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Structures of Two Polymorphs of *cis*-$TaBr_4(PhPMe_2)_2$

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Abstract. The title compound, tetrabromobis[dimethyl(phenyl)phosphine]tantalum(IV), $[TaBr_4(C_8H_{11}P)_2]$, $M_r = 776{\cdot}89$, is polymorphic. Monoclinic (1), $P2_1/c$, $a = 8{\cdot}493\,(8)$, $b = 30{\cdot}369\,(9)$, $c = 8{\cdot}898\,(5)$ Å, $\beta = 99{\cdot}22\,(2)°$, $V = 2265{\cdot}5$ Å^3, $Z = 4$, $D_x = 2{\cdot}28$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 119{\cdot}2$ cm^{-1}, $F(000) = 1444$, room temperature, $R = 0{\cdot}0514$ for 2065 observed reflections. Orthorhombic (2), $P2_12_12_1$, $a = 14{\cdot}38\,(1)$, $b = 19{\cdot}17\,(1)$, $c = 8{\cdot}28\,(2)$ Å, $V = 2282{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}28$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 119{\cdot}2$ cm^{-1}, $F(000) = 1444$, room temperature, $R = 0{\cdot}0455$ for 1448 observed reflections. The structures of the two forms (1) and (2) consist of octahedrally coordinated Ta atoms with comparable values of interatomic distances, and differ mainly in the angles between the average planes of the phenyl groups: 10·1 and 42·6°, respectively. The crystals were obtained by reduction of $TaBr_5$ with either one or two equivalents of sodium amalgam in toluene and in the presence of the phosphorus ligand.

Experimental. All compounds are air sensitive; manipulations were performed under argon with anhydrous and deoxygenated solvents. Sodium amalgam (95 mg, 9·4 ml) was added to $TaBr_5$ (Alfa Inorganics) (825 mg) in 30 ml toluene and $PhPMe_2$ (Aldrich) (0·75 ml) at room temperature. Stirring was maintained for 2 h, and after filtration and concentration, diffusion of pentane at room temperature offered 450 mg (35%) of brown-red needles of *cis*-$TaBr_4(PhPMe_2)_2$, (1). A comparable reduction applied to $TaBr_5$ (0·723 g) in 20 ml toluene and $PhPMe_2$ (0·60 ml) with one equivalent of sodium amalgam gave, after $3\frac{1}{2}$ h reaction time, an olive-green filtrate. Concentration induced formation of crystals of different shapes, corresponding mainly to *cis*-$TaBr_4(PhPMe_2)_2$, (2), while (1) appears as a minor compound. Analysis: Calc. for $C_{16}H_{22}Br_4P_2Ta$: C: 24·74 H: 2·83 P: 7·97 Br: 41·16. Found: C: 24·40 H: 2·82 P: 7·15 Br: 38·58.

The monocrystals were introduced under argon into sealed Lindemann capillaries and mounted on an Enraf–Nonius automatic diffractometer. The basic information about data collection and structural refinement is shown in Table 1. Cell parameters from setting angles of 25 reflections ($2° \leq \theta \leq 25°$) for (1) and for (2). Range of *hkl*: −10, 10; 0, 36; 0, 10 for (1) and 0, 17; 0, 22; 0, 9 for (2). Three standard reflections showed some decay of intensities [total loss of 6·1% during 48 h of exposure time for (1) and of 16·2% during 29 h for (2)]. A time-decay correction was applied for both. Lorentz and polarization effects were corrected. An empirical absorption correction, using *DIFABS* (Walker & Stuart, 1983), was applied for (2), no correction for (1).

The structures were solved on a PD11/60 computer using the Enraf–Nonius *SDP* package (Frenz, 1982). Atomic positions were found with *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier maps. Atomic scattering factors and anomalous-dispersion values were obtained from *International Tables for X-ray Crystallography* (1974). Anisotropic thermal parameters were used for all non-H atoms for (1) and for (2). H atoms were introduced in calculated (and non-refined) positions for (1), but not for (2) (low parameter-to-data ratio). Final max. shift/e.s.d. <0·02 for (1) and (2), final residual electron density 3·05 e Å^{-3} (near Ta)

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Table 1. *Intensity collection for cis*-$TaBr_4(PhPMe_2)_2$

