Cyclometallated compounds of palladium(II) with a 2,4-pentanedionate: the X-ray crystal structure of [Pd{4-(CHO)C₆H₃C(H)=NCy}(H₃CCOCHCOCH₃)]
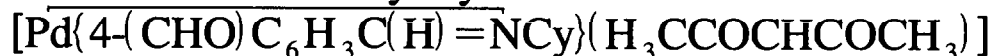
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Abstract

The structure of the cyclometallated palladium(II) complex [Pd{4-(CHO)C₆H₃C(H)=NCy}(H₃CCOCHCOCH₃)] is described. There are four different crystallographic molecules per asymmetric unit.

Keywords: Palladium; X-ray diffraction; Schiff base; Imine; Acetylacetonate; Cyclometallation

1. Introduction

Cyclometallated complexes are known with a wide range of ligands and this and other aspects of their chemistry are covered in various general reviews [1–5]. We have studied different types of organic ligand that undergo cyclometallation reactions [6]. In some cases the ligand itself is the key step in the metallation process, as when the regioselectivity of metallation is involved [7–9]. In others, the ligand may undergo structural changes, so that the organic moiety in the cyclometallated complex is totally different from that in the starting material. We have recently studied the metallation of Schiff bases derived from dialdehydes such a terephthalaldehydes [10] and isophthalaldehydes [11]. Thus reaction of N,N-terephthalylidenebis(cyclohexylamine), 1,4-(CyN=CH)₂C₆H₄ or N,N-isophthalylidenebis(cyclohexylamine), 1,3-(CyN=CH)₂C₆H₄ with palladium(II) acetate gave dinuclear cyclometallated complexes in which one of the C=N double bonds was cleaved to produce complexes with a free formyl group on each of the metallated phenyl rings. This produced cyclometallated complexes with an altered organic ligand. The original C=N double bond could

then be regenerated giving complexes with coordinated and uncoordinated C=N groups.

Although complexes prepared by us earlier [10] were correctly characterized by the usual techniques, no crystallographic evidence was provided. Since then we have been able to obtain suitable crystals for their X-ray analysis. Here we describe the crystal structure of one such compound, [Pd{4-(CHO)C₆H₃C(H)=NCy}-(H₃CCOCHCOCH₃)]. However, although the ¹H NMR spectrum showed that only one chemical species was present in solution, in the solid state the structure shows that, owing to the different orientations of the free formyl group in the crystal, there are four crystallographically distinct molecules present per asymmetric unit.

