Journal of Organometallic Chemistry, 433 (1992) 311–321
Elsevier Sequoia S.A., Lausanne
JOM 22642

The synthesis and structural characterization of a pentapalladium cluster, $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$, with linear bridging isocyanide ligands

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(Received January 9, 1992)

Abstract

The cluster compound $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$ (Xyl = $C_6H_3(CH_3)_2$-2,6) has been obtained in high yield from the reaction between the palladium(0) compound $[Pd_2(dba)_3] \cdot CHCl_3$ (dba = $\{PhCH{:}CH\}_2CO$) and XylNC under an atmosphere of sulphur dioxide. The molecular structure of $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5] \cdot THF$ has been determined by single-crystal X-ray diffraction. The structure is based on an edge-bridged tetrahedron of palladium atoms, with three edges bridged by sulphur dioxide ligands and two edges bridged by isocyanide ligands. Each palladium atom also carries a terminal isocyanide ligand. The CNC angles in the bridging isocyanides are almost linear, which is most unusual. This leads to higher than expected values for the ν(NC) stretching modes in the infrared spectrum of this compound.

Introduction

The palladium(0) compounds $[Pd_2(dba)_3] \cdot Sol$ (Sol = $CHCl_3$, dba) have been used to synthesize a number of cluster compounds such as $[Pd_5(SO_2)_4(PPh_3)_5]$ [1], $[Pd_8(CO)_8(PMe_3)_7]$ [2] and $[Pd_3(CNXyl)_6]$ [3]. $[Pd_2(dba)_3] \cdot CHCl_3$ also undergoes ligand substitution reactions to give monomeric compounds such as [Pd(dba)(bipy)] [4] and $[Pd(MeO_2CCH{=}CHCO_2Me)\{P(OPh)_3\}_2]$ [5] and has been used as a catalyst in a wide range of organic reactions [6]. Xylyl isocyanide (Xyl = $C_6H_3Me_2$-2,6) is a versatile ligand that can bond terminally to one metal atom or bridge between two, and has been shown to substitute for $P(C_6H_{11})_3$ in $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ to give $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNXyl)_2(CNXyl)\{P(C_6H_{11})_3\}_2]$ with three equivalents of XylNC and $[Pt_3(\mu\text{-}CNXyl)_3(CNXyl)_2\{P(C_6H_{11})_3\}]$ with five equivalents of XylNC [7]. This paper reports the reaction of $[Pd_2(dba)_3] \cdot CHCl_3$ with XylNC under an atmosphere of sulphur dioxide, which was studied in order to determine whether this represented a good route into palladium cluster compounds with isocyanides. It

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was also of interest how these compounds compared with the cluster compounds formed in the analogous reaction with phosphines.

Results and discussion

When a sulphur dioxide saturated solution of XylNC in toluene was added to a solution of $[Pd_2(dba)_3] \cdot CHCl_3$, also in toluene, and SO_2 was bubbled through the mixture for 10 min, the colour of the solution changed to red. After removal of the solvent under reduced pressure, the crude product was washed with ether to remove the dba, and recrystallized from dichloromethane/ether to give the compound $[Pd_5(SO_2)_3(CNXyl)_7]$ as red crystals in good yield.

$[Pd_5(SO_2)_3(CNXyl)_7]$ was characterized on the basis of FAB-MS, ^1H NMR, $^{13}C\{^1H\}$ NMR and IR spectroscopy. The $[M]^+$ peak was not observed in the FAB mass spectrum, and the peaks that were present are summarized in Table 1. The highest observed peak at $m/z = 1449$ corresponded to the ion $[Pd_5(CNXyl)_7]^+$, in which all three SO_2 ligands had been lost from the compound. This loss of all of the SO_2 ligands before any other ligand is the same pattern as that observed for the phosphine clusters $[Pd_5(SO_2)_4(PPh_3)_5]$ and $[Pd_4(SO_2)_3(PMe_3)_5]$ [1]. The most intense peak resulted from the loss of the three SO_2 ligands and two of the isocyanides. There was no evidence in the spectrum of decomposition products containing fragments of the isocyanide ligands. The FAB mass spectrum also showed small peaks at $m/z = 1663$ and 2117 which may correspond to higher nuclearity clusters also formed in the reaction in low yields and present as trace impurities.

The IR spectrum showed evidence of both sulphur dioxide and isocyanide ligands. Three peaks, at 1216m, 1063s and 1060s cm^{-1} indicated the presence of bridging SO_2 ligands. There were also three peaks in the $\nu(NC)$ region at 2142vs, 2047s and 1990w cm^{-1}. In previously characterized palladium and platinum cluster compounds, $\nu(NC)$ was observed between 2221 and 2080 cm^{-1} for terminal isocyanides, and between 1911 and 1589 cm^{-1} for bridging isocyanides. The strongest band at 2142 cm^{-1} in this compound is clearly from a terminal isocyanide ligand, but the other two bands fall between the usual ranges.

