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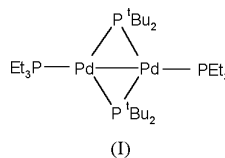
## Key indicators

Single-crystal X-ray study  
T = 233 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$   
R factor = 0.043  
wR factor = 0.134  
Data-to-parameter ratio = 22.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis( $\mu$ -di-*tert*-butylphosphido)bis[(triethylphosphine)palladium(I)](*Pd*—*Pd*)

The title compound,  $[\text{Pd}_2(\text{C}_8\text{H}_{18}\text{P})_2(\text{C}_6\text{H}_{15}\text{P})_2]$ , has been obtained by the reaction of di-*tert*-butylphosphine–phosphanylidene- $\sigma^4$ -di-*tert*-butyl(methyl)phosphorane and bis(triethylphosphine)palladium(II) chloride with sodium naphthalide.  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{PEt}_3)\}_2](\text{Pd}-\text{Pd})$  is not a primary product. It crystallizes in space group  $P\bar{1}$  with one molecule in the unit cell. The molecule has a centre of symmetry at the mid-point of the Pd—Pd bond.

## Comment

Di-*tert*-butylphosphine–phosphanylidene- $\sigma^4$ -di-*tert*-butyl(methyl)phosphorane,  ${}^t\text{Bu}_2\text{P}-\text{P}=\text{P}^t\text{Bu}_2(\text{Me})$  is a convenient source for the di-*tert*-butylphosphine-phosphanylidene ligand  ${}^t\text{Bu}_2\text{P}-\text{P}$  (Fritz & Scheer, 2000; Olkowska-Oetzel & Pikies, 2003). Until now only the  $\text{Pt}^0 d^{10} ML_2$  metal centre was found to be capable of stabilizing this ligand (Krautscheid *et al.*, 1997). Despite having many quite similar properties, the  $\text{Pd}^0 d^{10} ML_2$  centre does not stabilize this species. In the reaction of  ${}^t\text{Bu}_2\text{P}-\text{P}=\text{P}^t\text{Bu}_2(\text{Me})$  and  $(\text{Et}_3\text{P})_2\text{PdCl}_2$  with Na/naphthalide, crystalline  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{PEt}_3)\}_2](\text{Pd}-\text{Pd})$ , (I), was isolated, among other products which could not be fully characterized, instead of the expected product  $(\text{Et}_3\text{P})_2\text{Pd}(\eta^2\text{-}{}^t\text{Bu}_2\text{P}-\text{P})$ .



The molecular structure of (I) is shown in Fig. 1. There is a centre of symmetry at the mid-point of the Pd—Pd bond. To the best of our knowledge, only three similar examples are known, *viz.*  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{PMe}_3)\}_2](\text{Pd}-\text{Pd})$  (Arif *et al.*, 1987),  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{P}^t\text{Bu}_2\text{H})\}_2](\text{Pd}-\text{Pd})$  (Leoni *et al.*, 1992) and  $[\{\text{Pd}(\mu\text{-P}^c\text{Hex}_2)(\text{P}^c\text{Hex}_2\text{OPh})\}_2](\text{Pd}-\text{Pd})$  (Sommovigo *et al.*, 1994). The Pd—Pd distance of 2.5782 (9) Å in (I) is slightly longer than in  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{PMe}_3)\}_2](\text{Pd}-\text{Pd})$  (2.571 Å). The P2—Pd—Pd angle of 179.95 (6)° in (I) is similar to the  $\text{Me}_3\text{P}-\text{Pd}-\text{Pd}$  angle in  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{PMe}_3)\}_2](\text{Pd}-\text{Pd})$  (178.4°). For related complexes with bulky phosphine ligands, a significant deviation of the  $R_3\text{P}-\text{Pd}-\text{Pd}-\text{PR}_3$  moiety from linearity was observed. For  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{P}^t\text{Bu}_2\text{H})\}_2](\text{Pd}-\text{Pd})$  the  ${}^t\text{Bu}_2(\text{H})\text{P}-\text{Pd}-\text{Pd}$  angle is 173.2° and for  $[\{\text{Pd}(\mu\text{-P}^c\text{Hex}_2)(\text{P}^c\text{Hex}_2\text{OPh})\}_2](\text{Pd}-\text{Pd})$  the corresponding P—Pd—Pd angle is 170.5°.

