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Synthesis and structure of a gold-capped palladium *triangulo*-cluster compound containing an azide ligand

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Abstract

Reaction of $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ with $PPN[N_3]$ gave the *triangulo*-palladium cluster compound $PPN^+[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_3]^-$, **1**, which has been characterised spectroscopically. **1** reacts with $Au(PPh_3)NO_3$ to give $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$, **2**, the molecular stucture of which has been determined by single-crystal X-ray diffraction studies. The molecule contains a distorted tetrahedral metal core with Pd–Pd metal distances of between 2.843(2) Å and 2.876(2) Å and Pd–Au metal distances of between 2.725 (1) Å and 2.757(1) Å.

1. Introduction

The reactions of 42- and 44-electron *triangulo*-platinum cluster compounds such as $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ $(Cy = C_6H_{11})$ $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3]^-$ and $[Pt_3\text{-}(\mu\text{-}CO)_3(PCy_3)_2(dppp)]$ $(dppp = (Ph_2P)_2C_3H_6)$ with $MPPh_3^+$ or M^+ (M = Cu, Ag, Au) fragments have received considerable attention [1–5]. When $[Pt_3\text{-}(\mu\text{-}CO)_3(PCy_3)_3]$ reacts with $Au(PPh_3)^+$ the tetrahedral cluster $[Pt_3Au(\mu\text{-}CO)_3(PCy_3)_3(PPh_3)]$ results, whereas the reaction of $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3]^-$ with $Au\{P(C_6H_4F\text{-}p)_3\}^+$ gives rise to either the tetrahedral compound $[Pt_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3\{P(C_6\text{-}H_4F\text{-}p)_3\}]$ or the trigonal bipyramidal compound $[Pt_3Au_2(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_3\{P(C_6H_4F\text{-}p)_3\}_2]^+$. In the latter the gold atoms occupy the axial sites of the trigonal bipyramid. Far fewer metal-capping reactions have been reported for palladium clusters. We have previously shown [6] that the *triangulo*-palladium cluster $[Pd_3(\mu\text{-}SO_2)_2\text{-}(\mu\text{-}Cl)(PPh_3)_3]^-$ reacts with $Au(PPh_3)NO_3$ and $TlNO_3$ to give the capped triangles $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_4]$ and $[Pd_3Tl(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$ respectively. However, it has not proved possible to obtain single crystals of these compounds. A single-crystal X-ray analysis has been carried out on $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_4]$, synthesised from the reaction of $[Pd_4(SO_2)_3(PCy_3)_4]$ and $Au(PPh_3)Cl$ [7], and it has confirmed the tetrahedral metal core, but considerable crystallographic disorder prevented a really accurate determination of the bond lengths and angles. The similarities in the sizes and shapes of SO_2 and Cl leads to indiscriminate molecular packing. Use of the pseudo-halide N_3^- gave a further option for synthesising a novel *triangulo*-palladium cluster analogous to $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$. This *triangulo*-cluster would, if capped with $Au(PPh_3)^+$, give a product in which disorder was less likely given the different sizes and shapes of the SO_2 and N_3 ligands.

2. Results and discussion

When an ethanolic solution containing two equivalents of bis(triphenylphosphoranylidene)ammonium

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(PPN) azide 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 dichroic dark green to yellow. After stirring for 30 min the volume of solution was decreased under reduced pressure to give a yellow precipitate. This was recrystallised from acetone-diethyl ether to give yellow crystals of $PPN^+[Pd_3(SO_2)_2(N_3)(PPh_3)_3]^-$, **1**. The compound gave an IR spectrum that contained four peaks in the $\nu(SO_2)$ region, indicating the presence of bridging sulphur dioxide ligands and a strong peak at 2050 cm^{-1} assigned to the $\nu(N_3)$ stretching mode. The $^{31}P\{^1H\}$ NMR spectrum gave a doublet at 9.3 ppm and a triplet at 6.6 ppm. The intensity ratio of the doublet to the triplet was 2:1, and the coupling constant within the doublet and triplet was 44 Hz. This provides good evidence that the product has a structure analogous to that for $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ with two bridging SO_2 ligands and one bridging azide as shown below:

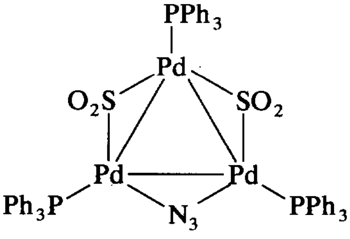
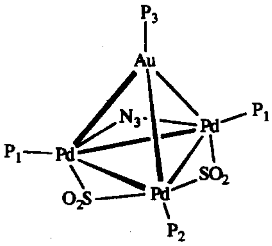


TABLE 1. Crystal data for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]\cdot 2EtOH$, **2**

Formula	$C_{72}H_{60}AuN_3O_4P_4Pd_3S_2\cdot 2EtOH$
M	1735.46 (1827.59 including ethanol)
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a	14.65(7) Å
b	15.90(2) Å
c	19.03(6) Å
α	75.87(5)°
β	72.67(3)°
γ	61.54(6)°
U	3693.09 $Å^3$
Z	2
D_c	1.60 g cm^{-3}
$F(000)$	1808
Linear absorption coefficient	28.11 cm^{-1}
Crystal colour	red
Data collection	
X-radiation	Mo-K_α, $\lambda = 0.71069$ Å
θ_{min}, θ_{max}	0°, 21°
min., max. h, k, l	−1, 14; −16, 16; −19, 19
ω-scan width	0.75° + 0.35 tan θ
Horizontal aperture	3.5 mm
Total data collected	8766
Total unique data	7851
Total observed data $[I > 3\sigma(I)]$	4523
Merging R factor	0.0245
Absorption	DIFABS (correction 0.808, 1.113)
Refinement	
No. of parameters	461
Ratio data:parameters	9.81
Weighting scheme	Chebyshev (coefficients 6.47, −8.33, 6.07, −2.68, 0.79)
Final R	0.048
Final R_w	0.054

When a dichloromethane solution containing one equivalent of $[Au(PPh_3)NO_3]$ was added to a solution of $PPN[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_3]$, 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 cold ethanol. Recrystallisation from dichloromethane-hexane gave red crystals that analysed correctly for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$. The identity of this heteronuclear cluster compound was confirmed by IR and $^{31}P\{^1H\}$ NMR spectroscopy and a single-crystal X-ray analysis. In the IR spectrum the $\nu(SO_2)$ stretching modes were observed at 1202 m, 1062 s and 1051 vs cm^{-1} and the $\nu(N_3)$ stretching mode was observed at 2050 s cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum showed three signals at 21.0 ppm, 15.1 ppm and 13.4 ppm in the ratio 1:2:1. The 21.0 ppm resonance was a doublet of triplets, with the coupling constants of 18 Hz and 15 Hz, the 15.1 ppm resonance was a doublet of doublets with the same coupling constants, and the 13.4 ppm signal was a quartet with a coupling constant of 18 Hz. On the basis of this information, together with the observation that phosphines bonded to gold atoms generally give signals at higher chemical shifts than those bonded to palladium, the spectrum can be assigned to the gold-capped tripalladium cluster compound $[Pd_3Au(\mu\text{-}SO_2)(\mu\text{-}N_3)PPh_3)_3]$:



$\delta(P_1) = 15.1$ ppm
$\delta(P_2) = 13.4$ ppm
$\delta(P_3) = 21.0$ ppm
$^3J(P_1\text{–}P_2) = 18$ Hz
$^3J(P_1\text{–}P_3) = 15$ Hz
$^3J(P_2\text{–}P_3) = 18$ Hz

In order to verify this, a single-crystal X-ray analysis was undertaken. Experimental details relating to the data collection are summarised in Table 1. Fractional atomic coordinates and selected bond lengths and angles are summarised in Tables 2 and 3. The molecule is

TABLE 2. Fractional atomic coordinates for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$

