Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

trans-Chlorido[6-chloro-4-(4-methoxybenzyl)-3-oxo-3,4-dihydropyrazin-2-yl]-bis(triphenylphosphine)palladium(II)

Koen Robeyns,[a] Jo Alen,[b] Wim M. De Borggraeve,[b] Frans Compernolle[b] and Luc Van Meervelt[a]*

[a]Biomolecular Architecture, Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium, and [b]Molecular Design and Synthesis, Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium
Correspondence e-mail: luc.vanmeervelt@chem.kuleuven.be

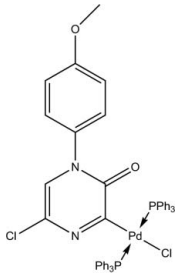
Received 19 November 2007; accepted 26 November 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 16.4.

The title compound, $[Pd(C_{12}H_{10}ClN_2O_2)Cl(C_{18}H_{15}P)_2]$, is the intermediate of the reduction of a 3,5-dichloropyrazinone [Loosen, Tutonda, Khorasani, Compernolle & Hoornaert (1991). *Tetrahedron*, **47**, 9259–9268]. This species is formed by oxidative addition of coordinatively unsaturated Pd^0 to the reactive 3-position of the heterocycle. The coordination around the Pd atom is square planar, with two *trans* PPh_3 ligands. π–π interactions are observed between the centroid of the pyrazinone ring and planes of two adjacent phenyl rings, one from each PPh_3 group (3.25 and 3.078 Å), stabilizing the intermediate structure. This could explain the reduced reactivity towards substitution of the Cl atom by the formate anion, resulting in poor yield of the reduced compound. 3-Substituted pyrazinones are important precursors in the synthesis of 5-aminopiperidinone-2-carboxylate (APC) systems.

Related literature

For related literature on the reduction of 3,5-dichloropyrazinones, see: Loosen *et al.* (1991). For related literature on 3,5-dichloropyrazinones, see: Pawar & De Borggraeve (2006). For related literature on APC systems, see: De Borggraeve *et al.* (2004); Alen *et al.* (2007). For the Cambridge Structural Database (Version 5.28), see: Allen (2002).



Experimental

Crystal data

$[Pd(C_{12}H_{10}ClN_2O_2)Cl(C_{18}H_{15}P)_2]$
M_r = 916.06
Triclinic, $P\overline{1}$
a = 10.7544 (1) Å
b = 13.1526 (1) Å
c = 16.9967 (1) Å
α = 91.811 (1)°
β = 94.39 (1)°
γ = 98.451 (1)°
V = 2368.83 (3) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 5.13 mm^{-1}
T = 100 (2) K
0.5 × 0.24 × 0.24 mm

Data collection

Bruker SMART 6000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.175, T_{max} = 0.292
23121 measured reflections
8422 independent reflections
7879 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 1.08
8422 reflections
515 parameters
318 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

The Katholieke Universiteit Leuven is gratefully acknowledged for financial support. The authors thank the FWO [Fund for Scientific Research–Flanders (Belgium)] for financial support. JA and WMDB (Postdoctoral Fellows of the FWO–Flanders) thank the FWO for Fellowships received. WMDB also thanks the FWO for a 'Krediet aan Navorsers'.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2294).

References

Alen, J., Smets, W. J., Dobrzańska, L., De Borggraeve, W. M., Compernolle, F. & Hoornaert, G. J. (2007). *Eur. J. Org. Chem.* **6**, 965–971.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (1997). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
De Borggraeve, W. M., Verbist, B. M. P., Rombouts, F. J. R., Pawar, V. G., Smets, W. J., Kamoune, L., Alen, J., Van der Eycken, E. V., Compernolle, F. & Hoornaert, G. J. (2004). *Tetrahedron*, **60**, 11597–11612.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Loosen, P. K., Tutonda, M. G., Khorasani, M. F., Compernolle, F. & Hoornaert, G. J. (1991). *Tetrahedron*, **47**, 9259–9268.
Pawar, V. G. & De Borggraeve, W. M. (2006). *Synthesis*, **17**, 2799–2814.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2008). E**64**, m93 [https://doi.org/10.1107/S1600536807063441]

trans-Chlorido[6-chloro-4-(4-methoxybenzyl)-3-oxo-3,4-dihydropyrazin-2-yl]bis(triphenylphosphine)palladium(II)

Koen Robeyns, Jo Alen, Wim M. De Borggraeve, Frans Compernolle and Luc Van Meervelt