The compound $[Pd_2Cl_2(\mu\text{-}CNXyl)_2(py)_2]$ contains two bridging isocyanide groups in which the C–N–C angles are 175.2(13)° and 157.6(9)° [8]. The former is almost linear and the latter is larger by about 20° than those that have been observed in other bridging isocyanide ligands. The linearity of the bridging iso-

Table 1

Important peaks in the FAB mass spectrum of $[Pd_5(SO_2)_3(CNXyl)_7]$

m/z	Intensity (rel.)	Assignment [a]
1149	17	$[M-3SO_2]^+$
1317	24	$[M-3SO_2-XylNC]^+$
1187	100	$[M-3SO_2-2XylNC]^+$
790	84	$[M-3SO_2-5XylNC]^+$
660	43	$[M-3SO_2-6XylNC]^+$
554	39	$[M-Pd-3SO_2-6XylNC]^+$

[a] $M = Pd_5(SO_2)_3(CNXyl)_7$.

cyanide ligands leads to a lower degree of backbonding and hence higher C–N stretching frequencies in the IR spectrum. ν(NC) was observed at 2056 and 1976 cm^{-1} in this compound. These stretching frequencies are very similar to those observed in [$Pd_5(SO_2)_3(CNXyl)_7$] leading to the possibility that this cluster compound also contains linear bridging isocyanides.

There were three peaks in the methyl region of the ^1H NMR spectrum, at 2.54 ppm, 2.51 ppm and 2.31 ppm, in the intensity ratio 2:2:3. This confirmed that there were seven isocyanide ligands in the cluster. The $^{13}C\{^1H\}$ NMR spectrum showed four weak peaks that were assigned to the M–*C*NR carbon atoms of the isocyanides. These were observed at 157.3, 153.0, 150.2 and 151.8 ppm. In the *triangulo*-platinum cluster [$Pt_3(\mu\text{-}CN^tBu)_3(CN^tBu)_3$] the sample needed to be enriched with 10% ^{13}C in the NC isocyanide groups in order for these carbon atoms to be observed in the $^{13}C\{^1H\}$ NMR spectrum [9]. The carbon atoms of the terminal isocyanides in the spectrum of the enriched compound were observed at $\delta = 163.3$ ppm, and those from the bridging isocyanides at $\delta = 231.3$ ppm. In the spectrum of [$Pd_5(SO_2)_3(CNXyl)_7$] there was no evidence of a peak at around 230 ppm, and the lowering of the chemical shift is consistent with the unusual nature of the bridging isocyanide ligands in this complex. The occurrence of four peaks in the M–*C*NR region and also four peaks in the methyl region of the $^{13}C\{^1H\}$ NMR spectrum suggested there are four inequivalent isocyanide ligands and that in the ^1H NMR spectrum there were two peaks coincident, leading to the most intense observed peak.

The spectroscopic data suggested that the structure of [$Pd_5(SO_2)_3(CNXyl)_7$] contains linear bridging isocyanide ligands. In order to verify this, a single-crystal X-ray analysis was undertaken. Crystals suitable for X-ray diffraction were obtained from the slow diffusion of diethyl ether into a tetrahydrofuran solution of the compound. Details of the study are given in Table 2, final fractional atomic coordinates are given in Table 3 and important bond lengths and angles are summarized in Table 4. The cluster is illustrated in Fig. 1 and, with the xylyl groups removed to emphasize the geometry of the cluster core, in Fig. 2.

The compound crystallizes in the space group $P\bar{1}$, and the structure consists of well separated molecules of [$Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5$] and occluded tetrahydrofuran molecules. The metal core geometry is based on an edge-bridged tetrahedron, with the Pd–Pd bond distances lying between 2.7172(6) and 2.9299(7) Å. The shortest bond is that between Pd(1) and Pd(4), the bond bridged by the fifth palladium atom, Pd(3), and the two longest are those between these two Pd atoms, and those in the half of the tetrahedron away from the bridging metal atom Pd(1)–Pd(5) (2.9299(7)) and Pd(2)–Pd(4) (2.8582(6) Å). Both of the bonds to the bridging palladium atom are themselves bridged by μ-SO_2 ligands, as is the bond furthest from the metal bridge, between Pd(2) and Pd(5). These three Pd–Pd bonds have distances of 2.8006(6), 2.7844(6) and 2.7720(7) Å which are typical for Pd–Pd bonds bridged by SO_2. Two bonds within the tetrahedron, Pd(1)–Pd(2) and Pd(1)–Pd(5), are bridged by isocyanide ligands, and each palladium atom in the molecule also carries a terminal isocyanide ligand.

The Pd–C_{term} bond lengths range from 1.973(7) to 2.024(6) Å, a similar range to that of the bond lengths in [$Pd_3(\mu\text{-}SO_2)_2(CN^tBu)_5$], which lie between 1.99(3) and 2.13(3) Å [10], [$Pd_3(\mu\text{-}SO_2)_2(CNXyl)_2(PPh_3)_3$], which average 2.049(4) Å [11], and [$Pd_3(\mu\text{-}CNCy)_3(CNCy)_3$] which average 2.004(14) Å [12]. The Pd–C_{br} bond lengths

