

Di- and Tri-nuclear Complexes of Palladium(II) containing Doubly- and Triply-bridging Pyridine-2-thionato (pyS) Ligands: Crystal Structure of $[\text{Pd}_3(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3(\text{pyS})_2][\text{BF}_4]^\dagger$

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The complex $[\text{Pd}_2\text{Cl}_2(\text{dmp})_2]$ [$\text{dmp} = 2$ - (dimethylaminomethyl)phenyl] reacts with 1*H*-pyridine-2-thione (pySH) or with the 6-methyl substituted derivative (mpySH) in the presence of triethylamine to generate the dinuclear complexes $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ and $[\text{Pd}_2(\text{dmp})_2(\text{mpyS})_2]$. These exist as head-to-tail isomers with folded conformations so that the palladium co-ordination planes are approximately parallel. Fluxional enantiomerisation of the mpyS-bridged compound leading to *N*-methyl group exchange has been studied. These bridged dimers behave as cyclic bidentate sulphur ligands. $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ reacts with $[\text{Pd}(\text{dmp})(\text{solvent})_2]^+$ to give $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2]^+$; the X-ray structure of $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$ is reported. The cation contains a cage of three palladium atoms linked by two triply-bridging pyS ligands. Related η^3 -2-methylallyl trimers and mixed-ligand trimers have also been synthesised by the same method.

1*H*-Pyridine-2-thione (pySH), or its conjugate anion pyridine-2-thionate (pyS⁻) can co-ordinate as monodentate ligands through the sulphur atoms.¹⁻⁵ The anion can also co-ordinate as a doubly-bridging ligand through both sulphur and nitrogen atoms and through sulphur alone,⁵⁻¹⁰ as a chelating ligand with a very small bite,^{1,2,11-15} and as a triply-bridging ligand,^{5,16} such as in a RhPd_2 complex we reported recently.¹⁶ Although pyS possesses a feature common to many bidentate bridging ligands, the 1,3-relation of donor atoms,¹⁷ there are only a few well-characterised complexes with bridging pyS ligands. This contrasts with the oxygen analogue, the 2-pyridonate anion, which commonly bridges.¹⁷⁻¹⁹ A series of platinum dimeric and tetrameric complexes containing bridging 2-pyridonate¹⁷ adopt the folded or 'basket' structure common with many palladium acetato-complexes.²⁰

We chose the cyclometallated derivative of *N,N*-dimethylbenzylamine, $[\text{Pd}_2\text{Cl}_2(\text{dmp})_2]$ [$\text{dmp} = 2$ - (dimethylaminomethyl)phenyl], as our starting material intending to replace bridging chloride by bridging pyS or 6-methylpyridine-2-thionate (mpyS). The ligand dmp exerts very different *trans* influences through its C and N atoms and we hoped that this would limit the available isomers of derived complexes. Furthermore the ¹H n.m.r. spectra of dmp in its complexes would provide useful structural information.

Results and Discussion

Dinuclear Complexes.—The complexes $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ and $[\text{Pd}_2(\text{dmp})_2(\text{mpyS})_2]$ were isolated as yellow-orange crystals in good yield from the reaction of the chloro-bridged complex with the appropriate ligand (pySH or mpySH) followed by dehydrochlorination with triethylamine. The ¹H n.m.r. spectrum of $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ (Table 1) shows the *N*-methyl groups to be diastereotopic while the CH₂ groups give an AB quartet. Therefore there is no plane of symmetry

in the Pd co-ordination plane.²¹ This rules out a monomeric compound with chelating pyS or a symmetrical dimer with pyS bridged through sulphur atoms alone. A folded 'basket' structure related to that in acetato-bridged dimers is likely.²⁰ Since both dmp and pyS are unsymmetrical there are five possible diastereomers for the bridged complex, two with head-to-head and three with head-to-tail arrangements of the bridging pyS ligands, but only one isomer is present in solution. Only the head-to-tail structures (**1a**) and (**1b**) of the possible structures (**1a**)—(**1e**) (Figure 1) are consistent with the symmetry shown by ¹H n.m.r. data. However, we have shown for $[\text{PdCl}(\text{dmp})(\text{py})]$ (py = pyridine) (Figure 2) that the chemical shift for H^a is significantly shifted to low δ by the effect of anisotropic shielding of the adjacent pyridine ring.²¹ No such effect was observed for $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ (there are no aromatic resonances below δ 6.68), which strongly indicates that the arene ring of the dmp ligand and the heterocycle are not *cis* to each other. The pyridine ring is *trans* to the carbon atom of the dmp chelate on this evidence and the structure is (**1a**). This arrangement of atoms is maintained in the tripalladium derivative described below except that the alignment of co-ordination planes is readjusted on adding the extra palladium atom (see the discussion below).

For structure (**1a**), one Me group of each dmp ligand is directed inwards and lies in the aromatic shielding zone of the other dmp ligand, while the other Me groups face outwards. This accounts for the difference in chemical shift between these groups. The structure of the succinimido dimer $[\text{Pd}_2(\text{dmp})_2(\text{NCOC}_2\text{H}_4\text{CO})_2]$ (Pd...Pd 2.98 Å)²² is closely related to that we propose for $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$. There is a close correspondence between the ¹H n.m.r. spectra of these dmp complexes.

