Synthesis, Structure and Reactivity of Anionic Tripalladium Cluster Compounds[‡]

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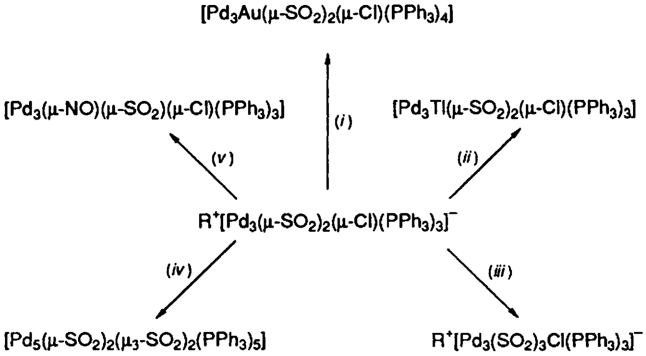
The cluster compounds $R^+[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}X)(PPh_3)_3]^-$ [R = NEt_4, X = Cl **1** or Br **2**; R = $NEt_3(CH_2Ph)$, X = Cl **3**; R = $PPh_3(CH_2Ph)$, X = Cl **4**; R = NBu_4, X = I **5**] have been synthesised from the reaction of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ and R^+X^-. The molecular structure of $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]\cdot 0.5Me_2CO$ has been determined by single-crystal X-ray diffractometry. The study, though limited by disorder of the bridging ligands, has demonstrated that the Pd–Pd bond distances are within the expected range for a 44-electron *triangulo*-palladium cluster. These *triangulo*-cluster compounds undergo a variety of reactions: one SO_2 ligand may be substituted by NO^+, giving the neutral *triangulo* cluster $[Pd_3(\mu\text{-}NO)(\mu\text{-}SO_2)(\mu\text{-}Cl)(PPh_3)_3]$ **6** which has been characterised by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and fast atom bombardment mass spectrometry. The triangle may be capped by the metal fragments $Au(PPh_3)^+$ and Tl^+, giving $[Pd_3Au(SO_2)_2Cl(PPh_3)_4]$ **7** and $[Pd_3Tl(SO_2)_2Cl(PPh_3)_3]$ **8** respectively and the chloride ligand may be abstracted by $AgNO_3$ leading by cluster aggregation to $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$. The compound $[Pd_3(SO_2)_2X(PPh_3)_3]^-$ reacts in a reversible manner with SO_2 to give $[Pd_3(SO_2)_3X(PPh_3)_3]^-$ (X = Cl **9** or I **10**). The reversibility of this reaction and the greater stability of the adduct formed from the iodo-*triangulo*-palladium cluster suggested that the additional SO_2 ligand is co-ordinated to the halide ligand.

The 44-electron anionic triplatinum cluster compounds $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}X)(PR_3)_3]^-$ (X = Cl, Br or N_3; R = Ph or C_6H_{11}) have been synthesised from the reaction of X^- with $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$, though for R = C_6H_{11} trimethylamine *N*-oxide needs to be added to labilise a sulfur dioxide ligand.[1,2] The reactions of these compounds with metal fragments to give capped *triangulo* clusters have been studied. Reactions of $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3]^-$ with 1 equivalent of $[Au\{P(C_6H_4F\text{-}p)_3\}Cl]$ gives the gold-capped *triangulo* cluster $[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}]$,[3] whereas reaction with an excess in the presence of $TlPF_6$ gives trigonal-bipyramidal $[Pt_3Au_2(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}_2]^+$.[4] Other *triangulo*-platinum cluster compounds have been capped with $CuPPh_3^+$,[5] $AgPPh_3^+$,[6] Ag^+[7] and Tl^+.[8] The research described in this paper details the synthesis from $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ of the palladium analogues of the *triangulo*-platinum anionic clusters, $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}X)(PPh_3)_3]^-$ (X = Cl, Br or I), and then seeks to explore the chemistry of these compounds by studying their substitution, addition and aggregation reactions. The reactions of $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}X)(PPh_3)_3]^-$ are summarised in Scheme 1.



Scheme 1 (*i*) $[Au(PPh_3)(NO_3)]$; (*ii*) $TlNO_3$; (*iii*) SO_2; (*iv*) Ag^+; (*v*) $NOBF_4$

Results and Discussion

The reaction of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ with R^+X^- leads to the formation of the ionic cluster compounds $R^+[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}X)(PPh_3)_3]^-$ [R = NEt_4, X = Cl **1** or Br **2**; R = $NEt_3(CH_2Ph)$, X = Cl **3**; R = $PPh_3(CH_2Ph)$, X = Cl **4**; R = NBu_4, X = I **5**]. These results have been characterised by IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and, in the case of **3**, by a single-crystal X-ray structural analysis. When an ethanolic solution containing 2 equivalents of R^+X^- was added to a toluene solution of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ there was a rapid lightening of colour from a dichroic dark green-red to yellow. After stirring for 1 h, the volume of solution was decreased under reduced pressure to give a yellow precipitate. This was recrystallised to give crystals of the product. The compounds all gave IR spectra that contained four peaks in the $\nu(SO_2)$ stretching mode region, indicating the presence of bridging sulfur dioxide ligands. Two peaks were observed between 1051 and 1036 cm^{-1}, and another two between 1192 and 1167 cm^{-1}. Compounds **1** and **2** were not soluble enough for $^{31}P\text{-}\{^1H\}$ NMR spectra to be obtained. Spectra were recorded for $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **3**, which gave a doublet at δ 8.3 and a triplet at δ 5.0 and for $[NBu_4][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}I)(PPh_3)_3]$ **5**, which gave a doublet at δ 14.0 and a triplet at δ 5.5. In both cases the intensity ratio of the doublet to the triplet was 2:1, and the coupling constant within the doublet and triplet was 44 Hz. These spectra provided good evidence that the products are *triangulo*-palladium cluster compounds with two phosphines in equivalent positions and the third in a different environment. Confirmation of the structure was

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

Table 1 Crystal data for compound **3**

Formula	$C_{67}H_{67}ClNO_4P_3Pd_3S_2\cdot0.5C_3H_6O$
M	1490.89 (1729.21 including solvent)
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	13.677(10)
b/Å	20.081(4)
c/Å	24.278(3)
α/°	90.43(1)
β/°	90.94(4)
γ/°	103.49(4)
U/Å^3	6482
Z	4
D_c/g cm^{-3}	1.53
$F(000)$	3024
μ/cm^{-1}	10.37
Crystal colour	Yellow
Crystal dimensions/mm	0.2 × 0.4 × 0.5
Data collection	
X-radiation	Mo-Kα, λ = 0.710 69 Å
$\theta_{min,max}$	1, 20
ω-scan width/°	$0.70 + 0.35\tan\theta$
total data collected	14 289
total unique and observed data $[I > 3\sigma(I)]$	6335
merging R factor	0.0197
Absorption correction	DIFABS
Refinement	
no. of parameters	731
ratio data : parameters	8.67
weighting scheme	Chebyshev (coefficients 6.311, −11.378, 4.891, −3.976)
Final R	0.0473
Final R'	0.0436

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

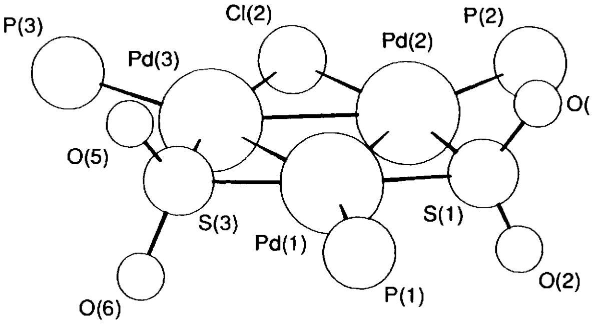


Fig. 1 Structure of one of the anionic units in $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **3**, with the phenyl groups omitted for clarity

obtained by a single-crystal X-ray structural analysis on one of this group of compounds.

Crystal and Molecular Structure of $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **3**.—Single crystals of X-ray quality were grown from the slow diffusion of hexane into an acetone solution of compound **3**. Details of the data collection and structure solution are given in Table 1, final fractional atomic coordinates in Table 2 and important bond lengths and angles in Table 3. The compound crystallises in the space group $P\bar{1}$. The asymmetric unit consists of two $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ anions, two $[NEt_3(CH_2Ph)]^+$ cations and one occluded molecule of acetone, all well separated. One of the cluster anion units is illustrated in Fig. 1. There is a crystallographic disorder between one of the bridging SO_2 ligands and the bridging chloride ligand on each palladium triangle. The two palladium triangles in the asymmetric unit are not equilateral, and the palladium–palladium bond lengths are 2.907(1), 2.876(1) and 2.899(1) Å in one triangle, and 2.994(1), 2.882(1) and 2.878(1) Å in the other.