Compound	$TaBr_4(PMe_2Ph)_2$ (1) (red)	$TaBr_4(PMe_2Ph)_2$ (2) (orange)
Crystal dimensions (mm)	0·42 × 0·40 × 0·40	0·51 × 0·33 × 0·20
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Scan type	ω–2θ	ω–2θ
Scan range (°)	1·00 + 0·35 tanθ	1·00 + 0·35 tanθ
θ limits (°)	1–25	1–25
Data collected	4342	2312
Unique data used	2065 [$I > 3\sigma(I)$]	1448 [$I > 3\sigma(I)$]
R	0·0514	0·0455
wR	0·0606	0·0535
Standard error of a unit weight observation (e)	1·87	2·12

for (1) and 2·1 e Å^{-3} (near Ta) for (2). Final values of R and wR are given in Table 1. For (2), refinement was achieved by block-approximation least-squares calculations on F with constraints (Waser, 1963; Rollett, 1969) applied to ill-resolved structural features. For the phenyl rings, unconstrained refinement led to unreasonable bond lengths and large discrepancy between the isotropic thermal parameters of C atoms. These problems were certainly related to the poor quality of the data. The following constraints were applied using the *CRYSTALS* package (Watkin, Carruthers & Betteridge, 1985): (*a*) C—C = 1·390 (4) Å, (*b*) C—C—C = 120 (1)°, (*c*) the phenyl rings to be planar with an e.s.d. of 0·01 Å, (*d*) the difference in r.m.s. amplitude of vibration in the direction of the C—C bond of two bonded C atoms in the ring to be 0·00 (1) Å^2. The weighting scheme used was $w = 1/\sum_{r=1}^{3} A_rT_r(X)[1 - \Delta F/6\sigma(F)^2]^2$ with three coefficients A_r (6·24, −2·13, 4·695), for the Chebyshev polynomial $T_r(X)$ where X is $F_c/F_c(\max)$ (Prince, 1982). Final atomic coordinates and equivalent isotropic thermal parameters are shown in Tables 2 and 3* for (1) and (2) respectively.

Table 2. *Atomic and isotropic thermal parameters of cis*-$TaBr_4(PhPMe_2)_2$ (1) *with e.s.d.'s in parentheses*

	x	y	z	B (Å^2)
Ta	−0·00012 (7)	0·12351 (2)	0·25369 (7)	3·12 (1)
Br1	0·2580 (2)	0·16384 (7)	0·3503 (2)	6·28 (5)
Br2	0·0274 (3)	0·07989 (7)	0·4991 (2)	6·81 (5)
Br3	0·1293 (2)	0·07248 (6)	0·0953 (2)	5·40 (4)
Br4	−0·1941 (2)	0·17569 (6)	0·3324 (2)	5·45 (4)
P1	−0·2455 (4)	0·0706 (1)	0·1677 (4)	3·24 (8)
P2	−0·0210 (5)	0·1793 (1)	0·0208 (5)	3·60 (9)
C1	−0·403 (2)	0·0787 (7)	0·276 (2)	5·6 (5)
C2	−0·195 (2)	0·0133 (5)	0·205 (2)	5·0 (4)
C3	−0·341 (2)	0·0694 (5)	−0·031 (2)	3·3 (3)
C4	−0·488 (2)	0·0912 (6)	−0·079 (2)	4·1 (4)
C5	−0·565 (2)	0·0868 (6)	−0·224 (2)	4·8 (4)
C6	−0·497 (2)	0·0640 (6)	−0·329 (2)	5·3 (4)
C7	−0·352 (2)	0·0436 (6)	−0·288 (2)	5·6 (5)
C8	−0·275 (2)	0·0482 (6)	−0·138 (2)	4·5 (4)
C9	0·038 (2)	0·2347 (6)	0·087 (2)	6·8 (5)
C10	0·113 (2)	0·1663 (7)	−0·111 (2)	6·6 (5)
C11	−0·212 (2)	0·1889 (5)	−0·095 (2)	3·1 (3)
C12	−0·253 (2)	0·1704 (5)	−0·239 (2)	4·0 (4)
C13	−0·399 (2)	0·1790 (6)	−0·328 (2)	4·6 (4)
C14	−0·507 (2)	0·2051 (6)	−0·275 (2)	4·7 (4)
C15	−0·468 (2)	0·2226 (5)	−0·134 (2)	4·5 (4)
C16	−0·325 (2)	0·2156 (5)	−0·046 (2)	3·8 (4)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (4/3) \times [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. *Atomic and isotropic thermal parameters of cis*-$TaBr_4(PhPMe_2)_2$ (2) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11}U_{12}U_{33})^{1/3}$.

