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Trinuclear Palladium(II) Complexes with Triply-Bridging Sulfide Ligands

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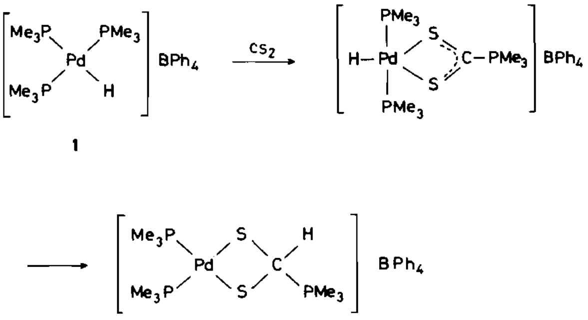
The complexes $[(PMe_3)_6Pd_3(\mu\text{-}S)_2](BPh_4)$ *(4) and* $[(PMePh_2)_6Pd_3(\mu\text{-}S)_2](BPh_4)_2$ *(6) are formed from* $[Pd(CH_3CN)_4](BF_4)_2$ *(5),* H_2S *and the corresponding phosphine in presence of* $NaBPh_4$*. Complex 4 is also obtained, although in low yields, as a secondary product in the reaction of* $[(PMe_3)_3PdH]BPh_4$ *with COS. 4 crystallizes in the space group* $P2_1/c$ $(Z = 4)$ *with* a = 1551(2), b = 2517(7), c = 1830(3) *pm and* $\beta = 94.74(9)°$*. The palladium and sulfur atoms of the dication* $[(PMe_3)_6Pd_3S_2]^{2+}$ *form a slightly distorted trigonal bipyramid in which one of the Pd–Pd distances is significantly shorter than the other two. The coordination sphere around each palladium atom is nearly square-planar with angles S–Pd–S = 79.3, P–Pd–P = 97.4 and S–Pd–P = 91.6° (mean values).*

Introduction

In the course of our studies dealing with the reactivity of CS_2 [1] and similar CS-containing molecules like CSSe [2] towards transition metal complexes, we recently observed that both neutral and cationic palladium(II) complexes of the type *trans*-$[(PMe_3)_2Pd(R)I]$ and $[(PMe_3)_3PdR]^+$ (R = Me, Ph, COMe) react readily with CS_2 by insertion either into the Pd–C or into one of the Pd–PMe_3 bonds [3]. In the reaction of the cationic hydrido complex $[(PMe_3)_3PdH]^+$ (*1*) with CS_2, also insertion into a Pd–PMe_3 bond is favoured; however, this process is followed by migration of the hydridic hydrogen atom from palladium to carbon with the formation of *2* [3].

Results and Discussion

As a consequence of this work, we were interested to learn whether COS behaves in a similar manner towards $[(PMe_3)_3PdH]^+$ and thus reacted this molecule with complex *1*. In this case, the course of the reaction is less clear. By using acetone as solvent, we isolated a colourless solid which most probably contains the expected compound *3* as the major component.



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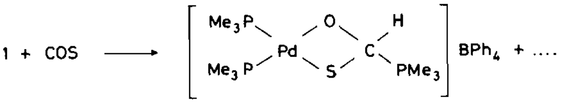

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The proposed structure is strongly supported by the ^1H and ^{13}C n.m.r. data which (together with the corresponding data of complex *2* [3]) are summarized in Table I.

The solubility and, in particular, the stability in solution of complex *2* and the product containing *3* are remarkably different. Whereas *2* dissolves easily in solvents like CH_3NO_2, CH_2Cl_2, DMSO and acetone, the substance obtained from COS is completely soluble and relatively stable in acetone only. In CH_3NO_2 and CH_2Cl_2 rapid reaction occurs which leads mainly to a neutral palladium(II) complex, the structure of which is presently under investigation [4].