Atom	x	y	z	U_{eq}
Au(1)	0.04105(5)	0.34046(5)	0.73921(4)	0.0455
Pd(1)	0.03638(9)	0.18510(8)	0.70654(6)	0.0397
Pd(2)	−0.05202(9)	0.24120(8)	0.85181(6)	0.0426
Pd(3)	0.17422(9)	0.16071(8)	0.79645(7)	0.0432
P(1)	0.0120(3)	0.1194(3)	0.6199(2)	0.0451
P(2)	−0.1872(3)	0.2752(3)	0.9571(2)	0.0481
P(3)	0.3376(3)	0.0863(3)	0.8319(2)	0.0503
P(4)	0.0333(3)	0.4879(3)	0.6908(2)	0.0501
S(1)	−0.1365(3)	0.2465(3)	0.7719(2)	0.0518
S(2)	0.2189(3)	0.1205(3)	0.6839(2)	0.0453
N(1)	0.074(1)	0.215(1)	0.9002(8)	0.0603
N(2)	0.083(1)	0.268(1)	0.9229(8)	0.0485
N(3)	0.098(2)	0.319(2)	0.954(1)	0.1110
O(1)	−0.1836(9)	0.180(1)	0.7915(7)	0.0742
O(2)	−0.2074(9)	0.3447(9)	0.7487(6)	0.0678
O(3)	0.2715(9)	0.1734(8)	0.6276(6)	0.0642
O(4)	0.2735(8)	0.0170(7)	0.6793(6)	0.0566
O(100)	0.561(4)	0.198(3)	0.422(2)	0.31(1)
O(101)	0.483(4)	0.146(3)	0.550(2)	0.31(1)
O(200)	0.395(4)	0.522(3)	0.307(2)	0.31(1)
O(201)	0.437(3)	0.444(3)	0.207(2)	0.31(1)
C(100)	0.561(4)	0.198(3)	0.422(2)	0.31(1)
C(101)	0.483(4)	0.145(3)	0.549(2)	0.31(1)
C(200)	0.395(4)	0.523(3)	0.307(2)	0.31(1)
C(201)	0.437(3)	0.444(3)	0.207(2)	0.31(1)
C(102)	0.506(5)	0.135(4)	0.469(3)	0.31(1)
C(202)	0.478(2)	0.468(4)	0.254(3)	0.31(1)
C(111)	0.091(1)	0.115(1)	0.5267(8)	0.050(4)
C(112)	0.047(1)	0.145(1)	0.4650(9)	0.058(4)
C(113)	0.112(1)	0.136(1)	0.393(1)	0.071(5)
C(114)	0.216(2)	0.104(1)	0.382(1)	0.075(5)
C(115)	0.262(2)	0.074(2)	0.443(1)	0.089(6)
C(116)	0.200(2)	0.081(1)	0.515(1)	0.076(5)
C(121)	0.034(1)	−0.005(1)	0.6572(9)	0.050(4)
C(122)	0.124(2)	−0.081(1)	0.624(1)	0.083(6)
C(123)	0.143(2)	−0.178(2)	0.660(1)	0.100(7)
C(124)	0.085(2)	−0.194(2)	0.726(1)	0.088(6)
C(125)	−0.002(2)	−0.119(1)	0.757(1)	0.078(5)
C(126)	−0.023(1)	−0.023(1)	0.724(1)	0.068(5)
C(131)	−0.121(1)	0.178(1)	0.6027(8)	0.049(4)
C(132)	−0.175(1)	0.277(1)	0.595(1)	0.066(5)
C(133)	−0.271(2)	0.323(1)	0.576(1)	0.087(6)
C(134)	−0.319(2)	0.272(2)	0.566(1)	0.087(6)
C(135)	−0.270(2)	0.176(1)	0.573(1)	0.082(6)
C(136)	−0.170(1)	0.126(1)	0.594(1)	0.064(5)
C(211)	−0.205(1)	0.388(1)	0.981(1)	0.062(5)
C(212)	−0.215(2)	0.460(2)	0.924(1)	0.089(6)
C(213)	−0.224(2)	0.550(2)	0.941(2)	0.130(9)
C(214)	−0.219(2)	0.550(2)	1.009(1)	0.094(7)
C(215)	−0.216(2)	0.487(2)	1.064(1)	0.101(7)