S1. Comment

The target structure 5-chloro-1-(4-methoxybenzyl)-2(1*H*)-pyrazinone) was synthesized as a starting product for the synthesis of dipeptide mimics (Alen *et al.*, 2007; De Borggraeve *et al.*, 2004). This compound can be formed by reduction of a 3,5-dichloropyrazinone with sodium formate using $Pd(PPh_3)_4$ as a catalyst. Surprisingly, the title compound (I) was isolated as an intermediate (Scheme 1, Fig. 1). This means that substitution of the chlorine atom with sodium formate and subsequent proton shift leading to the desired compound, did not occur. In similar reactions the yields are high and no traces of the intermediate substance are found. However, the presence of a hydrogen atom *para* to the palladium atom and a *para*-methoxybenzyl substituent on the N-1 nitrogen atom of the pyrazinone scaffold, seem to increase the stability of the intermediate. This stability might arise from the π–π interactions between the pyrazinone and two phenyl rings of the PPh_3 groups. The centroid of the pyrazinone makes a distance of 3.25 Å and 3.078 Å with the planes formed by the two adjacent phenyl rings. Searches in the CSD database (Version 5.28) (Allen, 2002) for similar structures (59 hits in 50 crystal structures) revealed that the angle between the pyrazinone ring and an adjacent phenyl ring is on average 27.6° (range 13.0° - 65.2°). As fragment for the CSD search a Pd atom with only four substituents (2 PPh_3 groups, any halogen and an aromatic ring consisting of any atom type) was used. In the represented structure the angles are 15.4° and 13.9°, resulting in almost parallel pyrazinone and adjacent phenyl rings.

S2. Experimental

To a solution of 570 mg (2 mmol) 3,5-dichloropyrazinone in 20 ml DMF, 204 mg (3 mmol) sodium formate and 115 mg $Pd(PPh_3)_4$ are added. The solution is stirred for 4 h at 110 °C under inert atmosphere. After removal of the solvent, the residue is treated with 50 ml of water and extracted with 3x 50 ml dichloromethane. After drying over magnesium sulfate and evaporation of the solvent, the product was chromatographically purified (Heptane/EtOAc 50:50). The title compound was formed as a by-product with a yield of 45% and spontaneously crystallized from the Heptane/EtOAc mixture.

S3. Refinement

Hydrogen atoms were positioned geometrically; $U_{iso}(H) = xU_{eq}(C)$, where x = 1.5 for methyl and 1.2 for all other H atoms.

The asymmetric unit contains a solvent accessible void (164.3 Å^3). The contribution of the disordered solvent atoms were taken into acount by the squeeze algorithm implemented in the *PLATON* program (Spek, 2003) for a total of 52.4 electrons.

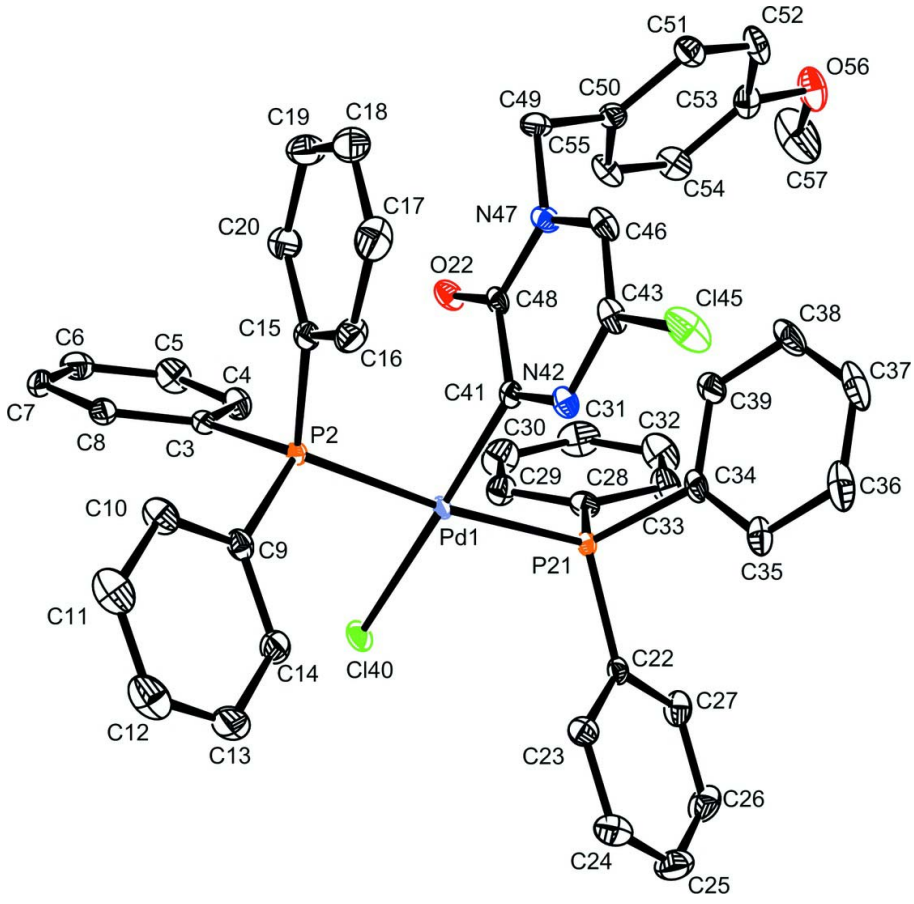
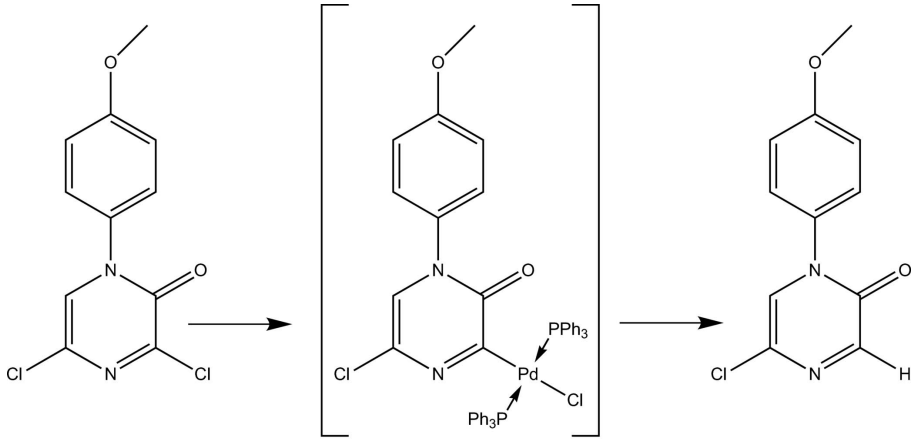