Table 2

Crystal data for $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$

Formula	$C_{63}H_{63}N_7O_6Pd_5S_3 \cdot C_4H_8O$
M	1641.00 (1713.11 including THF)
Crystal system	Triclinic
Space group	$P1$ (no. 2)
a (Å)	12.737(3)
b (Å)	15.495(3)
c (Å)	18.085(3)
α (°)	92.56(2)
β (°)	97.56(2)
γ (°)	87.06(2)
U (Å^3)	3530.96
Z	2
D_c (g cm^{-3})	1.61
$F(000)$	1712
Linear absorption coefficient (cm^{-1})	13.71
Crystal colour	Red
Data collection	
X-Radiation	Mo-K_α, $\lambda = 0.71069$ Å
θ_{min}, θ_{max} (°)	0, 23
min, max h, k, l	$-14,14$; $-17,17$; $-1,19$
ω-scan width (°)	$1.0 + 0.35 \tan\theta$
Horizontal aperture (mm)	2.5
Total data collected	12069
Total unique data	9721
Total observed data $[I > 3\sigma(I)]$	6617
Merging R factor	1.37%
Absorption correction	Empirical; min/max Correction 1.16, 1.53
Refinement	
No. of parameters	803
Ratio data/parameters	8.24
Weighting scheme	Unit weights
Final R	2.80%
Final R_w	2.94%

$$R = \frac{\Sigma \| F_o| - |F_c\|}{\Sigma |F_o|} \qquad R_w = \left[\frac{\Sigma\left[w(|F_o| - |F_w|)^2 \right]}{\Sigma\left(w|F_o|^2 \right)} \right]^{1/2}$$

show that both bridging isocyanide ligands are asymmetric, with bonds to Pd(1) on average 0.23 Å longer than those to Pd(2) and Pd(5). The Pd–C bonds to Pd(1), 2.266(6) and 2.303(7) Å are considerably longer than those Pd–C_{br} bonds observed in $[Pd_3(\mu\text{-}CNCy)_3(CNCy)_3]$ which average 2.072(13) Å [12] and $[Pd_2Cl_2(CNXyl)_2(py)_2]$, which average 2.011(14) Å [8].

The C–N–C angles in the bridging isocyanide ligands are C(6)–N(6)–C(61) = 168.4(7)° and C(7)–N(7)–C(71) = 171.4(8)°. As anticipated by the spectroscopic data these are unusually high for bridging isocyanides; all previously characterized palladium and platinum clusters containing bridging isocyanide ligands have C–N–

Table 3

Fractional atomic coordinates for $[Pd_5(SO_2)_3(CNXyl)_7]$

Atom	x	y	z
Pd(1)	0.32257(4)	0.78481(3)	0.20361(2)
Pd(2)	0.37295(4)	0.62809(3)	0.27293(3)
Pd(3)	0.16879(4)	0.88643(3)	0.26906(3)
Pd(4)	0.15797(4)	0.70756(3)	0.25097(3)
Pd(5)	0.25128(4)	0.62527(3)	0.13406(3)
S(1)	0.0543(1)	0.7957(1)	0.31171(9)
S(2)	0.3357(1)	0.5126(1)	0.1963(1)
S(3)	0.3039(1)	0.9319(1)	0.2125(1)
N(1)	0.5058(4)	0.7871(4)	0.1018(3)
N(2)	0.5339(4)	0.5177(4)	0.3819(3)
N(3)	0.1163(4)	1.0739(3)	0.3312(3)
N(4)	0.0365(4)	0.5385(3)	0.2608(3)
N(5)	0.2187(4)	0.5289(4)	−0.0242(3)
N(6)	0.4287(5)	0.7942(3)	0.3705(3)
N(7)	0.1437(5)	0.7928(4)	0.0651(3)
C(1)	0.4470(5)	0.7851(4)	0.1447(4)
C(2)	0.4764(5)	0.5612(4)	0.3440(4)
C(3)	0.1253(5)	1.0041(4)	0.3067(3)
C(4)	0.0855(5)	0.5991(4)	0.2571(3)
C(5)	0.2235(5)	0.5649(4)	0.0336(4)
C(6)	0.3929(5)	0.7499(4)	0.3207(3)
C(7)	0.1950(6)	0.7478(4)	0.1066(4)
C(11)	0.5625(5)	0.7859(5)	0.0404(4)
C(12)	0.5719(6)	0.7081(6)	0.0023(4)
C(13)	0.6219(9)	0.709(1)	−0.0614(6)
C(14)	0.658(1)	0.784(1)	−0.0805(7)
C(15)	0.649(1)	0.857(1)	−0.0428(8)
C(16)	0.6002(8)	0.8613(7)	0.0215(5)
C(21)	0.5999(5)	0.4624(5)	0.4287(4)
C(22)	0.6531(6)	0.4978(6)	0.4942(4)
C(23)	0.7172(7)	0.4410(8)	0.5389(5)
C(24)	0.7281(8)	0.356(1)	0.5196(7)
C(25)	0.6731(8)	0.3227(6)	0.4557(7)
C(26)	0.6072(7)	0.3759(6)	0.4072(5)
C(31)	0.1102(5)	1.1583(4)	0.3610(3)
C(32)	0.1551(5)	1.2226(4)	0.3262(3)
C(33)	0.1488(6)	1.3043(4)	0.3584(4)
C(34)	0.1030(6)	1.3208(4)	0.4215(4)
C(35)	0.0598(6)	1.2571(4)	0.4549(4)
C(36)	0.0627(5)	1.1724(4)	0.4262(4)
C(41)	−0.0245(5)	0.4693(4)	0.2716(4)
C(42)	−0.0292(6)	0.3997(4)	0.2207(4)
C(43)	−0.0908(7)	0.3311(5)	0.2366(6)
C(44)	−0.1423(7)	0.3376(6)	0.2991(7)
C(45)	−0.1361(7)	0.4071(7)	0.3463(5)
C(46)	−0.0766(6)	0.4749(5)	0.3348(4)
C(51)	0.2213(6)	0.4777(5)	−0.0904(4)
C(52)	0.2809(6)	0.5049(6)	−0.1434(4)
C(53)	0.2856(8)	0.4474(7)	−0.2043(5)
C(54)	0.2361(9)	0.3727(7)	−0.2118(5)
C(55)	0.1738(8)	0.3500(6)	−0.1605(5)
C(56)	0.1658(6)	0.4019(5)	−0.0965(4)
C(61)	0.4839(6)	0.8320(4)	0.4336(4)