The inclusion of the occupancies of the distorted bridging atoms in the refinement gave values different from $\frac{1}{2}$ though similar in the two triangles. The final occupancies of the disordered atoms in the first triangle were S(1), Cl(2), O(1) and O(2) 0.5907, S(2), Cl(1), O(3) and O(4) 0.4093 and in the second triangle S(4), Cl(5), O(7) and O(8) 0.4025 and S(5), Cl(4), O(9) and O(10) 0.5975. The disorder makes consideration of individual palladium–palladium bond lengths meaningless, but it may be noted that the average Pd–Pd bond lengths in $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$, which contains 44 valence electrons, of 2.894 and 2.918 Å for the two triangles fall in the range 2.734(4)–3.000(5) Å observed for previously characterised 44-electron *triangulo*-cluster compounds of palladium.[9,10]

The structure of the analogous platinum compound $[NEt_4][Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Br)\{P(C_6H_{11})_3\}_3]$ has been determined,[2] and a disorder between the SO_2 and halide ligands was observed. In this compound occupation of a stabilised a_2' molecular orbital leads to a cluster characterised by 44 valence electrons. The a_2' molecular orbital has some M–M antibonding character, and hence the Pt–Pt bonds are longer than in 42-valence-electron cluster compounds. The same argument may be applied to 44-electron palladium cluster compounds such as **3**. In both $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ and $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Br)\{P(C_6H_{11})_3\}_3]^-$ the metal triangle, phosphorus atoms and bridging atoms are essentially coplanar. The distances from the palladium to the full-occupancy bridging SO_2 ligands are Pd(1)–S(3) 2.229(4), Pd(3)–S(3), 2.233(4), Pd(4)–S(6) 2.239(4) and Pd(6)–S(6) 2.233(4) Å. These fall within the limits of 2.152(3) and 2.374(3) Å for Pd to μ-SO_2 distances observed in previously characterised structures. The Pd–P bond distances range from 2.315(4) to 2.337(3) Å and therefore fall between 2.273(6) and 2.345(3) Å which is the observed range for 44-electron *triangulo*-palladium cluster compounds.

Reaction with $NOBF_4$.—When an ethanolic solution of $NOBF_4$ was added to a solution of compound **4** also in ethanol the solution rapidly darkened and a fine yellow precipitate formed. Recrystallsation of this from benzene–hexane gave brown crystals formulated as $[Pd_3(\mu\text{-}NO)(\mu\text{-}SO_2)(\mu\text{-}Cl)(PPh_3)_3]$ **6** on the basis of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and fast atom bombardment (FAB) mass spectrometry. The IR spectrum of the product confirmed that both bridging NO and SO_2 ligands were present. The ν(NO) stretching mode was observed at 1602vs cm^{-1} and the $\nu(SO_2)$ stretching modes at 1207s and 1057vs cm^{-1}. There was no evidence for either the $[PPh_3(CH_2Ph)]^+$ cation or the BF_4^- anion, demonstrating that the cluster product was neutral. The $^{31}P\text{-}\{^1H\}$ NMR spectrum consisted of three signals, at δ 21.3, 12.8 and 6.9, all of equal intensity, and is shown in Fig. 2. The signals were broad at room temperature but cooling to 280 K revealed that two of the signals were doublets of doublets, whereas the third, at δ 12.8, appeared as a triplet. Examination of the other signals suggested that in reality this signal was also a doublet of doublets, but with the two coupling constants very similar. The spectrum indicated that there were three different phosphine environments in the molecule which is consistent with the formulation $[Pd_3(\mu\text{-}NO)(\mu\text{-}SO_2)(\mu\text{-}Cl)(PPh_3)_3]$.

It was possible to assign the phosphorus resonances to the different chemical environments by consideration of the following points. First, for all known compounds of the type $[Pt_3(SO_2)_2Cl(PR_3)_3]^-$ the $^3J_{PP}$ coupling across the Pt–Pt bond bridged by SO_2 is greater than that over the bond bridged by chloride.[1,2,11] For the palladium analogues it is not possible to obtain the latter coupling constant from the spectrum, though it is reasonable to assume that the observation from platinum chemistry is equally valid when applied to the related palladium compounds. Secondly, for the $[M_3(SO_2)_2Cl(PR_3)_3]^-$ (M = Pd or Pt) clusters the triplet is always observed at higher field than the doublet,[1,11] hence co-ordination to the chloride ion increases the chemical shift of the resonance. Thirdly, for platinum *triangulo* clusters of the type $[Pt_3(\mu\text{-}X)_3(PR_3)_3]$, $^3J_{PP}$

