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{4-Allyloxy-2,6-bis[(dimethylamino)methyl]phenyl-κ^3C^1,N,N'}iodidopalladium(II)

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Key indicators

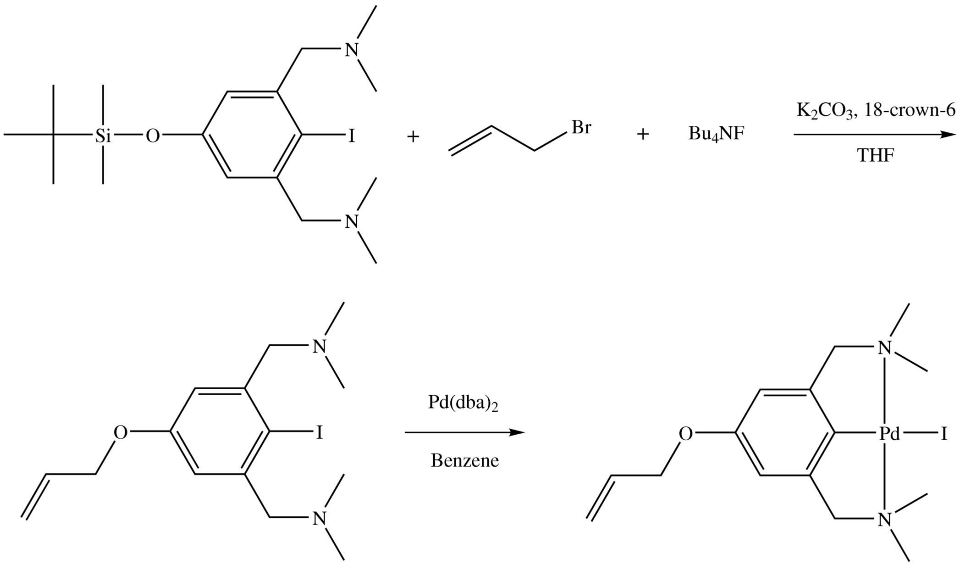
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.018
wR factor = 0.041
Data-to-parameter ratio = 21.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, [PdI($C_{15}H_{23}N_2O$)], the coordination environment of the central Pd^{II} atom is distorted square-planar. The Pd^{II} atom is coordinated by two neutral N atoms, an anionic C atom, and an I$^-$ anion with a long Pd—I distance of 2.72985 (19) Å. The molecules are packed on top of each other in an antiparallel fashion *via* intermolecular C—H$\cdots\pi$ and C—H$\cdots$O interactions.

Comment

In the title compound, (I), the coordination environment of the central Pd^{II} atom is defined by the monoanionic ligand 2,6-bis[(dimethylamino)methyl]-4-allyloxyphenyl and an I$^-$ anion (Fig. 1). The ligand coordinates to the metal in a tridentate fashion *via* the anionic atom C1 [Pd1—C1 = 1.9281 (18) Å] and the two neutral amine N atoms [Pd1—N1 = 2.1126 (16) Å and Pd1—N2 = 2.1210 (16) Å]. These distances compare well with those observed in similar Pd^{II} complexes, such as [(NCN)Pd(μ-Cl)Pd(NCN)]BF_4 {NCN = 2,6-bis[(dimethylamino)methyl]phenyl, $C_{12}H_{19}N_2$} reported by Terheijden *et al.* (1987), with Pd—C = 1.909 (4) and 1.929 (4)Å and Pd—N = 2.094 (3)–2.150 (3) Å.



(I)

The I$^-$ anion of (I) is coordinated *trans* to C1 [C1—Pd1—I1 = 178.42 (5)°], an sp^2 donor with a large *trans* influence. Therefore, the Pd1—I1 distance of 2.72985 (19) Å is rather long. This is similar to the Pd—I distance of 2.7731 (10) Å found in the [PdI(NCN)]·$2I_2$ complex (Mills *et al.*, 2002), where the distance involving the coordinated I$^-$ anion is

