

# $[\eta^2-(E)\text{-But-2-enedinitrile}](N,N'\text{-di-phenyl-1,7,7-trimethylbicyclo[2.2.1]-heptane-2,3-diimine-}N,N'\text{-palladium(0)})$

Dianne D. Ellis\* and Anthony L. Spek

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands  
Correspondence e-mail: d.d.ellis@chem.uu.nl

Received 6 October 2000

Accepted 8 November 2000

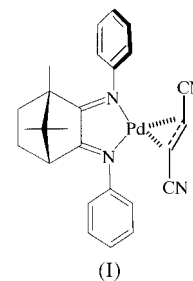
The zero-valent palladium in  $[\text{Pd}(\text{C}_4\text{H}_2\text{N}_2)(\text{C}_{22}\text{H}_{24}\text{N}_2)]$  is coordinated to two imine N atoms of a derivatized camphor ligand, and to the olefinic C atoms of a  $\pi$ -bonded fumaronitrile group. The N—Pd—N bite angle of  $77.31(9)^\circ$  is similar to angles observed in other zero-valent palladium diiminoalkene species. The asymmetry of the camphor moiety leads to two different orientations of the *N*-aryl groups relative to the  $\text{PdN}_2$  plane [ $\text{C}=\text{N}-\text{C}-\text{C}$  torsion angles of  $102.4(4)$  and  $39.4(4)^\circ$ ].

## Comment

Group 10 complexes of chiral bicyclic nitrogen ligands have been used in the study of homogeneous hydrogenation, polymerization and other catalytic reactions (Schleis *et al.*, 1998; van Asselt *et al.*, 1997; van Asselt & Elsevier, 1992). The reactivity and selectivity in these zero-valent complexes can be controlled by varying the groups on the nitrogen or by changing the electron-poor alkene (van Asselt *et al.*, 1994).

The Y-shaped trigonal-planar geometry of the title complex, (I), is shown in Fig. 1, with selected geometric parameters presented in Table 1. The palladium centre is coordinated to two imine N atoms attached to a camphor backbone, and to the alkenic C atoms of fumaronitrile. The metal distances [Pd—N 2.157(2) and 2.157(2) Å; Pd—C 2.037(3) and 2.047(3) Å] are comparable to those found in dimethyl[2-(phenylimino)-3-(2,6-dimethylphenylimino)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-diylidene]palladium(II), (II) (Schleis *et al.*, 1998). The metal distances in (I) are more symmetrical than in (II) due to the more crowded coordination sphere of the 2,6-dimethylphenyl group in the latter. The phenyl rings in (I) are tilted relative to the  $\text{PdN}_2\text{C}_2$  plane to a greater extent than in (II) [the dihedral angles between aryl rings and the  $\text{PdN}_2\text{C}_2$  plane are  $74.54(16)$  and  $35.54(14)^\circ$  in (I), compared with  $69.6$  and  $87.6^\circ$  in (II)]. Presumably, there are unfavourable interactions between the methyl groups on either the camphor backbone or the phenyl ring in (II), the latter being absent in (I).

The disposition of the N atoms ensures a *cis* orientation at the metal; constrained  $\sigma$ -donating ligands are known to induce small bite angles in similar systems (Tatsumi *et al.*, 1981). The N1—Pd—N2 bite angle of  $77.31(9)^\circ$  is comparable to that



(I)

found in (II) [ $77.2(1)^\circ$ ] and is of a similar magnitude to related complexes in the Cambridge Structural Database (Allen & Kennard, 1993). The imine  $\text{C}=\text{N}$  bonds of 1.281(5) and 1.271(4) Å are marginally different, one of them is slightly longer than those found in (II) [1.272(5) and 1.273(5) Å].