The complex $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ has temperature independent ¹H n.m.r. spectra up to room temperature whereas the mpyS analogue is fluxional. The spectra of $[\text{Pd}_2(\text{dmp})_2(\text{mpyS})_2]$ between -40 and 35 °C can be interpreted in terms of rapid enantiomerisation at the higher temperatures leading to a time-averaged plane of symmetry through the co-ordination planes. The rates (k_M) of exchange of the diastereotopic methyl groups on nitrogen were measured at various temperatures by standard line-shape analysis methods (see Experimental section and Figure 3). There is an associated coalescence of the AB quartet due to the CH₂ groups of the dmp ligands over the same

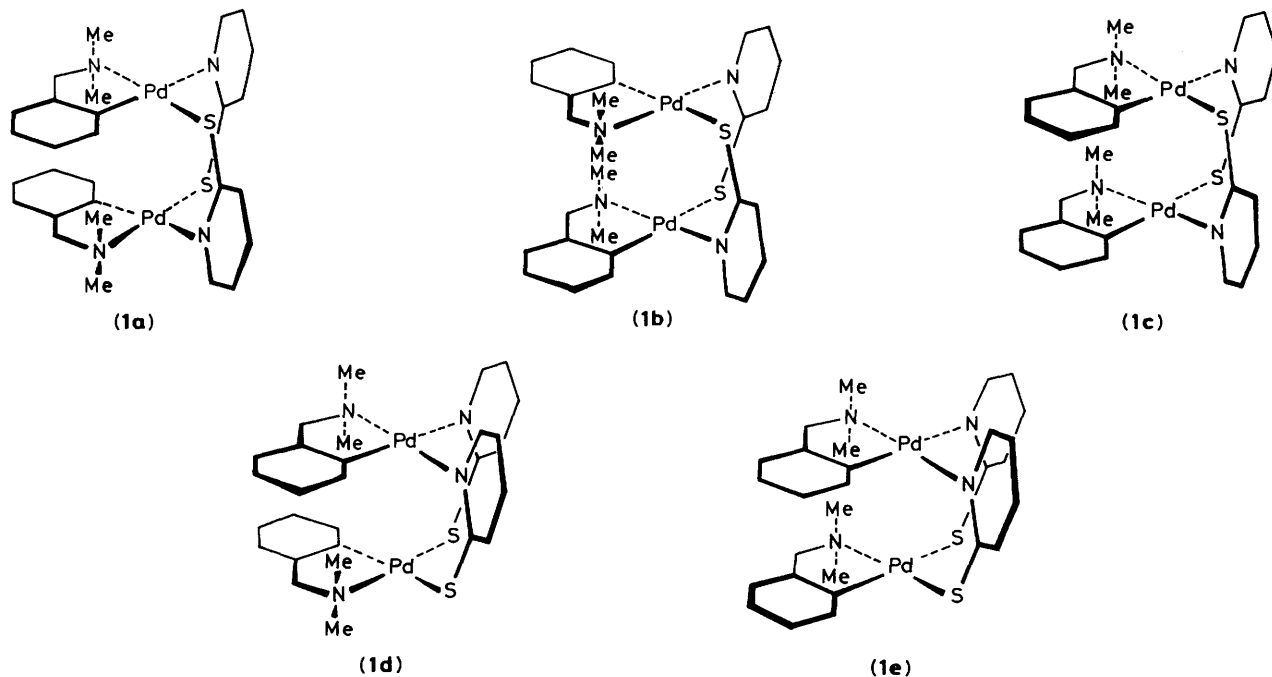
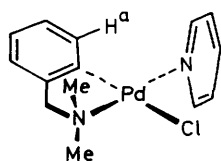
† 1,2,3-Tris[2-(dimethylaminomethyl)phenyl-*C*¹*N*]- μ_3 -[1*H*-pyridine-2-thionato-*N*(Pd¹)S(Pd^{2,3})]- μ_3 -[1*H*-pyridine-2-thionato-*N*(Pd³)S(Pd^{1,2})]-tripalladium(II) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. 200-MHz ^1H n.m.r. data for the complexes $[\text{Pd}_2(\text{dmp})_2\text{L}_2]$ where $\text{L} = \text{pyS}$ or mpyS

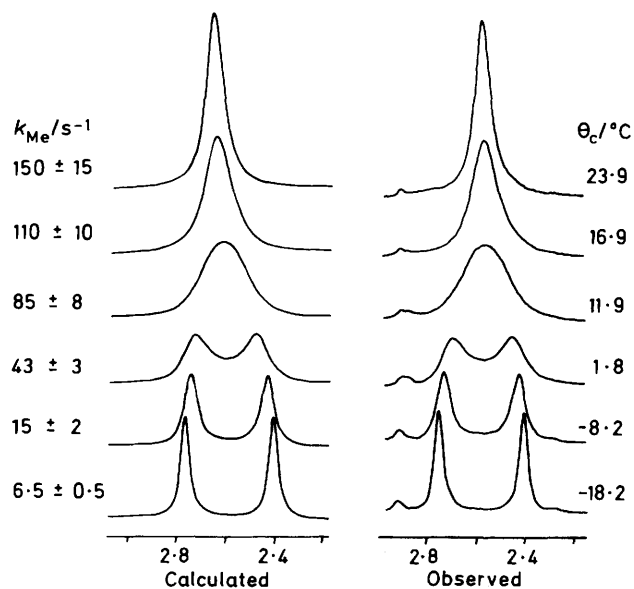
L	pyS or mpyS signals ^a				dmp signals		
	H ⁶ or Me ⁶	H ⁵	H ⁴	H ³	C ₆ H ₄	NCH ₂	NMe ₂
pyS ^b	8.54 (d)	6.97 (t)	7.54 (m)	7.21 (m)	6.69 (m)	2.86 (d) ^c	2.32 (s)
mpyS ^d	3.10 (s)	6.55 (d)	6.85 (m)	7.48 (d)	6.83 (m)	3.09 (d) ^c	2.47 (s)
					6.52 (m)	3.58 (s) ^e	2.76 (s)
					6.85 (m)		2.41 (s)

^a Multiplicities in parentheses describe the signal shape approximately. ^b Recorded at 24 °C in CD_2Cl_2 . ^c AB quartet; J 18 Hz. ^d Recorded at -38.7 °C in CDCl_3 . ^e AB quartet at -28 °C which coalesces at ca. 0 °C.