Table 3 (continued)

Atom	*x*	*y*	*z*
C(62)	0.5934(7)	0.8197(5)	0.4432(4)
C(63)	0.6467(7)	0.8525(6)	0.5098(5)
C(64)	0.5926(9)	0.8968(6)	0.5611(5)
C(65)	0.4862(8)	0.9102(5)	0.5485(4)
C(66)	0.4268(6)	0.8783(4)	0.4843(4)
C(71)	0.0900(7)	0.8399(4)	0.0075(4)
C(72)	−0.0137(8)	0.8714(5)	0.0139(5)
C(73)	−0.0654(9)	0.9139(6)	−0.0465(7)
C(74)	−0.017(1)	0.9263(7)	−0.1080(6)
C(75)	0.083(1)	0.8960(6)	−0.1128(5)
C(76)	0.141(1)	0.8513(5)	−0.0534(5)
C(121)	0.5314(8)	0.6295(6)	0.0272(6)
C(161)	0.594(1)	0.9423(8)	0.0688(8)
C(221)	0.6408(7)	0.5911(7)	0.5148(5)
C(261)	0.5469(9)	0.3406(6)	0.3361(7)
C(321)	0.2077(7)	1.2034(5)	0.2571(4)
C(361)	0.0210(7)	1.1000(5)	0.4638(5)
C(421)	0.0275(7)	0.3968(5)	0.1541(5)
C(461)	−0.0693(8)	0.5525(7)	0.3877(5)
C(521)	0.3344(7)	0.5875(7)	−0.1354(5)
C(561)	0.0983(8)	0.3789(6)	−0.0388(5)
C(621)	0.6509(8)	0.7738(6)	0.3848(6)
C(661)	0.3106(8)	0.8951(5)	0.4680(4)
C(721)	−0.0622(9)	0.8614(7)	0.0819(7)
C(761)	0.253(1)	0.8221(7)	−0.0550(6)
C(200)	0.634(1)	0.068(1)	0.2532(9)
C(300)	0.677(2)	−0.017(1)	0.289(1)
C(400)	0.798(2)	−0.017(1)	0.291(2)
C(500)	0.800(1)	0.080(1)	0.313(1)
O(1)	0.716(1)	0.1242(9)	0.2719(9)
O(11)	0.0707(4)	0.7825(3)	0.3917(2)
O(12)	−0.0556(4)	0.8031(3)	0.2794(3)
O(21)	0.2715(4)	0.4493(3)	0.2235(3)
O(22)	0.4270(4)	0.4759(3)	0.1645(3)
O(31)	0.2732(5)	0.9720(3)	0.1415(3)
O(32)	0.3872(4)	0.9729(3)	0.2607(3)

C angles that are much smaller. Examples are given in Table 5. It is apparent from Fig. 1 that there is no obvious steric reason for this linearity. In $[Pd_2Cl_2(\mu\text{-}CNXyl)_2(py)]$ the steric factors are not important in determining the C–N–C angles, and the more bent isocyanide is associated with the less hindered position [8]. This suggests that in $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$ the linearity of the isocyanide ligands has an electronic origin, and we are currently undertaking theoretical calculations to investigate the nature of these interactions. The terminal isocyanide ligands are all essentially linear, with typical C–N–C angles between 170.1(7) and 177.6(6)°.

Another way of describing the metal geometry of this molecule is to consider two Pd_3 triangles sharing a common vertex, Pd(1). C(6), C(7), C(2), C(5) and S(2) lie approximately in the plane defined by Pd(1), Pd(2) and Pd(5) whereas C(1), C(3), C(7), S(1) and S(3) lie approximately in the plane defined by Pd(1), Pd(3) and Pd(4).

