metal-organic compounds

Tetraallyl (2,2′-bipyridyl)-*rac*-3,3,7,7-tetramethyl-*trans*-5-palladatricyclo-[4.1.0.0^{2,4}]heptane-1,2,4,6-tetra-carboxylate above and below the phase-transition temperature of 194 K

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The crystal structure of the title compound, (2,2′-bipyridyl-$\kappa^2 N,N'$)(tetraallyl 3,3,3′,3′-tetramethyl-1,1′-bicyclopropane-1,1′,-2,2′-tetracarboxylato-$\kappa^2 C^2,C^{2'}$)palladium(II), [Pd(C$_{26}$H$_{32}$-O$_8$)(C$_{10}$H$_8$N$_2$)], is disordered above 194 K. A doubling of the unit cell is observed on cooling. The structure at 143 K contains two ordered molecules related by a pseudo-translation vector of approximately (0.44,0.00,0.50) or a pseudo-inversion center at approximately (0.22,0.00,0.25). Weak intermolecular C—H···O interactions are enhanced in the low-temperature structure.

Comment

In an effort to synthesize the first palladepane derivatives and in the course of an investigation covering polymer-bound organometallic catalysts, we reacted diallyl 3,3-dimethyl-cyclopropene-1,2-dicarboxylate with a Pd^0 compound. One of the two products was the desired palladepane derivative, the other turned out to be the title compound, (I) (Hashmi *et al.*, 1999). Compound (I) is also a promising substrate for the
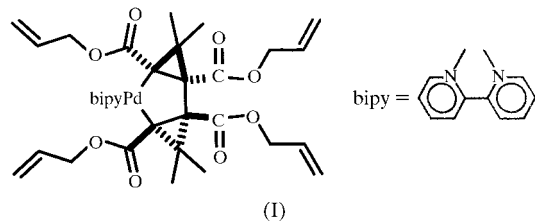
formation of polymer-bound organometallic catalysts by co-metathesis with other 1,*n*-dienes. During X-ray diffraction experiments on (I), a reversible phase transition was observed at 194 K. The crystal structure of the high-temperature phase has been determined at room temperature (292 K) and at 205 K. The high-temperature phase has one molecule in the asymmetric unit (Fig. 1). Two propene side chains are disor-

dered. The structures at 292 and 205 K are similar. Thus, the room-temperature results are not reported here.

The crystal structure of the low-temperature phase has been determined at 143 K. At this temperature, the crystal structure contains two independent ordered molecules (Fig. 2). The cell axes transform according to: $a_{\text{low}} = a_{\text{high}}$, $b_{\text{low}} = -c_{\text{high}}$ and $c_{\text{low}} = 2b_{\text{high}} - a_{\text{high}}$. The fractional coordinates between the low- and the high-temperature phases are related by: $x_{\text{low}} = x_{\text{high}} + \frac{1}{2}y_{\text{high}}$, $y_{\text{low}} = -z_{\text{high}}$ and $z_{\text{low}} = \frac{1}{2}y_{\text{high}}$. Thus, the low-temperature structure should be approximately B-centered. Surprisingly, the reflection intensities do not show approximate B-centering. The two independent molecules are related by a pseudo-translation of about (0.44,0.00,0.50).

A combination of this pseudo-translation vector with the crystallographic inversion center at (0,0,0) results in a non-crystallographic pseudo-inversion center at (0.22,0.00,0.25) (Desiraju *et al.*, 1991). The presence of this pseudo-center is confirmed by the program *BUNYIP* (Hester & Hall, 1996). The conformations of both independent molecules are very similar. The molecules differ mainly in the orientations of the propene groups attached to O2, O10, O8 and O16. Those are the propene groups which are disordered above the phase-transition temperature. Below the phase-transition temperature, both molecules are fully ordered. The conformations of the molecules in the high-temperature and low-temperature phases are compared in Fig. 3. This figure shows the relative positions of the molecules of the low-temperature structure as they would appear in the high-temperature cell. The phase transition not only corresponds to an order–disorder transition of the two propene side chains, but also results in small translations of the molecules along **a**. Thus, the deviation from
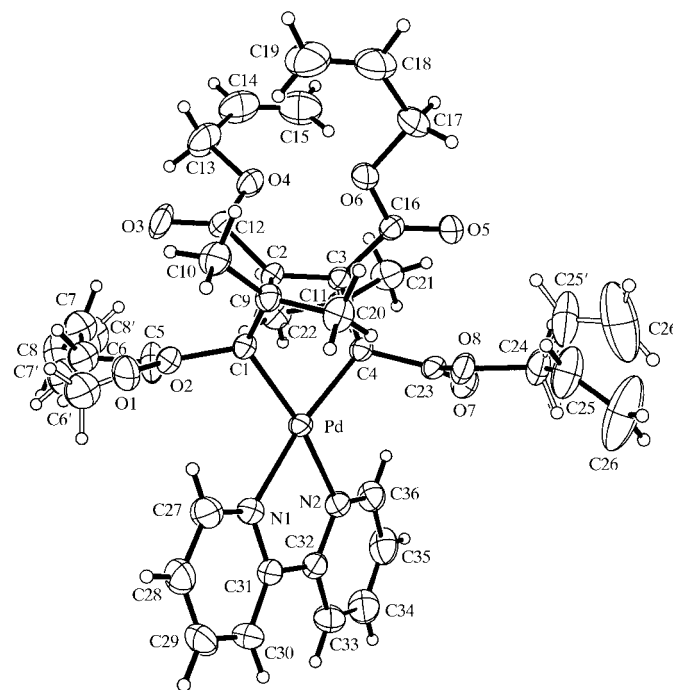