Attempts to recrystallize the product from the reaction of *1* and COS (in order to obtain single crystals of complex *3*) led to a surprising result. When the

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TABLE I ^{1}H and ^{13}C N m r Data for *2* (in CD_3NO_2) and *3* (in CD_3COCD_3) [δ in ppm, J and N in Hz, int TMS]

	2			*3*			Assignment
^{1}H	1 50 (vt)	N = 11 0	(18H)	1 60 (vt)	N = 11 0	(18H)	$PdPCH_3$
	1 85 (d)	$^2J_{PH}$ = 13 0	(9H)	1 70 (d)	$^2J_{PH}$ = 14 0	(9H)	$\rangle CHPCH_3$
	5 67 (dxt)	$^2J_{PH}$ = 4 8 $^4J_{PH}$ = 1 4	(1H)	5 72 (d)	$^2J_{PH}$ = 6 3	(1H)	$\rangle CHPMe_3$
	7 09 (m)		(20H)	7 09 (m)			BPh_4
^{13}C	5 16 (d)	$^1J_{PC}$ = 58 8		4 82 (d)	$^1J_{PC}$ = 50 7		$\rangle CHPCH_3$
	15 09 (vt)	N = 31 6		16 21 (vt)	N = 30 0		$PdPCH_3$
	45 17 (d)	$^1J_{PC}$ = 53 7		30 6^a			$\rangle CHPMe_3$

^{a}Signal partially hidden by the solvent

acetone solution had been stored for several days, a few well-shaped colourless prisms together with a larger quantity of a powdery material were formed According to the results of the X-ray analysis, the composition of the crystals does not correspond to compound *3* but to the new complex $[(PMe_3)_6Pd_3(\mu\text{-}S)_2](BPh_4)_2$ (*4*)

Trinuclear cations $[(PR_3)_6M_3(\mu\text{-}S)_2]^{2+}$ isostructural with $[(PMe_3)_6Pd_3(\mu\text{-}S)_2]^{2+}$ have been described by Chatt and Mingos [5] for M = Pt and PR_3 = PMe_2Ph and, more recently, by Sacconi *et al* [6] for M = Ni and PR_3 = PEt_3 The platinum complex was prepared (in fairly low yields) from *cis*-$[PtCl_2(PMe_2Ph)_2]$ and Na_2S whereas for the analogous nickel compound $Ni(BF_4)_2{\cdot}6H_2O$, PEt_3 and H_2S were used as starting materials Since the synthetic procedure to obtain $[(PEt_3)_6Ni_3(\mu\text{-}S)_2](BPh_4)_2$ [6] seemed particularly straightforward and since the yield of *4* according to our original method was very low, we tried a similar route for the preparation of the trinuclear palladium complex

The reaction of $[Pd(CH_3CN)_4](BF_4)_2$ (*5*) with PMe_3 and H_2S does indeed lead to the cation $[(PMe_3)_6Pd_3(\mu\text{-}S)_2]^{2+}$ which, after addition of $NaBPh_4$, gives *4* in 40% yield The advantage of this method is further demonstrated by the synthesis of $[(PMePh_2)_6Pd_3(\mu\text{-}S)_2](BPh_4)_2$ (*6*), isolated in 84% yield The starting compound *5* which has first been prepared by Schramm and Wayland [7] from palladium sponge and $[NO]BF_4$ in CH_3CN, can be obtained more easily from $PdCl_2$ and $AgBF_4$ in acetonitrile

$$PdCl_2 + 2AgBF_4 + 4CH_3CN \xrightarrow[-2AgCl]{} [Pd(CH_3CN)_4](BF_4)_2 \quad \mathit{5}$$

$$\mathit{5} + H_2S + PR_3 \xrightarrow{NaBPh_4} [(PR_3)_6Pd_3(\mu\text{-}S)_2](BPh_4)_2$$

4 $PR_3 = PMe_3$
6 $PR_3 = PMePh_2$

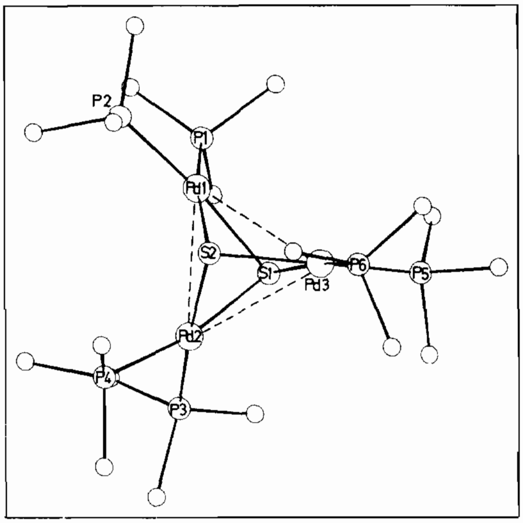

Fig 1 A perspective drawing of the dication of *4* The anions are omitted for clarity