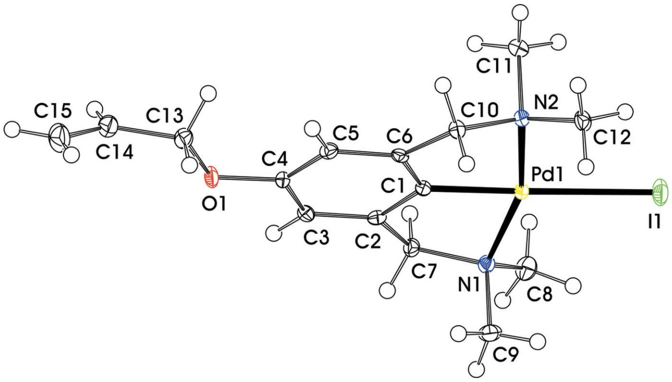


Figure 1
The molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

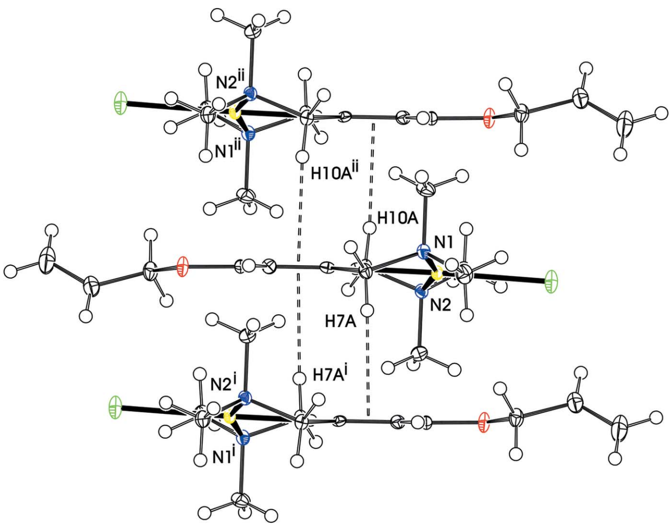


Figure 2
A packing diagram for (I). C—H$\cdots\pi$ interactions are shown as dashed lines. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.]

influenced by the interaction with two neutral I_2 molecules at a distance of ~3.3 Å. In general, Pd—I distances are much shorter, as can be seen in a search of the four-coordinated PdINCN fragment in the Cambridge Structural Database (Version 5.28, November 2006; Allen, 2002), which revealed a Pd–I distance range of 2.569–2.596 Å (34 hits).

The small bite angles of the chelate ligand [C1—Pd1—N1 = 80.60 (7)° and C1—Pd1—N2 = 80.74 (7)°] result in a distorted square-planar geometry of the central Pd^{II} atom. The sum of the *cis* angles is 360°, although they deviate from the ideal value of 90° by up to 10° for N1—Pd1—I1. The largest deviation for the *trans* angles is 19° (N1—Pd1—N2) from the ideal value of 180°. A conformational analysis of the ring puckering results in coefficients of 96.6% for the cosine form of the PdC_3N1 chelate ring, and 84.9% for the cosine form of the PdC_3N2 chelate ring (Evans & Boeyens, 1989). Therefore, the two five-membered PdC_3N chelate rings are best described as envelope conformations and are puckered in opposite directions, with the N atoms mutually *trans*. The torsion angles Pd1—N1—C7—C2 [−31.88 (17)°] and Pd1—N2—C10—C6 [−30.86 (17)°] indicate local non-crystallographic C_2 symmetry. The PdINCN coordination plane is tilted by 13.03 (7)° with respect to the plane of the aromatic ring.

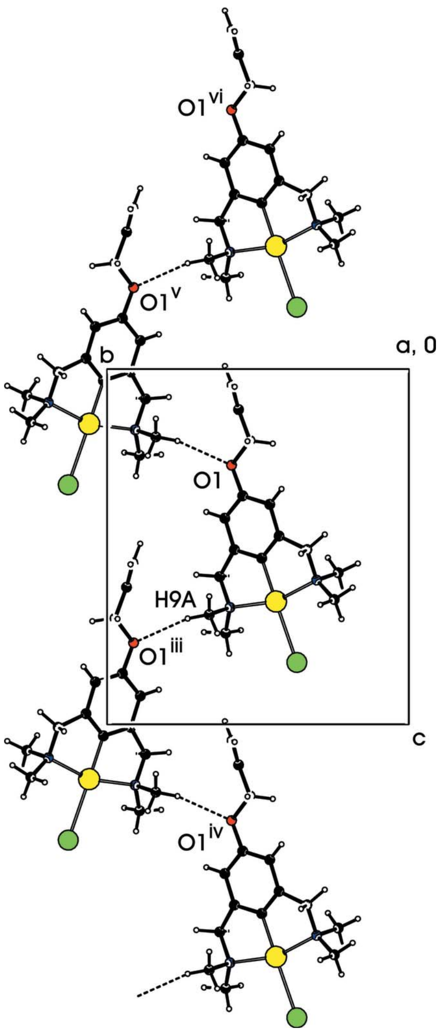


Figure 3
The hydrogen-bond interactions in (I), viewed along the crystallographic *a* axis. The C—H$\cdots$O contact are shown as dashed lines. [Symmetry codes: (iii) $x, 3/2 - y, \frac{1}{2} + z$; (iv) $x, y, 1 + z$; (v) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (vi) $x, y, z - 1$.]