Table 4

Selected bond lengths (Å) and angles (°) for $[Pd_5(SO_2)_3(CNXyl)_7]$

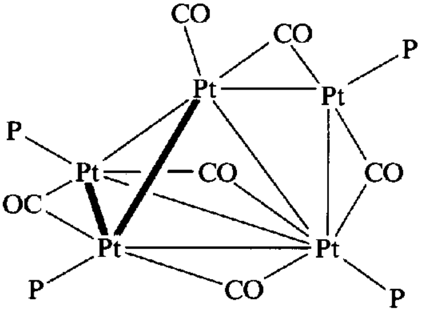
Pd(1)–Pd(2)	2.7894(6)	Pd(5)–C(7)	2.054(7)
Pd(1)–Pd(3)	2.8006(6)	S(1)–O(11)	1.456(5)
Pd(1)–Pd(4)	2.7172(6)	S(1)–O(12)	1.445(5)
Pd(1)–Pd(5)	2.8582(6)	S(2)–O(21)	1.451(5)
Pd(1)–S(3)	2.280(2)	S(2)–O(22)	1.444(5)
Pd(1)–C(1)	2.024(6)	S(3)–O(31)	1.449(5)
Pd(1)–C(6)	2.266(6)	S(3)–O(32)	1.437(5)
Pd(1)–C(7)	2.303(7)	N(1)–C(1)	1.149(7)
Pd(2)–Pd(4)	2.9299(7)	N(1)–C(11)	1.401(8)
Pd(2)–Pd(5)	2.7720(7)	N(2)–C(2)	1.149(7)
Pd(2)–S(2)	2.245(2)	N(2)–C(21)	1.400(8)
Pd(2)–C(2)	1.999(7)	N(3)–C(3)	1.156(7)
Pd(2)–C(6)	2.055(6)	N(3)–C(31)	1.395(7)
Pd(3)–Pd(4)	2.7844(6)	N(4)–C(4)	1.162(7)
Pd(3)–S(1)	2.302(2)	N(4)–C(41)	1.391(8)
Pd(3)–S(3)	2.271(2)	N(5)–C(5)	1.158(7)
Pd(3)–C(3)	1.995(6)	N(5)–C(51)	1.409(8)
Pd(4)–Pd(5)	2.7882(6)	N(6)–C(7)	1.165(7)
Pd(4)–S(1)	2.209(2)	N(6)–C(71)	1.382(8)
Pd(4)–C(4)	1.973(7)	N(7)–C(7)	1.160(8)
Pd(5)–S(2)	2.266(2)	N(7)–C(71)	1.384(8)
Pd(5)–C(5)	2.004(6)		

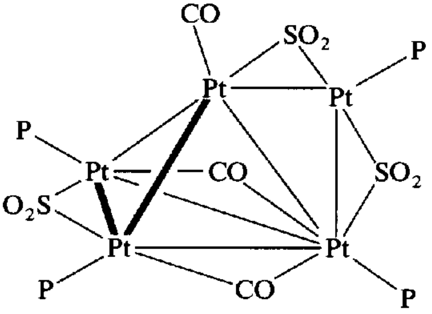
Pd(3)–Pd(1)–Pd(2)	112.88(2)	S(1)–Pd(4)–Pd(2)	138.91(5)
Pd(4)–Pd(1)–Pd(2)	64.28(2)	S(1)–Pd(4)–Pd(3)	53.41(4)
Pd(4)–Pd(1)–Pd(3)	60.59(2)	S(1)–Pd(4)–Pd(5)	160.67(5)
Pd(5)–Pd(1)–Pd(2)	58.77(2)	S(4)–Pd(4)–Pd(1)	146.8(2)
Pd(5)–Pd(1)–Pd(3)	115.06(2)	C(4)–Pd(4)–Pd(2)	95.4(2)
Pd(5)–Pd(1)–Pd(4)	59.95(2)	C(4)–Pd(4)–Pd(3)	151.8(2)
S(3)–Pd(1)–Pd(2)	149.26(5)	C(4)–Pd(4)–Pd(5)	86.4(2)
S(3)–Pd(1)–Pd(3)	51.89(5)	C(5)–Pd(4)–S(1)	98.9(5)
S(3)–Pd(1)–Pd(4)	112.11(5)	Pd(2)–Pd(5)–Pd(1)	59.37(2)
S(3)–Pd(1)–Pd(5)	148.74(5)	Pd(4)–Pd(5)–Pd(1)	57.51(2)
C(1)–Pd(1)–Pd(2)	98.3(2)	Pd(4)–Pd(5)–Pd(2)	63.60(2)
C(1)–Pd(1)–Pd(3)	145.6(2)	S(2)–Pd(5)–Pd(1)	109.93(5)
C(1)–Pd(1)–Pd(4)	152.3(2)	S(2)–Pd(5)–Pd(2)	51.75(4)
C(1)–Pd(1)–Pd(5)	92.9(2)	S(2)–Pd(5)–Pd(4)	98.83(5)
C(1)–Pd(1)–S(3)	93.8(2)	C(5)–Pd(5)–Pd(1)	141.5(2)
C(6)–Pd(1)–Pd(2)	46.5(2)	C(5)–Pd(5)–Pd(2)	146.5(2)
C(6)–Pd(1)–Pd(3)	87.2(2)	C(5)–Pd(5)–Pd(4)	145.0(2)
C(6)–Pd(1)–Pd(4)	78.7(2)	C(5)–Pd(5)–S(2)	97.6(2)
C(6)–Pd(1)–Pd(5)	104.5(2)	C(7)–Pd(5)–Pd(1)	52.9(2)
C(6)–Pd(1)–S(3)	103.0(2)	C(7)–Pd(5)–Pd(2)	110.6(2)
C(6)–Pd(1)–C(1)	105.5(3)	C(7)–Pd(5)–Pd(4)	69.2(2)
C(7)–Pd(1)–Pd(2)	102.7(2)	C(7)–Pd(5)–S(2)	162.3(2)
C(7)–Pd(1)–Pd(3)	89.3(2)	C(7)–Pd(5)–C(5)	99.5(3)
C(7)–Pd(1)–Pd(4)	67.7(2)	Pd(4)–S(1)–Pd(3)	76.19(5)
C(7)–Pd(1)–Pd(5)	45.3(2)	O(11)–S(1)–Pd(3)	115.7(2)
C(7)–Pd(1)–S(3)	103.5(2)	O(11)–S(1)–Pd(4)	112.0(2)
C(7)–Pd(1)–C(1)	97.9(3)	O(12)–S(1)–Pd(3)	117.0(2)
C(7)–Pd(1)–C(6)	143.1(2)	O(12)–S(1)–Pd(4)	115.8(2)
Pd(4)–Pd(2)–Pd(1)	56.67(2)	O(12)–S(1)–O(11)	114.6(3)
Pd(5)–Pd(2)–Pd(1)	61.85(2)	Pd(5)–S(2)–Pd(2)	75.83(5)
Pd(5)–Pd(2)–Pd(4)	58.47(2)	O(21)–S(2)–Pd(2)	115.9(2)
S(2)–Pd(2)–Pd(1)	113.02(5)	O(21)–S(2)–Pd(5)	118.1(2)