The ^{1}H n m r spectra of *4* and *6* (in CH_2Cl_2) show one broad signal for the P–CH_3 protons (*4* δ = 1 45, *6* δ = 1 32 ppm, int TMS) which is due to the fact that each of these protons couple to three different phosphorus nuclei which also couple to one another The ^{31}P n m r spectra show one sharp signal (*4* δ = −15 15, *6* δ = 6 45 ppm, ext 85% H_3PO_4) and thus clearly confirm the equivalence of the six phosphine groups

Crystal Data and Structure Determination of 4

Crystals of *4* are monoclinic with *a* = 1551(2), *b* = 2517(7), *c* = 1830(3) pm, β = 94 74(9)°, V = 7120 10^6 pm^3 Space group $P2_1/c$ (*Z* = 4) determined by precession photographs, σ (calc) = 1 38 g/cm^3 Intensity data were collected on a Syntex $P2_1$ four circle automatic diffractometer using Mo-K_α radiation (graphite monochromator, λ = 71 069 pm, ω-scan, Δω = 0 9°, 5208 independent

TABLE II. Final Atomic Coordinates with Their E.s.d's.

Atom	x/*a*	y/*b*	z/*c*	B
Pd(1)	0.2579(1)	0.1475(1)	0.1878(1)	
Pd(2)	0.2335(1)	0.0374(1)	0.2469(1)	
Pd(3)	0.3854(1)	0.1066(1)	0.3207(1)	
S(1)	0.3555(4)	0.0764(2)	0.2010(3)	
S(2)	0.2370(4)	0.1182(2)	0.3075(3)	
P(1)	0.3007(5)	0.1650(3)	0.0744(3)	
C(11)	0.397(2)	0.208(1)	0.084(2)	
C(12)	0.226(2)	0.196(1)	0.000(1)	
C(13)	0.335(2)	0.108(1)	0.024(1)	
P(2)	0.1501(4)	0.2102(3)	0.1860(3)	
C(21)	0.052(2)	0.189(1)	0.126(1)	
C(22)	0.178(1)	0.278(1)	0.155(1)	
C(23)	0.110(2)	0.224(1)	0.277(1)	
P(3)	0.2469(5)	−0.0363(2)	0.1740(4)	
C(31)	0.210(1)	−0.103(1)	0.201(1)	
C(32)	0.356(2)	−0.048(1)	0.158(2)	
C(33)	0.182(2)	−0.025(1)	0.085(1)	
P(4)	0.1045(5)	0.0172(3)	0.2893(4)	
C(41)	0.019(2)	0.020(1)	0.218(1)	
C(42)	0.092(2)	−0.047(1)	0.335(2)	
C(43)	0.074(3)	0.058(2)	0.362(2)	
P(5)	0.5268(5)	0.0912(3)	0.3114(4)	
C(51)	0.546(2)	0.020(1)	0.299(1)	
C(52)	0.611(2)	0.107(1)	0.383(2)	
C(53)	0.567(2)	0.121(1)	0.232(1)	
P(6)	0.3963(4)	0.1285(2)	0.4428(3)	
C(61)	0.295(2)	0.150(1)	0.477(1)	
C(62)	0.471(2)	0.180(1)	0.476(1)	
C(63)	0.427(2)	0.069(1)	0.499(1)	
B(1)	0.780(2)	0.275(1)	0.059(1)	3.7(6)
C(110)	0.872)1)	0.289(1)	0.027(1)	3.4(5)
C(111)	0.920(2)	0.331(1)	0.058(1)	5.8(6)
C(112)	1.008(2)	0.340(1)	0.030(1)	6.0(7)
C(113)	1.039(2)	0.310(1)	−0.024(1)	5.2(6)
C(114)	0.991(2)	0.268(1)	−0.050(1)	6.2(7)
C(115)	0.906(1)	0.256(1)	−0.026(1)	4.5(6)
C(120)	0.802(1)	0.241(1)	0.132(1)	4.3(5)
C(121)	0.815(2)	0.185(1)	0.129(1)	6.9(7)
C(122)	0.842(2)	0.157(1)	0.194(1)	6.9(7)
C(123)	0.865(2)	0.181(1)	0.259(1)	6.4(7)
C(124)	0.852(2)	0.236(1)	0.262(2)	7.7(8)
C(125)	0.827(2)	0.267(1)	0.205(2)	7.9(8)
C(130)	0.729(2)	0.331(1)	0.078(1)	4.7(6)
C(131)	0.665(2)	0.330(1)	0.130(1)	6.3(7)
C(132)	0.619(2)	0.378(1)	0.149(1)	5.6(6)
C(133)	0.641(2)	0.425(1)	0.114(1)	5.6(6)
C(134)	0.699(2)	0.427(1)	0.062(1)	7.3(8)
C(135)	0.742(2)	0.380(1)	0.044(1)	5.2(6)
C(140)	0.713(1)	0.247(1)	−0.001(1)	4.4(5)
C(141)	0.652(2)	0.211(1)	0.022(1)	5.6(6)
C(142)	0.589(2)	0.185(1)	−0.033(1)	6.2(7)
C(143)	0.590(2)	0.197(1)	−0.106(1)	7.0(7)
C(144)	0.643(2)	0.233(1)	−0.131(1)	6.7(7)
C(145)	0.708(2)	0.257(1)	−0.079(1)	5.5(6)
B(2)	0.241(2)	0.436(1)	0.290(1)	2.5(5)
C(210)	0.298(1)	0.475(1)	0.344(1)	2.7(4)
C(211)	0.384(1)	0.464(1)	0.366(1)	3.3(5)
C(212)	0.432(1)	0.500(1)	0.413(1)	4.4(5)
C(213)	0.397(2)	0.546(1)	0.438(1)	5.6(6)