Table 2 Fractional atomic coordinates for compound 3

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(1)	−0.003 48(7)	0.176 67(5)	0.181 07(4)
Pd(2)	0.175 54(7)	0.251 83(5)	0.126 36(4)
Pd(3)	0.174 13(7)	0.237 45(5)	0.245 08(4)
S(3)	0.023 4(3)	0.178 8(2)	0.271 9(2)
O(5)	0.025 4(8)	0.119 4(5)	0.299 2(4)
O(6)	−0.038 4(7)	0.221 6(5)	0.300 3(4)
S(1)	0.022 1(3)	0.202 1(2)	0.088 7(2)
Cl(1)	0.022 1(3)	0.202 1(2)	0.088 7(2)
S(2)	0.307 4(3)	0.288 7(2)	0.189 3(1)
Cl(2)	0.307 4(3)	0.288 7(2)	0.189 3(1)
O(1)	0.274 4(11)	0.143 4(8)	0.053 6(6)
O(2)	−0.023 2(11)	0.245 9(8)	0.071 3(6)
O(3)	0.329 8(15)	0.361 5(11)	0.194 3(8)
O(4)	0.372 4(14)	0.253 4(10)	0.184 2(8)
Pd(4)	0.084 31(7)	−0.312 11(5)	0.316 19(4)
Pd(5)	0.275 00(7)	−0.245 64(5)	0.376 67(4)
Pd(6)	0.262 47(7)	−0.246 13(5)	0.258 22(4)
S(6)	0.111 0(3)	−0.300 4(2)	0.225 7(1)
O(11)	0.104 3(7)	−0.364 5(5)	0.194 8(4)
O(12)	0.061 3(7)	−0.254 5(5)	0.199 6(4)
S(4)	0.119 4(2)	−0.301 6(2)	0.411 0(1)
Cl(4)	0.119 4(2)	−0.301 6(2)	0.411 0(1)
S(5)	0.388 6(3)	−0.187 1(2)	0.315 7(1)
Cl(5)	0.388 6(3)	−0.187 1(2)	0.315 7(1)
O(7)	0.078 2(12)	−0.258 4(9)	0.438 9(7)
O(8)	0.127 0(15)	−0.367 6(11)	0.437 6(9)
O(9)	0.385 8(9)	−0.113 8(7)	0.316 8(5)
O(10)	0.480 1(9)	−0.201 6(6)	0.312 6(5)
P(1)	−0.171 9(3)	0.119 4(2)	0.173 1(1)
P(2)	0.267 1(3)	0.285 9(2)	0.047 9(1)
P(3)	0.269 9(3)	0.249 8(2)	0.325 9(1)
C(1)	−0.198 8(9)	0.073 9(6)	0.107 9(5)
C(2)	−0.265 6(11)	0.088 0(8)	0.068 9(6)
C(3)	−0.283 8(12)	0.048 6(8)	0.018 9(7)
C(4)	−0.237 2(12)	−0.002 2(8)	0.011 4(7)
C(5)	−0.173 3(13)	−0.016 4(9)	0.047 5(7)
C(6)	−0.150 2(12)	0.023 0(8)	0.098 0(7)
C(7)	−0.233 4(9)	0.056 0(6)	0.223 5(5)
C(8)	−0.295 4(11)	−0.006 4(8)	0.207 1(6)
C(9)	−0.346 3(12)	−0.050 8(8)	0.248 1(7)
C(10)	−0.337 8(11)	−0.033 0(8)	0.300 2(6)
C(11)	−0.274 5(11)	0.028 0(8)	0.319 4(6)
C(12)	−0.221 8(10)	0.073 5(7)	0.279 5(6)
C(13)	−0.254 1(10)	0.180 1(7)	0.172 4(5)
C(14)	−0.228 1(11)	0.237 0(8)	0.139 9(6)
C(15)	−0.290 1(13)	0.283 5(9)	0.138 7(7)
C(16)	−0.375 7(14)	0.274 5(10)	0.167 7(8)
C(17)	−0.402 0(15)	0.219 0(11)	0.198 8(9)
C(18)	−0.340 1(14)	0.167 9(9)	0.200 4(7)
C(19)	0.210 9(10)	0.259 8(7)	−0.019 4(5)
C(20)	0.121 4(11)	0.278 1(8)	−0.033 8(6)
C(21)	0.076 5(12)	0.260 4(8)	−0.086 2(7)
C(22)	0.118 7(12)	0.226 6(8)	−0.122 7(7)
C(23)	0.207 5(14)	0.207 1(9)	−0.108 7(8)
C(24)	0.250 7(11)	0.224 2(8)	−0.058 0(6)
C(25)	0.319 1(10)	0.378 7(7)	0.041 9(6)
C(26)	0.292 9(13)	0.417 3(9)	0.002 7(7)
C(27)	0.332 8(16)	0.491 0(11)	0.003 9(9)
C(28)	0.397 1(15)	0.517 7(10)	0.041 0(8)
C(29)	0.426 7(14)	0.482 2(10)	0.080 2(8)
C(30)	0.385 0(13)	0.411 2(9)	0.081 7(7)
C(31)	0.378 7(10)	0.250 1(7)	0.045 6(5)
C(32)	0.367 1(11)	0.187 1(8)	0.066 8(6)
C(33)	0.452 1(17)	0.153 5(11)	0.058 7(9)
C(34)	0.529 5(15)	0.186 6(11)	0.034 1(8)
C(35)	0.545 6(14)	0.248 7(10)	0.016 0(8)
C(36)	0.466 0(12)	0.283 9(8)	0.020 4(7)
C(37)	0.218 3(9)	0.269 4(6)	0.392 2(5)
C(38)	0.274 9(11)	0.284 0(7)	0.439 0(6)
C(39)	0.236 7(12)	0.305 0(8)	0.487 0(7)
C(40)	0.140 4(11)	0.309 9(8)	0.487 6(6)
C(41)	0.079 0(11)	0.295 7(7)	0.441 6(6)
C(42)	0.118 0(10)	0.275 8(7)	0.391 8(6)
C(43)	0.386 2(9)	0.316 2(6)	0.327 0(5)
C(44)	0.375 7(11)	0.383 4(8)	0.321 1(6)
C(45)	0.458 6(13)	0.439 0(9)	0.325 3(7)
C(46)	0.550 3(12)	0.426 3(9)	0.333 8(7)
C(47)	0.560 2(13)	0.361 6(10)	0.340 1(7)
C(48)	0.481 0(11)	0.307 0(7)	0.336 6(6)
C(49)	0.314 7(9)	0.171 4(6)	0.336 0(5)
C(50)	0.304 8(10)	0.136 4(7)	0.383 0(6)
C(51)	0.341 2(12)	0.076 5(8)	0.384 8(7)
C(52)	0.385 8(12)	0.053 1(9)	0.341 7(7)
C(53)	0.397 9(13)	0.089 5(9)	0.294 9(7)
C(54)	0.359 3(11)	0.148 4(8)	0.290 9(6)
P(4)	−0.085 7(2)	−0.367 9(2)	0.317 9(1)
P(5)	0.382 7(2)	−0.232 1(2)	0.453 8(1)
P(6)	0.350 4(2)	−0.237 7(2)	0.176 4(1)
C(55)	−0.116 9(9)	−0.425 7(6)	0.374 4(5)
C(56)	−0.208 7(10)	−0.439 2(7)	0.401 4(6)
C(57)	−0.228 9(11)	−0.488 2(8)	0.442 4(6)
C(58)	−0.161 5(12)	−0.523 1(8)	0.458 1(7)
C(59)	−0.071 0(12)	−0.511 4(8)	0.434 2(6)
C(60)	−0.046 6(11)	−0.462 7(7)	0.390 5(6)
C(61)	−0.165 8(9)	−0.308 1(6)	0.327 6(5)
C(62)	−0.145 8(9)	−0.263 2(7)	0.373 2(5)
C(63)	−0.205 8(10)	−0.218 3(7)	0.382 2(6)
C(64)	−0.279 8(11)	−0.213 0(8)	0.346 9(6)
C(65)	−0.300 5(11)	−0.253 0(8)	0.301 3(6)
C(66)	−0.242 1(10)	−0.303 0(7)	0.290 0(6)
C(67)	−0.145 1(9)	−0.419 8(6)	0.258 6(5)
C(68)	−0.136 2(10)	−0.393 0(7)	0.206 7(5)
C(69)	−0.184 6(11)	−0.430 6(8)	0.162 5(6)
C(70)	−0.243 2(12)	−0.495 2(8)	0.169 4(7)
C(71)	−0.254 1(11)	−0.521 7(8)	0.218 8(6)
C(72)	−0.204 5(10)	−0.484 9(7)	0.264 9(6)
C(73)	0.339 0(10)	−0.229 2(7)	0.523 8(5)
C(74)	0.388 8(10)	−0.183 0(7)	0.563 2(5)
C(75)	0.355 5(11)	−0.185 5(8)	0.617 4(6)
C(76)	0.270 3(12)	−0.231 5(8)	0.630 3(7)
C(77)	0.218 3(11)	−0.278 8(8)	0.593 2(7)
C(78)	0.252 2(11)	−0.275 8(7)	0.540 3(6)
C(79)	0.445 8(9)	−0.303 7(6)	0.456 4(5)
C(80)	0.488 7(10)	−0.318 1(7)	0.408 6(5)
C(81)	0.535 8(12)	−0.373 3(8)	0.405 1(7)
C(82)	0.534 7(12)	−0.412 2(8)	0.452 8(7)
C(83)	0.496 7(12)	−0.398 3(8)	0.501 5(7)
C(84)	0.448 0(11)	−0.343 6(7)	0.501 6(6)
C(85)	0.487 4(9)	−0.156 5(6)	0.452 7(5)
C(86)	0.585 4(10)	−0.159 9(7)	0.464 0(5)
C(87)	0.662 3(11)	−0.100 2(8)	0.466 3(6)
C(88)	0.638 3(11)	−0.039 6(8)	0.455 0(6)
C(89)	0.543 8(11)	−0.033 9(8)	0.442 8(6)
C(90)	0.466 9(10)	−0.094 8(7)	0.440 5(6)
C(91)	0.437 2(10)	−0.293 4(7)	0.180 6(5)
C(92)	0.431 8(12)	−0.334 1(8)	0.224 7(7)
C(93)	0.496 6(13)	−0.382 1(9)	0.228 0(7)
C(94)	0.560 7(12)	−0.386 9(8)	0.189 3(7)
C(95)	0.565 7(16)	−0.347 9(11)	0.146 3(9)
C(96)	0.498 6(15)	−0.301 5(10)	0.139 5(8)
C(97)	0.415 6(9)	−0.151 7(6)	0.156 2(5)
C(98)	0.391 0(12)	−0.097 1(8)	0.181 3(7)
C(99)	0.429 9(14)	−0.029 8(10)	0.161 7(8)
C(100)	0.494 6(12)	−0.018 2(8)	0.121 4(7)
C(101)	0.523 1(13)	−0.070 9(9)	0.095 8(7)
C(102)	0.484 0(13)	−0.139 7(9)	0.114 3(7)
C(103)	0.278 0(10)	−0.267 1(7)	0.113 8(5)
C(104)	0.239 5(11)	−0.220 2(7)	0.083 0(6)
C(105)	0.178 1(12)	−0.241 3(8)	0.036 5(6)
C(106)	0.160 1(12)	−0.307 7(9)	0.018 9(7)
C(107)	0.200 6(13)	−0.352 6(9)	0.048 6(7)
C(108)	0.257 5(11)	−0.333 6(8)	0.095 5(6)
C(200)	0.085 6(11)	−0.131 4(8)	0.350 1(6)
C(201)	0.180 5(13)	−0.099 6(9)	0.385 1(7)