Figure 1

The molecular structure of the title compound (I), showing the atom-labeling scheme with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.



I

Figure 2

The title compound (I) is the stable intermediate in the synthesis of 5-chloro-1-(4-methoxybenzyl)-2(1*H*)-pyrazinone.

trans-Chlorido[6-chloro-4-(4-methoxybenzyl)-3-oxo-3,4-dihydropyrazin-2-yl]bis(triphenylphosphine)palladium(II)

Crystal data

$[Pd(C_{12}H_{10}ClN_2O_2)Cl(C_{18}H_{15}P)_2]$
$M_r = 916.06$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 10.7544$ (1) Å
$b = 13.1526$ (1) Å
$c = 16.9967$ (1) Å
$\alpha = 91.811$ (1)°
$\beta = 94.39$ (1)°
$\gamma = 98.451$ (1)°
$V = 2368.83$ (3) Å^3
$Z = 2$
$F(000) = 936$
$D_x = 1.284$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 6414 reflections
$\theta = 2.6$–$70.6°$
$\mu = 5.13$ mm^{-1}
$T = 100$ K
Block, transparent
0.5 × 0.24 × 0.24 mm

Data collection

Bruker SMART 6000 diffractometer
Radiation source: fine-focus sealed tube
Crossed Goebel mirrors monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.175$, $T_{max} = 0.292$
23121 measured reflections
8422 independent reflections
7879 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 68.8°$, $\theta_{min} = 2.6°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.073$
$S = 1.08$
8422 reflections
515 parameters
318 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.3456P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pd1	0.882642 (11)	0.283301 (9)	0.798987 (7)	0.00908 (6)
P2	0.83318 (4)	0.22202 (3)	0.92192 (2)	0.00951 (10)

