103.7(1)	S(2)–Pd(3)–Pd(2)	85.25(9)	S(3)–Pd(4)–Pd(3)	120.94(9)	O(4)–S(2)–Pd(3)	109.0(4)
P(1)–Pd(1)–S(3)	104.7(1)	S(2)–Pd(3)–Pd(4)	51.11(9)	S(3)–Pd(4)–S(2)	164.8(1)	O(4)–S(2)–Pd(4)	117.8(4)
Pd(3)–Pd(2)–Pd(1)	76.11(4)	S(2)–Pd(3)–S(1)	128.6(1)	P(4)–Pd(4)–Pd(1)	146.18(9)	O(4)–S(2)–O(3)	114.1(6)
Pd(4)–Pd(2)–Pd(1)	60.92(3)	P(3)–Pd(3)–Pd(2)	156.6(1)	P(4)–Pd(4)–Pd(2)	144.99(9)	Pd(4)–S(1)–Pd(1)	78.1(1)
Pd(4)–Pd(2)–Pd(3)	62.54(3)	P(3)–Pd(3)–Pd(4)	139.0(1)	P(4)–Pd(4)–Pd(3)	135.91(9)	O(5)–S(1)–Pd(1)	120.3(4)
S(1)–Pd(2)–Pd(1)	53.80(9)	P(3)–Pd(3)–S(1)	132.6(1)	P(4)–Pd(4)–S(2)	92.9(1)	O(5)–S(1)–Pd(4)	113.0(4)
S(1)–Pd(2)–Pd(3)	68.46(9)	P(3)–Pd(3)–S(2)	97.6(1)	P(4)–Pd(4)–S(3)	96.0(1)	O(6)–S(1)–Pd(1)	109.7(4)
S(1)–Pd(2)–Pd(4)	104.35(9)	O(2)–Pd(3)–Pd(2)	73.7(2)	Pd(2)–S(1)–Pd(1)	75.8(1)	O(6)–S(1)–Pd(4)	115.4(4)
P(2)–Pd(2)–Pd(1)	154.82(9)	O(2)–Pd(3)–Pd(4)	113.3(2)	Pd(3)–S(1)–Pd(1)	82.9(1)	O(6)–S(1)–O(5)	115.3(6)
P(2)–Pd(2)–Pd(3)	109.20(9)	O(2)–Pd(3)–S(1)	30.5(2)	Pd(3)–S(1)–Pd(2)	66.89(9)	S(1)–O(2)–Pd(3)	99.9(4)
P(2)–Pd(2)–Pd(4)	143.88(9)	O(2)–Pd(3)–S(2)	158.8(2)	O(1)–S(1)–Pd(1)	125.4(4)	N–C(73)–C(74)	177.6(17)
P(2)–Pd(2)–S(1)	104.2(1)	O(2)–Pd(3)–P(3)	102.5(2)	O(1)–S(1)–Pd(2)	115.1(4)	C(73)–N–Pd(2)	168.5(12)

Table 4 Examples of palladium compounds containing bound acetonitrile

Compound	Pd–N/Å	Ref.
$[\{Pd(\eta^3\text{-}C_3H_5)(MeCN)_2\}_2(B_{10}Br_{10})]$	2.10(1)	11
$[(MeCN)Cl_2Pd(\mu\text{-}L^1)PdCl_2]$	2.065(14)	12
$[(MeCN)_2Pd(\mu\text{-}L^2)PdCl_2]$	2.115(4), 2.086(7)	13
$[Pd(\eta^5\text{-}CH_2CHCHMeCH_2CH_2CH{=}CMe_2)(MeCN)]BF_4$	2.086(7)	14

L^1 = Bis(diphenylphosphinomethyl)phenylphosphine, L^2 = 2,3-bis(diphenylphosphino)-*N*-methylmaleimide.