Figure 1
The partly disordered molecule of (I) at 205 K with 50% probability displacement ellipsoids.

ideal *B*-centering of the low-temperature structure results from molecular rearrangements at the phase transition. Both molecules have approximately *C*2 symmetry. The propene side chains, however, show considerable deviations from this *C*2
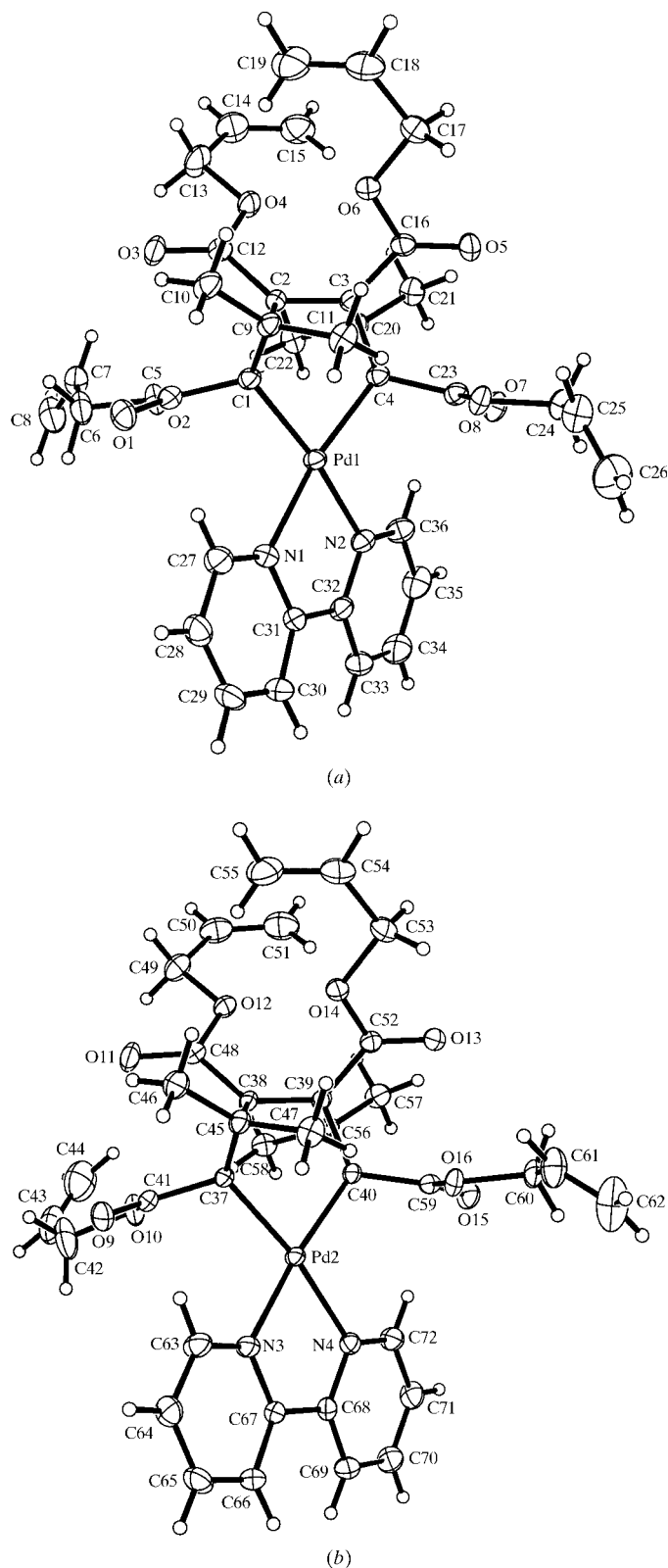

(a)

(b)