C3	0.84174 (17)	0.08526 (14)	0.92756 (11)	0.0124 (3)
C4	0.83393 (19)	0.02691 (15)	0.85665 (11)	0.0177 (4)
H4	0.8301	0.0594	0.8076	0.021*
C5	0.8318 (2)	−0.07905 (15)	0.85853 (12)	0.0221 (4)
H5	0.8258	−0.1189	0.8104	0.027*
C6	0.83855 (19)	−0.12702 (15)	0.93000 (13)	0.0210 (4)
H6	0.8377	−0.1993	0.9308	0.025*
C7	0.84646 (18)	−0.06874 (15)	1.00047 (12)	0.0184 (4)
H7	0.8512	−0.1013	1.0495	0.022*
C8	0.84748 (17)	0.03648 (15)	0.99934 (11)	0.0152 (4)
H8	0.8521	0.0758	1.0476	0.018*
C9	0.93153 (18)	0.28969 (14)	1.00503 (11)	0.0141 (4)
C10	0.8973 (2)	0.28020 (16)	1.08230 (12)	0.0196 (4)
H10	0.8211	0.2379	1.0921	0.023*
C11	0.9737 (2)	0.33190 (17)	1.14494 (12)	0.0255 (4)
H11	0.9503	0.3243	1.1974	0.031*
C12	1.0844 (2)	0.39479 (16)	1.13073 (13)	0.0272 (5)
H12	1.1367	0.4303	1.1736	0.033*
C13	1.1187 (2)	0.40580 (15)	1.05453 (14)	0.0252 (5)
H13	1.1943	0.4493	1.0452	0.030*
C14	1.0431 (2)	0.35355 (14)	0.99098 (12)	0.0188 (4)
H14	1.0672	0.3613	0.9386	0.023*
C15	0.67328 (18)	0.23049 (15)	0.94789 (10)	0.0139 (4)
C16	0.6417 (2)	0.32462 (15)	0.97354 (12)	0.0196 (4)
H16	0.7061	0.3821	0.9845	0.023*
C17	0.5173 (2)	0.33501 (17)	0.98318 (13)	0.0265 (5)
H17	0.4970	0.3993	1.0010	0.032*
C18	0.4222 (2)	0.25182 (18)	0.96699 (13)	0.0264 (5)
H18	0.3368	0.2594	0.9725	0.032*
C19	0.4529 (2)	0.15776 (17)	0.94274 (13)	0.0238 (4)
H19	0.3883	0.1003	0.9326	0.029*
C20	0.5775 (2)	0.14669 (16)	0.93306 (11)	0.0186 (4)
H20	0.5975	0.0819	0.9163	0.022*
P21	0.90967 (4)	0.34277 (3)	0.67295 (2)	0.00962 (10)
C22	1.06025 (17)	0.42371 (13)	0.66477 (11)	0.0123 (3)
O22	0.63099 (13)	0.14734 (10)	0.74606 (8)	0.0164 (3)
C23	1.11981 (18)	0.47685 (15)	0.73317 (11)	0.0162 (4)
H23	1.0858	0.4651	0.7826	0.019*
C24	1.2293 (2)	0.54722 (16)	0.72865 (13)	0.0234 (4)
H24	1.2687	0.5846	0.7749	0.028*
C25	1.2805 (2)	0.56260 (17)	0.65720 (14)	0.0265 (5)
H25	1.3551	0.6105	0.6544	0.032*
C26	1.2236 (2)	0.50845 (17)	0.58949 (13)	0.0242 (4)
H26	1.2601	0.5182	0.5406	0.029*
C27	1.1130 (2)	0.43986 (15)	0.59306 (11)	0.0187 (4)
H27	1.0732	0.4038	0.5464	0.022*
C28	0.89390 (18)	0.23888 (15)	0.59781 (11)	0.0155 (4)
C29	0.9105 (2)	0.14114 (15)	0.62008 (12)	0.0191 (4)