Table 2 (*continued*)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
C(202)	−0.031 2(10)	−0.131 0(7)	0.272 0(6)	C(304)	0.000 8(15)	0.453 7(10)	0.163 9(9)
C(203)	−0.090 8(12)	−0.090 6(8)	0.236 8(7)	C(305)	−0.010 3(20)	0.404 7(14)	0.110 3(11)
C(204)	0.048 5(11)	−0.018 7(8)	0.322 3(6)	C(306)	0.060 9(11)	0.488 5(8)	0.256 1(6)
C(205)	−0.033 7(12)	−0.026 3(8)	0.365 6(7)	C(307)	0.133 9(11)	0.495 5(8)	0.301 8(6)
C(206)	0.154 2(11)	−0.078 3(7)	0.262 9(6)	C(308)	0.210 8(12)	0.553 3(8)	0.305 5(7)
C(207)	0.142 3(10)	−0.046 4(7)	0.210 4(6)	C(309)	0.276 4(13)	0.567 2(9)	0.348 1(8)
C(208)	0.117 1(11)	−0.087 1(8)	0.163 5(6)	C(310)	0.265 8(14)	0.521 5(10)	0.390 8(8)
C(209)	0.098 2(13)	−0.059 9(9)	0.112 0(7)	C(311)	0.192 4(13)	0.464 8(9)	0.389 3(7)
C(210)	0.110 1(14)	0.009 7(10)	0.109 7(8)	C(312)	0.129 5(12)	0.449 9(8)	0.344 6(7)
C(211)	0.140 7(14)	0.050 6(9)	0.153 3(8)	C(400)	0.047 0(17)	0.112 8(12)	0.476 1(9)
C(212)	0.157 1(11)	0.025 7(8)	0.204 3(6)	C(401)	−0.067 3(14)	0.091 6(10)	0.472 4(7)
C(300)	0.165 8(14)	0.043 5(10)	0.194 3(8)	C(402)	−0.120 9(14)	0.140 0(10)	0.444 6(8)
C(301)	0.255 1(16)	0.501 1(11)	0.168 6(9)	O(400)	−0.113 6(10)	0.037 4(7)	0.491 3(6)
C(302)	0.011 8(14)	0.363 1(10)	0.230 8(8)	N(200)	0.063 4(8)	−0.088 8(6)	0.302 1(4)
C(303)	−0.095 7(15)	0.351 2(10)	0.252 4(8)	N(300)	0.061 6(10)	0.435 0(7)	0.210 3(5)

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

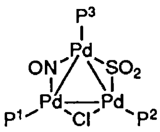
Pd(1)–Pd(2)	2.907(1)	Pd(2)–Cl(1)	2.277(4)	Pd(4)–Pd(5)	2.994(1)	Pd(5)–Cl(4)	2.334(3)
Pd(1)–Pd(3)	2.876(1)	Pd(2)–S(2)	2.325(4)	Pd(4)–Pd(6)	2.882(1)	Pd(5)–S(5)	2.289(3)
Pd(1)–S(3)	2.229(4)	Pd(2)–Cl(2)	2.325(4)	Pd(4)–S(6)	2.239(4)	Pd(5)–Cl(5)	2.289(3)
Pd(1)–S(1)	2.318(4)	Pd(2)–P(2)	2.315(4)	Pd(4)–S(4)	2.342(4)	Pd(5)–P(5)	2.337(3)
Pd(1)–Cl(1)	2.318(4)	Pd(3)–S(3)	2.233(4)	Pd(4)–Cl(4)	2.342(4)	Pd(6)–S(6)	2.233(4)
Pd(1)–P(1)	2.326(4)	Pd(3)–S(2)	2.332(4)	Pd(4)–P(4)	2.334(3)	Pd(6)–S(5)	2.295(4)
Pd(2)–Pd(3)	2.899(1)	Pd(3)–Cl(2)	2.332(4)	Pd(5)–Pd(6)	2.878(1)	Pd(6)–Cl(5)	2.295(4)
Pd(2)–S(1)	2.277(4)	Pd(3)–P(3)	2.320(3)	Pd(5)–S(4)	2.334(3)	Pd(6)–P(6)	2.326(3)
Pd(3)–Pd(1)–Pd(2)	60.17(3)	S(2)–Pd(2)–S(1)	162.3(1)	Pd(6)–Pd(4)–Pd(5)	58.62(3)	S(5)–Pd(5)–S(4)	158.4(1)
S(3)–Pd(1)–Pd(2)	110.1(1)	P(2)–Pd(2)–Pd(1)	151.7(1)	S(6)–Pd(4)–Pd(5)	108.39(9)	P(5)–Pd(5)–Pd(4)	152.3(1)
S(3)–Pd(1)–Pd(3)	49.9(1)	P(2)–Pd(2)–Pd(3)	148.2(1)	S(6)–Pd(4)–Pd(6)	49.77(9)	P(5)–Pd(5)–Pd(6)	145.50(9)
S(1)–Pd(1)–Pd(2)	50.13(9)	P(2)–Pd(2)–S(1)	100.9(1)	S(4)–Pd(4)–Pd(5)	50.07(8)	P(5)–Pd(5)–S(4)	103.8(1)
S(1)–Pd(1)–Pd(3)	110.2(1)	P(2)–Pd(2)–S(2)	96.7(1)	S(4)–Pd(4)–Pd(6)	108.69(9)	P(5)–Pd(5)–S(5)	97.4(1)
S(1)–Pd(1)–S(3)	159.9(1)	Pd(2)–Pd(3)–Pd(1)	60.45(3)	S(4)–Pd(4)–S(6)	158.5(1)	Pd(5)–Pd(6)–Pd(4)	62.62(3)
Cl(1)–Pd(1)–Pd(2)	50.13(9)	S(3)–Pd(3)–Pd(1)	49.8(1)	Cl(4)–Pd(4)–Pd(5)	50.07(8)	S(6)–Pd(6)–Pd(4)	49.96(9)
Cl(1)–Pd(1)–Pd(3)	110.2(1)	S(3)–Pd(3)–Pd(2)	110.2(1)	Cl(4)–Pd(4)–Pd(6)	108.69(9)	S(6)–Pd(6)–Pd(5)	112.6(1)
Cl(1)–Pd(1)–S(3)	159.9(1)	S(2)–Pd(3)–Pd(1)	111.8(1)	Cl(4)–Pd(4)–S(6)	158.5(1)	S(5)–Pd(6)–Pd(4)	113.02(9)
P(1)–Pd(1)–Pd(2)	147.4(1)	S(2)–Pd(3)–Pd(2)	51.40(9)	P(4)–Pd(4)–Pd(5)	149.57(9)	S(5)–Pd(6)–Pd(5)	51.01(9)
P(1)–Pd(1)–Pd(3)	152.1(1)	S(2)–Pd(3)–S(3)	161.5(1)	P(4)–Pd(4)–Pd(6)	151.6(1)	S(5)–Pd(6)–S(6)	161.8(1)
P(1)–Pd(1)–S(3)	102.2(1)	P(3)–Pd(3)–Pd(1)	151.9(1)	P(4)–Pd(4)–S(6)	102.0(1)	P(6)–Pd(6)–Pd(4)	146.83(9)
P(1)–Pd(1)–S(1)	97.3(1)	P(3)–Pd(3)–Pd(2)	146.2(1)	P(4)–Pd(4)–S(4)	99.6(1)	P(6)–Pd(6)–Pd(5)	146.31(9)
P(1)–Pd(1)–Cl(1)	97.3(1)	P(3)–Pd(3)–S(3)	103.0(1)	P(4)–Pd(4)–Cl(4)	99.6(1)	P(6)–Pd(6)–S(6)	98.7(1)
Pd(3)–Pd(2)–Pd(1)	50.39(3)	P(3)–Pd(3)–S(2)	95.1(1)	Pd(6)–Pd(5)–Pd(4)	58.76(3)	P(6)–Pd(6)–S(5)	99.2(1)
S(1)–Pd(2)–Pd(1)	51.4(1)	Pd(3)–S(3)–Pd(1)	80.2(1)	S(4)–Pd(5)–Pd(4)	50.31(9)	Pd(6)–S(6)–Pd(4)	80.3(1)
S(1)–Pd(2)–Pd(3)	110.7(1)	Pd(2)–S(1)–Pd(1)	78.5(1)	S(4)–Pd(5)–Pd(6)	109.07(9)	Pd(5)–S(4)–Pd(4)	79.6(1)
S(2)–Pd(2)–Pd(1)	110.9(1)	Pd(3)–S(2)–Pd(2)	77.0(1)	S(5)–Pd(5)–Pd(4)	109.40(9)	Pd(6)–S(5)–Pd(5)	77.8(1)
S(2)–Pd(2)–Pd(3)	51.61(9)			S(5)–Pd(5)–Pd(6)	51.21(9)		