**Figure 1.** Possible structures of $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ of which (1a) and (1b) are consistent with the C_2 symmetry deduced from the ^1H n.m.r. spectrum**Figure 2.** Proposed structure for $[\text{PdCl}(\text{dmp})(\text{py})]$ showing the cause of the shift to low δ for H^a (ref. 19)

temperature range but this was not analysed quantitatively. Rates do not vary over a 3.3-fold change in concentration which suggests an intramolecular process and not one involving dimer breakdown into monomers with chelating mpyS. One mechanism would be the inversion of the eight-membered ring associated with the $\text{Pd}_2(\text{mpyS})_2$ system without bond cleavage but much more likely is the cleavage of a Pd-N bond to mpyS allowing rotation about the Pd-S and remaining Pd-N bonds before recyclisation. This is how related acetato-bridged compounds are believed to invert.²³ The barrier to this process is much higher for the pyS-bridged analogue and it is probably repulsions between the 6-methyl substituent and the ancillary ligands that reduces the barrier to Pd-N cleavage in the mpyS compound.

The reaction of pySH or mpySH with the 2-methylallyl compound $[\text{Pd}_2\text{Cl}_2(\eta^3\text{-C}_4\text{H}_7)_2]$ in the presence of triethylamine

**Figure 3.** Observed ^1H n.m.r. spectra for the NMe_2 groups of $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ in CDCl_3 and ones calculated using the program DNMR3 (ref. 26)

gave no isolable products related to the above pyS- or mpyS-bridged dimers. Removal of solvent from these reaction solutions gave intensely coloured oils which gave insoluble and uncharacterisable materials on standing. The only isolable product from these reagents was $[\text{PdCl}(\eta^3\text{-C}_4\text{H}_7)(\text{mpySH})]$ which is the chloride-bridge cleaved product (see Experimental section). This compound gave a ^1H n.m.r. spectrum (15 °C) with four separate signals for the two terminal CH_2 groups of the allyl. Coalescence at 30 °C was consistent with *syn-syn*, *anti-*

anti exchange in accord with much that is known about palladium allyl systems of this kind.²⁴

Trinuclear Complexes.—We believed that $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ might behave as a neutral cyclic bidentate ligand towards other metal centres. To test this we reacted this compound with $[\text{Pd}(\text{dmp})(\text{solvent})_2][\text{ClO}_4]$ (solvent = H_2O or Me_2CO), prepared by treating $[\text{Pd}_2\text{Cl}_2(\text{dmp})_2]$ with AgClO_4 in acetone, and obtained the tripalladium compound $[\text{Pd}_3(\text{dmp})_3-$

