consistent with values found for other *trans*-Mo^{IV} chloride complexes such as *trans*-$[MoCl_2(ttp)]$ (ttp = 5,10,15,20-tetra-*p*-tolylporphyrin), $(MoCl)_{av}$ = 2·311 Å, $[MoOCl_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), Mo—Cl = 2·46 Å and *trans*-$[MoCl_2\{N(CH_3)CH_3C_6H_4O\}_2]$, Mo—Cl = 2·388 (2) Å. While other complexes containing the $[MoCl_6]^{2-}$ anion have been prepared (Homer & Tyree, 1963; Davison, Howe & Shawl, 1967), this is the first accurately determined X-ray crystal structure of this anion. From unit-cell dimensions the Mo—Cl bond distances in $K_2[MoCl_6]$ (Edwards, Peacock & Said, 1962) have been determined from Debye X-ray powder photographs. The Mo—Cl bond distance of 2·31 (5) Å is in agreement with that obtained for $[ClPPh_3]_2[MoCl_6]$.

The chlorophosphonium cation $[PClPh_3]^+$ has the expected tetrahedral geometry, with the P—Cl(1) bonds directed towards the centre of opposite faces of the $[MoCl_6]^{2-}$ octahedron on a threefold axis of symmetry. This unusual cation has also been fortuitously prepared (Davison, Howe & Shawl, 1967; Enemark & Ibers, 1968) by reaction between $S_2C_2(CF_3)_2$ and $[Ph_3PAuCl]$ to give $[ClPPh_3][Au\{S_2C_2(CF_3)_2\}_2]$. This complex has been structurally characterized and the bond angles and bond lengths of the chlorophosphonium cation are similar to those found in $[ClPPh_3]_2[MoCl_6]$.

Analyses for C and H were made by Mr C. Macdonald, AFRC Unit of Nitrogen Fixation, while Cl analyses carried out by Mion Analysis Ltd, Devon.

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Structure of Bromo(trimethylsilylethynyl)bis(triphenylphosphine)palladium(II)–Chloroform–Dichloromethane (2/2/1) Solvate

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Abstract. $[PdBr\{(C_6H_5)_3P\}_2(C_5H_9Si)].CHCl_3.\frac{1}{2}CH_2Cl_2$, M_r = 969·94, triclinic, $P\bar{1}$, a = 11·603 (3), b = 11·909 (3), c = 16·811 (7) Å, α = 104·49 (3), β = 99·71 (3), γ = 93·20 (3)°, V = 2205 (1) Å^3, Z = 2, D_m = 1·49, D_x = 1·461 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 17·4 cm^{-1}, $F(000)$ = 978, T = 295 K, R = 0·0622 for 6899 observed reflections with $I > 2{\cdot}5\sigma(I)$. The molecular structure consists of a central Pd atom, coordinated in a square-planar fashion by Br [Pd—Br = 2·481 (2) Å], a σ-bonded trimethylsilylethynyl moiety [Pd—C(*sp*) = 1·974 (6) Å] and two *trans*-positioned triphenylphosphine groups [Pd—P = 2·327 (2) and 2·333 (2) Å].

Introduction. The generally accepted mechanism (Yamamoto, Yamamoto & Ozawa, 1985; Kumada,

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1980) of Pd^0-catalysed cross-coupling reactions involves a sequence of oxidative addition, *trans*-metallation and reductive elimination. The title compound was isolated from the reaction of Pd(PPh_3)$_4$ with Me$_3$-Si—C≡C—Br and constitutes an example of the first step of this mechanism. The X-ray study was undertaken to investigate the coordination about the Pd atom in this case.