Table 4 (continued)

S(2)–Pd(2)–Pd(4)	95.34(5)	O(22)–S(2)–Pd(2)	113.0(2)
S(2)–Pd(2)–Pd(5)	52.43(5)	O(22)–S(2)–Pd(5)	114.4(3)
C(2)–Pd(2)–Pd(1)	146.4(2)	O(22)–S(2)–O(21)	114.3(3)
C(2)–Pd(2)–Pd(4)	143.8(2)	Pd(3)–S(3)–Pd(1)	75.96(5)
C(2)–Pd(2)–Pd(5)	145.4(2)	O(31)–S(3)–Pd(1)	114.0(2)
C(2)–Pd(2)–S(2)	93.7(2)	O(31)–S(3)–Pd(3)	115.6(3)
C(6)–Pd(2)–Pd(1)	53.2(2)	O(32)–S(3)–Pd(1)	114.6(3)
C(6)–Pd(2)–Pd(4)	77.1(2)	O(32)–S(3)–Pd(3)	115.8(3)
C(6)–Pd(2)–Pd(5)	114.1(2)	O(32)–S(3)–O(31)	115.1(4)
C(6)–Pd(2)–S(2)	166.2(2)	C(11)–N(1)–C(1)	170.1(7)
C(6)–Pd(2)–C(2)	99.2(2)	C(21)–N(2)–C(2)	177.3(7)
Pd(4)–Pd(3)–Pd(1)	58.22(2)	C(31)–N(3)–C(3)	177.6(6)
S(1)–Pd(3)–Pd(1)	108.32(4)	C(41)–N(4)–C(4)	174.6(6)
S(1)–Pd(3)–Pd(4)	50.40(4)	C(51)–N(5)–C(5)	173.3(7)
S(3)–Pd(3)–Pd(1)	52.16(4)	C(61)–N(6)–C(6)	168.4(7)
S(3)–Pd(3)–Pd(4)	110.02(4)	C(71)–N(7)–C(7)	171.4(8)
S(3)–Pd(3)–S(1)	160.41(6)	N(1)–C(1)–Pd(1)	169.3(6)
C(3)–Pd(3)–Pd(1)	146.4(2)	N(2)–C(2)–Pd(2)	175.2(6)
C(3)–Pd(3)–Pd(4)	155.0(2)	N(3)–C(3)–Pd(3)	169.6(6)
C(3)–Pd(3)–S(1)	104.6(2)	N(4)–C(4)–Pd(4)	175.4(6)
C(3)–Pd(3)–S(3)	95.0(2)	N(5)–C(5)–Pd(5)	172.9(6)
Pd(2)–Pd(4)–Pd(1)	59.06(2)	Pd(2)–C(6)–Pd(6)	80.3(2)
Pd(3)–Pd(4)–Pd(1)	61.19(2)	N(6)–C(6)–Pd(6)	129.7(5)
Pd(3)–Pd(4)–Pd(2)	109.19(2)	N(6)–C(6)–Pd(6)	149.3(5)
Pd(5)–Pd(4)–Pd(1)	62.54(2)	Pd(5)–C(7)–Pd(7)	81.8(2)
Pd(5)–Pd(4)–Pd(2)	57.93(2)	N(7)–C(7)–Pd(7)	128.5(6)
Pd(5)–Pd(4)–Pd(3)	117.91(5)	N(7)–C(7)–Pd(7)	148.9(6)
S(1)–Pd(4)–Pd(1)	114.27(5)		