H29	0.9347	0.1297	0.6736	0.023*
C30	0.8916 (2)	0.05938 (17)	0.56403 (14)	0.0278 (5)
H30	0.9043	−0.0074	0.5793	0.033*
C31	0.8544 (2)	0.07548 (17)	0.48620 (14)	0.0293 (5)
H31	0.8393	0.0193	0.4485	0.035*
C32	0.8392 (2)	0.17322 (19)	0.46310 (13)	0.0295 (5)
H32	0.8152	0.1842	0.4094	0.035*
C33	0.8591 (2)	0.25544 (17)	0.51857 (12)	0.0226 (4)
H33	0.8491	0.3226	0.5027	0.027*
C34	0.79522 (19)	0.42356 (15)	0.63620 (10)	0.0153 (4)
C35	0.8235 (2)	0.53018 (15)	0.64354 (11)	0.0192 (4)
H35	0.9064	0.5619	0.6616	0.023*
C36	0.7301 (2)	0.59064 (18)	0.62441 (12)	0.0274 (5)
H36	0.7494	0.6635	0.6294	0.033*
C37	0.6096 (2)	0.5446 (2)	0.59829 (13)	0.0304 (5)
H37	0.5464	0.5860	0.5850	0.037*
C38	0.5802 (2)	0.4381 (2)	0.59132 (12)	0.0274 (5)
H38	0.4969	0.4067	0.5738	0.033*
C39	0.67304 (19)	0.37767 (17)	0.61004 (11)	0.0197 (4)
H39	0.6533	0.3048	0.6050	0.024*
Cl40	1.08823 (4)	0.23058 (3)	0.81045 (3)	0.01784 (10)
C41	0.71073 (17)	0.32121 (14)	0.78835 (10)	0.0112 (3)
N42	0.68875 (15)	0.41388 (12)	0.80409 (9)	0.0134 (3)
C43	0.56729 (19)	0.43210 (15)	0.79552 (11)	0.0155 (4)
Cl45	0.54465 (5)	0.55731 (4)	0.82009 (3)	0.02764 (12)
C46	0.46835 (18)	0.36031 (15)	0.77103 (10)	0.0156 (4)
H46	0.3853	0.3772	0.7655	0.019*
N47	0.49052 (15)	0.26179 (12)	0.75423 (9)	0.0136 (3)
C48	0.61075 (17)	0.23561 (14)	0.76109 (10)	0.0122 (3)
C49	0.38425 (18)	0.18064 (15)	0.72664 (11)	0.0168 (4)
H49A	0.3067	0.1955	0.7497	0.020*
H49B	0.4025	0.1135	0.7456	0.020*
C50	0.36165 (18)	0.17346 (14)	0.63773 (12)	0.0157 (4)
C51	0.25756 (19)	0.20966 (15)	0.60036 (12)	0.0185 (4)
H51	0.2003	0.2384	0.6312	0.022*
C52	0.2369 (2)	0.20408 (15)	0.51874 (12)	0.0222 (4)
H52	0.1656	0.2287	0.4939	0.027*
C53	0.3206 (2)	0.16237 (14)	0.47317 (12)	0.0188 (4)
C54	0.4253 (2)	0.12637 (16)	0.50919 (12)	0.0216 (4)
H54	0.4831	0.0986	0.4782	0.026*
C55	0.44411 (19)	0.13164 (16)	0.59098 (12)	0.0203 (4)
H55	0.5148	0.1062	0.6157	0.024*
O56	0.29196 (16)	0.15893 (12)	0.39257 (9)	0.0268 (3)
C57	0.3688 (3)	0.1064 (3)	0.34498 (15)	0.0500 (8)
H57A	0.4568	0.1394	0.3539	0.075*
H57B	0.3399	0.1095	0.2891	0.075*
H57C	0.3623	0.0344	0.3594	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.00829 (8)	0.01200 (8)	0.00741 (8)	0.00311 (5)	−0.00019 (5)	0.00213 (5)
P2	0.0098 (2)	0.0118 (2)	0.0068 (2)	0.00126 (16)	−0.00014 (16)	0.00116 (15)
C3	0.0102 (8)	0.0130 (8)	0.0138 (8)	0.0015 (6)	−0.0006 (7)	0.0018 (6)
C4	0.0197 (10)	0.0199 (9)	0.0136 (9)	0.0042 (8)	−0.0006 (7)	−0.0001 (7)
C5	0.0253 (11)	0.0175 (9)	0.0228 (10)	0.0045 (8)	−0.0016 (8)	−0.0062 (8)
C6	0.0152 (10)	0.0148 (9)	0.0331 (11)	0.0028 (7)	0.0002 (8)	0.0028 (8)
C7	0.0127 (9)	0.0197 (9)	0.0240 (10)	0.0034 (7)	0.0024 (7)	0.0111 (8)
C8	0.0119 (9)	0.0201 (9)	0.0140 (9)	0.0030 (7)	0.0020 (7)	0.0034 (7)
C9	0.0169 (9)	0.0120 (8)	0.0130 (8)	0.0033 (7)	−0.0029 (7)	−0.0008 (6)
C10	0.0210 (10)	0.0233 (10)	0.0141 (9)	0.0049 (8)	−0.0014 (8)	−0.0048 (7)
C11	0.0313 (12)	0.0287 (11)	0.0164 (9)	0.0097 (9)	−0.0030 (8)	−0.0093 (8)
C12	0.0332 (12)	0.0202 (10)	0.0261 (11)	0.0063 (9)	−0.0110 (9)	−0.0099 (8)
C13	0.0246 (11)	0.0121 (9)	0.0351 (12)	−0.0028 (8)	−0.0104 (9)	0.0000 (8)
C14	0.0210 (10)	0.0130 (9)	0.0214 (9)	0.0010 (7)	−0.0030 (8)	0.0026 (7)
C15	0.0134 (9)	0.0203 (9)	0.0085 (8)	0.0034 (7)	0.0021 (7)	0.0026 (7)
C16	0.0204 (10)	0.0184 (9)	0.0212 (10)	0.0038 (8)	0.0068 (8)	0.0043 (7)
C17	0.0295 (12)	0.0243 (10)	0.0305 (11)	0.0142 (9)	0.0121 (9)	0.0066 (9)
C18	0.0175 (10)	0.0363 (12)	0.0292 (11)	0.0101 (9)	0.0110 (8)	0.0110 (9)
C19	0.0159 (10)	0.0311 (11)	0.0235 (10)	0.0000 (8)	0.0033 (8)	0.0020 (8)
C20	0.0186 (10)	0.0222 (10)	0.0149 (9)	0.0026 (8)	0.0021 (7)	−0.0007 (7)
P21	0.0116 (2)	0.0115 (2)	0.0060 (2)	0.00296 (16)	0.00008 (15)	0.00123 (15)
C22	0.0127 (9)	0.0123 (8)	0.0132 (8)	0.0056 (7)	0.0013 (7)	0.0035 (6)
O22	0.0156 (7)	0.0142 (6)	0.0195 (7)	0.0057 (5)	−0.0031 (5)	−0.0020 (5)
C23	0.0150 (9)	0.0175 (9)	0.0166 (9)	0.0036 (7)	0.0022 (7)	0.0000 (7)
C24	0.0184 (10)	0.0245 (10)	0.0260 (10)	0.0012 (8)	−0.0012 (8)	−0.0028 (8)
C25	0.0173 (10)	0.0242 (10)	0.0378 (12)	−0.0003 (8)	0.0061 (9)	0.0037 (9)
C26	0.0244 (11)	0.0248 (10)	0.0264 (10)	0.0058 (8)	0.0133 (8)	0.0086 (8)
C27	0.0238 (10)	0.0193 (9)	0.0147 (9)	0.0074 (8)	0.0046 (8)	0.0021 (7)
C28	0.0149 (9)	0.0177 (9)	0.0131 (9)	0.0014 (7)	−0.0012 (7)	−0.0030 (7)
C29	0.0220 (10)	0.0165 (9)	0.0182 (9)	0.0018 (8)	0.0010 (8)	−0.0001 (7)
C30	0.0356 (13)	0.0178 (10)	0.0287 (11)	0.0012 (9)	0.0024 (9)	−0.0059 (8)
C31	0.0334 (12)	0.0241 (11)	0.0271 (11)	−0.0026 (9)	0.0006 (9)	−0.0140 (9)
C32	0.0353 (13)	0.0362 (12)	0.0164 (10)	0.0093 (10)	−0.0047 (9)	−0.0081 (9)
C33	0.0300 (11)	0.0242 (10)	0.0139 (9)	0.0084 (9)	−0.0033 (8)	−0.0028 (8)
C34	0.0176 (9)	0.0231 (9)	0.0071 (8)	0.0078 (7)	0.0019 (7)	0.0044 (7)
C35	0.0248 (11)	0.0214 (10)	0.0141 (9)	0.0106 (8)	0.0032 (8)	0.0055 (7)
C36	0.0380 (13)	0.0315 (11)	0.0195 (10)	0.0230 (10)	0.0087 (9)	0.0100 (8)
C37	0.0315 (12)	0.0505 (14)	0.0181 (10)	0.0291 (11)	0.0081 (9)	0.0154 (9)
C38	0.0177 (10)	0.0545 (14)	0.0128 (9)	0.0131 (10)	0.0009 (8)	0.0125 (9)
C39	0.0162 (10)	0.0343 (11)	0.0094 (8)	0.0045 (8)	0.0014 (7)	0.0074 (7)
Cl40	0.0125 (2)	0.0251 (2)	0.0184 (2)	0.00943 (17)	0.00230 (16)	0.00715 (17)
C41	0.0136 (9)	0.0156 (8)	0.0045 (7)	0.0024 (7)	0.0010 (6)	0.0010 (6)
N42	0.0158 (8)	0.0163 (7)	0.0084 (7)	0.0048 (6)	−0.0007 (6)	−0.0007 (5)
C43	0.0191 (10)	0.0169 (9)	0.0119 (8)	0.0091 (7)	−0.0011 (7)	−0.0025 (7)
Cl45	0.0266 (3)	0.0223 (2)	0.0346 (3)	0.01454 (19)	−0.0088 (2)	−0.0137 (2)