Experimental. A pale yellow crystal (0·88 × 0·48 × 0·20 mm) suitable for single-crystal X-ray work was obtained by crystallization from chloroform and recrystallization from dichloromethane and mounted on a glass fibre. D_m by flotation in CCl_4/pentane. Data collection on an Enraf–Nonius CAD-4F diffractometer. Unit-cell parameters and their standard deviations were obtained from a least-squares fit of the setting angles of 22 reflections ($10 < \theta < 11°$). Unique dataset: h $-15 \to 14$, k $-15 \to 14$, l $0 \to 21$, $\theta_{max} = 27\cdot5°$, ω–2θ scan; $\Delta\omega = (0\cdot5 + 0\cdot35\tan\theta)°$, Zr-filtered Mo $K\alpha$ radiation, 10102 reflections scanned, 6896 observed [$I > 2\cdot5\sigma(I)$]. Standard deviations were calculated following McCandlish, Stout & Andrews (1975), $\sigma^2(I) = \sigma^2_{cs}(I) + (PI)^2$, $P = 0\cdot045$. The intensities of three reference reflections (200, 222, 002) were measured every hour of X-ray exposure time. A linear decay of 35% and fluctuations of the order of 2% were observed during the 145 h exposure time. The diffraction data were corrected for Lp and the observed decay. Empirical absorption correction was applied using the program *DIFABS* (Walker & Stuart, 1983) with corrections in the range 0·728–1·310. The structure was solved with standard Patterson and difference Fourier techniques. A difference Fourier map showed the presence of ordered $CHCl_3$. Residual density near (0,0,0) was interpreted in terms of disordered CH_2Cl_2. The non-hydrogen atoms, with the exception of those of the disordered CH_2Cl_2 molecule, were refined with anisotropic thermal parameters. H atoms were introduced on calculated positions (C—H = 1·08 Å) and refined with fixed geometries with respect to the atoms to which they are attached, with common thermal parameters for the H atoms of the methyl groups and for those of the phenyl groups. The positions of the atoms of the CH_2Cl_2 molecule were refined with bond restraints. Weights, $w = 1/\sigma^2(F)$, were introduced in the final refinement cycles. Blocked full-matrix least-squares refinement on F converged at $R = 0\cdot0622$ and $wR = 0\cdot0828$, $S = 2\cdot12$, 464 parameters, 6896 reflections, $(\Delta/\sigma)_{ave} = 0\cdot2$, $(\Delta/\sigma)_{max} = 0\cdot8$. Final positional parameters for the non-hydrogen atoms appear in Table 1.* A final difference Fourier map was essentially featureless apart from some residual peaks ($< 1\cdot6$ e Å^{-3}) in the region of the disordered CH_2Cl_2 and residual absorption artefacts ($< 1\cdot1$ e Å^{-3}) near Pd. Scattering factors of Cromer & Mann (1968) were used and anomalous-dispersion terms were taken from Cromer & Liberman (1970).

Table 1. *Final positional parameters for the non-hydrogen atoms, equivalent isotropic thermal factors and their e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Pd	0·27010 (4)	0·17680 (4)	0·29130 (3)	0·0364 (2)
Br	0·2069 (1)	0·3763 (1)	0·31820 (5)	0·0556 (3)
P(1)	0·1461 (1)	0·1052 (1)	0·3666 (1)	0·0390 (5)
P(2)	0·4226 (1)	0·2395 (1)	0·2332 (1)	0·0389 (5)
Si	0·3549 (2)	−0·2363 (2)	0·2215 (2)	0·0654 (8)
C(1)	0·0592 (5)	0·2094 (5)	0·4247 (4)	0·046 (2)
C(2)	0·0800 (6)	0·2438 (6)	0·5112 (5)	0·058 (2)
C(3)	0·0138 (7)	0·3227 (7)	0·5514 (5)	0·072 (3)
C(4)	−0·0736 (8)	0·3698 (7)	0·5069 (6)	0·076 (3)
C(5)	−0·0924 (7)	0·3371 (6)	0·4224 (6)	0·075 (4)
C(6)	−0·0257 (6)	0·2581 (6)	0·3791 (5)	0·056 (3)
C(7)	0·0330 (5)	−0·0130 (5)	0·3090 (4)	0·047 (2)
C(8)	−0·0605 (6)	−0·0410 (6)	0·3458 (5)	0·059 (3)
C(9)	−0·1461 (7)	−0·1289 (7)	0·3031 (6)	0·073 (3)
C(10)	−0·1402 (8)	−0·1919 (8)	0·2223 (7)	0·090 (4)
C(11)	−0·0465 (8)	−0·1658 (8)	0·1872 (6)	0·088 (3)
C(12)	0·0388 (7)	−0·0775 (7)	0·2280 (5)	0·071 (3)
C(13)	0·2354 (5)	0·0535 (5)	0·4476 (4)	0·041 (2)
C(14)	0·2050 (6)	−0·0511 (6)	0·4646 (4)	0·052 (2)
C(15)	0·2774 (7)	−0·0829 (6)	0·5298 (5)	0·067 (3)
C(16)	0·3767 (7)	−0·0166 (7)	0·5736 (5)	0·071 (3)
C(17)	0·4096 (6)	0·0894 (7)	0·5541 (4)	0·061 (3)
C(18)	0·3370 (6)	0·1222 (6)	0·4912 (4)	0·053 (2)
C(19)	0·5208 (6)	0·1335 (5)	0·1950 (4)	0·045 (2)
C(20)	0·4717 (7)	0·0401 (6)	0·1266 (4)	0·056 (3)
C(21)	0·5415 (8)	−0·0407 (6)	0·0906 (5)	0·069 (3)
C(22)	0·6588 (9)	−0·0324 (7)	0·1239 (6)	0·081 (4)
C(23)	0·7095 (8)	0·0581 (8)	0·1923 (7)	0·087 (4)
C(24)	0·6377 (6)	0·1421 (6)	0·2280 (5)	0·061 (3)
C(25)	0·5151 (5)	0·3509 (5)	0·3159 (4)	0·044 (2)
C(26)	0·5523 (7)	0·4599 (6)	0·3059 (5)	0·064 (3)
C(27)	0·6218 (8)	0·5438 (7)	0·3739 (6)	0·082 (4)
C(28)	0·6534 (7)	0·5201 (7)	0·4512 (5)	0·069 (3)
C(29)	0·6128 (6)	0·4140 (7)	0·4597 (4)	0·063 (3)
C(30)	0·5466 (6)	0·3314 (6)	0·3952 (4)	0·056 (2)
C(31)	0·3873 (6)	0·3000 (5)	0·1435 (4)	0·047 (2)
C(32)	0·4757 (7)	0·3215 (6)	0·0994 (4)	0·059 (3)
C(33)	0·4501 (9)	0·3642 (6)	0·0317 (5)	0·070 (3)
C(34)	0·338 (1)	0·3814 (7)	0·0020 (5)	0·083 (4)
C(35)	0·2490 (8)	0·3592 (8)	0·0425 (5)	0·081 (3)
C(36)	0·2738 (7)	0·3192 (7)	0·1144 (5)	0·067 (3)
C(37)	0·3214 (5)	0·0185 (5)	0·2715 (4)	0·044 (2)
C(38)	0·3432 (6)	−0·0778 (6)	0·2570 (5)	0·056 (3)
C(39)	0·5092 (7)	−0·2680 (7)	0·2140 (6)	0·081 (3)
C(40)	0·299 (1)	−0·3088 (8)	0·2953 (8)	0·122 (5)
C(41)	0·266 (1)	−0·2881 (8)	0·1142 (6)	0·114 (5)
Cl(1)	0·8191 (5)	0·4698 (5)	0·2266 (3)	0·229 (3)
Cl(2)	0·9689 (5)	0·4911 (7)	0·1138 (6)	0·317 (5)
Cl(3)	0·891 (1)	0·2823 (7)	0·1328 (5)	0·388 (8)
C(100)	0·9424 (7)	0·4267 (6)	0·1805 (6)	0·122 (6)
(Disordered CH_2Cl_2)				
Cl(4)	0·1308 (8)	0·9941 (7)	0·0334 (8)	0·224 (3)
Cl(5)	0·0137 (9)	1·1257 (7)	0·1243 (8)	0·224 (3)
C(101)	−0·0044 (8)	1·0107 (8)	0·0332 (9)	0·224 (3)

