Cyclopalladation of $C_6H_4(CH_2SBu^t)_2$-1,3 and the Crystal Structure of $[\overline{PdCl\{C_6H_3(CH_2S}Bu^t)_2\text{-}2,6\}]$ †

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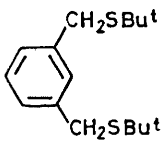
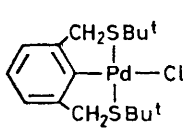
The new disulphide $C_6H_4(CH_2SBu^t)_2$-1,3 has been prepared from 1,3-di(bromomethyl)benzene and Bu^tSH using phase-transfer catalysis. It has been shown to cyclopalladate readily into the 2-position giving the title complex (2), the crystal structure of which has been determined: (2) reacts with PPh_3 to give $[PdCl\{C_6H_3(CH_2SBu^t)_2\text{-}2,6\}(PPh_3)_2]$ which is extensively dissociated in solution. Crystals of (2) are orthorhombic, space group *Pbcn*, with $a = 9.654(2)$, $b = 14.509(3)$, $c = 12.797(3)$ Å, and $Z = 4$. The structure has been determined from 1 024 independent F_o values and the final R is 0.043. The molecules have crystallographic symmetry C_2.

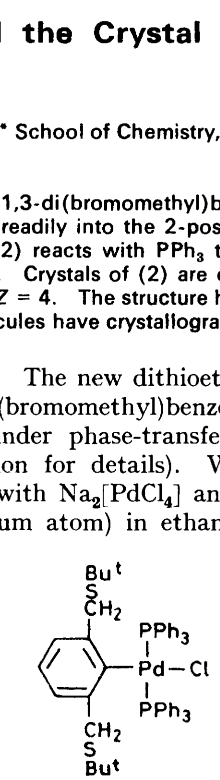
CYCLOMETALLATION is a quite widely occurring reaction in organotransition-metal chemistry and is being increasingly used in organic synthesis.[1-3] It is mainly a reaction associated with nitrogen or phosphorus donors although there are several examples of the cyclometallation of sulphur donors.[4] Although tertiary benzylamines are readily *ortho*-palladated (or *ortho*-platinated) it has been reported that benzyl phenyl sulphide is not *ortho*-palladated.[5] However, in this behaviour sulphur parallels that of phosphorus since phosphines such as $PPh(CH_2Ph)_2$ or $PR_2(CH_2Ph)$ (R = Me, Ph, or CH_2Ph) are reported not to cyclopalladate.[6-8] We showed, however, that the more sterically demanding benzylphosphines $PBu^t(CH_2Ph)_2$ and $PBu^t_2(CH_2Ph)$ could be *ortho*-palladated quite readily.[9] We have therefore attempted to cyclopalladate $Bu^tS(CH_2Ph)$ with sodium tetrachloropalladate(II) in ethanol [with or without added base (sodium acetate)] or with bis(benzonitrile)dichloropalladium(II) in either dichloromethane or toluene: in all cases we have been unsuccessful.[10] We therefore tried to doubly activate an *ortho* position towards palladation by introducing a t-butylthiomethyl group on either side, as in the dithioether (1). We have shown that 1,3-bis(di-t-butylphosphinomethyl)benzene is cyclometallated very readily in the 2-position by nickel, palladium, platinum, rhodium, or iridium.[11] The new dithioether was prepared by treating 1,3-di(bromomethyl)benzene with sodium t-butyl sulphide under phase-transfer conditions (see Experimental section for details). When this dithioether was treated with $Na_2[PdCl_4]$ and sodium acetate (1 mol per palladium atom) in ethanol the hoped for palladium complex [2,6-bis(t-butylthiomethyl)phenyl]-chloropalladium(II) (2) was formed. This complex, for which characterizing data are in the Experimental section, was sufficiently volatile to give a well defined set of peaks corresponding to the molecular ion in its mass spectrum, the most intense peak being at $m/e = 424$, as expected.



(1)



(2)



(3)

The crystal structure of this complex has been determined by *X*-ray diffraction. The molecular structure and atom numbering are shown in the Figure and Table 1 lists the bond lengths and angles with their estimated standard deviations. The molecules have crystallographically imposed C_2 symmetry and are thus the isomer having the t-butyl substituents on opposite sides of the molecular plane. The five-membered chelate rings have an envelope conformation with the sulphur atom 0.60 Å from the mean plane of the other atoms, and the t-butyl groups are in axial rather than equatorial positions. This avoids the non-bonded interaction between the t-butyl and Pd–Cl groups.