C46	0.0155 (9)	0.0230 (9)	0.0102 (8)	0.0104 (7)	0.0004 (7)	−0.0016 (7)
N47	0.0116 (8)	0.0176 (7)	0.0113 (7)	0.0026 (6)	−0.0003 (6)	−0.0008 (6)
C48	0.0134 (9)	0.0166 (9)	0.0069 (8)	0.0038 (7)	−0.0010 (6)	0.0015 (6)
C49	0.0108 (9)	0.0197 (9)	0.0190 (9)	0.0002 (7)	0.0004 (7)	0.0008 (7)
C50	0.0133 (9)	0.0126 (8)	0.0200 (9)	−0.0002 (7)	−0.0013 (7)	0.0011 (7)
C51	0.0166 (10)	0.0176 (9)	0.0213 (10)	0.0046 (7)	−0.0013 (8)	−0.0006 (7)
C52	0.0257 (11)	0.0180 (9)	0.0230 (10)	0.0090 (8)	−0.0087 (8)	0.0016 (8)
C53	0.0254 (10)	0.0131 (8)	0.0163 (9)	0.0009 (7)	−0.0040 (8)	−0.0005 (7)
C54	0.0220 (10)	0.0233 (10)	0.0196 (10)	0.0055 (8)	0.0003 (8)	−0.0052 (8)
C55	0.0172 (10)	0.0227 (10)	0.0211 (10)	0.0080 (8)	−0.0056 (8)	−0.0018 (8)
O56	0.0393 (9)	0.0273 (8)	0.0151 (7)	0.0131 (7)	−0.0047 (6)	−0.0004 (6)
C57	0.0578 (19)	0.084 (2)	0.0150 (11)	0.0361 (17)	−0.0002 (11)	−0.0048 (12)

Geometric parameters (Å, º)