Table 4 Important peaks in the FAB mass spectrum of compound **6**

Peak	*m/z*	Relative intensity	Assignment
A	1236	20	M^+
B	1140	51	$[M - NO - SO_2]^+$
C	1107	39	$[M - NO - SO_2 - Cl]^+$
D	1061	24	$[M - NO - SO_2 - Ph]^+$
E	1031	54	$[M - NO - SO_2 - Cl - Ph]^+$
F	953	45	$[M - NO - SO_2 - Cl - 2Ph]^+$
G	876	48	$[M - NO - SO_2 - Cl - 3Ph]^+$
H	842	48	$[M - NO - SO_2 - Cl - PPh_3]^+$
I	799	38	$[M - NO - SO_2 - Cl - 4Ph]^+$
J	766	93	$[M - NO - SO_2 - Cl - PPh_3 - Ph]^+$
K	738	100	$[M - Pd - NO - SO_2 - Cl - PPh_3]^+$
L	721	19	$[M - NO - SO_2 - Cl - 5Ph]^+$
M	688	45	$[M - NO - SO_2 - Cl - PPh_3 - 2Ph]^+$
N	661	58	$[M - Pd - NO - SO_2 - Cl - PPh_3 - Ph]^+$
O	644	27	$[M - NO - SO_2 - Cl - 6Ph]^+$
P	614	29	$[M - NO - SO_2 - Cl - PPh_3 - 3Ph]^+$
Q	533	69	$[M - NO - SO_2 - Cl - PPh_3 - 4Ph]^+$

$M = [Pd_3(NO)(SO_2)Cl(PPh_3)_3]$.

is greater when X is CO than when X is SO_2.[11] Since the NO ligand is the same size as CO, coupling across the bond bridged by it would also be expected to be greater than that across the SO_2 ligand. This led to the interpretation of the $^{31}P-\{^1H\}$ NMR data which is summarised below.



$\delta(P^1) = 21.3$
$\delta(P^2) = 12.8$
$\delta(P^3) = 6.9$
$^3J(P^1-P^2) = 28$ Hz
$^3J(P^1-P^3) = 55$ Hz
$^3J(P^2-P^3) = 30$ Hz

This is the first reported case of a palladium triangle with a bridging nitrosyl group, and also of a palladium triangle with three different bridging substituents. Both have precedents in platinum cluster chemistry that have been characterised crystallographically: $[Pt_3(\mu\text{-}NO)_2(\mu\text{-}OH)\{P(C_6H_{11})_3\}_3]BF_4$ has been synthesised[12] from the reaction of $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ and $NOBF_4$ in a benzene–methanol mixture, and $[Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3]$ has been synthesised[13] from refluxing the monomeric compound $[Pt(1,2\text{-}\eta\text{-}C_4H_5R)(SO_2)(PPh_3)_2]$ (R = H or Me) in benzene. Compound **6** is only the second example of a palladium cluster compound containing a nitrosyl

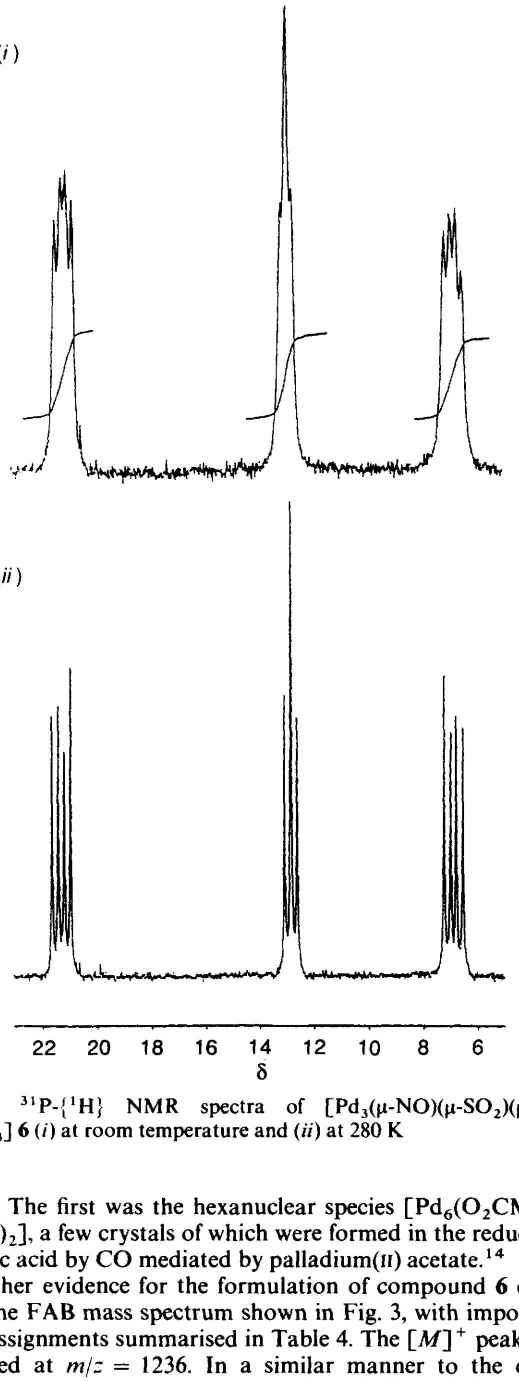


Fig. 2 $^{31}P-\{^1H\}$ NMR spectra of $[Pd_3(\mu-NO)(\mu-SO_2)(\mu-Cl)(PPh_3)_3]$ **6** (*i*) at room temperature and (*ii*) at 280 K

ligand. The first was the hexanuclear species $[Pd_6(O_2CMe)_8(\mu-NO)_2]$, a few crystals of which were formed in the reduction of nitric acid by CO mediated by palladium(II) acetate.[14]

Further evidence for the formulation of compound **6** came from the FAB mass spectrum shown in Fig. 3, with important peak assignments summarised in Table 4. The $[M]^+$ peak was observed at $m/z = 1236$. In a similar manner to the other palladium cluster compounds studied by this technique,[15,16] the bridging ligands were lost readily under the conditions of the experiment. The $[Pd_3(PPh_3)_3]^+$ peak was observed at $m/z = 1107$ and peaks were observed at lower m/z values corresponding to the loss of phenyl fragments and triphenylphosphine ligands from this species. This is again similar to the results observed for other palladium cluster compounds.

Reaction with $[Au(PPh_3)(NO_3)]$.—When a dichloromethane solution containing 1 equivalent of $[Au(PPh_3)(NO_3)]$ was added to a solution of compound **4**, also in dichloromethane, the colour immediately darkened to red. After allowing the mixture to stir for 30 min the solvent was removed under reduced pressure and the crude product washed with ethanol. Recrystallisation from dichloromethane–hexane gave orange crystals that analysed correctly for $[Pd_3Au(\mu-SO_2)_2(\mu-Cl)(PPh_3)_4]$ **7**. The identity of this heteronuclear cluster compound was confirmed by IR and $^{31}P-\{^1H\}$ NMR spectroscopy.