C(216)	−0.209(2)	0.394(1)	1.055(1)	0.083(6)
C(221)	−0.166(1)	0.187(1)	1.0383(9)	0.051(4)
C(222)	−0.065(1)	0.113(1)	1.0398(9)	0.058(4)
C(223)	−0.050(2)	0.044(1)	1.101(1)	0.079(6)
C(224)	−0.131(1)	0.048(1)	1.162(1)	0.071(5)
C(225)	−0.228(2)	0.120(1)	1.161(1)	0.080(6)
C(226)	−0.248(1)	0.192(1)	1.099(1)	0.065(5)
C(231)	−0.316(1)	0.296(1)	0.9507(8)	0.048(4)
C(232)	−0.325(1)	0.217(1)	0.9410(9)	0.054(4)
C(233)	−0.420(1)	0.222(1)	0.935(1)	0.071(5)
C(234)	−0.507(2)	0.305(1)	0.941(1)	0.078(6)
C(235)	−0.504(2)	0.387(2)	0.950(1)	0.094(6)
C(236)	−0.405(2)	0.381(1)	0.955(1)	0.081(6)
C(311)	0.412(1)	0.158(1)	0.796(1)	0.067(5)
C(312)	0.355(2)	0.256(1)	0.787(1)	0.081(6)
C(313)	0.408(2)	0.315(2)	0.767(1)	0.114(8)
C(314)	0.515(2)	0.270(2)	0.754(1)	0.100(7)
C(315)	0.574(2)	0.178(2)	0.762(1)	0.110(8)
C(316)	0.523(2)	0.114(1)	0.783(1)	0.087(6)
C(321)	0.319(1)	0.076(1)	0.9315(8)	0.050(4)
C(322)	0.372(1)	0.105(1)	0.966(1)	0.069(5)
C(323)	0.356(2)	0.093(1)	1.042(1)	0.080(6)
C(324)	0.287(2)	0.060(1)	1.086(1)	0.076(5)
C(325)	0.230(1)	0.033(1)	1.054(1)	0.070(5)
C(326)	0.247(1)	0.043(1)	0.978(1)	0.068(5)
C(331)	0.433(1)	−0.036(1)	0.8099(9)	0.050(4)
C(332)	0.476(1)	−0.050(1)	0.737(1)	0.068(5)
C(333)	0.550(2)	−0.144(1)	0.719(1)	0.085(6)
C(334)	0.571(2)	−0.217(2)	0.772(1)	0.096(7)
C(335)	0.528(1)	−0.206(1)	0.847(1)	0.070(5)
C(336)	0.458(1)	−0.113(1)	0.8644(9)	0.062(5)
C(411)	0.165(1)	0.484(1)	0.6489(8)	0.048(4)
C(412)	0.247(1)	0.402(1)	0.625(1)	0.067(5)
C(413)	0.345(2)	0.395(1)	0.592(1)	0.079(6)
C(414)	0.362(2)	0.474(2)	0.584(1)	0.092(6)
C(415)	0.288(2)	0.557(2)	0.609(1)	0.094(7)
C(416)	0.181(2)	0.565(1)	0.644(1)	0.083(6)
C(421)	−0.044(1)	0.544(1)	0.6218(9)	0.053(4)
C(422)	−0.020(2)	0.599(1)	0.558(1)	0.078(6)
C(423)	−0.088(2)	0.648(2)	0.509(1)	0.091(6)
C(424)	−0.181(2)	0.641(2)	0.525(1)	0.102(7)
C(425)	−0.211(2)	0.592(2)	0.588(1)	0.113(8)
C(426)	−0.138(2)	0.539(1)	0.637(1)	0.086(6)
C(431)	−0.025(1)	0.572(1)	0.7593(9)	0.053(4)
C(432)	−0.105(1)	0.663(1)	0.750(1)	0.067(5)
C(433)	−0.141(2)	0.724(1)	0.803(1)	0.079(6)
C(434)	−0.099(1)	0.698(1)	0.864(1)	0.064(5)
C(435)	−0.022(1)	0.609(1)	0.872(1)	0.065(5)
C(436)	0.017(1)	0.544(1)	0.8225(9)	0.058(4)