	x	y	z	U_{eq}
Ta(1)	0·04718 (7)	0·27998 (5)	−0·0842 (1)	0·0357
Br(1)	−0·0283 (2)	0·3996 (2)	−0·0808 (5)	0·0616
Br(2)	−0·0394 (3)	0·2489 (2)	0·1720 (4)	0·0602
Br(3)	−0·0639 (2)	0·2282 (2)	−0·2825 (4)	0·0647
Br(4)	0·1984 (2)	0·3083 (2)	0·0388 (4)	0·0514
P(1)	0·0993 (6)	0·1479 (4)	−0·0590 (9)	0·0477
P(2)	0·1303 (6)	0·3231 (4)	−0·3542 (8)	0·0444
C(1)	0·166 (3)	0·131 (2)	0·127 (4)	0·0576
C(2)	0·002 (3)	0·088 (2)	−0·040 (4)	0·0619
C(3)	0·172 (1)	0·1093 (7)	−0·231 (2)	0·0506
C(4)	0·119 (1)	0·0785 (8)	−0·351 (2)	0·0599
C(5)	0·176 (2)	0·0547 (7)	−0·475 (2)	0·0702
C(6)	0·273 (2)	0·0627 (8)	−0·467 (2)	0·0748
C(7)	0·320 (1)	0·0948 (8)	−0·339 (3)	0·0769
C(8)	0·266 (1)	0·1199 (7)	−0·213 (2)	0·0641
C(9)	0·054 (3)	0·368 (2)	−0·490 (5)	0·0655
C(10)	0·179 (3)	0·255 (2)	−0·477 (3)	0·0461
C(11)	0·226 (1)	0·3916 (9)	−0·337 (2)	0·0562
C(12)	0·194 (1)	0·454 (1)	−0·270 (2)	0·0628
C(13)	0·261 (2)	0·5058 (9)	−0·261 (2)	0·0734
C(14)	0·350 (2)	0·490 (1)	−0·319 (2)	0·0755
C(15)	0·375 (1)	0·425 (1)	−0·385 (2)	0·0777
C(16)	0·311 (2)	0·371 (1)	−0·397 (2)	0·0709

Discussion. Crystals of *cis*-$TaBr_4(PhPMe_2)_2$, suitable for X-ray analysis, were grown from the reaction medium resulting from the reduction of $TaBr_5$ with sodium amalgam in toluene and in the presence of an excess of the phosphine $PhPMe_2$. This adduct crystallizes as two different forms, namely as red-brown needles [monoclinic, (1)] or as orange-red polyhedra [orthorhombic, (2)]. The atomic labelling scheme is defined in Fig. 1 for both crystalline forms. Selected bond distances and angles are collected in Table 4. The monoclinic form is isomorphous with the chloro counterpart *cis*-$TaCl_4(PhPMe_2)_2$ (Cotton, Duraj & Roth, 1984), while the overall molecular geometry is analogous to it for both crystallographic forms. The tantalum(IV) centre has a pseudo-octahedral surrounding, with quite similar average values of bond distances and angles. The Ta—Br bond *trans* to P is larger than the Ta—Br bond *trans* to Br, as also observed for the metal–chlorine bonds of $TaCl_4(PhPMe_2)_2$. The tantalum–phosphorus lengths display the usual values observed for Ta^{IV} as well as Ta^{III} adducts (Sattelberger, Wilson & Huffman, 1982). The relative orientation of the phenyl groups

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* Lists of structure factors, anisotropic thermal parameters, non-essential ligand parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52721 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the two *cis* phosphorus ligands [angles between the average planes of 10·1 and 42·6° in (1) and (2), respectively] represents the main difference between the two crystalline forms.

We believe that the polymorphism is due mainly to that difference of conformation of the molecule which results from changing the conditions under which the compounds are crystallized. Although the Ta···Me distances are shorter than the Ta···Ph ones, their values [Ta···C_1, Ta···C_2: 3·729, 3·726; 3·740 and 3·765 Å for (1) and (2), respectively] exclude agostic CH→Ta interactions (Brookart & Green, 1983).

It is surprising that all bis[dimethyl(phenyl)-phosphine] Ta^{IV} adducts display a *cis* geometry. $TaCl_4(PEt_3)_2$ (Cotton, Duraj & Roth, 1984) is so far the only Ta^{IV} phosphine adduct for which a *trans* geometry has been established by X-ray analysis, but a similar geometry has also been suggested for $MCl_4(PBu_3)_2$ (M = Nb, Ta) on the basis of ESR data (Samuel, Labauze & Livage, 1977). The steric requirement of the ligand probably determines the geometry of these adducts.