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$

Atom	Molecule 1			Atom	Molecule 2		
	x	y	z		x	y	z
Pd(11)	5 616(1)	3 713.2(4)	6 890(1)	Pd(21)	677(1)	1 464.8(4)	2 097(1)
Pd(12)	5 824(1)	2 968.2(4)	8 051(1)	Pd(22)	550(1)	644.2(4)	1 009(1)
Pd(13)	5 484(1)	3 087.2(4)	5 603(1)	Pd(23)	814(1)	903.1(4)	3 418(1)
S(11)	4 758(2)	3 104(1)	7 327(2)	S(21)	-316(2)	873(1)	1 870(2)
S(12)	6 524(2)	3 066(1)	6 367(2)	S(22)	1 646(2)	816(1)	2 494(2)
N(11)	4 892(6)	2 477(4)	6 186(5)	N(21)	63(6)	297(4)	3 028(5)
N(12)	6 229(6)	2 359(4)	7 387(5)	N(22)	1 080(6)	43(5)	1 657(5)
N(13)	6 352(7)	4 382(4)	6 777(6)	N(23)	1 496(8)	2 103(5)	2 042(6)
N(14)	6 826(7)	2 983(4)	8 687(5)	N(24)	1 371(7)	580(5)	219(6)
N(15)	4 536(6)	3 266(5)	4 952(6)	N(25)	25(7)	1 163(5)	4 178(6)
C(11)	4 642(7)	2 523(5)	6 831(7)	C(21)	-362(7)	319(5)	2 427(7)
C(12)	4 261(9)	2 097(6)	7 155(8)	C(22)	-871(8)	-82(6)	2 230(8)
C(13)	4 161(10)	1 620(6)	6 782(8)	C(23)	-897(9)	-537(7)	2 649(9)
C(14)	4 409(10)	1 577(7)	6 119(8)	C(24)	-456(9)	-565(6)	3 238(9)
C(15)	4 774(8)	2 012(6)	5 830(7)	C(25)	0(8)	-136(6)	3 419(7)
C(16)	6 486(8)	2 426(6)	6 742(7)	C(26)	1 480(7)	160(5)	2 231(7)
C(17)	6 741(8)	1 997(5)	6 318(7)	C(27)	1 779(8)	-249(6)	2 653(7)
C(18)	6 721(9)	1 490(7)	6 603(9)	C(28)	1 639(9)	-774(6)	2 463(8)
C(19)	6 444(10)	1 424(6)	7 277(8)	C(29)	1 221(9)	-896(6)	1 868(8)
C(110)	6 233(8)	1 845(6)	7 654(8)	C(210)	955(8)	-475(6)	1 467(8)
C(111)	4 929(9)	4 289(6)	7 293(8)	C(211)	-53(8)	2 051(5)	1 849(7)
C(112)	5 359(10)	4 694(6)	7 540(8)	C(212)	342(12)	2 455(7)	1 518(9)
C(113)	4 989(11)	5 112(6)	7 907(9)	C(213)	-54(17)	2 932(7)	1 295(9)
C(114)	4 220(14)	5 093(8)	8 051(12)	C(214)	-873(17)	2 941(11)	1 417(13)
C(115)	3 768(13)	4 685(10)	7 737(12)	C(215)	-1 237(14)	2 536(9)	1 757(12)
C(116)	4 122(9)	4 265(7)	7 360(9)	C(216)	-814(10)	2 093(6)	1 951(8)
C(117)	5 451(8)	3 498(6)	8 729(7)	C(217)	66(8)	1 149(5)	347(7)
C(118)	4 714(9)	3 659(6)	8 845(7)	C(218)	-678(10)	1 362(6)	349(8)
C(119)	4 547(11)	4 041(7)	9 364(9)	C(219)	-936(11)	1 704(7)	-186(9)
C(120)	5 149(12)	4 254(6)	9 775(9)	C(220)	-431(12)	1 860(7)	-684(10)
C(121)	5 911(11)	4 089(7)	9 656(9)	C(221)	313(13)	1 645(7)	-708(9)
C(122)	6 040(10)	3 714(6)	9 140(8)	C(222)	576(11)	1 308(7)	-180(8)
C(123)	6 026(7)	3 584(5)	4 980(6)	C(223)	1 490(9)	1 433(5)	3 864(7)
C(124)	6 812(7)	3 650(5)	4 873(7)	C(224)	2 303(9)	1 450(6)	3 863(8)
C(125)	7 080(9)	4 002(6)	4 365(8)	C(225)	2 655(10)	1 872(8)	4 270(10)
C(126)	6 573(11)	4 297(7)	3 951(9)	C(226)	2 246(14)	2 214(9)	4 683(13)
C(127)	5 785(11)	4 252(6)	4 052(9)	C(227)	1 419(11)	2 202(8)	4 642(9)
C(128)	5 491(9)	3 888(6)	4 565(7)	C(228)	1 038(9)	1 803(6)	4 277(7)
C(129)	6 202(10)	4 693(6)	7 418(9)	C(229)	1 220(11)	2 400(7)	1 424(9)
C(130)	6 114(11)	4 712(6)	6 155(9)	C(230)	1 470(14)	2 462(7)	2 636(9)
C(131)	7 210(9)	4 253(6)	6 748(10)	C(231)	2 291(10)	1 957(8)	1 933(11)
C(132)	6 866(9)	3 558(6)	8 952(9)	C(232)	1 391(10)	1 115(6)	-129(8)
C(133)	6 729(11)	2 603(7)	9 297(9)	C(233)	1 154(11)	155(7)	-287(8)
C(134)	7 546(9)	2 852(9)	8 321(9)	C(234)	2 161(10)	470(8)	467(9)
C(135)	4 665(8)	3 830(6)	4 728(8)	C(235)	185(9)	1 737(6)	4 260(8)
C(136)	3 764(8)	3 225(8)	5 315(9)	C(236)	-819(9)	1 090(7)	3 942(9)
C(137)	4 508(9)	2 898(7)	4 323(8)	C(237)	144(9)	891(7)	4 859(7)
Disordered BF_4^- anions							
B(11)	8 010(7)	4 437(5)	441(7)	B(21)	2 812(6)	3 858(5)	3 303(7)
F(11)	7 365(6)	4 636(5)	814(6)	F(21)	2 428(7)	4 345(5)	3 451(6)
F(12)	8 589(8)	4 840(6)	426(8)	F(22)	3 606(6)	3 966(5)	3 169(7)
F(13)	7 766(9)	4 468(6)	-269(7)	F(23)	2 494(11)	3 664(8)	2 665(8)
F(14)	8 455(11)	4 098(8)	883(10)	F(24)	2 735(11)	3 440(7)	3 795(9)
F(15)	7 981(14)	3 873(5)	444(12)	F(25)	2 936(16)	3 917(12)	4 033(7)
				F(26)	2 029(9)	3 684(14)	3 255(19)

Table 3. Selected bond lengths and interatomic distances (Å) and angles (°) for [Pd₃(dmp)₃(pyS)₂][BF₄]

