Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.107$
$S = 1.031$
2054 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 2.7991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.412$ e Å^{-3}
$\Delta\rho_{\min} = -0.522$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Cu—O1	1.919 (2)	Cu—N2	1.989 (3)
Cu—N1	1.945 (2)	Cu—O3ⁱ	2.683 (2)
Cu—O2	1.975 (2)		
O1—Cu—N1	91.36 (9)	O2—Cu—N2	95.65 (11)
O1—Cu—O2	171.05 (10)	O1—Cu—O3ⁱ	98.94 (8)
N1—Cu—O2	82.97 (9)	N1—Cu—O3ⁱ	91.16 (9)
O1—Cu—N2	89.20 (11)	O2—Cu—O3ⁱ	88.14 (9)
N1—Cu—N2	173.38 (11)	N2—Cu—O3ⁱ	95.27 (10)

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

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···O3ⁱ	0.86	1.974	2.824 (4)	170

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

For both compounds, data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Express*; data reduction: *XCAD*-4 (Harms, 1997); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996); molecular graphics: *XP* (Siemens, 1996*b*); software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1215). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1593–1596

{1,2-Bis[*N*-(4-methylphenyl)imino-*N*]-acenaphthene}(η^2-maleic anhydride)-palladium(0)

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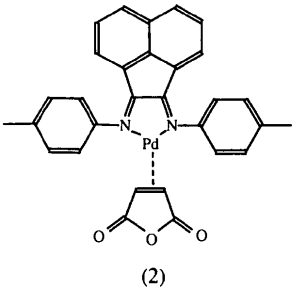
Abstract

The title compound, $[Pd(C_{26}H_{20}N_2)(C_4H_2O_3)]$, displays trigonal coordination of palladium by both N atoms and the double bond of maleic anhydride. The spatial arrangement of the *N*-aryl groups in the title compound, compared with a more sterically congested analogue, explains satisfactorily its enhanced reactivity towards organic substrates. The crystal packing involves weak C—H···O and C—H···π interactions.

Comment

Bidentate nitrogen ligands are useful ancillary ligands in palladium-catalyzed processes such as C—C coupling reactions (Süstmann, Lau & Zipp, 1986; van Asselt & Elsevier, 1992, 1994*a*). Among these, the rigid bidentate nitrogen compound bis[(*N*-aryl)imino]acenaphthene (Ar–BIAN) has been used as the spectator ligand in reaction sequences modeling the copolymerization of CO and alkenes (van Asselt, Gielens, Rülke, Vrieze & Elsevier, 1994; Markies *et al.*, 1995), as well as in propene polymerization (Johnson, Killian & Brookhart, 1995). For these selective reactions, evaluation of the spatial disposition of the *N*-aryl groups in *M*(Ar–BIAN) relative to the coordination plane appears to be important (Johnson, Killian & Brookhart, 1995; van Asselt & Elsevier, 1994*b*). We have studied previously the structure and dynamics of low valent Pd(Ar–BIAN) compounds and obtained the X-ray structure of {bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene}(maleic anhydride)-palladium(0), (1) (van Asselt, Elsevier, Smeets & Spek, 1994). In order to explain the enhanced reactivity of the title compound, (2) (the *N*-*p*-tolyl analogue, which lacks the bulky *ortho*-substituents on the *N*-aryl moiety), in C—C coupling and oxidative addition reactions (van Asselt & Elsevier, 1992, 1994*a*,*b*), a single crystal X-ray study was performed for the title compound which may quantitatively be compared with the known structure of the uncoordinated ligand bis[*N*-(4-methylphenyl)imino]-acenaphthene, (3) (van Asselt, Elsevier, Smeets, Spek & Benedix, 1994).