illustrated in Fig. 1. The $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$ molecular framework is essentially tetrahedral; the palladium atoms form a near equilateral triangle with a slightly greater distance between Pd(2) and Pd(3), the two atoms bonded to the azide ligand, (2.876(2) Å as opposed to 2.843(2) Å). The internal angles of the triangle are 59.9°, 59.5° and 60.6°. The Au–Pd bond lengths are slightly shorter, lying between 2.725(1) Å and 2.757(1) Å, with the bonds to Pd(2) and Pd(3) slightly longer than that to Pd(1) making the Au–Pd(2)–Pd(3) face more open than the other faces. The bond angles deviate from 60° a little more than in the palladium triangle, ranging from 58.2° to 62.9°. Each metal atom is coordinated to a triphenylphosphine ligand, with the three phosphorus atoms bonded to palladium approximately coplanar with the metal triangle (*i.e.* in equatorial positions), but all displaced slightly below the plane. The two sulphur dioxide ligands in the molecule are displaced slightly above the plane, as is the N_3 ligand.

The near equilateral triangle of the palladium atoms in the $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$ cluster compound has dimensions that are slightly larger than those recorded for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_4]$ which are between 2.71(3) Å and 2.74(2) Å [7]. This is unlikely to be a consequence of any electronic effects associated with the different phosphines as consideration of the platinum *triangulo*-clusters $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3]$ [8] and $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ [9] shows smaller metal–metal distances associated with triphenylphosphine in contrast to the observations made above. The enlargement is more likely to have a steric origin associated with the azide ligand. The Pd–Au bond lengths in $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_4]$ lie between 2.73(2) Å and 2.79(2) Å and because of the large standard deviation it is not possible to compare these meaningfully with those for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$.

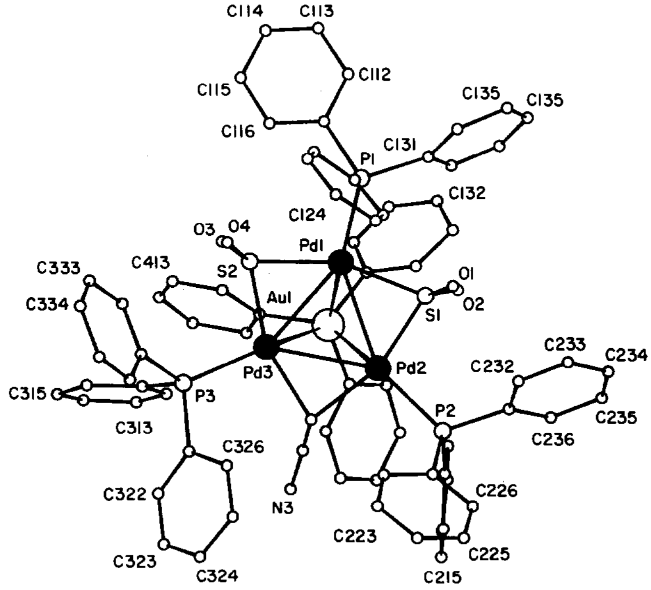


Fig. 1. Molecular structure of $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$. For reasons of clarity the hydrogen atoms have been omitted.

TABLE 3. Selected bond lengths (Å) and angles (°) for $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$

