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was characterized by microanalysis and NMR (^{1}H and ^{13}C) spectroscopy.

(I)
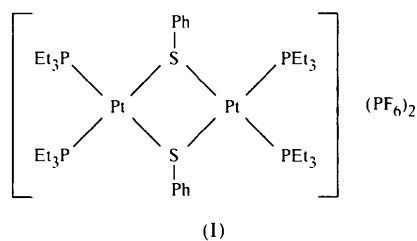
We report here the structure of (I), which crystallizes in space group $P\bar{1}$ with all atoms residing on general positions. The complex crystallizes as discrete cations and anions with no unusual contacts between them. The unit cell contains one formula unit. A view of the dinuclear cation, $[Pt_2(\mu\text{-}SPh)_2(PEt_3)_4]^{2+}$, which lies on an inversion centre at $(0,\frac{1}{2},\frac{1}{2})$, is shown in Fig. 1.

Di-μ-phenylthio-bis[bis(triethylphosphine-*P*)platinum(II)] Bis(hexafluorophosphate), [Pt2(μ-SPh)2(PEt3)4](PF6)2

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Abstract

The structure of $[Pt_2(C_6H_5S)_2(C_6H_{15}P)_4](PF_6)_2$ has been determined by single-crystal X-ray diffraction at room temperature. The cation has C_i symmetry with a square-planar-coordinated Pt atom. The central Pt_2S_2 ring is a rhombus with angles S—Pt—S' 81.34 (5) and Pt—S—Pt' 98.66 (5)°.

Comment

Insertion reactions of alkynes into metal–hydrogen bonds are important elementary steps in homogeneously catalyzed reactions (Cornils & Herrmann, 1996). We found that insertion reactions of the thiosubstituted alkynes $RSC\equiv CR'$ (R, R' = alkyl, aryl) into Pt—H bonds of neutral platinum complexes of the type $[PtClH(PR_3)_2]$ are characterized by unusual regio- and stereoselectivities (Steinborn *et al.*, 1998). Contrary to this, in the reaction of the cationic hydride complex *trans*-$[PtH(MeOH)(PEt_3)_2]PF_6$ with $PhSC\equiv CSiMe_3$, C—S bond cleavage occurs, giving the title complex, $[Pt_2(\mu\text{-}SPh)_2(PEt_3)_4](PF_6)_2$, (I), which

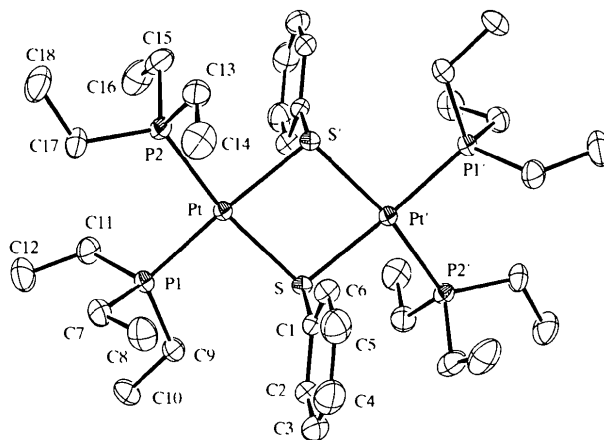Fig. 1. Perspective view of the cation $[Pt_2(\mu\text{-}SPh)_2(PEt_3)_4]^{2+}$. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