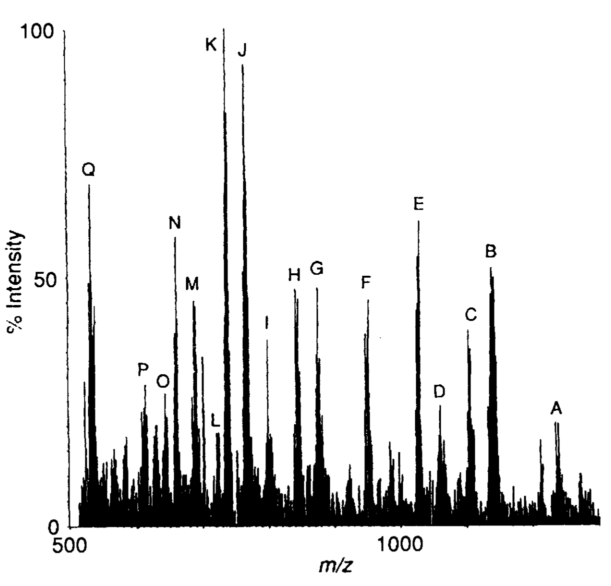


Fig. 3 The FAB mass spectrum of $[Pd_3(\mu-NO)(\mu-SO_2)(\mu-Cl)(PPh_3)_3]$

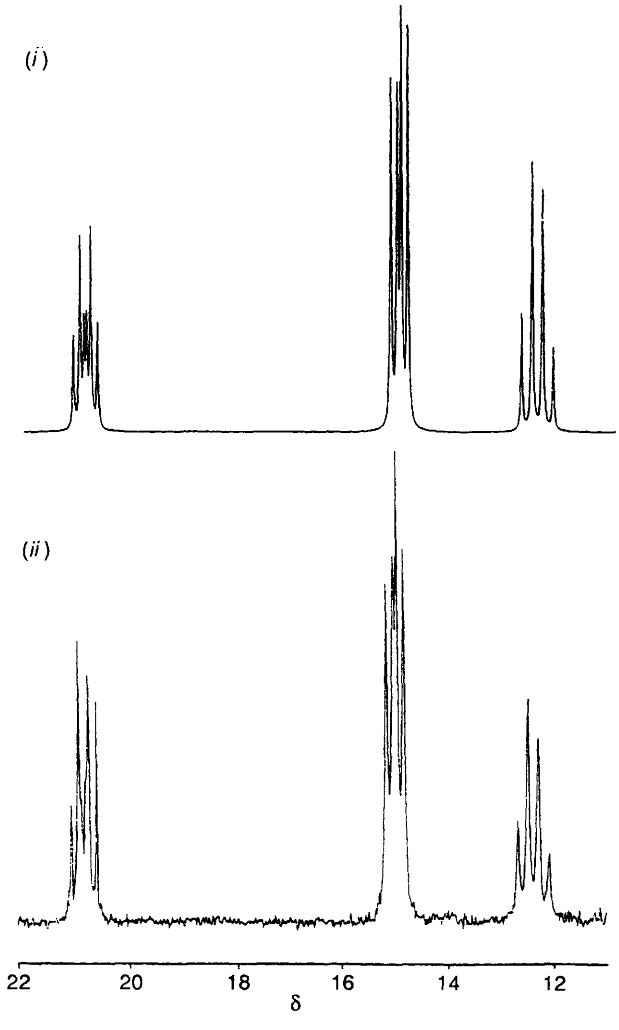


Fig. 4 $^{31}P-\{^1H\}$ NMR spectra of $[Pd_3Au(\mu-SO_2)_2(\mu-Cl)(PPh_3)_4]$ **7**, (*i*) simulated and (*ii*) observed

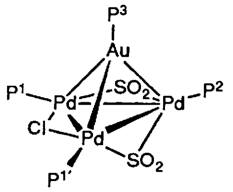
In the IR spectrum the $\nu(SO_2)$ stretching modes were observed at 1209m, 1062s and 1051vs cm^{-1} indicating the presence of bridging sulfur dioxide ligands. The $^{31}P-\{^1H\}$ NMR spectrum showed three signals, at δ 20.8, 14.9 and 12.4, in the

Table 5 Important peaks in the FAB mass spectrum of compound **8**

m/*z*	Relative intensity	Assignment
1346	33	$[M - 2SO_2]^+$
1313	33	$[M - 2SO_2 - Cl]^+$
1141	69	$[M - Tl - 2SO_2]^+$
1105	51	$[M - Tl - 2SO_2 - Cl]^+$
1029	65	$[M - Tl - 2SO_2 - Cl - Ph]^+$
842	54	$[M - Tl - 2SO_2 - Cl - PPh_3]^+$
738	100	$[M - Pd - Tl - 2SO_2 - Cl - PPh_3]^+$
630	79	$[M - 2Pd - Tl - 2SO_2 - Cl - PPh_3]^+$

$M = [Pd_3Tl(SO_2)_2Cl(PPh_3)_3]$.

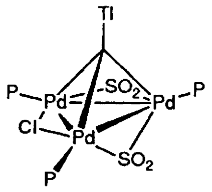
ratio 1:2:1 and it is shown in Fig. 4 together with a computer simulation based on the spin system A_2BC. The resonance at δ 20.8 was a doublet of triplets, with coupling constants of 24 and 15 Hz, that at δ 14.9 was a doublet of doublets with the same coupling constants, and that at δ 12.4 was a quartet with a coupling constant of 24 Hz. On this information, coupled with the observation that phosphines bonded to gold atoms generally give signals at higher chemical shifts that those bonded to palladium or platinum, the spectrum may be assigned to the $Au(PPh_3)^+$ capped triangle shown below.



$\delta(P^1) = 14.9$
$\delta(P^2) = 12.4$
$\delta(P^3) = 20.8$
$^3J(P^1\text{–}P^2) = 24$ Hz
$^3J(P^1\text{–}P^3) = 15$ Hz
$^3J(P^2\text{–}P^3) = 24$ Hz

The related cluster compound $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_4]$ has been synthesised from the reaction of $[Pd_4(SO_2)_3\{P(C_6H_{11})_3\}_4]$ with $[Au\{P(C_6H_{11})_3\}Cl]$,[17] and the platinum analogue $[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}]$ has been prepared from $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3]^-$ and $[Au\{P(C_6H_4F\text{-}p)_3\}(NO_3)]$.[3] A single-crystal X-ray analysis has been carried out on $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_4]$, and confirmed the tetrahedral structure, although considerable disorder has prevented any meaningful consideration of the bond lengths and angles.[17] The compound $[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}]$ reacts with a further equivalent of $[Au\{P(C_6H_4F\text{-}p)_3\}Cl]$ in the presence of $TlPF_6$ to give the bicapped *triangulo* cluster $[Pt_3Au_2(\mu\text{-}SO_2)_2(\mu\text{-}Cl)\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}_2]PF_6$.[4] Attempts to synthesise the palladium analogue of this compound have proved unsuccessful, as the extra $Au(PPh_3)^+$ has a tendency to abstract a phosphine from the palladium–gold cluster giving $Au(PPh_3)_2{}^+$. No cluster compounds have been isolated from this reaction.

Reaction with Tl^+.—It should be possible to abstract the chloride ligand from $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ to generate an unsaturated 40-electron species. This could then either react with a molecule that can act as a bridging ligand between two metal atoms to give a novel *triangulo* cluster or, in the absence of any such ligand, aggregate to give a larger cluster compound. Initial experiments were undertaken using Tl^+ as the halide abstracting agent. An aqueous solution of thallium nitrate was added to a solution of compound **3** in tetrahydrofuran. Over a period of 1 h the solution darkened from yellow to orange-red. Reduction of the volume of the solvent gave a yellow precipitate. This product did not dissolve appreciably in any solvent so it was not possible to purify it by recrystallisation or to obtain any NMR spectra. However, both analytical data and FAB mass spectrometry indicated that the anticipated abstraction had not occurred, and that thallium had been incorporated into the product.



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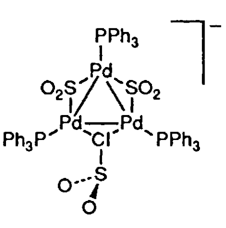
The analytical data gave a palladium to thallium ratio of 3:1 suggesting that the thallium atom was capping the palladium triangle. It also showed no nitrogen to be present in the product indicating that neither nitrate nor $[NEt_3(CH_2Ph)]^+$ ions were present, and hence the product was neutral and formulated as $[Pd_3Tl(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **8**. The FAB mass spectrum, though weak, showed the presence of at least two thallium-containing ions. The anticipated $[M]^+$ peak, which would have provided direct evidence of the Pd_3Tl compound, was not observed as the bridging SO_2 ligands were lost too readily under the conditions of the experiment. Important assigned peaks are summarised in Table 5.

The $\nu(SO_2)$ stretching modes were observed in the IR spectrum at 1150m, 1034m and 1009s cm^{-1}. These have shifted considerably from those observed for compound **3**, again suggesting interaction of the metal atom with the triangle. The proposed structure of the compound is as shown. This is the first example of a palladium–thallium cluster compound to be synthesised. There is, however, a platinum analogue. Reaction of $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ in benzene with an ethanolic solution of $TlPF_6$ gave orange crystals of $[Pt_3Tl(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]PF_6$ in high yield.[8] A crystal structure of this platinum–thallium cation has been obtained with $[RhCl_2(C_8H_{12})]^-$ as the counter ion. In this structure the cluster defines an elongated tetrahedron with the average platinum–thallium distance considerably longer at 3.038(1) Å than the average platinum–platinum bond length, 2.667(1) Å. This is a consequence of the filled 6s shell of the thallium atom. The thallium atom is weakly co-ordinated to a chlorine atom of the counter ion with a thallium–chlorine distance of 2.981(9) Å.

Reaction with Ag^+.—Although reaction with thallium salts gave a novel and interesting product the thallium ion did not act as the anticipated halide abstracting agent. More success in abstracting the chloride ligand was achieved using silver salts. When an ethanolic solution of silver nitrate was added to a solution of compound **4** in dichloromethane there was an immediate darkening of the colour of the solution to red. After stirring for 30 min the solution was filtered to remove an off-white powder, and the volume of the solution reduced to give a dark microcrystalline solid. A $^{31}P\text{-}\{^1H\}$ NMR spectrum of this solid showed a doublet at δ 19.3, a singlet at δ 19.0 and a triplet at δ 10.7. These signals were in the ratio 2:2:1, with the coupling constant in the doublet and triplet shown to be 29 Hz. This demonstrated the presence of the pentapalladium compound $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$.[15] A broad singlet was also present at δ 13.6 but the source of this has not been identified. These results demonstrate that silver salts can abstract the halide from $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ to generate an unsaturated 40-electron intermediate, which then aggregates to give $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$. Attempts to trap the intermediate by performing the reaction in the presence of potential bridging ligands proved unsuccessful.