The computations were carried out on the CDC-CYBER 855 computer of the University of Utrecht with programs of the *SHELX76* (Sheldrick, 1976) and *EUCLID* packages (Spek, 1982).

Discussion. The crystal structure consists of a triclinic unit cell, containing two molecules of the title com-

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44285 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pound, two chloroform molecules and one dichloromethane molecule that is disordered over an inversion centre. Fig. 1 shows the geometry of the title compound. Selected interatomic distances, bond angles and torsion angles appear in Table 2. The *trans*-positioned trimethylsilylethynyl moiety and Br are σ-bonded to Pd. The environment of Pd is approximately square-planar, the Pd, P(1), P(2), C(37) and Br are coplanar within 0·2 Å. The chloroform molecule donates its H atom to the Br atom of the $PdBr[PPh_3]_2[C{\equiv}CSiMe_3]$ molecule. [H(100)···Br = 2·696 (2) Å, C(100)—H(100)···Br = 153·5 (1)°]. The chloroform solvate of *N*-(diethylaminoethyl)salicylaldiminatobromocopper(II) also shows such an interaction (Elias, Hilms & Paulus, 1982) (H···Br = 2·677 Å, C—H···Br = 140·3°).

The Pd—P bond distances [2·327 (2) Å and 2·333 (2) Å] lie in the range (2·319–2·342 Å) that is reported for other square-planar Pd compounds (Del Piero & Cesari, 1979; McCrindle, Ferguson, McAlees, Parvez & Roberts, 1982; Van der Voort, Van der Sluis & Spek, 1987). The observed Pd—Br bond length [2·481 (2) Å] is normal (Kuhn, Burschka & Werner, 1982; Podlahova, Loub & Jecny, 1979; Chui & Powell, 1974).