The Pt atom is square-planar coordinated (sum of angles 361.15°) by two phosphine ligands and two bridging phenylthio ligands. However, the Pt_2S_2 and PtP_2 planes form a dihedral angle of 11.63 (8)°, indicating a small twist distortion of the square-planar coordination geometry of the Pt^{II} atom. Apparently, to decrease the steric interactions between the phosphine ligands, the P1—Pt—P2 angle is widened to 97.39 (6)°. Also for steric reasons, the complex plane (Pt, Pt', P1, P1', P2, P2', S, S'; symmetry code as in Table 1) and the planes of the phenyl rings (C1–C6) are almost perpendicular [interplanar angle 89.8 (1)°]. The central Pt_2S_2 ring is planar due to the inversion symmetry and is a rhombus with S—Pt—S' 81.34 (5) and Pt—S—Pt' 98.66 (5)°. The Pt—S bond lengths [Pt—S 2.392 (2) and Pt'—S 2.389 (2) Å] are equal within the 3σ criterion. They are in the range found for other complexes with $Pt(\mu\text{-}SR)Pt$ moieties (2.274–2.402 Å; Capdevila *et al.*,

1992, and references therein) and only slightly longer than those in complexes with terminal thiolato ligands *trans* to phosphine ligands (2.306–2.379 Å; Chen *et al.*, 1994; Gosselink *et al.*, 1981; Smith *et al.*, 1994). The Pt···Pt distance is 3.627 (1) Å, which is slightly longer than the van der Waals distance for platinum (3.4–3.6 Å; Bondi, 1964) and also the Pt···Pt distances found in other dinuclear platinum complexes with Pt_2S_2 rings (3.175–3.556 Å; Capdevila *et al.*, 1992, and references therein).

Experimental

The synthesis of [Pt$_2$(μ-SPh)$_2$(PEt$_3$)$_4$](PF$_6$)$_2$ was carried out by reaction of stoichiometric amounts of *trans*-[PtH(MeOH)-(PEt$_3$)$_2$]PF$_6$ (Clark *et al.*, 1977) and PhSC≡CSiMe$_3$ (Wakefield, 1988; Siebert *et al.*, 1968) in methanol solution at room temperature. After 2 h, the precipitate was filtered, washed with methanol and dried *in vacuo*. Crystals (5% yield, colourless, m.p. 590 K) suitable for X-ray diffraction study were obtained from an acetone–ethanol solution.

Crystal data
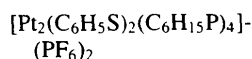
[Pt$_2$(C$_6$H$_5$S)$_2$(C$_6$H$_{15}$P)$_4$]-
(PF$_6$)$_2$
M_r = 1371.04
Triclinic
$P\bar{1}$
a = 11.150 (2) Å
b = 11.232 (2) Å
c = 12.176 (3) Å
α = 65.67 (2)°
β = 84.14 (2)°
γ = 65.641 (13)°
V = 1261.6 (4) Å^3
Z = 1
D_x = 1.805 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 4.36–34.93°
μ = 5.881 mm^{-1}
T = 293 (2) K
Prismatic
0.30 × 0.20 × 0.10 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.36, T_{max} = 0.56
5048 measured reflections
4454 independent reflections

4120 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25°
h = −13 → 13
k = −11 → 13
l = −11 → 14
1 standard reflection frequency: 60 min intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.088
S = 1.071
4450 reflections
298 parameters
Only H-atom U's refined

$\Delta\rho_{max}$ = 0.925 e Å^{-3}
$\Delta\rho_{min}$ = −0.550 e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0063 (5)

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.0415P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—C1	1.792 (7)	Pt—S	2.392 (2)
Pt—P1	2.294 (2)	Pt—S^i	2.3893 (15)
Pt—P2	2.293 (2)		
C1—S—Pt^i	101.2 (2)	P1—Pt—S^i	170.48 (5)
C1—S—Pt	100.2 (2)	P2—Pt—S	166.55 (6)
Pt^i—S—Pt	98.66 (5)	P1—Pt—S	93.46 (6)
P2—Pt—P1	97.39 (6)	S^i—Pt—S	81.34 (5)
P2—Pt—S^i	88.96 (5)		

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Data collection: *STADI4* (Stoe & Cie, 1996a). Cell refinement: *STADI-4*. Data reduction: *X-RED* (Stoe & Cie, 1996b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL93*.

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