Dixon and co-workers have managed to replace the chloride ion in the related *triangulo* clusters typified by $[Pd_3(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)(PPh_3)_3]^+$ with a range of other ligands such as PPh_2,[18] SMe [19] and Br.[20] Their reactions are helped by both the size and the inertness of the PPh_2 group. This group is larger than SO_2, which disfavours aggregation reactions, and unlike SO_2 it is not readily substituted, hence the only substitution chemistry likely



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to occur in $[Pd_3(\mu-PPh_2)_2(\mu-Cl)(PPh_3)_3]^+$ is for the chloride ligand.

Reaction with SO_2.—As a solid and in solution, $R[Pd_3(\mu-SO_2)_2(\mu-Cl)(PPh_3)_3]$ absorbs SO_2 reversibly with a change in colour. When a sulfur dioxide atmosphere was introduced above yellow crystals of $[NEt_3(CH_2Ph)][Pd_3(\mu-SO_2)_2(\mu-Cl)(PPh_3)_3]$ they became dark red. This colour change is reversible since heating the red crystals under reduced pressure led to a reversion to the yellow colour of the starting material. The red crystals analysed for $[NEt_3(CH_2Ph)][Pd_3(SO_2)_3Cl(PPh_3)_3]$ **9**. There was no evidence in the IR spectrum for rearrangement of the ligands to have occurred and for the chloride to have become terminally bound to a palladium atom. As well as bridging two metal atoms, SO_2 can also behave as a Lewis acid and bind to the ligand rather than the metal.[21] Ligand-bound SO_2 was first illustrated crystallographically in 1973, in the structure of $[PtMe(PPh_3)_2(I-SO_2)]$.[22] Several other complexes are known, including the iodo-bridged complex $[Cu_2(\mu-I)(\mu-I-SO_2)(PMePh_2)_4]$.[23] In this and other compounds containing ligand-bound SO_2 the I–S bond is long, 3.407 Å in this case. Ligand-bound sulfur dioxide is usually characterised by the reversibility of the co-ordination and unreactivity of the bound SO_2 to oxygen, which are both features of compound **9**. If the third SO_2 ligand is bound to the chloride, as shown, then the iodo complex would be expected to be more stable, since iodide is a better Lewis base than is chloride. Solid $[NBu_4][Pd_3(SO_2)_2I(PPh_3)_3]$ reacted with SO_2 in the same way as the chloro cluster, but the product needed to be heated under reduced pressure for longer and at a higher temperature to reverse the colour change. This provided further evidence for the ligand bound SO_2.

Both chloro and iodo products showed additional bands in the IR spectra due to the additional SO_2 ligand. For $[Pd_3(SO_2)_3Cl(PPh_3)_3]^-$ these occurred at $\nu(SO_2)$ 1231m, 1205m and 1065s cm^{-1}, and for $[Pd_3(SO_2)_3I(PPh_3)_3]^-$ at $\nu(SO_2)$ 1219m (br) and 1082m cm^{-1}. Ligand-bound SO_2 ligands have previously been reported to show bands for the $\nu(SO_2)$ stretching modes between 1317 and 1210 and between 1135 and 1051 cm^{-1}. Again the results were consistent with ligand-bound sulfur dioxide. Cross-polarisation magic angle spinning (CP MAS) solid-state $^{31}P-\{^1H\}$ NMR spectra have been recorded on compounds **3** and **9**. In both spectra there were two major signals which were in a 2:1 intensity ratio when the spectra were recorded without cross-polarisation. In the spectrum of **3** these were at δ 14.4 and 8.1. The spectrum of **9** was broader, with both signals shifted to higher chemical shifts: δ 30.7 and 16.9. The difference in chemical shifts on reaction with SO_2 was greater for the unique position than for the two equivalent phosphorus atoms. This was opposite to the shifts expected if simple co-ordination of the SO_2 ligand to the chloride ligand had occurred, and it is consistent with either co-ordination of SO_2 direct to the unique palladium atom or chloride co-ordination with some interaction with the unique palladium atom possibly *via* a μ_3-SO_2 in a similar manner to that observed in other palladium cluster compounds such as $[Pd_5(\mu-SO_2)_2(\mu_3-SO_2)_2(AsPh_3)_5]$.[15]

When SO_2 was passed through a dichloromethane solution of compound **3** the colour immediately darkened to red. However, reaction in solution was also reversible as reduction in volume of the solution followed by addition of hexane gave only yellow crystals of **3**. When $^{31}P-\{^1H\}$ NMR spectra of solutions of **3** under SO_2 were recorded only a singlet was observed. The chemical shift of this signal varied, suggesting that the solution species is undergoing fluxional processes that are rapid on the NMR time-scale.

There are other examples in the literature of compounds that absorb SO_2 in the solid state. For example, the manganese(II) compound $[MnI_2(PPh_3)]$ absorbs SO_2 both as a solid and in solution to give the adduct $[MnI_2(PPh_3)(SO_2)_x]$ where x = 0.66 for the solid and 0.65–0.76 for a tetrahydrofuran (thf) solution.[24] This occurs with a colour change from pink-orange to yellow.[25]

Experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen, with dry, dioxygen-free solvents. Microanalyses (C, H, N, Cl, Pd and Tl) 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, and recorded between KBr 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 $^{31}P-\{^1H\}$ NMR spectra were recorded on a Brüker MSL-200 spectrometer operating at 80.96 MHz, using CP and MAS techniques. The FAB mass spectra were recorded by Dr. J. Ballantine and his staff at the SERC Mass Spectometry 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 compound $[Pd_5(\mu-SO_2)_2(\mu_3-SO_2)_2(PPh_3)_5]$ was synthesised by the previously published route.[15]

Syntheses.—$[NEt_4][Pd_3(\mu-SO_2)_2(\mu-Cl)(PPh_3)_3]$ **1**. The compound $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.10 g, 0.048 mmol) was dissolved in benzene (20 cm^3), and a solution of NEt_4Cl (0.018 g, 0.11 mmol) in ethanol (3 cm^3) added. The mixture was stirred for 30 min and during this time a yellow precipitate of compound **1** was formed. This was found to be only sparingly soluble in all solvents, so was not recrystallised (Found: C, 57.3; H, 5.1; N, 0.9. $C_{62}H_{65}ClNO_4P_3Pd_3S_2\cdot 2C_6H_6$ requires C, 57.1; H, 5.0; N, 0.9%); $\nu(SO_2)$ at 1180m, 1171m, 1051m and 1037s cm^{-1}.

$[NEt_4][Pd_3(\mu-SO_2)_2(\mu-Br)(PPh_3)_3]$ **2**. The compound $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.10 g, 0.048 mmol) was dissolved in toluene (20 cm^3), and a solution of NEt_4Br (0.02 g, 0.095 mmol) in ethanol (3 cm^3) added. The mixture was stirred for 30 min and during this time a yellow precipitate of compound **2** was formed. This was recrystallised from acetone. Yield 0.099 g (86%) (Found: C, 51.5; H, 4.5; N, 1.0. $C_{62}H_{65}BrNO_4P_3Pd_3S_2$ requires C, 51.6; H, 4.5; N, 1.0%); $\nu(SO_2)$ at 1181m, 1168m, 1047s and 1036s cm^{-1}.

$[NEt_3(CH_2Ph)][Pd_3(\mu-SO_2)_2(\mu-Cl)(PPh_3)_3]$ **3**. The compound $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.39 g, 0.19 mmol) was dissolved in toluene (20 cm^3), and a solution of $NEt_3(CH_2Ph)Cl$ (0.085 g, 0.37 mmol) in ethanol (3 cm^3) added. The mixture was stirred for 30 min, and then the volume of solvent was decreased under reduced pressure to give a yellow precipitate of compound **3**, which was recrystallised from acetone. Yield 0.36 g (80%) (Found: C, 54.8; H, 4.7; N, 1.0. $C_{67}H_{67}ClNO_4P_3Pd_3S_2$ requires C, 55.0; H, 4.6; N, 1.0%); $\nu(SO_2)$ at 1184m, 1167m, 1049s and 1037vs cm^{-1}; $\delta(^{31}P)$ at 8.3 (2 P, d) and 5.0 (1 P, t), $^3J_{PP}$ = 44 Hz.