(2)

The Pd atom is coordinated by N1, N2 and the midpoint of C42═C43 in an approximately trigonal environment. Comparison of the molecular structures of (2) and the uncoordinated (*E*,*E*)-bis[*N*-(4-methylphenyl)imino]acenaphthene, (3), reveals several changes in bond angles and a puckering of the backbone. In (2), the torsion angle N1—C8—C19—N2 is 0.0 (11)°, whereas the equivalent torsion angle is −6.5° in compound (3) and 1.1° in compound (1). The *N*-aryl groups in (2) make angles of 55.1 (3) and 55.5 (3)° with the plane defined by the diimino–acenaphthene system, whereas this angle is 61° in (3) and 76–86° in (1). Hence, there is much less steric interference between the *N*-4-methylphenyl groups and the naphthalene backbone in (2) compared with the situation involving the two bulky *N*-2,6-diisopropylphenyl groups in (1). Interestingly, the *N*-aryl groups in (2) are also less tilted compared with (3), which may be ascribed to the expected decrease in bite angle in (2) upon coordination of the bidentate nitrogen ligand (3). This relieves the steric interference slightly between the *ortho*-H atoms of the =it N-*p*-tolyl group and the naphthalene backbone in (2). The resulting less perpendicular arrangement of the *N*-aryl groups leads to less shielding above and below the coordination plane of the palladium center, which explains the enhanced reactivity of (2) in oxidative addition and β-elimination reactions compared with (1). The *N*-aryl groups in (1), *mutatis mutandis*, shield the palladium center more effectively above and below the coordination plane, this being reflected in more sluggish reactions with organic compounds.

Compound (2) exhibits many similarities to compound (1) and the comparable known compounds (2,2′-bipyridyl)(dibenzylideneacetone)palladium(0), (4) (Pierpont, Buchanan & Downs, 1977), (η^2-tetracyanoethylene)(1,10-phenanthroline-*N*,*N*′)palladium(0), (5) (Zagorodnikov, Katser, Vargaftik, Porai-Koshits & Moiseev, 1989) and chloromethyl(η^2-maleic anhydride)(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)palladium(II), (6) (Albano, Castellari, Cucciolito, Panunzi & Vitagliano, 1990). The Pd—N and Pd—C distances as well as the N—Pd—N and C—Pd—C angles in (2) are similar to those in (1) and (4). As expected, the coordination distances mentioned here in (2) are larger and the angles smaller than corresponding ones in the TCNE complex (5); the opposite is observed in compound (6), a five-coordinate Pd$^{\rm II}$ compound. The Pd—C distances are shorter than in a number of other palladium–alkene complexes, *e.g.* Pd(DBA)$_3$ (Mazza & Pierpont, 1973) and Pd$_2$(DBA)$_3$.CH$_2$Cl$_2$ (Pierpont & Mazza, 1974). Other bond distances and angles in (2) show no anomalies. The maleic anhydride molecule is coordinated at an angle of 80.4 (4)° relative to the coordination plane. Atoms C42 and C43 show no significant pyramidalization.

The crystal structure of (2) displays two short intramolecular C—H···O contacts between aromatic H atoms and the maleic anhydride O atoms (C4—H4···O41 and C21—H21···O43). Weak intermolecular interactions include C—H···O contacts [C6—H6···O41$^{\rm i}$ and C25—H25···O43$^{\rm i}$; symmetry code: (i) $x-1$, y, z] as well as C—H···π interactions to the maleic anhydride [C3—H3···*Cg*$^{\rm ii}$, where *Cg* is the centre of the C═C bond; symmetry code (ii) $1-x$, $-y$, $-z$] (see Table 2).

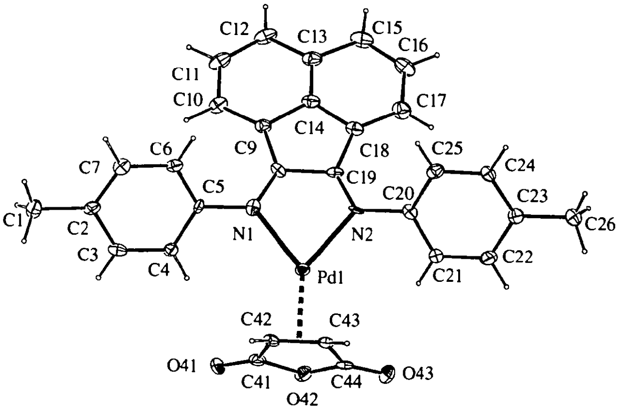


Fig. 1. Atomic displacement ellipsoid plot at the 30% probability level for (2).