Molecule 1			
Pd(12)···Pd(11)	2.946(4)	Pd(13)···Pd(11)	2.952(4)
S(11)–Pd(11)	2.308(6)	S(12)–Pd(11)	2.494(5)
N(13)–Pd(11)	2.134(13)	C(111)–Pd(11)	2.041(18)
S(11)–Pd(12)	2.330(5)	N(12)–Pd(12)	2.130(13)
N(14)–Pd(12)	2.115(13)	C(117)–Pd(12)	1.986(16)
S(12)–Pd(13)	2.316(5)	N(11)–Pd(13)	2.174(12)
N(15)–Pd(13)	2.108(13)	C(123)–Pd(13)	1.983(15)
C(11)–S(11)	1.765(16)	C(16)–S(12)	1.776(16)
Molecule 2			
Pd(22)···Pd(21)	2.958(4)	Pd(23)···Pd(21)	2.925(4)
S(21)–Pd(21)	2.318(6)	S(22)–Pd(21)	2.467(5)
N(23)–Pd(21)	2.154(14)	C(211)–Pd(21)	2.003(16)
S(21)–Pd(22)	2.324(5)	N(22)–Pd(22)	2.166(13)
N(24)–Pd(22)	2.104(14)	C(217)–Pd(22)	1.987(15)
S(22)–Pd(23)	2.317(6)	N(21)–Pd(23)	2.143(12)
N(25)–Pd(23)	2.121(13)	C(223)–Pd(23)	1.972(16)
C(21)–S(21)	1.769(15)	C(26)–S(22)	1.758(15)
Molecule 1			
Pd(13)–Pd(11)–Pd(12)	107.7(2)	S(11)–Pd(11)–Pd(12)	50.9(2)
S(11)–Pd(11)–Pd(13)	84.5(2)	S(12)–Pd(11)–Pd(12)	79.3(2)
S(12)–Pd(11)–Pd(13)	49.5(1)	S(12)–Pd(11)–S(11)	97.0(2)
N(13)–Pd(11)–Pd(12)	121.2(4)	N(13)–Pd(11)–Pd(13)	112.3(4)
N(13)–Pd(11)–S(11)	163.0(3)	N(13)–Pd(11)–S(12)	95.6(4)
C(111)–Pd(11)–Pd(12)	103.6(5)	C(111)–Pd(11)–Pd(13)	131.6(4)
C(111)–Pd(11)–S(11)	87.5(6)	C(111)–Pd(11)–S(12)	175.5(5)
C(111)–Pd(11)–N(13)	79.9(6)	S(11)–Pd(12)–Pd(11)	50.2(2)
N(12)–Pd(12)–Pd(11)	92.5(4)	N(12)–Pd(12)–S(11)	90.6(4)
N(14)–Pd(12)–Pd(11)	121.5(4)	N(14)–Pd(12)–S(11)	170.3(3)
N(14)–Pd(12)–N(12)	95.0(5)	C(117)–Pd(12)–Pd(11)	91.7(5)
C(117)–Pd(12)–S(11)	91.9(5)	C(117)–Pd(12)–N(12)	175.7(5)
C(117)–Pd(12)–N(14)	83.0(6)	S(12)–Pd(13)–Pd(11)	54.9(2)
N(11)–Pd(13)–Pd(11)	88.8(4)	N(11)–Pd(13)–S(12)	91.3(4)
N(15)–Pd(13)–Pd(11)	116.0(4)	N(15)–Pd(13)–S(12)	168.8(3)
N(15)–Pd(13)–N(11)	95.2(5)	C(123)–Pd(13)–Pd(11)	97.8(5)
C(123)–Pd(13)–S(12)	91.7(5)	C(123)–Pd(13)–N(11)	173.3(5)
C(123)–Pd(13)–N(15)	82.8(6)	Pd(12)–S(11)–Pd(11)	78.9(2)
C(11)–S(11)–Pd(11)	115.3(5)	C(11)–S(11)–Pd(12)	106.7(5)
Pd(13)–S(12)–Pd(11)	75.6(2)	C(16)–S(12)–Pd(11)	114.1(6)
C(16)–S(12)–Pd(13)	104.4(6)		
Molecule 2			
Pd(23)–Pd(21)–Pd(22)	106.3(2)	S(21)–Pd(21)–Pd(22)	50.5(2)
S(21)–Pd(21)–Pd(23)	84.5(2)	S(22)–Pd(21)–Pd(22)	78.3(2)
S(22)–Pd(21)–Pd(23)	50.0(2)	S(22)–Pd(21)–S(21)	97.5(2)
N(23)–Pd(21)–Pd(22)	122.4(4)	N(23)–Pd(21)–Pd(23)	111.1(4)
N(23)–Pd(21)–S(21)	164.4(3)	N(23)–Pd(21)–S(22)	93.8(4)
C(211)–Pd(21)–Pd(22)	108.0(5)	C(211)–Pd(21)–Pd(23)	127.8(5)
C(211)–Pd(21)–S(21)	88.2(5)	C(211)–Pd(21)–S(22)	173.5(4)
C(211)–Pd(21)–N(23)	81.3(6)	S(21)–Pd(22)–Pd(21)	50.3(2)
N(22)–Pd(22)–Pd(21)	93.3(4)	N(22)–Pd(22)–S(21)	92.1(4)
N(24)–Pd(22)–Pd(21)	121.5(4)	N(24)–Pd(22)–S(21)	169.9(3)
N(24)–Pd(22)–N(22)	94.5(5)	C(217)–Pd(22)–Pd(21)	91.9(5)
C(217)–Pd(22)–S(21)	91.6(5)	C(217)–Pd(22)–N(22)	174.8(5)
C(217)–Pd(22)–N(24)	82.4(6)	S(22)–Pd(23)–Pd(21)	54.7(2)
N(21)–Pd(23)–Pd(21)	89.9(4)	N(21)–Pd(23)–S(22)	92.4(4)
N(25)–Pd(23)–Pd(21)	113.9(4)	N(25)–Pd(23)–S(22)	166.8(3)
N(25)–Pd(23)–N(21)	94.1(5)	C(223)–Pd(23)–Pd(21)	95.3(5)
C(223)–Pd(23)–S(22)	91.6(5)	C(223)–Pd(23)–N(21)	174.6(5)
C(223)–Pd(23)–N(25)	82.7(6)	Pd(22)–S(21)–Pd(21)	79.2(2)
C(21)–S(21)–Pd(21)	115.9(5)	C(21)–S(21)–Pd(22)	105.6(5)
Pd(23)–S(22)–Pd(21)	75.3(2)	C(26)–S(22)–Pd(21)	115.5(5)
C(26)–S(22)–Pd(23)	102.1(6)		

(pyS)₂][ClO₄]. The tetrafluoroborate was prepared similarly. The ¹H n.m.r. of the Pd₃ cation is complex, showing three different sets of dmp resonances and two sets of pyS resonances. Clearly the molecule is asymmetric and furthermore is

stereochemically rigid in that the dmp resonances show six Me singlets (two of these overlapping) and a set of two doublets for each of the three CH₂ groups even at room temperature and above.

We have established the structure of [Pd₃(dmp)₃(pyS)₂][BF₄] by a single-crystal X-ray structure determination. Table 2 lists the atomic co-ordinates and Table 3 some selected bond lengths and angles. The unit cell contains two crystallographically distinct but chemically equivalent Pd₃ molecules (molecules 1 and 2) and Figure 4 shows the structure of molecule 1. The central Pd₃(pyS)₂ cage contains two μ₃-pyS ligands linking the three metal atoms. The Pd···Pd distances shown as broken lines in Figure 4 are 2.946(4) [Pd(12)–Pd(11)] and 2.952(4) Å [Pd(13)–Pd(11)]. Even though these are much shorter than the other Pd···Pd distance, which is more than 4.7 Å, we consider the molecule to contain three square-planar palladium(II) atoms and no metal–metal bond. All three palladium atoms are different; hence the complex ¹H n.m.r. spectrum described above. The non-equivalence of the Pd(12) and Pd(13) atoms results from the unsymmetrical nature of the chelate at Pd(11) which removes two-fold molecular symmetry. The different *trans* influences of this chelate are apparent in the bond lengths of Pd(11)–S(12) [2.494(5) Å, *trans* to C] and of Pd(11)–S(11) [2.308(6) Å, *trans* to N].