TABLE III. *(continued)*

Atom	x/*a*	y/*b*	z/*c*	B
C(214)	0.311(2)	0.558(1)	0.419(1)	5.6(6)
C(215)	0.259(2)	0.522(1)	0.374(1)	4.5(6)
C(220)	0.208(2)	0.466(1)	0.209(1)	5.8(6)
C(221)	0.209(2)	0.522(1)	0.208(1)	5.0(6)
C(222)	0.172(1)	0.545(1)	0.133(1)	4.6(6)
C(223)	0.148(2)	0.514(1)	0.072(1)	6.5(7)
C(224)	0.153(2)	0.459(1)	0.077(1)	6.3(7)
C(225)	0.186(2)	0.434(1)	0.144(1)	6.0(7)
C(230)	0.296(1)	0.383(1)	0.271(1)	4.7(6)
C(231)	0.295(2)	0.337(1)	0.320(1)	5.2(6)
C(232)	0.346(2)	0.290(1)	0.308(1)	6.0(7)
C(233)	0.402(2)	0.293(1)	0.254(1)	6.3(7)
C(234)	0.407(2)	0.335(1)	0.207(1)	7.3(8)
C(235)	0.353(2)	0.381(1)	0.217(1)	5.8(6)
C(240)	0.154(1)	0.417(1)	0.328(1)	
C(241)	0.094(2)	0.384(1)	0.288(1)	
C(242)	0.014(2)	0.361(1)	0.327(2)	
C(243)	0.007(2)	0.378(1)	0.398(1)	
C(244)	0.067(2)	0.411(1)	0.438(2)	
C(245)	0.138(2)	0.432(1)	0.400(1)	

reflections, $2^\circ \leqslant 2\theta \leqslant 44^\circ$). The data were corrected for Lorentz and polarization factors, but not for absorption (μ(Mo-K$_\alpha$) = 9.7 cm^{-1}). The structure was solved by MULTAN and difference Fourier maps (Syntex XTL) and refined by block-diagonal least squares. Only the Pd, S and P atoms and some of the carbon atoms were treated anisotropically. Hydrogen atoms were not located. For 4931 structure factors with $F_o \geqslant 4.2\ \sigma(F_o)$ final $R_1 = 0.102$ and $R_2 = 0.104$ were obtained. The rather poor R's can be attributed to the fact that despite high thermal motion (see C(240)–C(245)) the phenyl groups of the anions were only treated isotropically. The additional diffractometer and computer time needed for an improvement seemed not worth the effort, particularly since the parameters for the dication are of sufficient reliability. The final atomic parameters and thermal parameters are given in Tables II and III (Fig. 1).