This compound may be regarded as a higher homologue of the cluster $[Pd_3(\mu\text{-}SO_2)_2(CN^tBu)_5]$ [10] as the edge-bridging part of the molecule contains the $Pd_3(\mu\text{-}SO_2)_2(CNR)_3$ fragment. The Pd–Pd bonds bridged by SO_2 are somewhat shorter in the triangular cluster, being 2.734(4) Å as opposed to 2.7844(6) and 2.8006(6) Å for the larger cluster compound. The cluster valence electron count of $[Pd_5(SO_2)_3(CNXyl)_7]$ is 70, and this is the number expected for edge-bridged tetrahedral platinum cluster compounds [13]. However, this is the first example of this metal geometry in palladium cluster chemistry. Two isoelectronic pentaplatinum cluster compounds, $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$ and $[Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4]$, with edge-bridged tetrahedral structures have been synthesized [14,15] and are illustrated below.





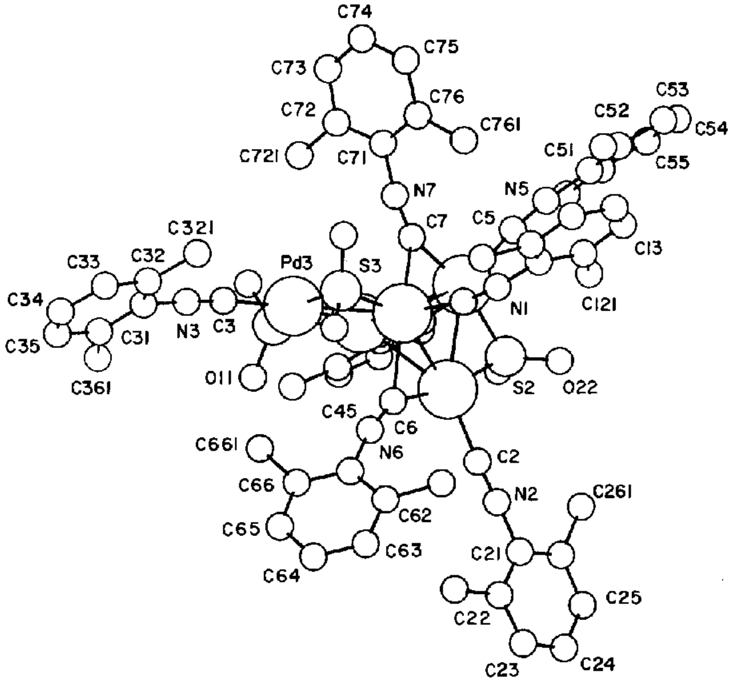


Fig. 1. Molecular structure of [$Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5$], with hydrogen atoms omitted for clarity.

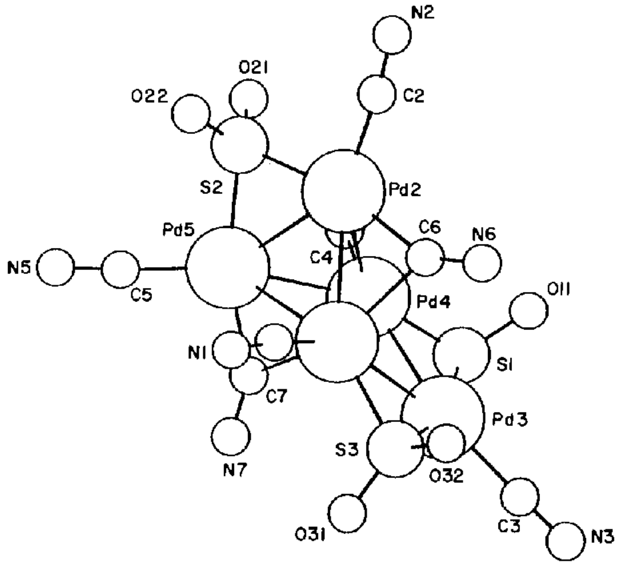


Fig. 2. Molecular structure of [$Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)]_5$, with xylyl groups omitted to emphasize the cluster core coordination.

Table 5

C–N–C angles in palladium and platinum cluster compounds containing bridging isocyanide ligands

Compound	CNC (°)	Ref.
$[Pd_3(\mu\text{-}CNCy)_3(CNCy)_3]$	128.9(12)	[12]
$[Pt_3(\mu\text{-}CN^tBu)_3(CN^tBu)_3]$	132(2), 133(2), 133(2)	[9]
$[Pt_3(\mu\text{-}CO)(\mu\text{-}CNXyl)_2(CNXyl)(PCy_3)_2]$	128(2), 129(2)	[7]
$[Pt_3(\mu\text{-}CNXyl)_3(CNXyl)_2(PCy_3)]$	131(1), 132(1), 133(1)	[7]
$[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$	164.4(7), 171.4(8)	This work

In both cases one of the platinum atoms carries a terminal carbonyl ligand instead of a phosphine. In $[Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4]$ the sulphur dioxide ligands occupy equivalent positions on the edge-bridged tetrahedral metal core as they do in the cluster compound $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$.