Experimental

Compound (2) was obtained following an established procedure (van Asselt, Elsevier, Smeets & Spek, 1994). Crystals suitable for X-ray diffraction were obtained by slow evaporation of diethyl ether into a solution of (2) in dichloromethane at 277 K.

Crystal data

[Pd($C_{26}H_{20}N_2$)($C_4H_2O_3$)]
$M_r = 564.94$

Mo *K*α radiation
$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 8.7507\ (16)$ Å
$b = 12.5722\ (13)$ Å
$c = 12.927\ (2)$ Å
$\alpha = 71.248\ (11)°$
$\beta = 70.267\ (14)°$
$\gamma = 86.458\ (12)°$
$V = 1265.9\ (4)$ Å^3
$Z = 2$
$D_x = 1.482$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10.07–25.10°$
$\mu = 0.77$ mm^{-1}
$T = 150$ K
block (four different crystals)
0.4 × 0.2 × 0.1 mm
Orange

Data collection

Enraf–Nonius CAD-4T diffractometer on a rotating anode
ω scans
Absorption correction: none
11333 measured reflections
4463 independent reflections
4463 reflections with $I \geq -3\sigma(I)$

$R_{\rm int} = 0.076$
$\theta_{\rm max} = 25°$
$h = -11 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 45%

Refinement

Refinement on F^2
$R(F) = 0.064$
$wR(F^2) = 0.144$
$S = 0.957$
4463 reflections
333 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.050$
$\Delta\rho_{\rm max} = 1.212$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.851$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—N1	2.147 (7)	O42—C41	1.421 (10)
Pd1—N2	2.148 (6)	O42—C44	1.396 (10)
Pd1—C42	2.060 (8)	O43—C44	1.189 (10)
Pd1—C43	2.070 (8)	C42—C43	1.422 (12)
O41—C41	1.178 (9)		
N1—Pd1—N2	77.6 (2)	Pd1—N2—C19	112.0 (5)
N1—Pd1—C42	119.9 (3)	Pd1—N2—C20	125.9 (5)
N1—Pd1—C43	160.2 (3)	N1—C8—C19	116.9 (7)
N2—Pd1—C42	162.3 (3)	N2—C19—C18	134.1 (7)
N2—Pd1—C43	122.2 (3)	Pd1—C42—C41	105.7 (5)
C42—Pd1—C43	40.3 (3)	Pd1—C42—C43	70.2 (5)
Pd1—N1—C5	125.5 (5)	Pd1—C43—C42	69.5 (5)
Pd1—N1—C8	112.0 (5)	Pd1—C43—C44	107.8 (6)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$O41	0.930 (9)	2.553 (6)	3.469 (11)	168.5 (5)
C6—H6$\cdots$O41$^{\rm i}$	0.930 (9)	2.439 (6)	3.345 (11)	164.7 (5)
C21—H21$\cdots$O43	0.931 (9)	2.571 (7)	3.465 (11)	161.1 (5)
C25—H25$\cdots$O43$^{\rm i}$	0.931 (9)	2.467 (7)	3.376 (12)	165.5 (5)
C3—H3$\cdots Cg^{\rm ii}$†	0.930 (9)	2.954 (7)	3.262 (12)	112.5 (5)

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

† *Cg* is the centre of the C42═C43 bond.

Since crystals of (2) decay rapidly, as is indicated by the intensity of the reference reflections; a total of four data sets were collected at high scan speed, each on a different crystal of approximately the same size. For two crystals, a full unique data set up to $\theta = 25°$ was measured; for the other crystals, only a part of the unique set was measured as a result of strong decay. Total data collection time was 91 h. For all data sets, reflections were measured with a scan angle of $\Delta\omega = 2.10 + 0.35\tan\theta°$; horizontal and vertical apertures were $3.00 + 1.50\tan\theta°$ and 4.00 mm, respectively. The individual data sets refine to $R(F)$ values in the range 0.10–0.14. The structure presented in this paper is refined against a merged data set. The scaling factors of the individual sets were determined from a least-squares refinement against all measured data. The H atoms of the maleic anhydride ligand were located on a difference Fourier map; their coordinates were included as parameters in the refinement. All other H atoms were included in the refinement at calculated positions, riding on their carrier atoms. The H atoms were refined with a fixed isotropic displacement parameter related to the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.5 for the methyl H atoms and a factor of 1.2 for all others. All non-H atoms were refined with anisotropic displacement parameters. The structure contains a 145 Å^3 hole at coordinates $0,\frac{1}{2},\frac{1}{2}$. The integral over the electron density in this hole amounts to 1.0 e, indicating that it is essentially empty. The reported maximum in the residual density is located 1.0 Å from the Pd atom. The largest shift/s.u. value is that of the torsion angle of the CH_3 rigid group. The cited R value is calculated for 2878 reflections with $F > 4\sigma(F)$; $wR(F^2)$ is calculated for all observed reflections.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *PLUTON* (Spek, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1007). Services for accessing these data are described at the back of the journal.