Figure 2
The two independent molecules of (I) at 143 K with 50% probability displacement ellipsoids.
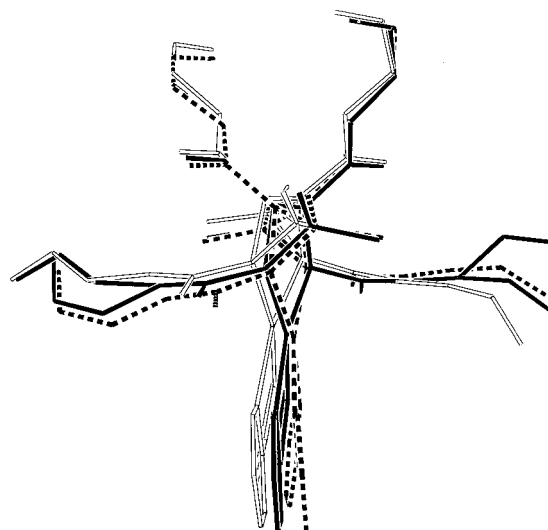

Figure 3
The relative positions of the two independent molecules of the low-temperature structure (open lines: molecule 1, dashed lines: molecule 2) transformed to the high-temperature setting (solid lines: disordered molecule at 205 K).

symmetry. The bipyridyl groups are non-planar; the angle between the planes of the pyridyl groups is 15.6 (1)° for molecule 1 and 11.0 (1)° for molecule 2. The Pd atoms have heavily distorted square-planar conformations. The angle between the C—Pd—C and N—Pd—N planes is 16.9 (1)° for molecule 1 and 15.0 (1)° for molecule 2. The non-planarity of the Pd atoms may result from intramolecular C—H···O interactions: O1···H27 2.33, O7···H36 2.41, O9···H63 2.28 and O15···H72 2.39 Å (see Table 1 for intra- and inter-molecular C—H···O interactions).

Intramolecular C—H···O interactions very similar to those in the title compound have been observed in the crystal structures of related palladatricyclo[4.1.0.0^{2,4}]heptanes (Hashmi *et al.*, 1997; Hashmi, Naumann & Bats, 1997; Hashmi *et al.*, 1998; Hashmi, Naumann & Bolte, 1998; Hashmi, Bats *et al.*, 1998). Thus, these interactions appear characteristic for this group. The crystal packing shows a number of weak intermolecular C—H···O interactions, with H···O distances between 2.5 and 2.6 Å. These interactions have been included in Table 1. Desiraju & Steiner (1999) have outlined the significance of such weak intermolecular interactions for crystal packing. All four weak intermolecular C—H···O interactions involve propene side chains. In the high-temperature structure, such weak intermolecular C—H···O interactions are only observed for two partially occupied propene groups (Table 2). Thus, the phase transition results in an enhancement of intermolecular C—H···O interactions below the transition temperature. A determination of the cell constants just above and below the phase-transition temperature shows no significant change in the volume occupied by a molecule. A similar result has been reported for an order–disorder transition by Thuéry *et al.* (1999). Herbstein & Samson (1994) showed this to be a prerequisite for a second-order transition.

metal-organic compounds

Experimental

Compound (I) was prepared according to the method of Hashmi *et al.* (1999). Crystals suitable for X-ray diffraction analysis were obtained by crystallization from a hexane/dichloromethane solution at 277 K.

Compound (I) at 143 K

Crystal data

[Pd(C$_{26}$H$_{32}$O$_8$)(C$_{10}$H$_8$N$_2$)]	$Z = 4$
$M_r = 735.10$	$D_x = 1.435$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.0197\ (6)$ Å	Cell parameters from 276
$b = 17.918\ (2)$ Å	reflections
$c = 21.375\ (3)$ Å	$\theta = 3$–$23°$
$\alpha = 95.641\ (12)°$	$\mu = 0.599$ mm^{-1}
$\beta = 97.375\ (11)°$	$T = 143\ (2)$ K
$\gamma = 93.083\ (9)°$	Plate, yellow
$V = 3401.7\ (7)$ Å^3	$0.44 \times 0.17 \times 0.04$ mm

Data collection

Siemens SMART diffractometer	$R_{int} = 0.059$
ω scans	$\theta_{max} = 32.2°$
Absorption correction: numerical	$h = -13 \rightarrow 13$
(*SHELXTL*; Sheldrick, 1996)	$k = -26 \rightarrow 24$
$T_{min} = 0.817$, $T_{max} = 0.977$	$l = -32 \rightarrow 31$
64 204 measured reflections	703 standard reflections
22 046 independent reflections	frequency: 1200 min
16 183 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.010$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
$wR(F^2) = 0.101$	$\Delta\rho_{min} = -0.61$ e Å^{-3}
$S = 1.212$	Extinction correction: *SHELXL*97
22 046 reflections	(Sheldrick, 1997)
856 parameters	Extinction coefficient: 0.00053 (14)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Compound (I) at 205 K