The difference between the products given by phosphines and isocyanide in the reaction with $[Pd_2(dba)_3] \cdot CHCl_3$ under a SO_2 atmosphere reflect the ability of isocyanides to exhibit both bridging and terminal coordination geometries, whereas phosphines are able to bond only in a terminal fashion.

Experimental

Reactions were carried out by 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 in this laboratory. IR spectra were recorded as Nujol mulls on a Perkin–Elmer FT-1710 spectrometer.

$^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 75.47 MHz for ^{13}C and referenced to the solvent. The FAB mass spectrum was recorded by Dr. J. Ballantine and his staff at the SERC Mass Spectrometry Service Centre at the University of Swansea using a VG ZAB-E high-resolution double-focussing mass spectrometer. Samples were suspended in a matrix of NOBA and bombarded with a high energy beam of xenon atoms to generate ions.

The $[Pd_2(dba)_3] \cdot CHCl_3$ was synthesised as previously described [4].

Synthesis of $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]$

The compound $[Pd_2(dba)_3] \cdot CHCl_3$ (0.40 g, 0.39 mmol) was dissolved in toluene (20 cm^3) and a SO_2-saturated solution of XylNC (0.142 g, 1.08 mmol) in toluene (10 cm^3) added. SO_2 was bubbled through the solution for 10 min and the mixture was stirred under SO_2 for 2 h. The solvent was removed under reduced pressure, and the solid obtained was washed several times with diethyl ether, then recrystallized from dichloromethane/diethyl ether to give red crystals of $[Pd_5(SO_2)_3(CNXyl)_7]$. Yield 0.19 g (74%). Anal. Found: C, 46.5; H, 4.0; N, 5.8. $C_{63}H_{63}N_7O_6Pd_5S_3$ calc.: C, 46.1; H, 3.9; N, 6.0%. ν(NC) at 2142vs, 2047s, 1990w cm^{-1}; $\nu(SO_2)$ at 1216 m, 1063s and 1060s cm^{-1}.

Crystal data for $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNXyl)_2(CNXyl)_5]\text{-}C_4H_8O$

Red crystals were grown by slow diffusion of diethyl ether into a tetrahydrofuran solution of $[Pd_5(SO_2)_3(CNXyl)_7]$. A single crystal of dimensions 0.1 × 0.1 × 1.0

mm was mounted on a glass fibre. X-Ray diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer at ambient temperature. Details of the data collection and structure are given in Table 2.

The positions of the palladium atoms were taken from a SHELXS direct methods calculation. The positions of all other atoms were found in Fourier difference maps. All atoms were refined anisotropically. The C–C and C–O distances in the tetrahydrofuran molecule were restrained to 1.545(1) and 1.43(1) Å respectively during final cycles of refinement. The model converged at $R = 0.028$, $R_w = 0.0294$. Programs and sources of scattering factor data are given in the refs. 16, 17. The carbon atoms in the xylyl groups are numbered so that C(n1)–C(n6) (n = 1–7) are the phenyl carbons, and C(n21) and C(n61) are the methyl carbon atoms bonded to C(n2) and C(n6), respectively. The carbon atoms in the THF molecule are numbered C(n00) (n = 2–5) with the oxygen atom O(1).

Acknowledgements

The SERC for financial support, Johnson-Matthey plc for generous loans of palladium salts and Dr. J. Ballantine (Swansea) for the FAB mass spectrum.

References

1 A.D. Burrows, D.M.P. Mingos and H.R. Powell, J. Chem. Soc., Dalton Trans., (1992) 261.
2 M. Bochmann, I. Hawkins, M.B. Hursthouse and R.L. Short, Polyhedron, 6 (1987) 1987.
3 A. Christofides, J. Organomet. Chem., 259 (1983) 355.
4 T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, J. Organomet. Chem., 65 (1974) 253.
5 Ts. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, J. Organomet. Chem., 73 (1974) 401.
6 A.Z. Rubezhov, Russ. Chem. Rev., 57 (1988) 1194.
7 C.E. Briant, D.I. Gilmour, D.M.P. Mingos and R.W.M. Wardle, J. Chem. Soc., Dalton Trans., (1985) 1693.
8 Y. Yamamoto and H. Yamazaki, Inorg. Chem., 25 (1986) 3327.
9 M. Green, J.A.K. Howard, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 1509.
10 S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumoto, H. Yoshioka and K. Nakatsu, J. Chem. Soc., Chem. Commun., (1973) 445.
11 A.D. Burrows, J.C. Machell, D.M.P. Mingos and H.R. Powell, J. Chem. Soc., Dalton Trans., (1992) 1521.
12 C.G. Francis, S.I. Khan and P.R. Morton, Inorg. Chem., 23 (1984) 3680.
13 D.G. Evans and D.M.P. Mingos, J. Organomet. Chem., 240 (1982) 321.
14 R. Bender, P. Braunstein, J. Fischer, L. Ricard and A. Mitschler, Nouv. J. Chim., 5 (1981) 81.
15 C.E. Briant, D.G. Evans and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1986) 1535.
16 D.J. Watkin, J.R. Carruthers and P.W. Retteridge, CRYSTALS User Manual, Chemical Crystallography Laboratory, University of Oxford, 1985.
17 International Tables of Crystallography, Kynoch Press, Birmingham, 1974.