2. Results and discussion

Suitable crystals of the title compound [Pd{4-(CHO)C₆H₃C(H)=NCy}(H₃CCOCHCOCH₃)] (1) were grown from a slowly evaporating chloroform solution. The molecular structure for the different molecules, with atom labelling, is illustrated in Fig. 1. The unit cell of 1 is shown in Fig. 2. Crystal data are given in Table 1. Fractional coordinates and isotropical parameters are listed in Table 2, and selected bond lengths and bond
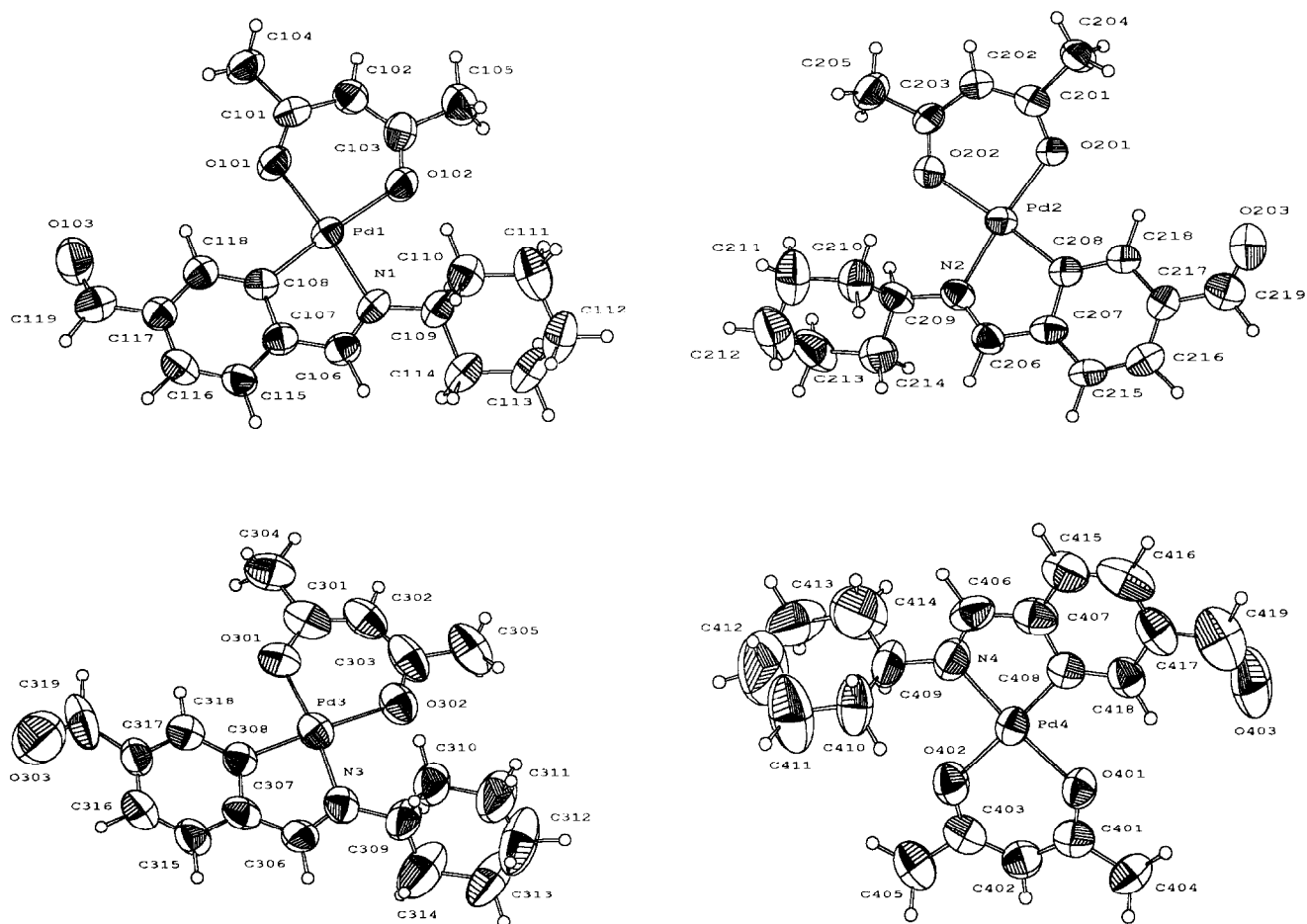
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[1] Deceased.

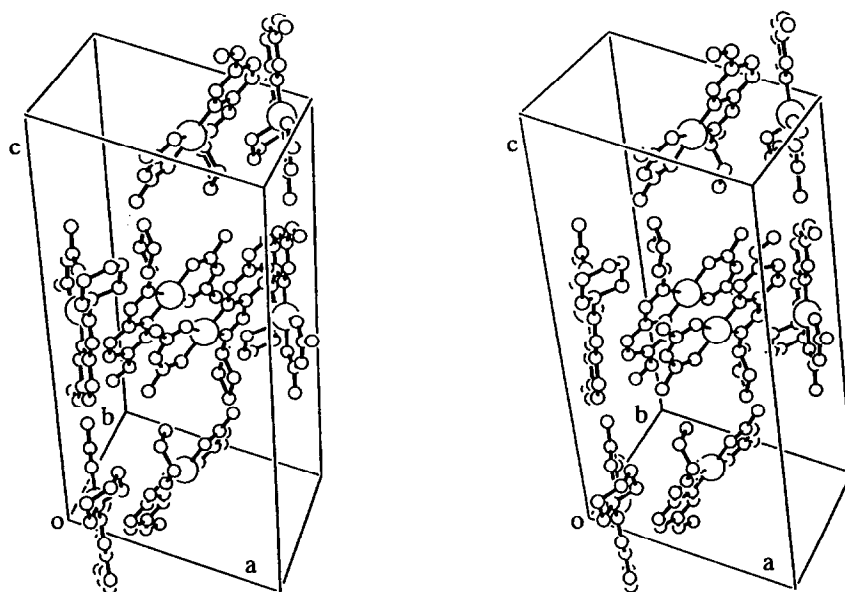Fig. 1. The molecular structure of the title compound.