The  $\text{C}=\text{C}$  bond distance in the fumaronitrile ligand [1.441(4) Å] is longer than in the free ligand [1.249(10) Å; Britton & Gleason, 1982] due to coordination to palladium; the  $\pi$ -back-bond donation from the filled metal orbital to the empty  $\pi^*$  orbital in the alkene causes an elongation of this bond. There is a concomitant shortening of the  $\text{C}-\text{C}(\text{N})$  single bonds from 1.480(8) Å in the free ligand to 1.435(4)/1.433(4) Å in (I). The secondary effect (of ligand coordination) is a bending of the substituents away from the metal plane, which has been quantified by Ittel & Ibers (1976). Two angles, designated  $\alpha$  and  $\beta/\beta'$ , describe deviations of the alkene ligands from the metal plane. Their values,  $66.3(3)$  and  $57.7(3)/55.8(3)^\circ$ , correlate well with those in other bidentate systems, for example,  $59.3(8)$  and  $60.8(6)/59.9(5)^\circ$  for the tetracyanoethane ligand in  $[\text{Pd}(\text{C}_{23}\text{H}_{16}\text{N}_6)]$  (Kranenburg *et al.*,

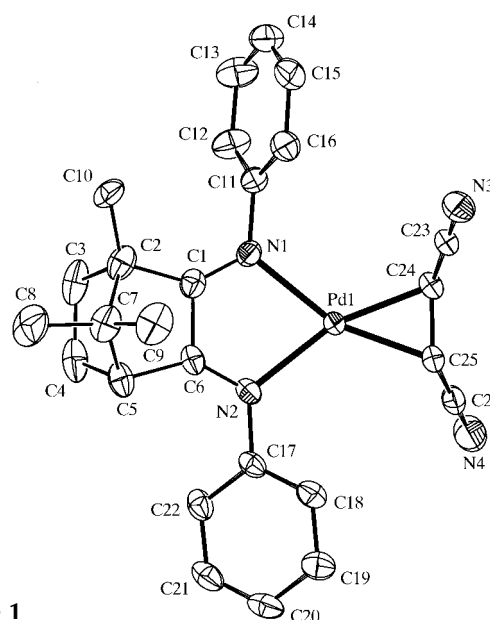


Figure 1

Displacement ellipsoid plot of the major disordered component in (I) drawn at the 50% probability level. H atoms have been omitted for clarity.

1997). The olefinic C atoms are notionally  $sp^2$  hybridized, as shown by the C—C—C angles of 119.7 (3) and 118.6 (3) $^\circ$ . The cyano groups are linear [C—C $\equiv$ N 179.0 (3) and 179.3 (4) $^\circ$ ] and form very weak C—H $\cdots$ N hydrogen-bond contacts, *i.e.* H3A $\cdots$ N3<sup>i</sup> of 2.58 Å and H4B $\cdots$ N4<sup>ii</sup> of 2.60 Å [symmetry codes: (i)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ii)  $-x, -y, -z$ ].

## Experimental

The synthesis of [Pd(C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>)] has been described previously (van Asselt *et al.*, 1997). The complex was recrystallized from a hexane/dichloromethane solution. The crystal selected for data collection was cut to size in inert oil and mounted under a liquid-nitrogen jet.

### Crystal data

[Pd(C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> )(C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> )]	$D_x = 1.451 \text{ Mg m}^{-3}$
$M_r = 500.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 11.8073 (13) \text{ \AA}$	$\theta = 11.4\text{--}13.8^\circ$
$b = 10.0751 (12) \text{ \AA}$	$\mu = 0.829 \text{ mm}^{-1}$
$c = 21.453 (3) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 116.024 (8)^\circ$	Block, orange
$V = 2293.3 (5) \text{ \AA}^3$	$0.55 \times 0.25 \times 0.25 \text{ mm}$
$Z = 4$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 27.46^\circ$
$\omega$ – $2\theta$ scans	$h = -10 \rightarrow 15$
7053 measured reflections	$k = -13 \rightarrow 0$
5235 independent reflections	$l = -27 \rightarrow 25$
4462 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.076$	frequency: 60 min
	intensity decay: <1%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 2.2454P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{\text{max}} < 0.002$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$
5235 reflections	$\Delta\rho_{\text{min}} = -1.44 \text{ e \AA}^{-3}$
317 parameters	
H atoms treated by a mixture of independent and constrained refinement	