Au(1)–Pd(1)	2.725(1)	Pd(2)–S(1)	2.194(4)
Au(1)–Pd(2)	2.757(1)	Pd(2)–N(1)	2.13(1)
Au(1)–Pd(3)	2.757(1)	Pd(3)–P(3)	2.337(4)
Au(1)–P(4)	2.261(4)	Pd(3)–S(2)	2.204(4)
Pd(1)–Pd(2)	2.843(2)	Pd(3)–N(1)	2.17(2)
Pd(1)–Pd(3)	2.855(2)	S(1)–O(1)	1.44(1)
Pd(1)–P(1)	2.343(4)	S(1)–O(2)	1.45(1)
Pd(1)–S(1)	2.296(4)	S(2)–O(3)	1.46(1)
Pd(1)–S(2)	2.302(4)	S(2)–O(4)	1.46(1)
Pd(2)–Pd(3)	2.876(2)	N(1)–N(2)	1.10(2)
Pd(2)–P(2)	2.318(4)	N(2)–N(3)	1.23(2)
Pd(2)–Au(1)–Pd(1)	62.47(4)	S(2)–Pd(3)–Pd(2)	111.7(1)
Pd(3)–Au(1)–Pd(1)	62.75(4)	N(1)–Pd(3)–Au(1)	81.8(4)
Pd(3)–Au(1)–Pd(2)	62.86(4)	N(1)–Pd(3)–Pd(1)	107.0(4)
Pd(2)–Pd(1)–Au(1)	59.31(4)	N(1)–Pd(3)–Pd(2)	47.6(4)
Pd(3)–Pd(1)–Au(1)	59.17(3)	N(1)–Pd(3)–S(2)	159.3(4)
Pd(3)–Pd(1)–Pd(2)	60.62(4)	N(1)–Pd(2)–Pd(1)	108.4(4)
S(1)–Pd(1)–Au(1)	85.3(1)	N(1)–Pd(2)–Au(1)	82.3(4)
S(1)–Pd(1)–Pd(2)	49.1(1)	N(1)–Pd(2)–Pd(3)	48.5(4)
S(1)–Pd(1)–Pd(3)	109.7(1)	N(1)–Pd(2)–S(1)	160.7(4)
S(2)–Pd(1)–Au(1)	84.9(1)	O(1)–S(1)–Pd(1)	114.3(5)
S(2)–Pd(1)–Pd(2)	109.8(1)	O(1)–S(1)–Pd(2)	115.7(6)
S(2)–Pd(1)–Pd(3)	49.2(1)	O(2)–S(1)–Pd(1)	117.8(5)
S(2)–Pd(1)–S(1)	158.7(1)	O(2)–S(1)–Pd(2)	111.6(5)
Pd(1)–Pd(2)–Au(1)	58.22(3)	O(2)–S(1)–O(1)	114.2(8)
Pd(3)–Pd(2)–Au(1)	58.57(4)	Pd(3)–S(2)–Pd(1)	78.6(1)
Pd(3)–Pd(2)–Pd(1)	59.89(4)	O(3)–S(2)–Pd(1)	118.0(5)
S(1)–Pd(2)–Au(1)	86.5(1)	O(3)–S(2)–Pd(3)	114.1(5)
S(1)–Pd(2)–Pd(1)	52.3(1)	O(4)–S(2)–Pd(1)	114.7(5)
S(1)–Pd(2)–Pd(3)	112.2(1)	O(4)–S(2)–Pd(3)	114.9(5)
Pd(1)–Pd(3)–Au(1)	58.08(3)	O(4)–S(2)–O(3)	112.6(6)
Pd(2)–Pd(3)–Au(1)	58.56(4)	Pd(3)–N(1)–Pd(2)	83.9(5)
Pd(2)–Pd(3)–Pd(1)	59.49(4)	N(2)–N(1)–Pd(2)	126.9(14)
S(2)–Pd(3)–Au(1)	86.0(1)	N(2)–N(1)–Pd(3)	121.5(13)
S(2)–Pd(3)–Pd(1)	52.2(1)	N(3)–N(2)–N(1)	172.8(19)

The effect of adding the gold phosphine unit on the palladium–palladium bond lengths in the triangle cannot be fully realised because the structure of $PPN[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_3]$ has not been solved, but comparison to the triangle $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ [6] shows the palladium triangles in both structures to be very similar in dimensions with Pd–Pd bond lengths of 2.843(2) Å, 2.855(2) Å and 2.876(2) Å associated with 2 and bond lengths of between 2.88(1) Å and 2.99(1) Å for $[NEt_3(CH_2Ph)][Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]$. An interesting observation from the stuctural analysis of 2 is the lack of disorder in the crystal structure. Crystallographic disorder was observed in the previously documented palladium triangles $[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PPh_3)_3]^-$ [6] and $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}Cl)(PCy_3)_4]$ [7]. The similarity in size of the chloride ligand to the SO_2 ligand makes the packing of the triangles in an ordered arrangement less important and hence disorder predominates. In the azide cluster, the intermolecular forces between the anions are sufficiently specific as to influence the packing and lead to a regular and ordered packing arrangement.