The shape of the Pd₃(pyS)₂ cage in the Pd₃ cation is topologically equivalent to that of the RhPd₂(pyS)₂ cage in [RhPd₂(μ₃-pyS)₂(pyS)₂(η³-C₄H₇)₂][BF₄].¹⁶ Figure 5 shows the Pd₃(pyS)₂ and RhPd₂(pyS)₂ cages in these two compounds which at first sight appear to be very different. The Pd₃(pyS)₂ cage is associated with two short and one long M···M distance while the RhPd₂(pyS)₂ cage has one short and two long M···M distances. Molecular models of M₃(pyS)₂ cages show that the geometries shown in Figure 5 are conformations that can be easily transformed into each other by rotation about bonds to sulphur without any bond breaking. The two conformations in Figure 5 appear to be close to two accessible extremes of possible conformations that can be adopted. The cage is apparently robust while allowing for a wide range of metal–metal distances.

In the Pd₃ cation the bidentate chelate 'ligand' Pd₂(dmp)₂(pyS)₂ [S,S-chelated to palladium(II)] adopts a different configuration to that believed to be present in the free ligand. Figure 6 shows that the co-ordination planes in this ligand must move from being essentially parallel to essentially perpendicular on co-ordination.

We have also synthesised the related η³-2-methylallyl system [Pd₃(η³-C₄H₇)₃(pyS)₂][ClO₄] and mixed dmp-allyl compounds which also appear to contain the Pd₃(pyS)₂ cage but these exist as isomers giving n.m.r. spectra that we have not unravelled.

Experimental

The starting palladium complexes [Pd₂Cl₂(dmp)₂] and [Pd₂Cl₂(η³-C₄H₇)₂] were prepared by reported methods.^{25,26} Pyridine-2-thione (pySH) (Aldrich) was used without purification. 6-Methylpyridine-2-thione (mpySH) was prepared by an established method.²⁷

Preparation of [Pd₂(dmp)₂(pyS)₂].[Pd₂Cl₂(dmp)₂] (0.300 g, 5.43 × 10⁻⁴ mol) was added to a solution of pySH (0.120 g, 1.08 × 10⁻³ mol) in dichloromethane (15 cm³) and after 5 min NEt₃ (0.15 cm³) was added and the mixture stirred under nitrogen for 20 min. The solution was washed with water, aqueous sodium chloride, and the organic layer dried over anhydrous sodium sulphate. The product after removal of the organic solvent was recrystallised from a chloroform-methanol mixture to give the product as bright yellow crystals (0.286 g,

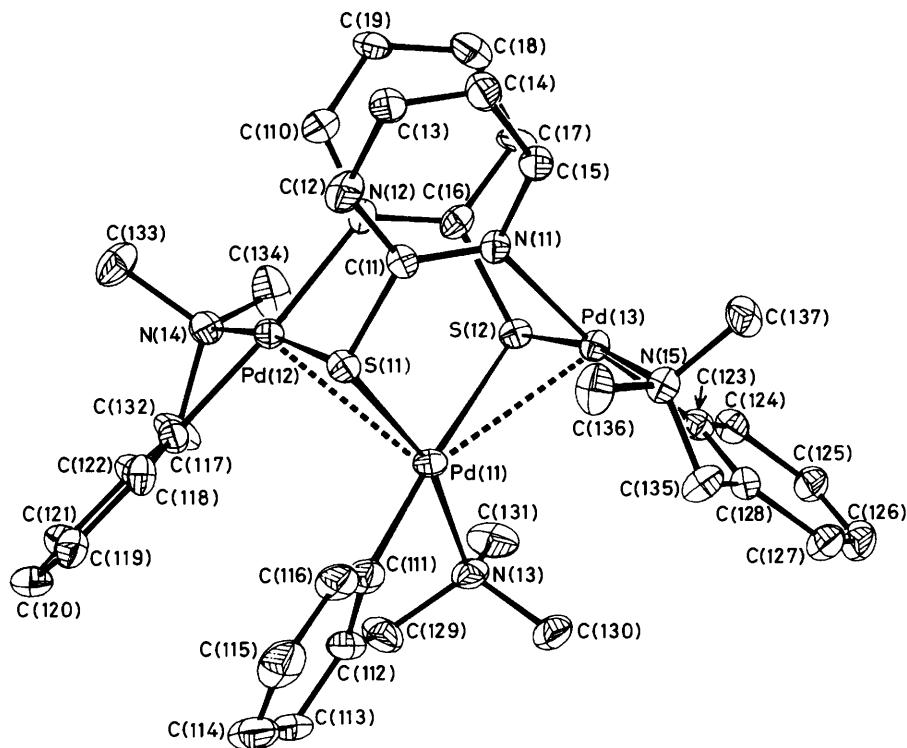


Figure 4. Molecular structure (molecule 1) of the cation of $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$