Table 5 Selected peaks in the FAB mass spectrum of $[Pd_4(SO_2)_3(PMePh_2)_5]$

m/z	Intensity	Assignment
1490	12	$[M - 2SO_2]^+$
1428	13	$[M - 3SO_2]^+$
1225	21	$[M - 3SO_2 - PMePh_2]^+$
1025	27	$[M - 3SO_2 - 2PMePh_2]^+$
948	32	$[M - 3SO_2 - 2PMePh_2 - Ph]^+$
871	31	$[M - 3SO_2 - 2PMePh_2 - 2Ph]^+$

$M = Pd_4(SO_2)_3(PMePh_2)_5$.

crystallographically, these compounds have been used as synthetic precursors to many *triangulo*-osmium cluster compounds, as the acetonitrile ligands are readily replaced by ligands such as PPh_3, $MeC_6H_4SO_2CH_2NC$, C_2H_4 and pyridine.

Reaction of $[Pd_4(SO_2)_3(MeCN)(PMePh_2)_4]$ *with* $PMePh_2$.—The structure of compound **2a** is very similar to that observed for $[Pd_4(SO_2)_3(PMe_3)_5]$.[8] As **2a** is synthesised from $[Pd_5(SO_2)_4(PPh_3)_5]$, it should be possible to convert a $[Pd_5(SO_2)_4L_5]$ cluster into a $[Pd_4(SO_2)_3L_5]$ cluster, *via* the acetonitrile complex, if the acetonitrile ligand is labile in a similar manner to that reported for $[Os_3(CO)_{11}(MeCN)]$. This proved problematic with the PPh_3 group of compounds as the acetonitrile complex is not stable in solution. Fortunately, the equivalent $PMePh_2$ compound is soluble in acetonitrile, and hence it was decided to start from $[Pd_5(SO_2)_4(PMePh_2)_5]$ **1b**. This has the additional advantage that the $[Pd_4(SO_2)_3(PMePh_2)_5]$ cluster compound is well documented as it is formed as a by-product in the synthesis of $[Pd_5(SO_2)_4(PMePh_2)_5]$ from $[Pd_2(dba)_3]\cdot CHCl_3$.[8]

The compound $[Pd_5(SO_2)_4(PMePh_2)_5]$ was dissolved in acetonitrile giving a red solution of $[Pd_4(SO_2)_3(MeCN)(PMePh_2)_4]$ **2b**. A toluene solution of $PMePh_2$ was added, and the acetonitrile removed under reduced pressure. Diethyl ether was added to precipitate a red solid, which was recrystallised from thf-ether to give a red microcrystalline solid that analysed for $[Pd_4(SO_2)_3(PMePh_2)_5]$ **3**. The identity of the product was confirmed by $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy and fast atom bombardment (FAB) mass spectrometry.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum, recorded at 240 K, was the same spectrum as that observed for samples of compound **3** synthesised directly from $[Pd_2(dba)_3]\cdot CHCl_3$. It has five resonances of equal intensity in the form of one doublet, three doublets of doublets, and one doublet of doublet of doublets.[8] The IR spectrum showed $\nu(SO_2)$ stretching modes at 1204m, 1181m, 1055s and 1043vs cm^{-1}, which again are identical to those observed for samples of **3** synthesised directly from $[Pd_2(dba)_3]\cdot CHCl_3$.[8] Further confirmation of the identity of the compound was obtained by FAB mass spectrometry. Although the $[M]^+$ peak was not observed, other important peaks were and these are summarised in Table 5. The intensities are relative to the $[Pd_2(PMePh_2)_2]^+$ peak, which was observed at $m/z = 612$. As in the other palladium cluster compounds studied using this technique[8,19] the SO_2 ligands were lost first from the co-ordination sphere. Then came the removal of fragments from the phosphine ligands which occurred concurrently with the loss of whole phosphine ligands. As with $[Pd_5(SO_2)_3(CO)_2(PMe_2Ph)_5]$[19] the phenyl fragments were lost before the methyl fragments from the phosphine ligands.

The synthesis of $[Pd_4(SO_2)_3(PMePh_2)_5]$ from $[Pd_4(SO_2)_3(MeCN)(PMePh_2)_4]$ has shown that, as with the *triangulo*-osmium clusters, it is possible to replace the acetonitrile by ligands which form stronger bonds to the cluster. It should also prove possible to synthesise novel cluster compounds by treating $[Pd_4(SO_2)_3(MeCN)L_4]$ clusters with mononuclear metal carbonyls which are capable of replacing MeCN and forming additional metal–metal bonds.