The Structure of 4

Like the analogous nickel complex [6] the overall geometry of the dication of *4* is best described as three square planar *cis*-PdS$_2$S$_2$ moieties, which have both sulfur atoms in common (Fig. 1). Despite this similarity there is a significant difference (Table IV): The central triangle of palladium atoms in *4* is not equilateral, as it is in [(PEt$_3$)$_6$Ni$_3$S$_2$]$^{2+}$ [6] and in (C$_5$H$_5$)$_3$Ni$_3$S$_2$ [8]. In *4*, Pd(1)–Pd(2) (301.1 pm) is considerably shorter than Pd(1)–Pd(3) and Pd(2)–Pd(3) (317.8 and 314.4 pm). Complexes with the isostructural [Cu$_3$Cl$_2$]$^+$ or [Ag$_3$Br$_2$]$^+$ cores ([Cu$_3$Cl$_2$(dpm)$_3$]Cl [9], Ag$_3$Br$_2$(dpm)$_3$]Br [10, 11], dpm

TABLE III. Final Anisotropic Thermal Parameters with Their E.s.d's. They are of the form: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd(1)	4.3(1)	3.3(1)	3.1(1)	0.1(1)	0.7(1)	0.0(1)
Pd(2)	3.6(1)	3.9(1)	3.4(1)	−0.5(1)	0.2(1)	0.3(1)
Pd(3)	3.6(1)	3.6(1)	3.7(1)	0.4(1)	0.2(1)	−0.9(1)
S(1)	3.5(4)	3.6(3)	3.3(3)	0.6(3)	0.2(3)	−0.4(2)
S(2)	3.1(4)	3.5(3)	2.3(2)	0.2(3)	0.6(2)	−0.9(2)
P(1)	6.1(5)	4.0(4)	3.0(3)	−0.2(3)	1.4(3)	−0.2(3)
C(11)	8.7(21)	5.5(17)	9.0(23)	−3.3(15)	2.3(16)	−1.2(15)
C(12)	11.4(23)	7.0(18)	3.6(13)	4.4(16)	−0.4(14)	−0.5(12)
C(13)	11.2(21)	5.3(15)	3.0(12)	3.1(15)	1.5(13)	−1.1(11)
P(2)	4.7(4)	4.1(4)	4.1(3)	0.8(3)	1.1(3)	0.6(3)
C(21)	3.4(17)	10.6(21)	7.1(17)	−1.6(15)	−1.3(13)	2.1(15)
C(22)	3.9(15)	2.8(11)	6.8(15)	−0.3(10)	−0.2(11)	1.2(10)
C(23)	12.1(23)	6.9(17)	4.7(14)	4.0(17)	5.5(15)	2.1(13)
P(3)	5.4(5)	3.2(3)	5.1(4)	−1.2(3)	0.6(3)	−0.1(3)
C(31)	0.0(13)	5.3(14)	11.3(19)	−2.3(11)	−1.7(12)	3.0(14)
C(32)	5.4(18)	4.9(15)	11.7(21)	2.0(13)	5.6(15)	−2.9(14)
C(33)	14.1(24)	4.7(14)	2.5(11)	−1.3(15)	2.1(13)	−0.3(10)
P(4)	3.8(4)	5.1(4)	4.9(4)	−1.7(3)	0.8(3)	−0.7(3)
C(41)	6.6(19)	7.6(17)	9.7(18)	5.3(14)	9.3(15)	5.0(14)
C(42)	7.8(21)	7.9(19)	12.0(22)	0.2(16)	3.9(17)	6.3(17)
C(43)	19.7(38)	15.2(31)	10.4(25)	−6.4(28)	10.5(26)	−8.0(23)
P(5)	3.5(4)	5.8(4)	4.9(4)	1.1(3)	0.2(3)	−1.5(3)
C(51)	3.1(16)	6.5(16)	8.7(18)	2.6(12)	0.9(13)	−2.9(14)
C(52)	4.4(18)	16.3(29)	7.9(19)	2.7(18)	−1.1(14)	−7.3(20)
C(53)	5.0(18)	10.2(21)	7.2(17)	−0.5(15)	3.3(14)	1.7(15)
P(6)	3.9(4)	4.2(3)	3.9(3)	0.9(3)	0.1(3)	−1.3(3)
C(61)	4.0(17)	10.0(20)	5.2(14)	−0.1(15)	1.6(12)	−1.7(14)
C(62)	6.6(18)	4.4(14)	6.0(15)	−2.3(12)	1.8(13)	−2.8(11)
C(63)	12.4(23)	4.3(14)	2.5(12)	−0.2(15)	1.9(13)	−0.2(10)
C(240)	3.0(14)	4.1(12)	5.0(13)	1.5(10)	−0.1(10)	1.1(10)
C(241)	6.4(18)	3.4(12)	9.5(17)	0.9(12)	0.1(14)	2.3(12)
C(242)	6.3(18)	2.2(10)	13.8(23)	1.2(11)	1.8(16)	−1.2(12)
C(243)	6.2(19)	7.1(16)	7.3(16)	0.6(14)	0.1(13)	2.6(13)
C(244)	5.4(19)	9.9(19)	11.3(20)	2.6(15)	5.0(15)	7.4(16)
C(245)	4.5(16)	9.2(18)	5.8(14)	1.8(13)	3.6(12)	3.7(13)