$[PPh_3(CH_2Ph)][Pd_3(\mu-SO_2)_2(\mu-Cl)(PPh_3)_3]$ **4**. The compound $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.20 g, 0.095 mmol) was dissolved in toluene (20 cm^3) and a solution of $PPh_3(CH_2Ph)Cl$ (0.074 g, 0.19 mmol) in ethanol (3 cm^3) added. The mixture was stirred for 30 min, and then the volume of the solvent was decreased under reduced pressure to give a yellow precipitate of compound **4**, which was recrystallised from dichloromethane–toluene to give crystals of the dichloromethane solvate. Yield 0.24 g (90%) (Found: C, 56.0; H, 4.1. $C_{79}H_{67}ClO_4P_4Pd_3S_2\cdot CH_2Cl_2$ requires C, 56.3; H, 4.1%); $\nu(SO_2)$ at 1184m, 1168m, 1049s and 1036s cm^{-1}.

$[NBu_4][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}I)(PPh_3)_3]$ **5**. The compound $[Pd_5(SO_2)_4(PPh_3)_5]$ (0.13 g, 0.062 mmol) was dissolved in toluene (20 cm^3), and a solution of NBu_4I (0.046 g, 0.12 mmol) in ethanol (3 cm^3) added. The mixture was stirred for 30 min and during this time an orange precipitate of compound **5** was formed. This was recrystallised from thf–diethyl ether. Yield 0.13 g (81%) (Found: C, 52.7; H, 5.1; N, 1.0. $C_{70}H_{81}INO_4P_3Pd_3S_2$ requires C, 52.4; H, 5.1; N, 0.9%); $\nu(SO_2)$ at 1192m, 1177m, 1051s and 1037vs cm^{-1}; $\delta(^{31}P)$ at 14.0 (2 P, d) and 5.5 (1 P, t), $^3J_{PP}$ = 44 Hz.

$[Pd_3(\mu\text{-}NO)(\mu\text{-}SO_2)(\mu\text{-}Cl)(PPh_3)_3]$ **6**. Compound **4** (0.15 g, 0.092 mmol) was dissolved in ethanol (20 cm^3) and a solution of $NOBF_4$ (0.032 g, 0.27 mmol) in ethanol (3 cm^3) added. The solution rapidly darkened, and after stirring for 60 min a fine yellow precipitate was produced. This was filtered off and recrystallised from benzene–hexane to give dark brown crystals of **6**. Yield 0.080 g (70%) (Found: C, 53.7; H, 3.9; N, 1.0. $C_{54}H_{45}ClNO_3P_3Pd_3S\cdot 0.5C_6H_6$ requires C, 53.7; H, 3.8; N, 1.1%); $\nu(NO)$ at 1602s cm^{-1}; $\nu(SO_2)$ at 1207m and 1057s cm^{-1}; $\delta(^{31}P)$ at 21.3 (1 P, dd, J = 28, 55), 12.8 (1 P, dd, J = 28, 30) and 6.9 (1 P, dd, J = 30, 55 Hz).

$[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_4]$ **7**. Compound **4** (0.20 g, 0.12 mmol) was dissolved in dichloromethane (20 cm^3) and a solution of $[Au(PPh_3)(NO_3)]$ (0.064 g, 0.12 mmol) in dichloromethane (10 cm^3) was added, leading to an immediate colour change from yellow to red. The mixture was stirred for 30 min then the solvent was removed under reduced pressure and the crude solid washed with ethanol before recrystallisation from dichloromethane–hexane, which gave red crystals of compound **7**. Yield 0.19 g (89%) (Found: C, 50.4; H, 3.7; Cl, 1.8. $C_{72}H_{60}AuClO_4P_3Pd_3S_2$ requires C, 50.0; H, 3.5; Cl, 2.0%); $\nu(SO_2)$ at 1209m, 1062s and 1051vs cm^{-1}; $\delta(^{31}P)$ at 20.8 (1 P, dt, J = 24, 15), 14.9 (2 P, dd, J = 24, 15) and 12.4 (1 P, q, J = 24 Hz).

$[Pd_3Tl(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **8**. Compound **3** (0.12 g, 0.082 mmol) was dissolved in thf (20 cm^3) and a solution of $TlNO_3$ (0.022 g, 0.082 mmol) in water (3 cm^3) was added. The mixture was stirred for 60 min, during which time it darkened from yellow to orange-red. The volume of the solution was decreased under reduced pressure giving a yellow precipitate of compound **8**. Yield 0.089 g, (74%) (Found: C, 44.4; H, 3.1; Pd, 21.1; Tl, 14.0. $C_{54}H_{45}ClO_4P_3Pd_3S_2Tl$ requires C, 44.0; H, 3.1; Pd, 21.6; Tl, 13.9%); $\nu(SO_2)$ at 1150m, 1034m and 1009s cm^{-1}.

Reaction of compound **4** *with* $AgNO_3$. This reaction was carried out in foil-covered Schlenk vessels. Compound **4** (0.085 g, 0.052 mmol) was dissolved in dichloromethane (20 cm^3), and a solution of $AgNO_3$ (0.009 g, 0.52 mmol) in ethanol (5 cm^3) was added. A rapid colour change from yellow to red occurred. The mixture was stirred for 30 min, filtered and the volume of the filtrate reduced to give a dark microcrystalline solid. Recrystallisation from dichloromethane–hexane gave $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$. Yield 43%. Identified on the basis of IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

$[NEt_3(CH_2Ph)][Pd_3(SO_2)_3Cl(PPh_3)_3]$ **9**. Solid compound **3** (0.10 g, 0.068 mmol) was placed under an atmosphere of SO_2 for 5 min. During this time the yellow crystals darkened to red-purple (Found: C, 52.7; H, 4.6; N, 1.0. $C_{67}H_{67}ClNO_6P_3Pd_3S_3$ requires C, 52.7; H, 4.4; N, 0.9%); $\nu(SO_2)$ at 1231m, 1205m, 1184m, 1167m, 1065s, 1049s and 1037vs cm^{-1}. The red-purple crystals of compound **9** can be converted back into **3** by heating under reduced pressure.

When compound **3** (0.10 g, 0.068 mmol) was dissolved in dichloromethane (20 cm^3), and SO_2 bubbled through the solution for 10 min, a rapid colour change from yellow to red occurred. The solvent was removed under reduced pressure and the solid obtained recrystallised from dichloromethane–hexane to give only yellow crystals of **3**, identified by IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

$[NBu_4][Pd_3(SO_2)_3I(PPh_3)_3]$ **10**. Solid compound **5** (0.10 g, 0.066 mmol) was placed under an atmosphere of SO_2 for 5 min. During this time the yellow crystals darkened to red-purple (Found: C, 50.2; H, 5.1; N, 1.0. $C_{70}H_{81}INO_6P_3Pd_3S_3$ requires C, 50.4; H, 4.9; N, 0.8%); $\nu(SO_2)$ at 1219 (br), 1192m, 1177m, 1082m, 1051s and 1037vs cm^{-1}. The red-purple crystals of **10** can be converted back into **5** by prolonged heating under reduced pressure.

Crystal Structure Determination of $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ **3**.—Crystals of compound **3** used in the analysis were grown from a slow diffusion of hexane into an acetone solution. 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 routine Patterson and direct methods, with all non-hydrogen atoms located in subsequent Fourier difference syntheses. After assigning anisotropic thermal parameters to the palladium and phosphorus atoms, the hydrogens were generated geometrically. The presence of disorder between one of the bridging sulfur dioxide ligands and the bridging chloride meant that the electron density corresponding to two of the bridging atoms in each triangle was best modelled with partial occupancy chlorine and sulfur atoms. On refinement with the disordered chlorine and sulfur and their associated oxygen atoms at an occupancy of 0.5 each, the thermal parameters of the oxygen atoms within each triangle were very different, indicating an error in the occupancy values. Consequently, the occupancies were included in the refinement and the thermal parameters of all the sulfur and chlorine atoms were constrained to be equal. The result was a fully converged satisfactory model with the disordered oxygen atoms in each triangle having similar thermal parameters. On application of a Chebyshev weighting scheme the model converged at R 0.0473 and R' 0.0436. The programs and sources of scattering factors used are given in refs. 26–28. 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), C(55), C(61) and C(67) to P(4), C(73), C(79) and C(85) to P(5) and C(91), C(97) and C(103) to P(6); C(200)–C(212) and C(300)–C(312) are the carbon atoms in the cations and C(400)–C(402) in the solvated acetone molecule.

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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