Since sulphur is a relatively weak donor towards

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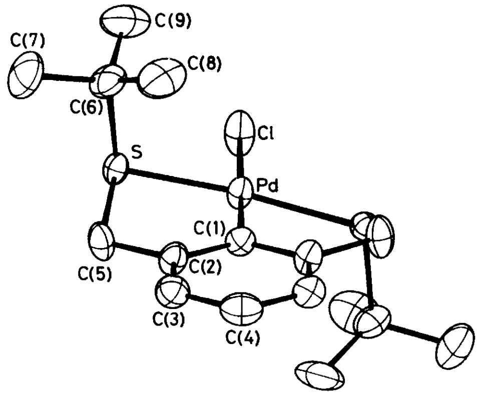
† [2,6-Bis(t-butylthiomethyl)phenyl-C^1SS']chloropalladium(II). This work is closely related to the series Transition Metal–Carbon Bonds, Parts 42 and 46 of which constitute refs. 11 and 1 respectively.

palladium we have attempted to open up the chelate ring by treatment with triphenylphosphine. With 2 mol of PPh_3 per palladium a white microcrystalline product was obtained which gave good microanalytical figures for the hoped for product (**3**), but a molecular-weight measurement in chloroform gave a value of 299 suggesting extensive dissociation. The ^{31}P n.m.r. resonance in $CDCl_3$ gave only a singlet at $\delta = -5.0$ p.p.m. (relative to 85% H_3PO_4) very close to the value for free triphenylphosphine. Moreover on adding more PPh_3 this peak increased in intensity. Hence from the melting point, 151—152 °C, and the i.r. spectrum, in which many of the bands present in the spectra of (**2**) or PPh_3 were absent, this white crystalline product probably has the structure (**3**), but it was very labile and highly dissociated in anything except highly concentrated solutions.



ORTEP drawing showing the molecular structure and atom numbering. There is a crystallographic C_2 axis passing through Cl, Pd, C(1), and C(4)

TABLE 1

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pd–Cl	2.406(3)	Cl–Pd–S	95.5(1)
Pd–S	2.308(2)	C(1)–Pd–S	84.5(1)
Pd–C(1)	1.988(11)	Pd–S–C(5)	98.5(2)
C(1)–C(2)	1.393(9)	Pd–S–C(6)	109.4(2)
C(2)–C(3)	1.386(12)	C(5)–S–C(6)	105.3(4)
C(3)–C(4)	1.408(10)	Pd–C(1)–C(2)	119.9(5)
C(2)–C(5)	1.515(11)	C(1)–C(2)–C(5)	118.9(7)
C(5)–S	1.816(9)	C(2)–C(5)–S	109.7(5)
S–C(6)	1.855(7)	C(2)–C(1)–C(2′)	120.2(7)
C(6)–C(7)	1.552(11)	C(1)–C(2)–C(3)	120.5(7)
C(6)–C(8)	1.532(12)	C(2)–C(3)–C(4)	119.1(7)
C(6)–C(9)	1.531(12)	C(3)–C(4)–C(3′)	120.5(8)

EXPERIMENTAL

The general techniques and apparatus were the same as in other recent papers from this laboratory.[12] The phase-transfer catalyst ADOGEN-464 [methyltrialkyl(C_8—C_{10})-ammonium chloride] was purchased from Aldrich Co. Ltd.

1,3-*Bis(t-butylthiomethyl)benzene* (1).—1,3-Di(bromomethyl)benzene (6.6 g, 25.0 mmol) and 1,1-dimethylethanethiol (4.5 g, 50 mmol) in degassed benzene (40 cm^3) were vigorously stirred under argon with a solution of sodium hydroxide (3.3 g, 83 mmol) in degassed water (50 cm^3) containing the phase-transfer catalyst ADOGEN-464 (0.4 g) for 1.75 h at *ca.* 20 °C. The mixture was then stirred under reflux for another 15 min, cooled, and the organic layer washed with water and dried over $Mg[SO_4]$. After removal of the solvent the product crystallized. It was purified by distillation under reduced pressure and obtained as a colourless liquid, b.p. 118—120 °C (0.02 mmHg),* which solidified to give a crystalline solid, yield 5.93 (84%) (Found: C, 68.4; H, 9.4; S, 22.4. $C_{16}H_{26}S_2$ requires C, 68.05; H, 9.3; S, 22.7%).

$[PdCl\{C_6H_3(CH_2SBu^t)_2\text{-}2,6\}]$ (2).—A mixture of sodium tetrachloropalladate(II) (0.26 g, 0.81 mmol), sodium acetate (0.07 g, 0.81 mmol), and 1,3-bis(t-butylthiomethyl)-benzene (0.24 g, 0.85 mmol) in ethanol (20 cm^3) was heated under reflux with stirring over a period of 25 min, after which time it was very dark. The solvent was removed under reduced pressure and the product extracted into dichloromethane and treated with charcoal. It formed greenish yellow prisms (0.18 g, 53%) from chloroform–hexane. The product sublimed at 210—219 °C and melted at 220—222 °C (decomp.) (Found: C, 45.35; H, 6.0; Cl, 8.05. $C_{16}H_{25}ClPdS_2$ requires C, 45.4; H, 5.95; Cl, 8.35%). The mass spectrum showed a parent molecular ion with the most intense peak at $m/e = 424$, as expected. Proton n.m.r. spectrum (in $CDCl_3$): $\delta = 6.91$ (s, aromatic H), 4.16 (s, CH_2), and 1.60 p.p.m. (CCH_3). There were only two bands in the i.r. spectrum (at 261m and 275m cm^{-1}) in the range 200—400 cm^{-1} one of which is presumably due to ν(Pd–Cl).

