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[2,6-Bis(isopropylthiomethyl)phenyl-κ^3S,C^1,S']bromopalladium(II)

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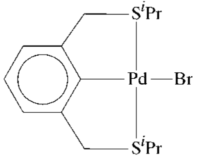
The title compound, $[PdBr(C_{14}H_{21}S_2)]$ or $[PdBr\{C_6H_3(CH_2S^iPr)_2\text{-}2,6\}]$, exhibits square-planar geometry at the Pd centre, with three atoms of the square plane provided by the rigid thiopincer ligand, *i.e.* 1,3-bis(thiomethyl)benzene.

Comment

Thiopincer ligand complexes are formed by the cyclometallation of 1,3-bis(disubstituted thiomethyl)benzene. The compounds $[PdCl\{C_6H_3(CH_2S^tBu)_2\text{-}2,6\}]$ (Errington *et al.*, 1980), and $[PdCl\{C_6H_3(CH_2SCH_2CH_3)_2\text{-}2,6\}]$ and $[PdCl\{C_6H_3(CH_2SC_6H_5)_2\text{-}2,6\}]$ (Lucena *et al.*, 1996) have been prepared by this method. These complexes have been used as catalysts for various reactions, such as the catalytic dehydrogenation of alkanes (Gupta *et al.*, 1996, 1997; Liu *et al.*, 1999), and ethers and alkylarenes (Dijkstra *et al.*, 2001; Gorla *et al.*, 1994; Langmire *et al.*, 1998; Stark *et al.*, 2000), and as Lewis acid catalysts (Dijkstra *et al.*, 2001). They are also used as catalysts for aldol reactions between benzaldehydes and methyl isocyanoacetate (Espinet *et al.*, 1994), as hydrogen transfer catalysts (Dani *et al.*, 2000) and as SO_2 reversible binding sites in gas sensor materials (Albrecht & van Koten, 1999; Albrecht *et al.*, 2000).



(I)

Recently, we have used pincer ligand complexes as starting materials for potential metallomesogens by reacting $[PdBr\{C_6H_3(CH_2S^iPr)_2\text{-}2,6\}]$ with long-chain alkoxy-arylthiols in the presence of Et_3N. This is a methodology employed in preparing a number of metal–thiolate complexes (Darkwa & Milius, 1996; Darkwa *et al.*, 1998; Nevondo *et al.*, 2000; Moutloali *et al.*, 2001). However, in an attempt to react $[PdBr\{C_6H_3(CH_2S^iPr)_2\text{-}2,6\}]$, (I), with thiols, compound (I) crystallized from the reaction mixture instead of forming a palladium–thiolate complex. This indicates that Et_3N might be too weak a base to effect the desired reaction. The structure of the title palladium complex, (I), is reported here.

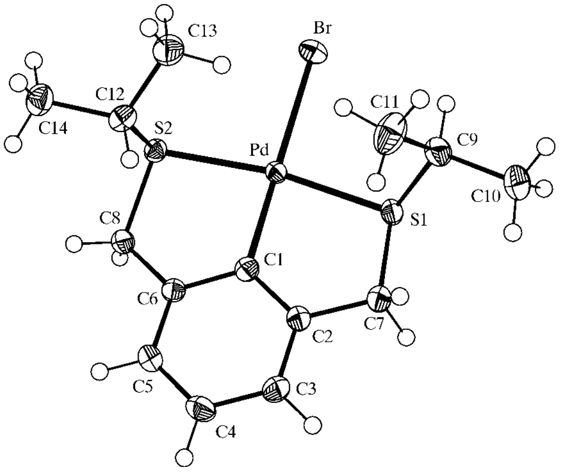


Figure 1
A view of the molecule of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecular structure of (I) is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The coordination number of the Pd atom in (I) is four and the donor atoms are arranged in a square plane, with the S atoms *trans* to each other. The two Pd—S distances differ only slightly. This is in contrast with similar compounds in which the S atoms are *cis* to each other. In these compounds, the Pd—S distances differ significantly. For example, the two Pd—S distances [2.274 (2) and 2.256 (2) Å] in $[Pd(C_6H_{12}S_3)Br_2]$ (Wieghart *et al.*, 1986) are noticeably different.