Pd1—C41	1.9812 (19)	C26—C27	1.389 (3)
Pd1—P21	2.3280 (4)	C26—H26	0.9500
Pd1—P2	2.3343 (4)	C27—H27	0.9500
Pd1—Cl40	2.4084 (4)	C28—C29	1.384 (3)
P2—C3	1.8198 (18)	C28—C33	1.402 (3)
P2—C9	1.8225 (18)	C29—C30	1.395 (3)
P2—C15	1.8259 (19)	C29—H29	0.9500
C3—C4	1.398 (3)	C30—C31	1.384 (3)
C3—C8	1.398 (3)	C30—H30	0.9500
C4—C5	1.392 (3)	C31—C32	1.385 (4)
C4—H4	0.9500	C31—H31	0.9500
C5—C6	1.388 (3)	C32—C33	1.393 (3)
C5—H5	0.9500	C32—H32	0.9500
C6—C7	1.392 (3)	C33—H33	0.9500
C6—H6	0.9500	C34—C35	1.390 (3)
C7—C8	1.383 (3)	C34—C39	1.396 (3)
C7—H7	0.9500	C35—C36	1.396 (3)
C8—H8	0.9500	C35—H35	0.9500
C9—C10	1.395 (3)	C36—C37	1.381 (4)
C9—C14	1.401 (3)	C36—H36	0.9500
C10—C11	1.388 (3)	C37—C38	1.390 (4)
C10—H10	0.9500	C37—H37	0.9500
C11—C12	1.388 (4)	C38—C39	1.390 (3)
C11—H11	0.9500	C38—H38	0.9500
C12—C13	1.380 (4)	C39—H39	0.9500
C12—H12	0.9500	C41—N42	1.299 (2)
C13—C14	1.398 (3)	C41—C48	1.474 (3)
C13—H13	0.9500	N42—C43	1.360 (3)
C14—H14	0.9500	C43—C46	1.345 (3)
C15—C20	1.396 (3)	C43—Cl45	1.7423 (19)
C15—C16	1.396 (3)	C46—N47	1.377 (2)
C16—C17	1.387 (3)	C46—H46	0.9500
C16—H16	0.9500	N47—C48	1.384 (2)

C17—C18	1.388 (3)	N47—C49	1.481 (2)
C17—H17	0.9500	C49—C50	1.510 (3)
C18—C19	1.385 (3)	C49—H49A	0.9900
C18—H18	0.9500	C49—H49B	0.9900
C19—C20	1.391 (3)	C50—C55	1.394 (3)
C19—H19	0.9500	C50—C51	1.397 (3)
C20—H20	0.9500	C51—C52	1.386 (3)
P21—C22	1.8199 (19)	C51—H51	0.9500
P21—C28	1.8208 (19)	C52—C53	1.392 (3)
P21—C34	1.8283 (19)	C52—H52	0.9500
C22—C27	1.393 (3)	C53—O56	1.379 (2)
C22—C23	1.398 (3)	C53—C54	1.391 (3)
O22—C48	1.235 (2)	C54—C55	1.387 (3)
C23—C24	1.395 (3)	C54—H54	0.9500
C23—H23	0.9500	C55—H55	0.9500
C24—C25	1.380 (3)	O56—C57	1.432 (3)
C24—H24	0.9500	C57—H57A	0.9800
C25—C26	1.385 (3)	C57—H57B	0.9800
C25—H25	0.9500	C57—H57C	0.9800

C41—Pd1—P21	87.89 (5)	C26—C27—C22	120.32 (18)
C41—Pd1—P2	86.59 (5)	C26—C27—H27	119.8
P21—Pd1—P2	174.088 (16)	C22—C27—H27	119.8
C41—Pd1—Cl40	177.83 (5)	C29—C28—C33	119.68 (18)
P21—Pd1—Cl40	92.403 (15)	C29—C28—P21	119.31 (15)
P2—Pd1—Cl40	93.033 (15)	C33—C28—P21	120.94 (15)
C3—P2—C9	108.29 (8)	C28—C29—C30	120.10 (19)
C3—P2—C15	102.83 (9)	C28—C29—H29	119.9
C9—P2—C15	103.12 (9)	C30—C29—H29	119.9
C3—P2—Pd1	111.86 (6)	C31—C30—C29	120.1 (2)
C9—P2—Pd1	114.02 (6)	C31—C30—H30	120.0
C15—P2—Pd1	115.72 (6)	C29—C30—H30	120.0
C4—C3—C8	119.60 (17)	C32—C31—C30	120.24 (19)
C4—C3—P2	117.83 (14)	C32—C31—H31	119.9
C8—C3—P2	122.43 (14)	C30—C31—H31	119.9
C5—C4—C3	119.52 (18)	C31—C32—C33	120.0 (2)
C5—C4—H4	120.2	C31—C32—H32	120.0
C3—C4—H4	120.2	C33—C32—H32	120.0
C6—C5—C4	120.65 (19)	C32—C33—C28	119.9 (2)
C6—C5—H5	119.7	C32—C33—H33	120.1
C4—C5—H5	119.7	C28—C33—H33	120.1
C5—C6—C7	119.69 (18)	C35—C34—C39	119.60 (18)
C5—C6—H6	120.2	C35—C34—P21	120.60 (15)
C7—C6—H6	120.2	C39—C34—P21	119.27 (15)
C8—C7—C6	120.18 (18)	C34—C35—C36	120.0 (2)
C8—C7—H7	119.9	C34—C35—H35	120.0
C6—C7—H7	119.9	C36—C35—H35	120.0
C7—C8—C3	120.35 (18)	C37—C36—C35	120.0 (2)