Fig. 2. The unit cell of the title compound.

angles with estimated standard deviations are listed in Tables 3 and 4 respectively.

The molecule comprises a palladium(II) to which is bonded a chelated *N*-(4-formylbenzylidene)cyclohexylamine-C^2,*N* group and a 2,4-pentanedionate-*O*,*O*. Because rotation of the formyl group in the solid state is hindered, there are four crystallographically distinct molecules per asymmetric unit, as opposed to only one chemical species in solution and, except for the orientation of the formyl group in each molecule, the bond distances and angles are within expected values (torsion angles for C(X18)–C(X17)–C(X19)–O(X03) are 3.83(1.33)° for $X = 1$, 176.63(0.98)° for $X = 2$, −174.42(1.07)° for $X = 3$, −179.80(1.57)° for $X = 4$ and for C(X16)–C(X17)–C(X19)–O(X03) are −176.42(0.85)° for $X = 1$, −1.00(1.49)° for $X = 2$, 3.10(1.72)° for $X = 3$ and 1.15(2.31)° for $X = 4$). Therefore, only one molecule will be described, for $X = 1$ (see Fig. 1).

The palladium atom adopts a square-planar geometry as expected for Pd^{2+}, the donor atoms of the Schiff base being *cis*, with the distortion most noticeable in the C(108)–Pd(1)–N(1) angle of 81.0(3)°. The sum of

angles at palladium is 359.9°. This is reflected in the value of the Pd(1)–C(108)–C(118) angle of 129.0(6)°. The Pd–C bond length (Pd(1)–C(108), 1.969(7) Å) is shorter than the expected value of 2.081 Å based on the sum of the covalent radii for carbon and palladium, 0.771 and 1.31 Å respectively [12]. This shortening is consistent with previous observations [13–15] and is attributable to partial multiple-bond character of the Pd–C bond. The Pd–N bond length (Pd(1)–N(1), 2.010(6) Å) is consistent with the sum of the covalent radii for nitrogen (sp²) 0.70 Å and palladium 1.31 Å. As in other cyclometallated complexes, the C=N distance (N(1)–C(106), 1.283(9) Å) is somewhat longer than the value of 1.237(7) Å observed for a related free donor [16] and typical of a coordinated Schiff base [17].

The Pd–O distances (Pd(1)–O(101), 2.018(5) Å; Pd(1)–O(102), 2.082(5) Å) are consistent with the value from the sum of the covalent radii for palladium 1.31 Å and oxygen 0.66 Å [12] and they represent single-bond interactions. The longer Pd–O distance, Pd(1)–O(102), reflects the greater *trans* influence of the phenyl carbon atom as compared to the imine nitrogen atom.

The aromatic (plane ii) and 2,4-penatnedionate (plane

Table 1
Crystal data for [Pd{4-(CHO)C₆H₃C(H)=NCy}(H₃CCOCHCOCH₃)] (1)

Formula	$C_{19}H_{23}NO_3Pd$
Formula weight	419.78
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal color	Yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	
a (Å)	11.887(3)
b (Å)	12.773(2)
c (Å)	25.187(4)
α (°)	99.15(2)
β (°)	103.11(3)
γ (°)	91.42(4)
Volume (Å³)	3669.9(12)
Z	8
Density (calculated) (g cm⁻¹)	1.520
$F(000)$	1712
Crystal size (mm)	0.32 × 0.15 × 0.15
Absorption coefficient (mm⁻¹)	1.027
θ range for data collection (°)	0.84–22.98
Index ranges	$0 < h < 13, -14 < k < 14, -27 < l < 26$
Number of reflections collected	10832
Number of independent reflections	10166 (R_{int} = 0.0300)
Refinement method	Full-matrix least-squares method on F^2
Number of data	10150
Number of restraints	0
Number of parameters	871
Goodness of fit on F^2	1.098
Final R indices ($I > 2.0\sigma(I)$)	R_1 = 0.0445, wR_2 = 0.0960
R indices (all data)	R_1 = 0.0893, wR_2 = 0.1333
Largest difference peak and hole (electrons Å⁻³)	0.517 and −0.602