## Experimental

The title compound was obtained using standard Schlenk methods under an atmosphere of carefully purified nitrogen: 4.1 ml of a 0.18 M solution of Na/naphthalide was added dropwise to a solution of 0.144 g (0.439 mmol)  $(\text{Et}_3\text{P})_2\text{PdCl}_2$  and 0.059 g (0.174 mmol)  ${}^t\text{Bu}_2\text{P}=\text{P}=\text{P}{}^t\text{Bu}_2(\text{Me})$  in 6 ml tetrahydrofuran. This solution turned slowly dark while it was stirred for 2 d at room temperature. The reaction mixture was evaporated to dryness in vacuum and naphthalene was sublimed from the residue. The residue was dissolved in  $\text{Et}_2\text{O}$ , filtered and recrystallized three times at 229 K from  $\text{Et}_2\text{O}$ , yielding a small amount of  $[\{\text{Pd}(\mu\text{-P}{}^t\text{Bu}_2)(\text{PEt}_3)_2\}_2(\text{Pd}-\text{Pd})]$ .  ${}^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.86 [PCH<sub>2</sub>, *d* of quartets,  ${}^2J(\text{H,H}) = 5$  Hz,  ${}^2J(\text{P,H}) = 3$  Hz],  $\delta$  1.52 ( ${}^t\text{Bu}_2\text{P}$ , pseudo-*t*,  $J = 5.7$  and 6.1 Hz),  $\delta$  1.12 [CH<sub>3</sub>, *d* of *t*,  ${}^2J(\text{H,H}) = 5$  Hz,  ${}^3J(\text{P,H}) = 7.6$  Hz];  ${}^{31}\text{P}$  { ${}^1\text{H}$ } NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  284.9 [PEt<sub>3</sub>, *t*,  ${}^2J(\text{P,P}) = 38.1$  Hz],  $\delta$  14.6 ( ${}^t\text{Bu}_2\text{P}$ , *t*)  ${}^{13}\text{C}$  { ${}^1\text{H}$ } ( $\text{C}_6\text{D}_6$ ):  $\delta$  34.2 (P ${}^t\text{Bu}_2$ , CH<sub>3</sub>, *t*,  $J = 6.1$  Hz),  $\delta$  30.9 ( ${}^t\text{Bu}_2\text{P}$ , C, *s*),  $\delta$  23.5 (PCH<sub>2</sub>, *d* of *t*),  $\delta$  10.2 (CH<sub>3</sub>, *s*).

### Crystal data

$[\text{Pd}_2(\text{C}_8\text{H}_{18}\text{P})_2(\text{C}_6\text{H}_{15}\text{P})_2]$	$Z = 1$
$M_r = 739.53$	$D_x = 1.327 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9820$ (9) Å	Cell parameters from 24 reflections
$b = 10.935$ (2) Å	$\theta = 11\text{--}14^\circ$
$c = 11.296$ (2) Å	$\mu = 1.16 \text{ mm}^{-1}$
$\alpha = 114.15$ (1) $^\circ$	$T = 233$ (1) K
$\beta = 103.67$ (1) $^\circ$	Cut fragment, red
$\gamma = 101.72$ (1) $^\circ$	$0.40 \times 0.25 \times 0.25 \text{ mm}$
$V = 925.8$ (3) Å <sup>3</sup>	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.019$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 26.0^\circ$
Absorption correction: $\psi$ scans (North <i>et al.</i> , 1968)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.695$ , $T_{\text{max}} = 0.749$	$k = -13 \rightarrow 13$
4955 measured reflections	$l = -13 \rightarrow 4$
3623 independent reflections	3 standard reflections
3266 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 0.5%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 8P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.30 \text{ e \AA}^{-3}$
3617 reflections	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$
163 parameters	
H-atom parameters constrained	

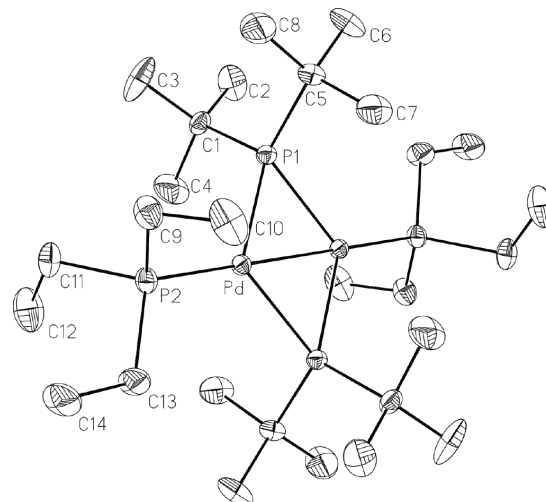
**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

Pd—P2	2.2584 (15)	Pd—P1	2.3293 (16)
Pd—P1 <sup>i</sup>	2.3240 (17)	Pd—Pd <sup>i</sup>	2.5782 (9)
P2—Pd—P1 <sup>i</sup>	123.52 (6)	P1 <sup>i</sup> —Pd—Pd <sup>i</sup>	56.45 (4)
P2—Pd—P1	123.77 (6)	P1—Pd—Pd <sup>i</sup>	56.26 (4)
P1 <sup>i</sup> —Pd—P1	112.71 (5)	Pd <sup>i</sup> —P1—Pd	67.29 (5)
P2—Pd—Pd <sup>i</sup>	179.95 (6)		

Symmetry code: (i)  $1 - x, 2 - y, 1 - z$ .

Backgrounds were obtained from analysis of the scan profile (Blessing *et al.*, 1974). All H atoms were treated as riding with fixed



**Figure 1**

The structure of (I) (Johnson, 1976), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 25% probability level and all H atoms have been omitted.

isotropic displacement parameters. The maximum electron-density peak is located 1.16 Å from the Pd atom.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *PROCESS MoLEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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