= bis(diphenylphosphino)methane) show similar distortions form an ideal threefold symmetry of the cores. The reason for the deviation from a more symmetric arrangement in *4* is not obvious, since the Pd_3S_2 trigonal bipyramid would be similar (in a geometrical sense) to that in $[(PEt_3)_6Ni_3S_2]^{2+}$, if mean bond lengths and angles are considered (the mean angles M–S–M and S–M–S and the ratio of the mean distances M–S/M–M (M = Ni, Pd) are about the same).

The PdS_2P_2 moieties are not strictly planar. If the corresponding PdS_2 planes are taken as reference planes, the phosphorus atoms are located somewhat below or above these planes: P(1) −8.4(7), P(2) 17.7(7), P(3) 9.3(7), P(4) 29.2(7), P(5) 4.5(7), P(6) −25.3(6) pm. As a consequence of the low S–Pd–S angles (mean value 79.3°) the P–Pd–P angles become obtuse (mean value 97.4°), whereas *cis* S–Pd–P angles remain close to 90° (mean value 91.6°).

Experimental

The starting compound $[(PMe_3)_3PdH]BPh_4$ (*1*) was prepared according to [12]. All reactions were carried out under purified nitrogen. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457 and n.m.r. spectra on Varian T 60, XL 100 and Bruker WH 90 instruments.

Preparation of $[Pd(CH_3CN)_4](BF_4)_2$ *(5)*

To 1.0 g $PdCl_2$ (5.64 mmol) in 25 ml acetonitrile was added 2.2 g $AgBF_4$ (11.3 mmol). The colour of the solution immediately turned to orange and a grey precipitate was formed. After stirring for 45

TABLE IV. Selected Interatomic Distances (in pm) and Angles (in °)