Table 2

Non-hydrogen atom coordinates and isotropic thermal parameters 1

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} (10^{-3} Å²)
Pd(1)	4130(1)	5763(1)	367(1)	54(1)
O(101)	4468(5)	7222(4)	207(2)	62(1)
O(102)	5147(5)	6149(4)	1170(2)	65(2)
O(103)	2357(7)	6708(6)	−1823(3)	104(2)
N(1)	3632(5)	4301(5)	460(3)	57(2)
C(101)	5109(7)	7960(6)	559(4)	60(2)
C(102)	5683(7)	7893(6)	1092(4)	66(2)
C(103)	5668(7)	7025(7)	1367(4)	65(2)
C(104)	5213(8)	8987(6)	352(4)	79(3)
C(105)	6367(9)	7142(8)	1958(4)	93(3)
C(106)	2905(7)	3775(6)	.41(4)	59(2)
C(107)	2567(7)	4283(6)	−434(3)	56(2)
C(108)	3121(6)	5291(6)	−374(3)	51(2)
C(109)	4062(7)	3892(6)	973(4)	63(2)
C(110)	3365(8)	4305(7)	1385(4)	77(3)
C(111)	3870(10)	3957(10)	1943(4)	110(4)
C(112)	3938(10)	2753(9)	1889(5)	105(4)
C(113)	4612(9)	2368(8)	1465(4)	93(3)
C(114)	4072(8)	2701(7)	916(4)	82(3)
C(115)	1791(7)	3835(7)	−924(3)	68(2)
C(116)	1567(7)	4379(7)	−1356(4)	69(2)
C(117)	2132(7)	5371(6)	−1318(3)	57(2)
C(118)	2898(7)	5813(6)	−822(3)	56(2)
C(119)	1870(8)	5879(7)	−1809(4)	76(3)
Pd(2)	1221(1)	749(1)	454(1)	51(1)
O(201)	678(5)	2147(4)	257(2)	58(1)
O(202)	1000(5)	1146(4)	1252(2)	60(1)
O(203)	746(7)	1546(7)	−1781(3)	113(2)
N(2)	1823(5)	−673(5)	576(3)	56(2)
C(201)	420(6)	2901(6)	610(3)	56(2)
C(202)	407(7)	2865(6)	1150(3)	61(2)
C(203)	699(7)	2033(6)	1446(3)	56(2)
C(204)	68(8)	3889(6)	371(4)	72(2)
C(205)	649(9)	2187(7)	2042(3)	86(3)
C(206)	2097(7)	−1204(6)	156(3)	59(2)
C(207)	1961(6)	−732(6)	−339(3)	57(2)
C(208)	1490(6)	277(6)	−280(3)	52(2)
C(209)	1905(7)	−1079(6)	1099(3)	61(2)
C(210)	2961(8)	−534(8)	1523(4)	81(3)
C(211)	2968(11)	−845(11)	2084(5)	124(4)
C(212)	2942(12)	−2038(12)	2049(6)	135(5)
C(213)	1921(12)	−2578(9)	1621(5)	110(4)
C(214)	1907(10)	−2272(7)	1053(4)	91(3)
C(215)	2221(7)	−1194(6)	−822(4)	67(2)
C(216)	1983(7)	−696(7)	−1273(4)	69(2)
C(217)	1497(7)	279(6)	−1239(3)	59(2)
C(218)	1261(6)	765(6)	−740(3)	53(2)
C(219)	1205(8)	749(8)	−1737(4)	80(3)
Pd(3)	3958(1)	5995(1)	5047(1)	71(1)
O(301)	4471(5)	7158(5)	4690(3)	83(2)
O(302)	4923(6)	6726(6)	5817(3)	90(2)
O(303)	1102(11)	5089(9)	2468(5)	172(4)
N(3)	3275(7)	4775(6)	5313(3)	74(2)
C(301)	5171(8)	7950(8)	4935(5)	85(3)
C(302)	5698(9)	8139(9)	5487(6)	99(4)
C(303)	5569(9)	7554(11)	5898(5)	98(4)
C(304)	5414(9)	8703(8)	4574(5)	110(4)
C(305)	6225(10)	7927(9)	6485(5)	122(4)
C(306)	2601(9)	4101(7)	4931(4)	76(3)
C(307)	2376(8)	4339(7)	4382(4)	69(2)
C(308)	2975(7)	5277(6)	4346(3)	62(2)

Table 2 (continued)