In the crystal structure of (I), molecules are packed on top of each other in an antiparallel fashion, with interplanar distances of 3.65 and 3.61 Å for molecules related by symmetry codes (i) $(-x, 1 - y, 1 - z)$ and (ii) $(1 - x, 1 - y, 1 - z)$, respectively (Fig. 2). There are two intermolecular C—H$\cdots\pi$ contacts to the C1–C6 aromatic ring (centroid *Cg*), $H7A\cdots Cg^{i}$ = 2.65 Å and $H10A\cdots Cg^{ii}$ = 2.63 Å. The molecules are additionally connected by an intermolecular C—H$\cdots$O contact, forming zigzag chains parallel to the crystallographic *c* axis [$H9A\cdots O1^{iii}$ = 2.52 Å; symmetry code: (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$] (Fig. 3).

Experimental

To a solution of 4-(*tert*-butyldimethylsilyloxy)-1-iodo-2,6-bis-[(dimethylamino)methyl]benzene (0.25 g, 0.56 mmol) (Dijkstra *et al.*, 2003) in tetrahydrofuran (THF; 3.5 ml) was added a 1 *M* Bu_4NF

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solution in THF (0.56 ml, 0.56 mmol) and the resulting solution was stirred at room temperature for 1 h. This solution was then added to a mixture of 18-crown-6 (15 mg, 0.06 mmol) and K_2CO_3 (0.23 g, 1.68 mmol) in THF (5.0 ml), followed by the dropwise addition of allyl bromide (0.058 ml, 0.67 mmol). The resulting mixture was heated to reflux for 12 h, cooled to room temperature and poured into H_2O (10 ml). This layer was extracted with Et_2O (3×5 ml), and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated, affording the ligand 4-allyloxy-1-iodo-2,6-bis-[(dimethylamino)methyl]benzene as a yellow oil (0.20 g, 0.53 mmol; yield 95%). This oil was subsequently dissolved in dry benzene (2 ml) and added to a solution of $Pd(dba)_2$ (dba = dibenzylidineaceto) (0.30 g, 0.55 mmol) in benzene (20 ml), and the resulting solution was stirred at room temperature for 18 h. The reaction mixture was then filtered over Celite and the filtrate was evaporated. The remaining solid was washed with Et_2O (3×5 ml) and dried *in vacuo*. Yellow crystals of (I) suitable for data collection were obtained by slow evaporation diffusion of pentane into a concentrated solution of the Pd complex in CH_2Cl_2.

Crystal data

$[PdI(C_{15}H_{23}N_2O)]$
$M_r = 480.65$
Monoclinic, $P2_1/c$
$a = 8.9404$ (1) Å
$b = 12.7563$ (1) Å
$c = 15.0229$ (2) Å
$\beta = 90.9663$ (7)°
$V = 1713.06$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.88$ mm^{-1}
$T = 100$ (2) K
$0.18 \times 0.15 \times 0.03$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: analytical (*ABST* in *PLATON*; Spek, 2003)
$T_{min} = 0.69$, $T_{max} = 0.89$
35105 measured reflections
3926 independent reflections
3613 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 1.05$
3926 reflections
185 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—Pd1	2.72985 (19)	Pd1—N1	2.1126 (16)
Pd1—C1	1.9281 (18)	Pd1—N2	2.1210 (16)
C1—Pd1—N1	80.60 (7)	C1—Pd1—I1	178.42 (5)
C1—Pd1—N2	80.74 (7)	N1—Pd1—I1	99.61 (4)
N1—Pd1—N2	161.31 (6)	N2—Pd1—I1	99.08 (4)
Pd1—N1—C7—C2	−31.88 (17)	Pd1—N2—C10—C6	−30.86 (17)

Table 2
C—H···π interactions (Å, °).

Cg is the centroid of the C1–C6 aromatic ring.

X—H···*Cg*	*X*—H	H···*Cg*	*X*···*Cg*	*X*—H···*Cg*
C7—H7*A*···*Cg*^{i}	0.99	2.65	3.586 (2)	159
C10—H10*A*···*Cg*^{ii}	0.99	2.63	3.567 (2)	157

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

Table 3
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O1^{iii}	0.98	2.52	3.561 (2)	161

Symmetry code: (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

All H atoms were introduced in geometrically idealized positions, with C—H = 0.95–0.99 Å, and refined using a riding model, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for H atoms of CH and CH_2 moieties and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. The methyl groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Version 1.11.0; Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *DIRDIF97* (Beurskens *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: manual editing of the *SHELXL97* output.

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