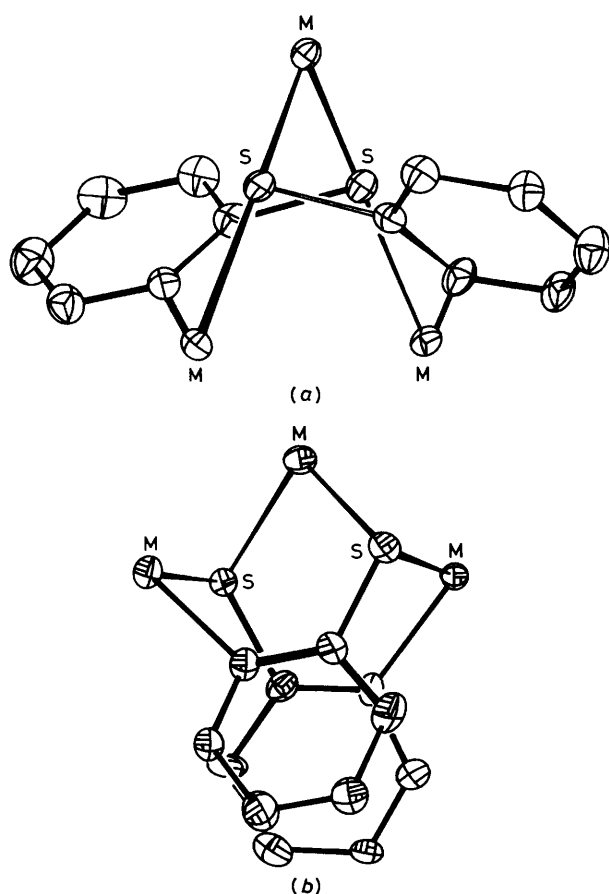


Figure 5. $\text{M}_3(\text{pyS})_2$ skeletons of $[\text{RhPd}_2(\mu_3\text{-pyS})_2(\text{pyS})(\eta^3\text{-C}_4\text{H}_7)_2][\text{BF}_4]^{16}$ (a) and $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$ (b) showing their grossly different conformations

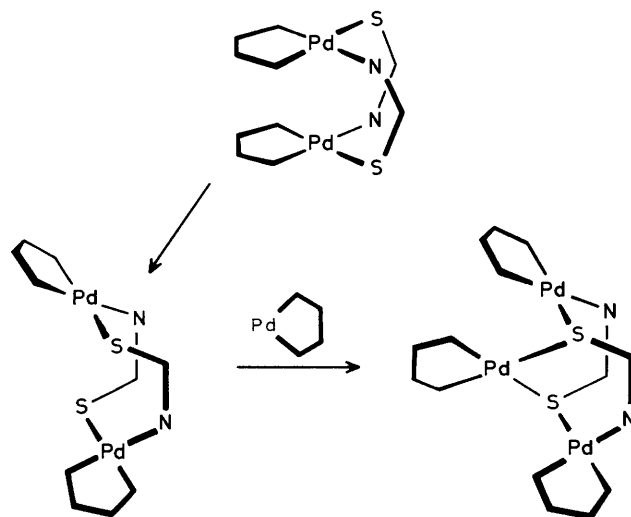


Figure 6. Changes in conformation of the eight-membered ring of the ligand $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ required by its co-ordination to the third palladium centre in $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$

75%) (Found: C, 47.7; H, 4.5; N, 7.9. $\text{C}_{28}\text{H}_{32}\text{N}_4\text{Pd}_2\text{S}_2$ requires C, 47.9; H, 4.5; N, 8.0%).

Preparation of $[\text{Pd}_2(\text{dmp})_2(\text{mpyS})_2]$.—This was prepared similarly as bright yellow crystals (68%) (Found: C, 49.2; H, 5.0; N, 7.7. $\text{C}_{30}\text{H}_{36}\text{N}_4\text{Pd}_2\text{S}_2$ requires C, 49.4; H, 4.9; N, 7.7%).

Preparation of $[\text{PdCl}(\eta^3\text{-C}_4\text{H}_7)(\text{mpySH})]$.—Addition of light petroleum (b.p. 30–40 °C) to a mixture of mpySH (0.0127 g, 1.02×10^{-4} mol) and $[\text{Pd}_2\text{Cl}_2(\eta^3\text{-C}_4\text{H}_7)_2]$ (0.020 g, 5.08×10^{-5} mol) in CDCl_3 (1 cm^3) afforded the product as yellow crystals (Found: C, 37.1; H, 4.3; Cl, 11.0; N, 4.3. $\text{C}_{10}\text{H}_{14}\text{ClN}_2\text{PdS}$ requires C, 37.3; H, 4.35; Cl, 11.0; N, 4.35%).

Preparation of $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{ClO}_4]$.—Silver perchlorate (0.030 g, 1.4×10^{-4} mol) was added to a suspension of $[\text{Pd}_2\text{Cl}_2(\text{dmp})_2]$ (0.039 g, 7.1×10^{-5} mol) in acetone (5 cm³). Dichloromethane (ca. 2 cm³) was added to dissolve the starting complex and after being stirred for 20 min the mixture was filtered to remove AgCl. The filtrate was added to a solution of $[\text{Pd}_2(\text{dmp})_2(\text{pyS})_2]$ (0.100 g, 1.42×10^{-4} mol) in dichloromethane (5 cm³) and the mixture stirred for 30 min. The volume of the solution was reduced to ca. 2 cm³ under vacuum and diethyl ether added to precipitate the product as bright yellow crystals (0.099 g, 67%) (Found: C, 42.2; H, 4.3; Cl, 3.5; N, 6.6. $\text{C}_{37}\text{H}_{44}\text{ClN}_5\text{O}_4\text{Pd}_3\text{S}_2$ requires C, 42.6; H, 4.3; Cl, 3.5; N, 6.7%). The tetrafluoroborate salt was prepared similarly using AgBF_4 and was used for the X-ray structure determination. ¹H N.m.r. (CDCl_3): CH_2 doublets: δ 4.53 and 3.68 (J 13.7 Hz), 4.47 and 3.35 (J 13.4 Hz), 3.66 and 2.91 (J 12.7 Hz); Me singlets: δ 2.75, 2.72 (two overlapping), 2.71, 2.45, and 2.39; pyS resonances between δ 8.2 and 6.2.