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Bis(2-aminomethylpyridine-*N*,*N'*)bis(nitrato-*O*)copper(II)

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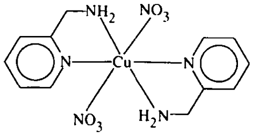
Abstract

In the title compound, $[Cu(NO_3)_2(C_6H_8N_2)_2]$, the copper(II) ion, which lies on a centre of symmetry, is coordinated by four N atoms of two 2-aminomethylpyridine ligands and two O atoms of two nitrate ions in an elongated octahedral geometry.

Comment

In the course of our investigations on models of superoxide dismutase (SOD) (Tainer, Getzoff, Beem, Richardson & Richardson, 1982), the tetradentate ligand 1,5-bis(2-pyridyl)-2,4-diazapentane was synthesized in good yield by a Mannich reaction. Reaction of this ligand with $[Cu(H_2O)_3(NO_3)_2]$ in ethanol unintentionally resulted in the title compound, (I). Apparently, the ligand had decomposed in its original components through a reverse Mannich reaction, which is not uncommon under these circumstances (Heany, 1991).



(I)

The copper(II) ion in bis(nitrato-*O*)bis(2-aminomethylpyridine-*N*,*N'*)copper(II) is coordinated by an O atom from each of the two nitrate ions and the four N atoms of the two ligands in an elongated octahedron. The Cu—N distances of 1.9984 (14) (amine N atom) and 2.0191 (15) Å (pyridine N atom) can be considered as normal, while the Cu—O distance of 2.5428 (14) Å is longer than the normal value of 2.0 Å (see, for example, Neenan, Driessen, Haasnoot & Reedijk, 1996) as a result of the Jahn–Teller effect. The coordination angles around the Cu^{II} ion (Table 2) are mostly very close to the regular octahedral angles, with the exception of the N(amine)—Cu—N(pyridine) angle of 81.99 (6)°, which is due to strain in the five-membered ring imposed by the three-bond ligand bite. Since O22 and O23 lie more than 3.4 Å from the Cu^{II} centre, the nitrate is clearly monodentate.

The amine H atoms are hydrogen bonded to the nitrate anions, forming a two-dimensional network in the *bc* plane, with H181 forming a bifurcated hydrogen bond, intramolecular to O22 and intermolecular to O21, and H182 forming an intermolecular hydrogen bond to O22. The O23 atom is not involved in the hydrogen-bonding network; its bond to the central N atom is significantly shorter than the other N—O bonds of the nitrate anion.

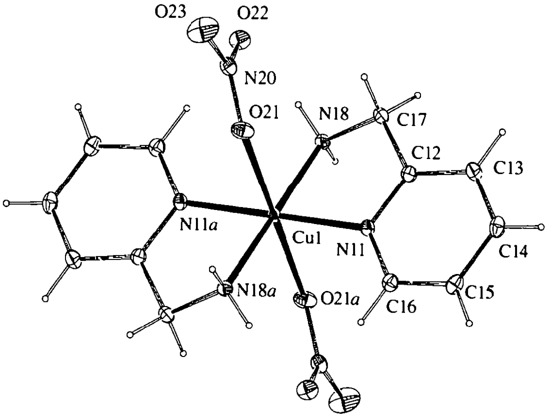


Fig. 1. A view of the title compound showing the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. Labels with suffix *a* denote atoms generated by symmetry operation $-x, -y, -z$.

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