[2,6-*Bis(t-butylthiomethyl)phenyl*]*chlorobis(triphenylphosphine)palladium*(II) (3).—Triphenylphosphine (0.07 g, 0.27 mmol) was added to a solution of complex (2) in a mixture of dichloromethane (1 cm^3) and ethanol (2 cm^3). The solution was boiled for 15 min and then evaporated to a volume of *ca.* 1 cm^3. The required product separated on cooling as white microcrystals, yield 0.10 g (88%) (Found: C, 66.05; H, 6.05; Cl, 4.0; S, 7.0. $C_{52}H_{55}ClP_2PdS_2$ requires C, 65.9; H, 5.85; Cl, 3.75; S, 6.75%). The product melted sharply at 151—152 °C with decomposition to diamond-shaped prisms which sublimed at 210—215 °C and melted at 219—221 °C (decomp.). These were probably of the cyclometallated compound (2). The product (3) showed two i.r. bands in the range 200—400 cm^{-1}, at 254m and 287m cm^{-1}, one of which is presumably due to ν(Pd–Cl).

Crystal Data.—$C_{16}H_{25}ClPdS_2$, $M = 423.35$, Orthorhombic, *Pbcn*, $a = 9.654(2)$, $b = 14.509(3)$, $c = 12.797(3)$ Å, $Z = 4$, $D_c = 1.569$ Mg m^{-3}, $U = 1\,792.5(6)$ Å^3, $F(000) = 864$, μ(Mo-K_α) = 1.386 mm^{-1}, λ(Mo-K_α) = 0.710 69 Å, crystal dimensions 0.2 × 0.2 × 0.2 mm.

Structure Analysis.—Measurements were made on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo-K_α radiation. Cell dimensions and their standard deviations were determined by least-squares analysis of the setting angles for 15 reflections having $35 < 2\theta < 40°$. The 1 181 independent reflections with $2\theta < 45°$ were measured in the ω—2θ scan mode and the structure analysis used the 1 024 of these having $I > 3\sigma(I)$. The intensities were reduced to F and $\sigma(F)$ values by application of Lorentz, polarization, and transmission factors (A = 1.231—1.369) and the structure was solved *via* Patterson and difference syntheses. Full-matrix least-squares refinement with allowance for anisotropic vibrations for all atoms converged to a final R of 0.043 and $R' = 0.074$.

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* Throughout this Note: 1 mmHg ≈ 13.6 × 9.8 Pa.

Weights were derived from the modified variances $\sigma^2(I) = \sigma_c^2(I) + (0.05I)^2$, $\sigma_c^2(I)$ being the variance from counting statistics. Atomic scattering factors were calculated from the analytical expression and coefficients given in ref. 13; hydrogen atoms were not included. The atomic co-ordinates and their estimated standard deviations are given in Table 2; vibration parameters and a list of observed and calculated structure factors are in Supplementary Publication No. SUP 22845 (9 pp.).*

TABLE 2

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Pd(1)	0	0.071 27(5)	$\frac{1}{4}$
Cl(1)	0	−0.094 54(22)	$\frac{1}{4}$
S(1)	0.233 19(16)	0.086 42(13)	0.285 72(14)
C(1)	0	0.208 3(8)	$\frac{1}{4}$
C(2)	0.124 8(7)	0.256 1(5)	0.243 6(5)
C(3)	0.126 4(8)	0.351 6(6)	0.244 3(5)
C(4)	0	0.399 7(9)	$\frac{1}{4}$
C(5)	0.258 4(8)	0.202 0(6)	0.234 6(6)
C(6)	0.258 6(7)	0.096 7(5)	0.428 9(5)
C(7)	0.413 1(9)	0.122 3(7)	0.445 8(7)
C(8)	0.164 0(10)	0.169 4(6)	0.478 4(6)
C(9)	0.230 8(12)	−0.000 2(6)	0.471 4(7)

We thank the S.R.C. for support.

[0/405 *Received, 12th March,* 1980]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] A. G. Constable, W. S. McDonald, and B. L. Shaw, *J.C.S. Dalton*, 1980, 1992.
[2] M. I. Bruce, *Angew. Chem. Internat. Edn.*, 1977, **16**, 73.
[3] J. Dehand and M. Pfeffer, *Co-ordination Chem. Rev.*, 1976, **18**, 327.
[4] I. Omae, *Co-ordination Chem. Rev.*, 1979, **28**, 97.
[5] Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1972, **35**, 415.
[6] 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973.
[7] R. L. Bennett, M. I. Bruce, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **38**, 325.
[8] J. H. Nelson and D. A. Redfield, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 807.
[9] B. L. Shaw and M. M. Truelock, *J. Organometallic Chem.*, 1975, **102**, 517.
[10] P. Pringle and B. L. Shaw, unpublished work.
[11] C. J. Moulton and B. L. Shaw, *J.C.S. Dalton*, 1976, 1020.
[12] H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.
[13] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.