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} (10^{-3} Å²)
C(309)	3516(13)	4695(9)	5904(4)	117(4)
C(310)	2816(12)	5506(9)	6185(4)	115(4)
C(311)	3114(23)	5494(13)	6797(6)	287(17)
C(312)	3324(15)	4710(16)	7005(6)	186(8)
C(313)	3961(13)	3883(12)	6726(5)	153(6)
C(314)	3617(18)	3832(13)	6087(6)	223(11)
C(315)	1583(9)	3773(7)	3933(4)	81(3)
C(316)	1373(9)	4109(8)	3434(4)	84(3)
C(317)	1985(9)	5015(8)	3383(4)	76(3)
C(318)	2769(7)	5583(7)	3828(4)	69(2)
C(319)	1849(12)	5511(12)	2863(5)	137(6)
Pd(4)	8713(1)	9096(1)	4527(1)	64(1)
O(401)	9498(5)	7879(4)	4838(2)	70(2)
O(402)	8870(5)	8463(5)	3732(2)	77(2)
O(403)	9539(11)	8837(11)	6824(4)	164(5)
N(4)	7895(7)	10364(7)	4305(4)	83(2)
C(401)	9919(8)	7126(7)	4555(4)	72(2)
C(402)	9848(8)	6988(7)	4002(4)	77(3)
C(403)	9367(8)	7610(8)	3617(4)	76(3)
C(404)	10513(8)	6341(7)	4887(4)	91(3)
C(405)	9414(9)	7329(9)	3025(4)	104(3)
C(406)	7643(8)	10991(7)	4691(5)	87(3)
C(407)	7958(8)	10710(8)	5237(5)	81(3)
C(408)	8522(7)	9750(6)	5251(4)	63(2)
C(409)	7659(11)	10556(9)	3718(5)	114(4)
C(410)	6564(9)	9892(10)	3415(5)	112(4)
C(411)	6353(18)	10007(19)	2808(8)	215(11)
C(412)	6523(24)	10920(22)	2678(9)	238(14)
C(413)	7542(19)	11612(12)	3002(7)	170(8)
C(414)	7752(18)	1546(12)	3609(6)	193(8)
C(415)	7741(9)	11269(9)	5703(6)	100(3)
C(416)	8076(10)	10919(11)	6202(5)	06(4)
C(417)	8652(10)	9999(10)	6232(4)	91(3)
C(418)	8860(7)	9412(7)	751(4)	71(2)
C(419)	024(13)	9637(15)	6758(7)	137(6)

Eqivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

iii) rings are planar (r.m.s. deviations, 0.010 and 0.004 Å, respectively) and approximately coplanar with the five-membered cyclometallated ring (plane i) (angles between i and ii, and between i and iii are 2.95° and 3.95° respectively). The geometry around the palladium atom is planar (r.m.s. deviation of coordination plane, 0.019 Å), from which the displacement of the palladium atom is only −0.019 Å. (Angles between planes for the other three molecules of the asymmetric unit are as follows; for $X = 2$, i and ii 2.78°, i and iii 4.81°; for $X = 3$, i and ii 4.49°, i and iii 0.89°; for $X = 4$, i and ii 0.45°, i and iii 1.65°).

3. Experimental details

The synthesis of the title compound has been reported previously [10]. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer operating in the θ–2θ scan mode with scan width $(1.0 + 0.35 \tan \theta)$

and a scan speed of 4.00–6.67° min^{-1}, using graphite-monochromated Mo Kα radiation. Unit-cell parameters were determined from least squares on setting angles of 24 reflections with $5 < \theta < 13°$. One standard reflection (740) varied $\pm 2.1\%$ of mean intensity over data collection. 10 832 reflections were measured with $\theta_{max} = 23°$; 10 166 unique reflections; $R_{int} = 0.03$; 6733 reflections were considered observed on the criterion $I < 2\sigma(I)$ and corrected for Lorentz and polarization effects. Absorption corrections were applied (average transmission factor of 0.95, with maximum and minimum absorption coefficients of 0.97 and 0.90). The structure was solved by centrosymmetric direct methods SHELXS86 [18] and

refined by least squares. After a full-matrix least-squares refinement (on F^2), with all non-hydrogen atoms anisotropic, the methyl-group H atoms were included at positions based on those found in difference synthesis and the rest were stereochemically positioned. Further refinements were performed with the H atoms riding on their bound carbon atoms with overall temperature factors. Refinement on F^2, SHELXL-93 [19], for 10 150 reflections (except 16 with very negative F^2 owing to potential systematic errors) converged at a final $R = 0.0445$; inspection of F_c and F_o values indicated that a correction for secondary extinction was necessary. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.032200P)^2 +$

