

FERGUSON, G., MCCRINDLE, R., MCALEES, A. J. & PARVEZ, M. (1982). *Acta Cryst.* **B38**, 2679–2681.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KITANO, Y., KINOSHITA, Y., NAKAMURA, R. & ASHIDA, T. (1983). *Acta Cryst.* **C39**, 1015–1017.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Acta Cryst. (1991). **C47**, 1729–1730

Chloro[7(*Z*)-chloromethylene-4,4,8,8-tetramethyl-2,10-dithiaundec-5(*Z*)-en-5-yl-S,S]palladium(II)

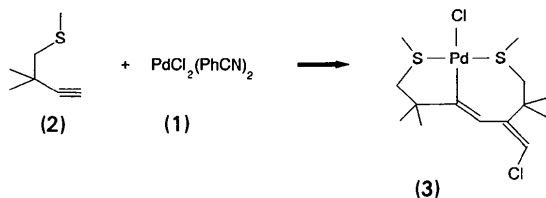
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(Received 26 September 1990; accepted 21 January 1991)

Abstract. $C_{14}H_{24}Cl_2PdS_2$, $M_r = 433.8$, monoclinic, $P2_1/c$, $a = 9.754$ (4), $b = 10.648$ (2), $c = 17.921$ (2) Å, $\beta = 99.95$ (2)°, $V = 1833$ (1) Å³, $Z = 4$, $D_x = 1.57$ g cm⁻³, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $\mu = 15.0$ cm⁻¹, $F(000) = 880$, $T = 294$ K. $R = 0.039$ for 1044 observed data. Space group unambiguously determined by the systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$). Reaction of dichlorobis(benzonitrile)palladium (1) with 2,2-dimethyl-3-butyn-1-yl methyl sulfide (2) (3 mol equiv.) gave a complex mixture of products; the structure and stereochemistry of the major product (3) was established by this X-ray analysis. The crystal structure contains discrete monomeric molecules separated by normal van der Waals distances. The Pd atom is four-coordinate in a close to square-planar environment; one methylthio moiety is disordered over two sites. Deviations of the atoms from the PdS_2ClC plane are Pd 0.036 (1), S(2) 0.479 (2), S(2') -0.492 (2), S(10) 0.008 (2), Cl 0.073 (2), C(5) -0.104 (3) Å. The exocyclic olefin is oriented so that the Cl atom on C(71) is *cis* to C(6) (Fig. 1). The seven-membered ring has a deformed boat conformation. Principal bond lengths are: Pd—Cl 2.408 (4), Pd—S 2.424 (6), 2.272 (6) and 2.303 (3) and Pd—C 1.980 (11) Å.

Experimental. A yellow prism crystal of (3) measuring $0.23 \times 0.20 \times 0.15$ mm was mounted on a glass fibre in a random orientation. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer from a least-squares refinement of data collected using the setting angles of 25 reflections in the range $10 < \theta < 15^\circ$. Intensities of reflections with indices $h - 9$ to 9, $k 0$ to 10, $l 0$ to 18, with $2 < 2\theta < 42^\circ$ measured; $\omega - 2\theta$ scans; ω -scan width $(0.60 + 0.35 \tan \theta)^\circ$. Intensities of three reflections measured at 3 h intervals showed no evidence of crystal decay. The crystals diffracted poorly and of the 2118 reflections measured only 1044 (49.3%) with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects. The structure was solved by the heavy-atom method using the *NRC Crystal Structure Package* (Larson & Gabe, 1978). One sulfur atom and its methyl group are disordered over two sites; these atoms were included with an occupancy factor of 0.5 (from difference map peak heights) for each of two sites. It is probable that carbon atom C(3) (to which the two disordered S atoms are bonded) is itself slightly disordered over two sites but we were unable to resolve this. The structure was refined by block-diagonal least-squares calculations on F , initially with isotropic and later with anisotropic thermal parameters for non-H atoms. H atoms were visible in difference syntheses [except for those of the disordered methyl carbons C(2) and C(2')] and were included at their idealized positions (C—H 0.95 Å, $U_{iso} = 0.05$ Å²) but not refined. The final refinement cycle included 190 variable parameters. Final $R = 0.039$, $wR = 0.034$, $w = 1/\sigma^2(F)$, $S = 1.96$, $\Delta/\sigma = 0.01$. Density in the final