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. Infrared spectra were recorded on a Perkin-Elmer FT-1710 or a Mattson Polaris spectrometer. Solid samples were mulled with Nujol or hexachlorobutadiene, and recorded between KBr or CsI discs. Spectra of solution samples were recorded in KBr cells. The $^{31}P-\{^1H\}$ NMR spectra were recorded on a Brüker AM-300 spectrometer operating at 121.49 MHz and referenced to $P(OMe)_3O$ in D_2O; computer simulations were carried out using the Oxford University VAX computer system using 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. Solid-state spectra were recorded on a Brüker MSL-200 spectrometer operating at 80.96 MHz, using CP MAS techniques. 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 (NOBA) and bombarded with a high-energy beam of xenon atoms to generate ions.

Compounds **1a** and **1b** were synthesised as reported previously.[8]

Syntheses.—$[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$ **2a**. Acetonitrile (30 cm^3) was added to $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.30 g, 0.14 mmol) and the suspension stirred for 2 h. The resulting orange-red precipitate of compound **2a** was filtered off, washed with acetonitrile, and dried by passing a stream of dinitrogen over it. Yield 0.24 g (79%) (Found: C, 50.5; H, 3.7; N, 1.0. $C_{74}H_{63}NO_6P_4Pd_4S_3\cdot CH_2Cl_2$ requires C, 50.2; H, 3.7; N, 0.8%). ν(SO_2) at 1212m, 1174s, 1062m and 1051s; ν(CH_3) at 2925w; ν(NC) at 2275w cm^{-1}. δ(^{31}P) (CD_2Cl_2, 253 K) 17.1 (br s) and 11.6 (br s); (CD_2Cl_2, 188 K) δ 21.6 (br s, 1P), 11.34, 11.20 and 11.05 (combined, 3P); δ(^1H) (CD_2Cl_2, 188 K) 1.96 (br s).

$[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(PMePh_2)_5]$ **3**. The compound $[Pd_5(SO_2)_4(PMePh_2)_5]$ (0.20 g, 0.11 mmol) was dissolved in acetonitrile (20 cm^3) giving a red solution of compound **2b**, and a solution of $PMePh_2$ (0.022 g, 0.11 mmol) in toluene (20 cm^3) was added. The mixture was stirred for 2 h, and the volume of the solution decreased under reduced pressure. Diethyl ether was then added to precipitate a red solid, which was recrystallised from thf–ether to give compound **3**. Yield 0.11 g (61%) (Found: C, 47.7; H, 4.0. $C_{65}H_{65}O_6P_5Pd_4S_3$ requires C, 48.2; H, 4.0%). ν(SO_2) at 1204m, 1181m, 1055s and 1043vs cm^{-1}. δ(^{31}P) (CD_2Cl_2, 250 K) 6.3 (ddd), −1.7 (d), −4.8 (dd), −5.0 (dd) and −7.7 (dd).

Crystal Structure Determination of $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$ **2a**.—Crystals of compound **2a** used in the analysis were grown from a slow diffusion of acetonitrile into a dichloromethane solution of compound **1a**. A single crystal was mounted in a Lindemann tube 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. The structure was solved by direct methods, with all non-hydrogen atoms located in subsequent Fourier difference syntheses. After assigning anisotropic thermal parameters to all of the palladium, phosphorus, oxygen and sulfur atoms, and the atoms of the acetonitrile, the hydrogens were generated geometrically. On application of a Chebyshev weighting scheme the model converged at R 0.0492 and R' 0.0575. The programs and sources of scattering factors used are given in refs. 10, 20 and 21. The carbon atoms are numbered such that C(1), C(7) and C(13) are bonded to P(1), C(19), C(25) and C(31) to P(2), C(37), C(43) and C(49) to P(3), and C(55), C(61) and C(67) to P(4). Atoms C(73) and C(74) are associated with the acetonitrile ligand and C(75) with the dichloromethane molecule of solvation.

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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