Table 4
Selected bond angles (°) with estimated standard deviations 1

C(108)–Pd(1)–N(1)	81.0(3)	C(208)–Pd(2)–N(2)	81.9(3)
C(308)–Pd(3)–N(3)	80.6(3)	C(408)–Pd(4)–N(4)	81.7(4)
C(108)–Pd(1)–O(101)	93.1(3)	C(208)–Pd(2)–O(201)	92.2(3)
C(308)–Pd(3)–O(301)	92.1(3)	C(408)–Pd(4)–O(401)	91.5(3)
N(1)–Pd(1)–O(101)	173.6(2)	N(2)–Pd(2)–O(201)	173.9(2)
N(3)–Pd(3)–O(301)	172.4(3)	N(4)–Pd(4)–O(401)	173.2(3)
C(108)–Pd(1)–O(102)	175.2(2)	C(208)–Pd(2)–O(202)	175.5(3)
C(308)–Pd(3)–O(302)	176.3(3)	C(408)–Pd(4)–O(402)	176.8(3)
N(1)–Pd(1)–O(102)	94.3(2)	N(2)–Pd(2)–O(202)	93.6(2)
N(3)–Pd(3)–O(302)	96.3(3)	N(4)–Pd(4)–O(402)	95.1(3)
O(101)–Pd(1)–O(102)	91.5(2)	O(201)–Pd(2)–O(202)	92.3(2)
O(301)–Pd(3)–O(302)	91.0(3)	O(401)–Pd(4)–O(402)	91.6(2)
C(106)–N(1)–C(109)	123.4(6)	C(206)–N(2)–C(209)	122.9(6)
C(306)–N(3)–C(309)	123.5(9)	C(406)–N(4)–C(409)	123.4(9)
C(106)–N(1)–Pd(1)	114.9(5)	C(206)–N(2)–Pd(2)	114.1(5)
C(306)–N(3)–Pd(3)	115.0(6)	C(406)–N(4)–Pd(4)	115.3(7)
C(109)–N(1)–Pd(1)	121.7(5)	C(209)–N(2)–Pd(2)	123.0(5)
C(309)–N(3)–Pd(3)	121.4(7)	C(409)–N(4)–Pd(4)	121.2(7)
N(1)–C(106)–C(107)	116.9(7)	N(2)–C(206)–C(207)	118.0(7)
N(3)–C(306)–C(307)	116.7(9)	N(4)–C(406)–C(407)	116.9(9)
C(115)–C(107)–C(108)	121.1(7)	C(215)–C(207)–C(208)	122.2(8)
C(315)–C(307)–C(308)	122.0(9)	C(415)–C(407)–C(408)	120.7(11)
C(115)–C(107)–C(106)	124.9(7)	C(215)–C(207)–C(206)	125.3(7)
C(315)–C(307)–C(306)	124.8(9)	C(415)–C(407)–C(406)	125.7(11)
C(108)–C(107)–C(106)	113.9(7)	C(208)–C(207)–C(206)	112.5(7)
C(308)–C(307)–C(306)	113.0(8)	C(408)–C(407)–C(406)	113.5(9)
C(118)–C(108)–C(107)	117.9(7)	C(218)–C(208)–C(207)	117.0(7)
C(318)–C(308)–C(307)	116.4(8)	C(418)–C(408)–C(407)	118.2(9)
C(118)–C(108)–Pd(1)	129.0(6)	C(218)–C(208)–Pd(2)	129.5(6)
C(318)–C(308)–Pd(3)	129.0(6)	C(418)–C(408)–Pd(4)	129.3(7)
C(107)–C(108)–Pd(1)	113.1(6)	C(207)–C(208)–Pd(2)	113.4(6)
C(307)–C(308)–Pd(3)	114.5(6)	C(407)–C(408)–Pd(4)	112.6(7)
C(116)–C(115)–C(107)	119.7(8)	C(216)–C(215)–C(207)	119.7(8)
C(316)–C(315)–C(307)	120.2(9)	C(416)–C(415)–C(407)	120.7(11)
C(115)–C(116)–C(117)	120.8(8)	C(215)–C(216)–C(217)	120.2(8)
C(315)–C(316)–C(317)	119.0(9)	C(415)–C(416)–C(417)	120.0(11)
C(118)–C(117)–C(116)	118.8(8)	C(218)–C(217)–C(216)	120.1(8)
C(318)–C(317)–C(316)	120.9(9)	C(418)–C(417)–C(416)	119.4(11)
C(118)–C(117)–C(119)	124.2(8)	C(218)–C(217)–C(219)	121.8(8)
C(318)–C(317)–C(319)	113.0(10)	C(418)–C(417)–C(419)	120.3(13)
C(116)–C(117)–C(119)	117.0(8)	C(216)–C(217)–C(219)	118.1(8)
C(316)–C(317)–C(319)	126.0(10)	C(416)–C(417)–C(419)	120.3(13)
C(108)–C(118)–C(117)	121.7(7)	C(208)–C(218)–C(217)	120.8(7)
C(308)–C(318)–C(317)	121.4(8)	C(408)–C(418)–C(417)	120.9(10)
O(103)–C(119)–C(117)	121.5(10)	O(203)–C(219)–C(217)	126.2(10)
O(303)–C(319)–C(317)	116 (2)	O(403)–C(419)–C(417)	125 (2)