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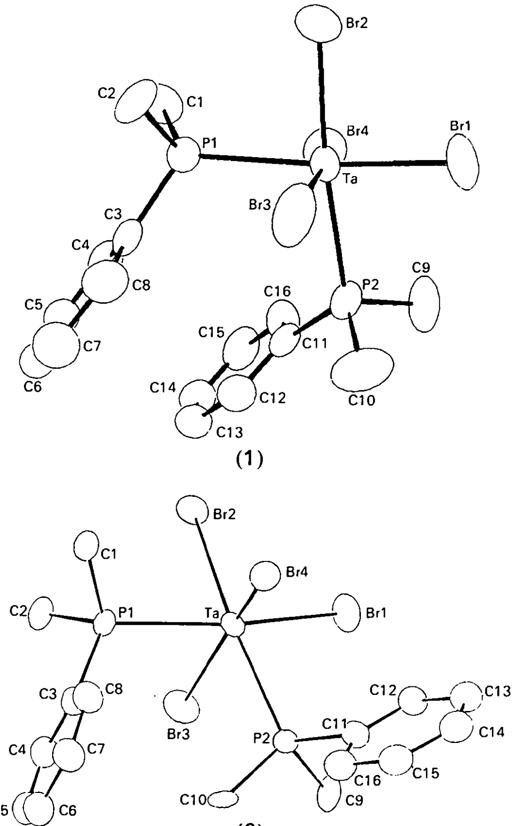

(1)

(2)

Fig. 1. *ORTEP* drawings of the *cis*-$TaBr_4(PhPMe_2)_2$ molecules [(1) and (2)] showing the non-H atoms.

Table 4. *Selected bond lengths* (Å) *and angles* (°) *in* *cis*-$TaBr_4(PhPMe_2)_2$ *with e.s.d.'s in parentheses*

Coordination polyhedron			
Monoclinic (1)		Orthorhombic (2)	
Ta—Br1	2·538 (1)	Ta—Br1	2·534 (3)
Ta—Br2	2·533 (1)	Ta—Br2	2·529 (3)
Ta—Br3	2·468 (1)	Ta—Br3	2·495 (2)
Ta—Br4	2·467 (1)	Ta—Br4	2·461 (2)
Ta—P1	2·645 (3)	Ta—P1	2·645 (5)
Ta—P2	2·660 (3)	Ta—P2	2·665 (6)
Br1—Ta—Br2	90·29 (5)	Br1—Ta—Br2	89·5 (1)
Br1—Ta—Br3	93·27 (5)	Br1—Ta—Br3	95·11 (8)
Br1—Ta—Br4	99·99 (5)	Br1—Ta—Br4	100·1 (1)
Br1—Ta—P1	171·40 (8)	Br1—Ta—P1	169·8 (2)
Br1—Ta—P2	84·41 (8)	Br1—Ta—P2	85·5 (2)
Br2—Ta—Br3	100·14 (6)	Br2—Ta—Br3	98·2 (1)
Br2—Ta—Br4	93·70 (6)	Br2—Ta—Br4	98·1 (1)
P1—Ta—P2	102·13 (9)	P1—Ta—P2	103·6 (2)
Br2—Ta—P1	83·77 (7)	Br2—Ta—P1	81·3 (2)
Br2—Ta—p2	171·92 (8)	Br2—Ta—P2	175·0 (2)
Br3—Ta—Br4	160·77 (6)	Br3—Ta—Br4	157·7 (1)
Br3—Ta—P1	81·71 (7)	Br3—Ta—P1	81·6 (2)
Br3—Ta—P1	86·63 (8)	Br3—Ta—P2	81·9 (2)
Br4—Ta—P1	86·63 (7)	Br4—Ta—P1	85·9 (2)
Br4—Ta—P2	81·26 (8)	Br4—Ta—P2	83·2 (2)
Ligand parameters			
P1—C1	1·789 (12)	P1—C1	1·86 (3)
P1—C2	1·811 (12)	P1—C2	1·81 (4)
P1—C3	1·822 (11)	P1—C3	1·91 (2)
P2—C9	1·827 (14)	P2—C9	1·80 (4)
P2—C10	1·804 (13)	P2—C10	1·80 (3)
P2—C11	1·799 (11)	P2—C11	1·90 (2)
C1—P1—C2	102·1 (7)	C1—P1—C2	102·3 (16)
C1—P1—C3	105·5 (5)	C1—P1—C3	105·3 (12)
C2—P1—C3	102·4 (6)	C2—P1—C3	103·9 (13)
C9—P2—C10	104·2 (8)	C9—P2—C10	105·1 (10)
C9—P2—C11	102·1 (6)	C9—P2—C11	99·1 (12)
C10—P2—C11	105·4 (6)	C10—P2—C11	105·1 (13)

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