3. Experimental details

Reactions were routinely carried out by use of Schlenk-line techniques under pure dry dinitrogen, with dry dioxygen-free solvents. Microanalyses (C, H, N, Au and Pd) were carried out by Mr. M. Gascoyne and his staff at Oxford. Infrared spectra were recorded on a

Perkin-Elmer FT1710 spectrometer as Nujol mulls between KBr discs and $^{31}P\{^1H\}$ NMR spectra using a Brüker AM-300 spectrometer operating at 121.49 MHz and referenced to TMP in D_2O. $[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ was prepared according to the method in Ref. 10.

3.1. Syntheses

3.1.1. $PPN[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_3]$, 1

$[Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)_2(PPh_3)_5]$ (0.40 g, 0.19 mmol) was dissolved in toluene (25 cm^3), and a solution of bis(triphenylphosphoranylidene)ammonium azide (0.205 g, 0.77 mmol) in ethanol (15 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 $PPN[Pd_3(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_3]$, which was recrystallised from acetone-ether to give yellow crystals. Yield 0.52 g (90%). Anal. Found: C, 59.2; H, 4.2; N, 3.1. $C_{78}H_{65}N_4O_4P_6Pd_3S_2$ calc.: C, 59.6; H, 4.2; N, 3.1%); $\nu(SO_2)$ at 1179m, 1169m, 1049s, 1034s cm^{-1}; $\nu(N_3)$ at 2050 cm^{-1}; ^{31}P NMR: 9.3 (d, 2P); 6.6 (t, 1P, $^3J_{PP} = 36$ Hz) ppm.

3.1.2. $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$, 2

1 (0.16 g, 0.09 mmol) was dissolved in dichloromethane (20 cm^3) and a solution of $[Au(PPh_3)NO_3]$ (0.046 g, 0.09 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 **2**. Yield 0.14 g (89%). Anal. Found: C, 49.7; H, 3.6; N, 2.5; Au, 11.8; Pd, 19.1. $C_{72}H_{60}AuN_3O_4P_3Pd_3S_2$ calc.: C, 49.7; H, 3.8; N, 2.3; Au, 11.9; Pd, 18.9%; $\nu(SO_2)$ at 1202m, 1062m, 1045vs cm^{-1}; $\nu(N_3)$ at 2045s cm^{-1}; ^{31}P NMR 21.0 (dt 1P, $J = 18$, 15 Hz), 15.1 (dd 2P, $J = 18$, 15 Hz), 12.4 (q, 1P, $J = 18$ Hz).

3.2. Crystal structure determination of $[Pd_3Au(\mu\text{-}SO_2)_2(\mu\text{-}N_3)(PPh_3)_4]$, 2

Crystals of compound **2** used in the analysis were grown by the slow evaporation of an ethanol solution. A single crystal of dimensions 0.30 × 0.20 × 0.12 mm 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 positions of the palladium atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located in subsequent Fourier difference syntheses [11,12]. An absorption correction using DIFABS was applied when the model was in place [13]. The hydrogen atoms were included in idealised positions. The metal, phosphorus, sulphur and nitrogen atoms were assigned anisotropic displacement parameters, as were the oxygen atoms in the SO_2 groups. The carbon atoms of the phenyl groups were assigned isotropic thermal parameters that were allowed to vary independently. The EtOH solvent molecules were considered to be two-fold disordered; each end atom was treated as 50% C, 50% O and present as only half a molecule per asymmetric unit. The central C atoms were modelled as 100% carbon. The non-hydrogen atoms of this group were refined with a common thermal parameter and the C–C–O bond angles were restrained to 110°, as in pure ethanol. The bond lengths were restrained to be 1.49 Å, an average between the C–O and C–C bond lengths in ethanol. All hydrogen atoms were given an isotropic thermal parameter, relating to that of the carbon atom to which they were attached, that was not refined. A five-parameter Chebychev polynomial weighting scheme was applied to the final model which converged at $R = 0.048$ and $R_w = 0.054$.

Additional information, including a list of observed and calculated structure factors, is available from the authors.

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