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Table 1. Final fractional coordinates with e.s.d.'s in parentheses and mean B_{iso}(Å²)
$$B_{\text{iso}} = 8 \pi^2 (U_{11}U_{22}U_{33})^{0.33}$$

	x	y	z	B _{iso}
Pd	0.21649 (12)	0.17401 (8)	0.10687 (5)	4.52 (6)
Cl(1)	0.1670 (4)	-0.0087 (3)	0.1768 (2)	7.4 (3)
C(1)	0.1649 (25)	-0.0359 (19)	-0.0367 (13)	5.4 (17)
C(1')	0.3561 (25)	-0.0374 (24)	0.0177 (12)	6.1 (19)
S(2)	0.3001 (7)	0.0804 (5)	-0.0002 (3)	4.1 (4)
S(2')	0.1829 (7)	0.0381 (5)	0.0077 (3)	3.8 (4)
C(3)	0.2370 (20)	0.1691 (13)	-0.0703 (7)	12.9 (20)
C(4)	0.1821 (15)	0.2953 (13)	-0.0431 (5)	7.7 (11)
C(41)	0.2028 (17)	0.4004 (16)	-0.0932 (7)	10.7 (15)
C(42)	0.0253 (16)	0.2882 (11)	-0.0440 (6)	7.6 (13)
C(5)	0.2481 (12)	0.3136 (11)	0.0388 (6)	5.1 (8)
C(6)	0.3365 (13)	0.4062 (11)	0.0626 (6)	5.5 (8)
C(7)	0.4165 (12)	0.4242 (10)	0.1417 (6)	4.6 (7)
C(71)	0.5386 (13)	0.3747 (11)	0.1601 (7)	6.6 (10)
Cl(71)	0.6230 (4)	0.2885 (4)	0.0993 (2)	10.6 (4)
C(8)	0.3495 (12)	0.5033 (10)	0.1956 (6)	4.5 (8)
C(81)	0.4256 (14)	0.4935 (12)	0.2791 (7)	7.4 (10)
C(82)	0.3490 (16)	0.6401 (11)	0.1697 (8)	8.3 (11)
C(9)	0.1994 (13)	0.4608 (10)	0.1912 (5)	4.7 (8)
S(10)	0.1847 (3)	0.2945 (3)	0.2092 (2)	4.1 (2)
C(11)	0.0014 (14)	0.2801 (12)	0.2047 (7)	7.4 (10)

Atoms S(2), S(2'), C(1) and C(1') have 0.5 occupancy.

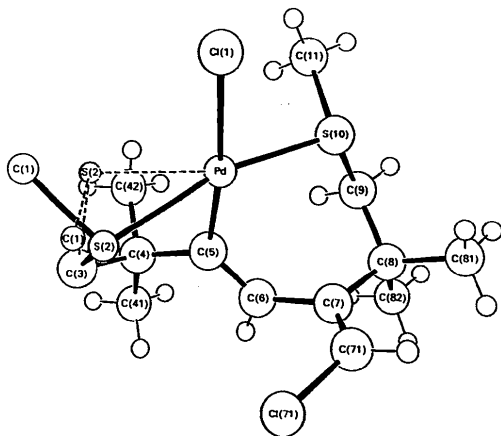


Fig. 1. A view of molecule (3) with the crystallographic numbering scheme. Atoms are shown as spheres of an arbitrary size. The atoms S(2), S(2'), C(1) and C(1') occur with 0.5 occupancy; atoms S(2') and C(1') are shown as small spheres and the bonds which they form are shown by dashed lines.

difference map $\pm 0.4 e \text{ \AA}^{-3}$ near disordered S atoms. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates and molecular dimensions are given in Tables 1 and 2,*

* Calculated hydrogen coordinates, anisotropic thermal parameters, selected torsion angles and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53941 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) and angles (°)