Preparation of $[\text{Pd}_3(\eta^3\text{-C}_4\text{H}_7)_3(\text{pyS})_2][\text{ClO}_4]$.—Triethylamine (0.28 cm³) was added to a solution of $[\text{Pd}_2\text{Cl}_2(\eta^3\text{-C}_4\text{H}_7)_2]$ (0.400 g, 1.02×10^{-3} mol) and pySH (0.226 g, 2.03×10^{-3} mol) in dichloromethane (15 cm³). After 30 min the orange solution was washed with water (50 cm³) and aqueous sodium chloride (50 cm³) and dried over anhydrous sodium sulphate. This solution was added to a stoichiometric amount of $[\text{Pd}(\eta^3\text{-C}_4\text{H}_7)(\text{solvent})_2][\text{ClO}_4]$ in dichloromethane (5 cm³) prepared from the chloro-bridged compound and AgClO_4 . After 30 min, diethyl ether was added to crystallise the product as yellow crystals (0.572 g, 70%) (Found: C, 32.3; H, 3.6; Cl, 5.0; N, 3.35. $\text{C}_{22}\text{H}_{29}\text{ClN}_2\text{O}_4\text{Pd}_3\text{S}_2 \cdot 0.10\text{CH}_2\text{Cl}_2$ requires C, 32.65; H, 3.55; Cl, 5.2; N, 3.4%).

Preparation of $[\text{Pd}_3(\eta^3\text{-C}_4\text{H}_7)(\text{dmp})_2(\text{pyS})_2][\text{ClO}_4]$.—This compound was prepared by an appropriate modification of the above method (90%) (Found: C, 38.2; H, 4.0; Cl, 8.85; N, 5.4. $\text{C}_{32}\text{H}_{36}\text{ClN}_4\text{O}_4\text{Pd}_3\text{S}_2 \cdot 0.8\text{CH}_2\text{Cl}_2$ requires C, 38.2; H, 3.65; Cl, 8.95; N, 5.4%).

Preparation of $[\text{Pd}_3(\eta^3\text{-C}_4\text{H}_7)_2(\text{dmp})(\text{pyS})_2][\text{ClO}_4]$.—This was also prepared by an appropriate modification of the above procedure (80.5%) (Found: C, 33.5; H, 3.4; Cl, 14.35; N, 4.05. $\text{C}_{27}\text{H}_{34}\text{ClN}_3\text{O}_4\text{Pd}_3\text{S}_2 \cdot \text{CHCl}_3$ requires C, 33.5; H, 3.4; Cl, 14.2; N, 4.2%).

¹H N.M.R. Line-shape Analysis for $[\text{Pd}_2(\text{dmp})_2(\text{mpyS})_2]$.—Experimental line shapes for the NMe₂ signals in the range -40 to 25 °C were matched against those calculated for different exchange rates k_{Me} using the program DNMR3.²⁸ Spectral parameters (peak widths and positions) were obtained at -40 °C. The observed temperature dependence of signal frequencies was allowed for by extrapolating from those values near the slow exchange limit to higher temperatures. Values obtained for $k_{\text{Me}}/\text{s}^{-1}$ with temperatures (K) in square brackets are: 2.5(5) [245.0], 6.5(5) [255.0], 15(2) [265.0], 43(3) [275.0], 85(8) [285.1], 110(10) [290.1], and 150(15) [297.1]. The errors in k_{Me} are obtained from our confidence in the best fit of spectra and the error in temperature is ± 0.2 K. These data give ΔG^\ddagger (273 K) = 58.9 ± 0.2 kJ mol⁻¹, ΔH^\ddagger = 49.0 ± 1.6 kJ mol⁻¹, and ΔS^\ddagger = $-(36 \pm 6)$ J K⁻¹ mol⁻¹.

X-Ray Crystal Structure of $[\text{Pd}_3(\text{dmp})_3(\text{pyS})_2][\text{BF}_4]$.—Crystal data. $\text{C}_{37}\text{H}_{44}\text{BF}_4\text{N}_5\text{Pd}_3\text{S}_2$. $M = 1028.91$, monoclinic, space group $P2_1/c$, $a = 17.339(2)$, $b = 25.308(3)$, $c = 19.288(4)$ Å, $\beta = 90.64(2)^\circ$, $U = 8463(2)$ Å³, $Z = 8$, $D_c = 1.615$ g cm⁻³, $\lambda = 0.71069$ Å, $F(000) = 4096$, $\mu(\text{Mo-K}\alpha) = 13.9$ cm⁻¹, crystal size $0.48 \times 0.18 \times 0.13$ mm.

Data collection. Unit-cell parameters and intensity data were

obtained by following the previously detailed procedures,²⁹ using a CAD4 diffractometer operating in the ω - 2θ scan mode with graphite-monochromated Mo-K_α radiation. A total of 10361 unique reflections were collected ($3 \leq 2\theta \leq 44^\circ$). The segment of reciprocal space scanned was: h 0→18, k 0→26, l -20→20.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX 86³⁰), and refined by blocked least squares (SHELX 76³¹). There are two chemically equivalent cations and two disordered anions per asymmetric unit. After isotropic refinement of all ordered non-hydrogen atoms, the DIFABS method of absorption correction³² was applied. (Maximum transmission factor, 1.10, minimum value, 0.90). All the non-hydrogen atoms of both cations were then refined anisotropically; hydrogen atoms were not included in the model.

At this stage a difference-Fourier synthesis revealed multiple positions for the F atoms of both BF_4^- anions. The more obvious positions were included in the model (B-F fixed at 1.430 Å). The B atoms were refined with unrestricted isotropic thermal parameters while thermal parameters for each of the disordered F atoms remained fixed ($U = 0.10$ Å²). Occupancy factors for the disordered F atoms were allowed to refine and the final values were in the range 0.29–0.90. The final difference-Fourier map showed the higher peaks to be associated with these disordered anions, 1.2 – 0.8 e⁻ Å⁻³.

The final residuals R and R' were 0.058 and 0.060 respectively for the 900 variables and 6755 data for which $F_o \geq 3\sigma(F_o)$. The function minimised was $\sum w(|F_o| - |F_c|)^2$ with the weight w being defined as $1/[\sigma^2(F_o) + 0.001F_o^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 33 and 34 respectively. All computations were made on a DEC VAX-11/750 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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