The Pd—C(*sp*) bond distance of 1·974 (6) Å is somewhat longer than the value of 1·952 (7) Å observed for *o*-ethynylphenylethynylisothiocyanato-*trans*-bis(triethylphosphine)palladium(II) (Behrens & Hoffmann, 1977) but significantly shorter than the distances 2·03 (2) and 2·04 (2) Å reported for [*trans*-$\{(MeO_2C)HC{=}C(Co_2Me)\}Pd(PEt_3)_2(C{\equiv}CPh)$] (Yasuda, Kai, Yasuoka & Kasai, 1977).

The Pd—C≡C—Si chain is slightly bent with Pd—C≡C = 175·0 (6)° and C≡C—Si = 170·6 (7)°, which is not unusual for Pd compounds with σ-bonded acetylenic ligands.

The X-ray data were kindly collected by A. J. M. Duisenberg. Part of this work (ALS) was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

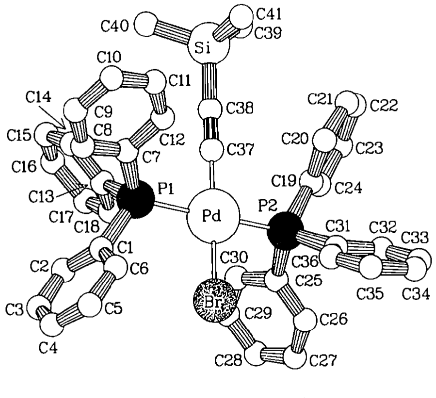

Fig. 1. *PLUTO* drawing (*EUCLID* version) with adopted numbering scheme; hydrogens omitted.

Table 2. *Bond distances* (Å), *angles* (°) *and torsion angles* (°)

Pd—Br	2·481 (2)	Si—C(38)	1·852 (8)
Pd—P(1)	2·327 (2)	Si—C(39)	1·869 (9)
Pd—P(2)	2·333 (2)	Si—C(40)	1·86 (1)
Pd—C(37)	1·974 (6)	Si—C(41)	1·86 (1)
P(1)—C(1)	1·837 (6)	⟨C(1)—C(6)⟩	1·378 (4)
P(1)—C(7)	1·823 (6)	⟨C(7)—C(12)⟩	1·383 (4)
P(1)—C(13)	1·823 (6)	⟨C(13)—C(18)⟩	1·391 (4)
P(2)—C(19)	1·818 (7)	⟨C(19)—C(24)⟩	1·385 (4)
P(2)—C(25)	1·805 (6)	⟨C(25)—C(30)⟩	1·387 (4)
P(2)—C(31)	1·825 (7)	⟨C(31)—C(36)⟩	1·380 (5)
C(37)—C(38)	1·16 (1)		
Br—Pd—P(1)	96·28 (5)	Pd—P(2)—C(25)	106·3 (2)
Br—Pd—P(2)	89·30 (5)	Pd—P(2)—C(31)	119·1 (2)
Br—Pd—C(37)	179·2 (2)	C(19)—P(2)—C(25)	105·0 (3)
P(1)—Pd—P(2)	169·23 (6)	C(19)—P(2)—C(31)	100·4 (3)
P(1)—Pd—C(37)	83·4 (2)	C(25)—P(2)—C(31)	107·2 (3)
P(2)—Pd—C(37)	90·9 (2)	C(38)—Si—C(39)	111·9 (4)
Pd—P(1)—C(1)	117·1 (2)	C(38)—Si—C(40)	108·7 (4)
Pd—P(1)—C(7)	117·7 (2)	C(38)—Si—C(41)	106·7 (4)
Pd—P(1)—C(13)	108·6 (2)	C(39)—Si—C(40)	110·5 (5)
C(1)—P(1)—C(7)	101·4 (3)	C(39)—Si—C(41)	107·0 (5)
C(1)—P(1)—C(13)	103·8 (3)	C(40)—Si—C(41)	111·9 (5)
C(7)—P(1)—C(13)	107·0 (3)	Pd—C(37)—C(38)	175·0 (6)
Pd—P(2)—C(19)	117·7 (2)	Si—C(38)—C(37)	170·6 (7)
C(37)—Pd—P(1)—C(1)	174·2 (3)	Pd—P(1)—C(1)—C(6)	65·4 (6)
C(37)—Pd—P(1)—C(7)	−64·5 (3)	Pd—P(1)—C(7)—C(12)	15·7 (6)
C(37)—Pd—P(1)—C(13)	57·2 (3)	Pd—P(1)—C(13)—C(18)	42·7 (5)
C(37)—Pd—P(2)—C(19)	0·3 (3)	Pd—P(2)—C(19)—C(20)	65·5 (6)
C(37)—Pd—P(2)—C(25)	−117·0 (3)	Pd—P(2)—C(25)—C(30)	45·7 (5)
C(37)—Pd—P(2)—C(31)	121·9 (3)	Pd—P(2)—C(31)—C(36)	6·0 (7)

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