In the penultimate stages of refinement, a large positive residual electron-density peak was located towards the centre of the camphor ring, indicating some minor disorder of the backbone. Subsequent analysis revealed a second orientation equivalent to 12.3 (4)% disorder of the camphor backbone. All distances and angles were restrained (using the *SAME* instruction), and additionally, the distances to the disordered methyl C10B atom were constrained with a *DFIX* command. The displacement parameters of the disordered camphor atoms (C1B to C10B) were refined isotropically and were tied to a free variable which converged to 0.028 (3). A large negative residual electron density of  $-1.44 \text{ e \AA}^{-3}$  (0.03 Å from Pd1) remained in the final difference maps.

All H atoms, except for H24 and H25 on the fumaronitrile ligand, were constrained and allowed to ride on their C atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C})$  for CH<sub>3</sub> groups. A sensible geometry was not obtained when atoms H24 and H25 were constrained using normal instructions; thus, both were located in the Fourier map, their distances constrained and their displacement parameters allowed to ride on their parent atom with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .  $360^\circ \psi$  scans showed no significant variations; thus, no correction for absorption was performed.

**Table 1**

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

Pd1—N1	2.157 (2)	N2—C6	1.271 (4)
Pd1—N2	2.157 (2)	C1—C6	1.495 (5)
Pd1—C24	2.037 (3)	C23—C24	1.435 (4)
Pd1—C25	2.047 (3)	C24—C25	1.441 (4)
N1—C1	1.281 (5)	C25—C26	1.433 (4)
N1—Pd1—N2	77.31 (9)	N3—C23—C24	179.0 (3)
C24—Pd1—C25	41.31 (11)	N4—C26—C25	179.3 (4)
C25—Pd1—N1	159.67 (10)	C23—C24—C25	119.7 (3)
C24—Pd1—N2	162.58 (11)	C24—C25—C26	118.6 (3)
C1—N1—C11—C12	−80.2 (4)	C6—N2—C17—C18	−143.1 (3)
C1—N1—C11—C16	102.4 (4)	C6—N2—C17—C22	39.4 (4)

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

Crystals were kindly provided by Dr R. P. de Boer, Professor Dr K. Vrieze and Professor Dr C. J. Elsevier, University of Amsterdam, The Netherlands. The investigations were supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization of Scientific Research (NWO).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1030). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Asselt, R. van & Elsevier, C. J. (1992). *Organometallics*, **11**, 1999–2001.
- Asselt, R. van, Elsevier, C. J., Amatore, C. & Jutand, A. (1997). *Organometallics*, **16**, 317–328.
- Asselt, R. van, Elsevier, C. J., Smeets, W. J. J., Spek, A. L. & Benedix, R. (1994). *Recl Trav. Chim. Pays-Bas*, **113**, 88–98.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1999). *DIRDIF99*. University of Nijmegen, The Netherlands.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Britton, D. & Gleason, W. B. (1982). *Cryst. Struct. Commun.* **11**, 1155–1158.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Ittel, S. D. & Ibers, J. A. (1976). *Adv. Organomet. Chem.* **14**, 33–61.
- Kranenburg, M., Delis, J. G. P., Kamer, P. C. J., van Leeuwen, P. W. N. M., Vrieze, K., Veldman, N., Spek, A. L., Goubitz, K. & Fraanje, J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1839–1849.
- Schleis, T., Heinemann, J., Spaniol, T. P., Mulhaupt, R. & Okuda, J. (1998). *Inorg. Chem. Commun.* **1**, 431–434.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
- Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.
- Tatsumi, K., Hoffmann, R., Yamamoto, A. & Stille, J. K. (1981). *Bull. Chem. Soc. Jpn.* **54**, 1857–1867.