In compound (I), the 1,3-bis(thiomethyl)benzene unit behaves as a tridentate ligand. Its two S atoms are separated by a distance of 4.587 (8) Å and are therefore suitably disposed to form two Pd—S bonds orientated *trans* to each other. The two isopropyl substituents are in axial positions on the same side of the molecular plane, whereas the *tert*-butyl groups are on opposite sides in $[PdCl(C_6H_4)(CH_2S^tPr)_2]$ (Errington *et. al.*, 1980). The axial conformation is preferred, as the isopropyl repulsions are minimized. Potential repulsion between the two isopropyl substituents is also minimized when they are on opposite sides. However, in contrast with the *tert*-butyl analogue, the two isopropyl groups in (I) are *cis* to each other. In this conformation, the shortest distance between H atoms is 2.315 (7) Å.

Experimental

Palladium acetate (0.5 g, 2.23 mmol) was dissolved in glacial acetic acid (40 ml) and then charged with compound (I) (0.71 ml, 2.23 mmol), and the mixture was refluxed for 30 min. To this was added LiBr (0.5 g, 12.2 mmol) and the reaction was stirred at room

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Table 1
Selected geometric parameters (Å, °).

Pd—C1	1.984 (2)	Pd—S2	2.3110 (6)
Pd—S1	2.2924 (6)	Pd—Br	2.5471 (3)
C1—Pd—S1	85.08 (7)	C1—Pd—Br	178.91 (7)
C1—Pd—S2	85.17 (7)	S1—Pd—Br	94.549 (17)
S1—Pd—S2	170.19 (2)	S2—Pd—Br	95.180 (16)

temperature for 1 h. The solvent was removed and the residue extracted with CH_2Cl_2 and passed through silica gel (7 cm), which was washed with a copious amount of CH_2Cl_2. The solvent was removed *in vacuo* from the combined CH_2Cl_2 washings to leave an orange residue, which was recrystallized from CH_2Cl_2–hexane (1:1 *v*/*v*) at 123 K to give an orange–yellow solid, (I) (0.83 g, 94%). Analysis calculated for $[PdBr\{C_6H_3(CH_2S^iPr)_2\text{-}2,6\}]$: C 38.23, H 4.81%; found: C 38.5, H 4.6%. ^1H NMR ($CDCl_3$, δ, p.p.m.): 6.97 (*s*, 3H, C_6H_3), 4.20 (*s*, 4H, CH_2), 3.64 (*q*, 2H, J_{HH} = 6.8 Hz, ^{i}Pr), 1.58 (*d*, 12H, J_{HH} = 6.8 Hz, ^{i}Pr).

Crystal data

$[PdBr(C_{14}H_{21}S_2)]$
$M_r = 439.77$
Monoclinic, $P2_1/c$
$a = 8.5591$ (2) Å
$b = 10.6777$ (2) Å
$c = 17.6816$ (4) Å
$\beta = 103.042$ (1)°
$V = 1574.3$ (1) Å^3
$Z = 4$
$D_x = 1.855$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3396 reflections
$\theta = 2.2$–$27.5°$
$\mu = 3.96$ mm^{-1}
$T = 173$ (2) K
Rectangular block, light yellow
0.30 × 0.26 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with θ offsets
Absorption correction: empirical (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.350$, $T_{max} = 0.490$
14 692 measured reflections
3557 independent reflections
3143 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.052$
$S = 1.08$
3557 reflections
168 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 1.0617P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00217 (17)

Although all H atoms could be located in the difference Fourier map, they were placed in idealized positions and refined as riding atoms, with C—H = 0.95–1.00 Å and $U_{iso}(H)$ = 1.2 or 1.5 times $U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1357). Services for accessing these data are described at the back of the journal.

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