Table 3
Selected bond lengths (Å) with estimated standard deviations for 1

Pd(1)–C(108)	1.969(7)	Pd(2)—C(208)	1.951(8)
Pd(3)–C(308)	1.953(8)	Pd(4)–C(408)	1.947(8)
Pd(1)–N(1)	2.010(6)	Pd(2)–N(2)	2.012(6)
Pd(3)–N(3)	2.012(8)	Pd(4)–N(4)	2.000(8)
Pd(1)–O(101)	2.018(5)	Pd(2)–O(201)	2.010(5)
Pd(3)–O(301)	2.005(6)	Pd(4)–O(401)	2.007(5)
Pd(1)–O(102)	2.082(5)	Pd(2)–O(202)	2.071(5)
Pd(3)–O(302)	2.078(7)	Pd(4)–O(402)	2.088(6)
O(103)–C(119)	1.202(10)	O(203)–C(219)	1.176(10)
O(303)–C(319)	1.213(14)	O(403)–C(419)	1.22(2)
N(1)–C(106)	1.283(9)	N(2)–C(206)	1.273(9)
N(3)–C(306)	1.289(11)	N(4)–C(406)	1.255(12)
N(1)–C(109)	1.461(9)	N(2)–C(209)	1.476(9)
N(3)–C(309)	1.474(12)	N(4)–C(409)	1.501(12)
C(106)–C(107)	1.432(10)	C(206)–C(207)	1.449(11)
C(306)–C(307)	1.431(12)	C(406)–C(407)	1.446(14)
C(107)–C(115)	1.391(10)	C(207)–C(215)	1.369(11)
C(307)–C(315)	1.383(12)	C(407)–C(415)	1.353(14)
C(107)–C(108)	1.402(10)	C(207)–C(208)	1.417(10)
C(307)–C(308)	1.404(11)	C(407)–C(408)	1.414(12)
C(108)–C(118)	1.379(10)	C(208)–C(218)	1.379(10)
C(308)–C(318)	1.392(11)	C(408)–C(418)	1.373(11)
C(115)–C(116)	1.363(11)	C(215)–C(216)	1.367(11)
C(315)–C(316)	1.364(12)	C(415)–C(416)	1.38(2)
C(116)–C(117)	1.398(11)	C(216)–C(217)	1.383(11)
C(316)–C(317)	1.391(12)	C(416)–C(417)	1.38(2)
C(117)–C(118)	1.394(10)	C(217)–C(218)	1.402(10)
C(317)–C(318)	1.374(12)	C(417)–C(418)	1.395(13)
C(117)–C(119)	1.463(12)	C(217)–C(219)	1.450(12)
C(317)–C(319)	1.52(2)	C(417)–C(419)	1.45(2)

11.058101P] where $P = 0.33333F_o^2 + 0.66666F_c^2$ was used in the latter stages of refinement.

Weighted R factors wR and goodness of fit are based on F^2, conventional R factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating R_{obs} and is not relevant to the choice of reflections for refinement.

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