Pd—Cl(1)	2.408 (4)	C(4)—C(42)	1.528 (22)
Pd—S(2)	2.424 (6)	C(5)—C(6)	1.330 (18)
Pd—S(2')	2.272 (6)	C(6)—C(7)	1.506 (16)
Pd—S(10)	2.303 (3)	C(7)—C(8)	1.513 (17)
Pd—C(5)	1.980 (11)	C(7)—C(71)	1.292 (17)
S(2)—C(1)	1.844 (22)	C(71)—Cl(71)	1.736 (14)
S(2')—C(1')	1.851 (23)	C(8)—C(9)	1.521 (17)
S(2)—C(3)	1.608 (14)	C(8)—C(81)	1.554 (16)
S(2')—C(3)	2.106 (18)	C(8)—C(82)	1.529 (16)
C(3)—C(4)	1.556 (19)	C(9)—S(10)	1.811 (11)
C(4)—C(5)	1.510 (14)	S(10)—C(11)	1.782 (14)
C(4)—C(41)	1.471 (20)		
Cl(1)—Pd—S(2)	101.8 (2)	C(5)—C(4)—C(41)	114.5 (11)
Cl(1)—Pd—S(2')	83.0 (2)	C(5)—C(4)—C(42)	106.0 (10)
Cl(1)—Pd—C(5)	173.5 (3)	C(41)—C(4)—C(42)	105.9 (11)
Cl(1)—Pd—S(10)	88.2 (1)	C(4)—C(5)—C(6)	123.5 (10)
S(2)—Pd—S(2')	30.9 (2)	C(4)—C(5)—Pd	114.5 (8)
S(2)—Pd—C(5)	73.3 (4)	Pd—C(5)—C(6)	121.3 (8)
S(2)—Pd—S(10)	165.8 (2)	C(5)—C(6)—C(7)	126.7 (10)
S(2')—Pd—C(5)	90.8 (4)	C(6)—C(7)—C(71)	119.6 (11)
S(2')—Pd—S(10)	163.2 (2)	C(6)—C(7)—C(8)	117.4 (9)
C(5)—Pd—S(10)	97.4 (3)	C(71)—C(7)—C(8)	123.0 (11)
Pd—S(2)—C(1)	103.9 (8)	C(7)—C(71)—Cl(71)	124.8 (10)
Pd—S(2)—C(3)	104.0 (5)	C(7)—C(8)—C(81)	113.0 (9)
C(1)—S(2)—C(3)	87.9 (11)	C(7)—C(8)—C(82)	108.4 (10)
Pd—S(2')—C(1')	101.3 (8)	C(7)—C(8)—C(9)	108.7 (8)
Pd—S(2')—C(3)	94.5 (4)	C(9)—C(8)—C(81)	109.0 (10)
C(1')—S(2')—C(3)	91.3 (9)	C(9)—C(8)—C(82)	108.3 (10)
S(2)—C(3)—C(4)	111.6 (8)	C(81)—C(8)—C(82)	109.4 (9)
S(2')—C(3)—C(4)	103.0 (9)	C(8)—C(9)—S(10)	112.7 (8)
C(3)—C(4)—C(5)	107.8 (10)	C(9)—S(10)—C(11)	100.7 (6)
C(3)—C(4)—C(41)	112.0 (11)	C(9)—S(10)—Pd	112.2 (4)
C(3)—C(4)—C(42)	110.6 (12)	Pd—S(10)—C(11)	100.8 (4)

respectively. Fig. 1 is a view of the molecule prepared using ORTEPII (Johnson, 1976).

Related literature. For leading references see McCrindle, Stephenson, McAlees & Willson (1986). Other products from the reaction which led to molecule (3) have been described previously (McCrindle, Ferguson, Arsenaault, McAlees & Parvez, 1983; Ferguson, McCrindle & Parvez, 1983).

We thank NSERC Canada for grants in aid of research.

References

- FERGUSON, G., MCCRINDLE, R. & PARVEZ, M. (1983). *Acta Cryst.* C39, 993–994.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. & GABE, E. J. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 81–89. Delt. Univ. Press.
- MCCRINDLE, R., FERGUSON, G., ARSENAULT, G. J., MCALEES, A. J. & PARVEZ, M. (1983). *J. Organomet. Chem.* 246, C19–22.
- MCCRINDLE, R., STEPHENSON, D. K., MCALEES, A. J. & WILLSON, J. M. (1986). *J. Chem. Soc. Dalton Trans.* pp. 641–644.