Crystal data

[Pd(C$_{26}$H$_{32}$O$_8$)(C$_{10}$H$_8$N$_2$)]	$Z = 2$
$M_r = 735.10$	$D_x = 1.422$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9583\ (8)$ Å	Cell parameters from 155
$b = 11.3245\ (18)$ Å	reflections
$c = 17.906\ (3)$ Å	$\theta = 3$–$23°$
$\alpha = 83.438\ (16)°$	$\mu = 0.594$ mm^{-1}
$\beta = 88.482\ (14)°$	$T = 205\ (2)$ K
$\gamma = 72.118\ (16)°$	Plate, yellow
$V = 1717.4\ (4)$ Å^3	$0.44 \times 0.17 \times 0.04$ mm

Data collection

Siemens SMART diffractometer	$R_{int} = 0.070$
ω scans	$\theta_{max} = 31.2°$
Absorption correction: numerical	$h = -12 \rightarrow 13$
(*SHELXTL*; Sheldrick, 1996)	$k = -15 \rightarrow 16$
$T_{min} = 0.791$, $T_{max} = 0.977$	$l = -24 \rightarrow 26$
31 971 measured reflections	444 standard reflections
10 543 independent reflections	frequency: 1200 min
8751 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
$wR(F^2) = 0.101$	$\Delta\rho_{min} = -0.55$ e Å^{-3}
$S = 1.306$	Extinction correction: *SHELXL*97
10 543 reflections	(Sheldrick, 1997)
451 parameters	Extinction coefficient: 0.0020 (6)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Hydrogen-bonding geometry (Å, °) for (I) at 143 K.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C10—H10$B\cdots$O3	0.96	2.22	2.916 (3)	128
C11—H11$C\cdots$O8	0.96	2.30	3.255 (3)	173
C21—H21$B\cdots$O5	0.96	2.26	3.016 (3)	135
C22—H22$C\cdots$O2	0.96	2.40	3.358 (3)	176
C27—H27$\cdots$O1	0.93	2.33	3.093 (3)	139
C36—H36$\cdots$O7	0.93	2.41	3.105 (3)	132
C46—H46$C\cdots$O11	0.96	2.28	2.982 (3)	129
C47—H47$B\cdots$O16	0.96	2.35	3.297 (3)	171
C57—H57$C\cdots$O13	0.96	2.25	2.979 (3)	132
C58—H58$B\cdots$O10	0.96	2.34	3.286 (3)	168
C63—H63$\cdots$O9	0.93	2.28	2.974 (3)	131
C72—H72$\cdots$O15	0.93	2.39	3.182 (3)	143
C8—H8$A\cdots$O13^i	0.93	2.57	3.346 (3)	141
C19—H19$B\cdots$O9^{ii}	0.93	2.53	3.397 (3)	156
C24—H24$B\cdots$O7^{iii}	0.97	2.58	3.483 (3)	156
C60—H60$A\cdots$O15^{iv}	0.97	2.46	3.392 (3)	161

Symmetry codes: (i) $-1-x, -y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, -1-y, -z$; (iv) $-1-x, 1-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I) at 205 K.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C10—H10$B\cdots$O3	0.96	2.28	2.950 (3)	126
C11—H11$C\cdots$O8	0.96	2.36	3.305 (3)	168
C21—H21$B\cdots$O5	0.96	2.22	2.959 (3)	133
C22—H22$C\cdots$O2	0.96	2.32	3.268 (3)	170
C27—H27$\cdots$O1	0.93	2.31	3.057 (3)	137
C36—H36$\cdots$O7	0.93	2.40	3.111 (3)	134
C8—H8$A\cdots$O5^i	0.93	2.57	3.370 (6)	144
C24—H24$B\cdots$O7^{ii}	0.96	2.52	3.446 (3)	161

Symmetry codes: (i) $x - 1, 1 + y, z$; (ii) $-x, -y, 1 - z$.

Two side chains of the 205 K structure were refined with split atoms. The occupancy factor was 0.613 (7) for C6, C7 and C8, and 0.387 (7) for C6′, C7′ and C8′. An occupancy factor of 0.596 (9) was found for C25 and C26, while 0.404 (9) was used for C25′ and C26′. Only a single position was found for C24. The split atoms C25, C26, C25′ and C26′ still had rather large displacement parameters and thus were refined with anisotropic displacement parameters to reduce residual density near this group. The H atoms in both determinations were placed at calculated positions and were refined with fixed individual displacement parameters [U(H) = 1.2U_{eq}(C) and U(H) = 1.5U_{eq}(C$_{methyl}$)] using a riding model with fixed distances: H—C(methyl) = 0.96, H—C(secondary) = 0.97 and H—C(planar) = 0.93 Å. Torsion angles about the C—C bonds of the methyl groups were allowed to refine.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *CIF* in *SHELXL*97.

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