C7—C8—H8	119.8	C37—C36—H36	120.0
C3—C8—H8	119.8	C35—C36—H36	120.0
C10—C9—C14	119.27 (17)	C36—C37—C38	120.4 (2)
C10—C9—P2	121.40 (15)	C36—C37—H37	119.8
C14—C9—P2	119.33 (15)	C38—C37—H37	119.8
C11—C10—C9	120.6 (2)	C37—C38—C39	119.7 (2)
C11—C10—H10	119.7	C37—C38—H38	120.2
C9—C10—H10	119.7	C39—C38—H38	120.2
C12—C11—C10	119.9 (2)	C38—C39—C34	120.3 (2)
C12—C11—H11	120.1	C38—C39—H39	119.9
C10—C11—H11	120.1	C34—C39—H39	119.9
C13—C12—C11	120.12 (19)	N42—C41—C48	123.17 (17)
C13—C12—H12	119.9	N42—C41—Pd1	122.49 (13)
C11—C12—H12	119.9	C48—C41—Pd1	114.33 (13)
C12—C13—C14	120.6 (2)	C41—N42—C43	118.09 (16)
C12—C13—H13	119.7	C46—C43—N42	124.11 (17)
C14—C13—H13	119.7	C46—C43—Cl45	120.40 (15)
C13—C14—C9	119.5 (2)	N42—C43—Cl45	115.49 (14)
C13—C14—H14	120.2	C43—C46—N47	118.31 (17)
C9—C14—H14	120.2	C43—C46—H46	120.8
C20—C15—C16	118.82 (18)	N47—C46—H46	120.8
C20—C15—P2	120.50 (15)	C46—N47—C48	121.92 (16)
C16—C15—P2	120.19 (15)	C46—N47—C49	119.99 (16)
C17—C16—C15	120.59 (19)	C48—N47—C49	118.08 (15)
C17—C16—H16	119.7	O22—C48—N47	122.10 (17)
C15—C16—H16	119.7	O22—C48—C41	123.50 (17)
C16—C17—C18	120.3 (2)	N47—C48—C41	114.40 (16)
C16—C17—H17	119.9	N47—C49—C50	112.06 (15)
C18—C17—H17	119.9	N47—C49—H49A	109.2
C19—C18—C17	119.5 (2)	C50—C49—H49A	109.2
C19—C18—H18	120.3	N47—C49—H49B	109.2
C17—C18—H18	120.3	C50—C49—H49B	109.2
C18—C19—C20	120.6 (2)	H49A—C49—H49B	107.9
C18—C19—H19	119.7	C55—C50—C51	118.42 (18)
C20—C19—H19	119.7	C55—C50—C49	121.16 (18)
C19—C20—C15	120.24 (19)	C51—C50—C49	120.43 (18)
C19—C20—H20	119.9	C52—C51—C50	120.69 (19)
C15—C20—H20	119.9	C52—C51—H51	119.7
C22—P21—C28	107.68 (9)	C50—C51—H51	119.7
C22—P21—C34	102.95 (9)	C51—C52—C53	119.96 (19)
C28—P21—C34	103.53 (9)	C51—C52—H52	120.0
C22—P21—Pd1	113.86 (6)	C53—C52—H52	120.0
C28—P21—Pd1	112.69 (6)	O56—C53—C54	123.74 (19)
C34—P21—Pd1	115.12 (6)	O56—C53—C52	115.97 (18)
C27—C22—C23	119.38 (18)	C54—C53—C52	120.28 (18)
C27—C22—P21	122.84 (14)	C55—C54—C53	119.10 (19)
C23—C22—P21	117.63 (14)	C55—C54—H54	120.5
C24—C23—C22	119.85 (18)	C53—C54—H54	120.5

C24—C23—H23	120.1	C54—C55—C50	121.55 (19)
C22—C23—H23	120.1	C54—C55—H55	119.2
C25—C24—C23	120.17 (19)	C50—C55—H55	119.2
C25—C24—H24	119.9	C53—O56—C57	116.97 (18)
C23—C24—H24	119.9	O56—C57—H57A	109.5
C24—C25—C26	120.3 (2)	O56—C57—H57B	109.5
C24—C25—H25	119.9	H57A—C57—H57B	109.5
C26—C25—H25	119.9	O56—C57—H57C	109.5
C25—C26—C27	120.0 (2)	H57A—C57—H57C	109.5
C25—C26—H26	120.0	H57B—C57—H57C	109.5
C27—C26—H26	120.0		