Pd(1)···Pd(2)	301.1(2)	Pd(1)···Pd(2)···Pd(3)	62.12(6)
Pd(1)···Pd(3)	317.8(2)	Pd(2)···Pd(3)···Pd(1)	56.89(5)
Pd(2)···Pd(3)	314.4(2)	Pd(3)···Pd(1)···Pd(2)	60.99(6)
Pd(1)–S(1)	234.4(6)	S(1)–Pd(1)–S(2)	78.6(2)
Pd(1)–S(2)	235.8(5)	S(1)–Pd(1)–P(1)	90.4(2)
Pd(2)–S(1)	234.8(6)	S(1)–Pd(1)–P(2)	171.5(2)
Pd(2)–S(2)	231.6(6)	S(2)–Pd(1)–P(1)	168.8(2)
Pd(3)–S(1)	232.9(6)	S(2)–Pd(1)–P(2)	94.2(2)
Pd(3)–S(2)	231.2(6)	P(1)–Pd(1)–P(2)	97.0(2)
Pd(1)–P(1)	227.3(6)	S(1)–Pd(2)–S(2)	79.4(2)
Pd(1)–P(2)	229.5(7)	S(1)–Pd(2)–P(3)	90.9(2)
Pd(2)–P(3)	230.4(7)	S(1)–Pd(2)–P(4)	168.0(2)
Pd(2)–P(4)	226.3(7)	S(2)–Pd(2)–P(3)	170.0(2)
Pd(3)–P(5)	224.8(7)	S(2)–Pd(2)–P(4)	91.1(2)
Pd(3)–P(6)	229.3(6)	P(3)–Pd(2)–P(4)	98.2(3)
P(1)–C (mean)	183(3)	S(1)–Pd(3)–S(2)	79.8(2)
P(2)–C (mean)	186(3)	S(1)–Pd(3)–P(5)	89.6(2)
P(3)–C (mean)	182(3)	S(1)–Pd(3)–P(6)	170.8(2)
P(4)–C (mean)	179(3)	S(2)–Pd(3)–P(5)	169.3(2)
P(5)–C (mean)	181(3)	S(2)–Pd(3)–P(6)	93.3(2)
P(6)–C (mean)	182(3)	P(5)–Pd(3)–P(6)	97.0(2)
B–C (mean)	164(3)	Pd(1)–S(1)–Pd(2)	79.9(2)
		Pd(1)–S(1)–Pd(3)	85.7(2)
		Pd(2)–S(1)–Pd(3)	84.5(2)
		Pd(1)–S(2)–Pd(2)	80.2(2)
		Pd(1)–S(2)–Pd(3)	85.7(2)
		Pd(2)–S(2)–Pd(3)	85.6(2)
		Pd–P–C (mean)	114.8(9)
		C–P–C (mean)	103.7(12)

min, the mixture was filtered and the filtrate concentrated *in vacuo* to about half of the original volume. To this 75 ml ether was added which led to the formation of a bright-yellow solid. After recrystallisation from acetonitrile (10 ml) and ether (75 ml) pale-yellow crystals of *5* were obtained (2.2 g; 88%). *Anal.* Calc. for $C_8H_{12}B_2F_8N_4Pd$: Pd, 23.95. Found: Pd, 23.15.

The i.r. data [3320 w, 3010 m, 2340 s, 2310 m] are consistent with those in [7].

Preparation of $[(PMe_3)_6Pd_3S_2](BPh_4)_2$ *(4) from* 5

357 mg *5* (1 mmol) and 0.6 ml PMe_3 (6 mmol) were dissolved in 20 ml acetonitrile. Through the solution H_2S was bubbled for 5 min. After continuous stirring for 20 h, the solution was concentrated to about 1/3 of its original volume and filtered. Addition of 50 ml ether to the filtrate led to the formation of a bright-yellow precipitate which was washed with ether and dried *in vacuo*. The product was dissolved in 10 ml methanol and the solution treated with an excess of $NaBPh_4$ (*ca.* 400 mg). Air stable colourless crystals were formed (360 mg; 40%). *Anal.* Calc. for $C_{66}H_{94}B_2P_6Pd_3S_2$: C, 53.63; H, 6.41; S, 4.34. Found: C, 53.97; H, 6.65; S, 4.23.

Preparation of $[(PMePh_2)_6Pd_3S_2](BPh_4)_2$ *(6)*

This complex was prepared from *5*, $PMePh_2$ and H_2S as was described for the analogous compound *4*. Air stable bright-yellow crystals were obtained (84%). *Anal.* Calc. for $C_{126}H_{118}B_2P_6Pd_3S_2$: C, 68.07; H, 5.35; Pd, 14.36; S, 2.88. Found: C, 67.82; H, 5.10; Pd, 14.17; S, 2.73.

Preparation of 4 *from* $[(PMe_3)_3PdH]BPh_4$ (1)

500 mg *1* (0.76 mmol) were dissolved in 20 ml acetone and the nitrogen atmosphere replaced by COS. The solution was stirred for 2 h and during this time, the flask was repeatedly filled (about every 30 min) with COS. Concentration of the solution *in vacuo* and addition of ether led to the formation of a colourless solid the composition of which approximately corresponds to *3* [*Anal.* Calc. for $C_{34}H_{58}$-BOP_3PdS: C, 57.12; H, 6.76. Found: C, 55.53; H, 6.46].

A saturated solution of this solid in acetone was kept under nitrogen for 7 days. During this time, a few colourless prisms were formed together with a greater quantity of a colourless powder. The crystals were separated from the powder by hand and one of them was used for the X-ray analysis.

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