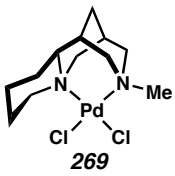
APPENDIX 3

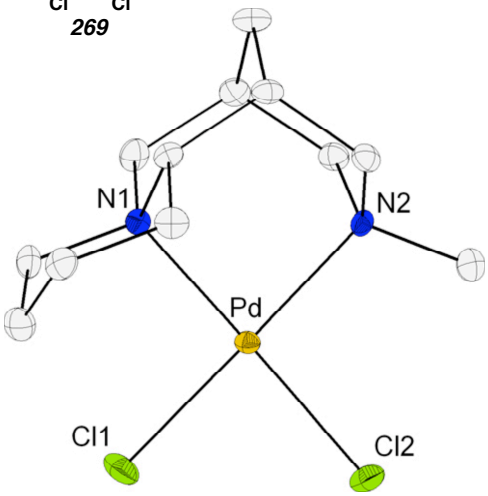
X-Ray Crystallographic Data Relevant to Chapter 4

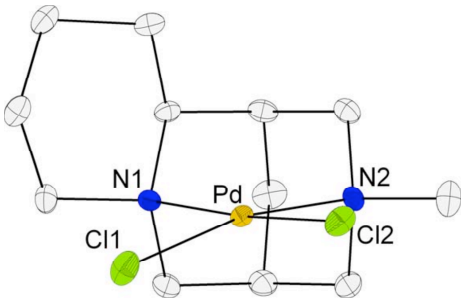
A3.1 Pd(N-Me Diamine)Cl_2 (269)

Figure A3.1.1 Pd(N-Me Diamine)Cl_2 (**269**).[1]



269





Select bond lengths (Å) and angles (°)			
Pd–N1	2.1116(14)	N1–Pd–N2	86.67(6)°
Pd–N2	2.1038(14)	Cl1–Pd–Cl2	84.895(18)°
Pd–Cl1	2.3197(4)	N2–Pd–Cl1	168.14(4)°
Pd–Cl2	2.3262(4)	N1–Pd–Cl2	175.64(4)°
		N1–Pd–Cl1	94.80(4)°
		N2–Pd–Cl2	94.52(4)°
		Σ ∠	704.67°

[1] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 274539.

Table A3.1.1 Crystal data and structure refinement for DCE03 (CCDC 274539).

Empirical formula	$C_{12}H_{22}N_2Cl_2Pd$
Formula weight	371.62
Crystal Habit	Square
Crystal size	0.27 x 0.25 x 0.10 mm^3
Crystal color	Orange

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 12945 reflections used in lattice determination	2.86 to 49.26°
Unit cell dimensions	a = 7.0251(3) Å b = 13.6041(5) Å β = 109.0170(10)° c = 7.5396(3) Å
Volume	681.23(5) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.812 Mg/m^3
F(000)	376
Data collection program	Bruker SMART v5.630
θ range for data collection	2.86 to 49.74°
Completeness to θ = 49.74°	93.9 %
Index ranges	$-14 \le h \le 11$, $-28 \le k \le 27$, $-14 \le l \le 15$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	23502
Independent reflections	11670 [R_{int}= 0.0389]
Absorption coefficient	1.734 mm^{-1}
Absorption correction	Face-indexed (SADABS)
Max. and min. transmission	0.8457 (1.000000) and 0.6517 (0.858406)

Structure Solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11670 / 1 / 242
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.159
Final R indices [I>2σ(I), 10050 reflections]	R1 = 0.0348, *w*R2 = 0.0634
R indices (all data)	R1 = 0.0457, *w*R2 = 0.0669
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.015(17)
Largest diff. peak and hole	1.711 and -0.893 e.$Å^{-3}$

Special Refinement Details

Data were collected from two different crystals (DCE01 and DCE03) and data from both crystals provided high quality structures. The results from the second crystal (DCE03) are reported herein. The structure refined against data from the second crystal resulted in more uniform hydrogen parameters and a lower goodness-of-fit. The data set from the second crystal was nearly 10% more complete and the residual for the merging of equivalent reflections was lower.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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

Figure A3.1.2 Pd(N-Me Diamine)Cl_2 (**269**).

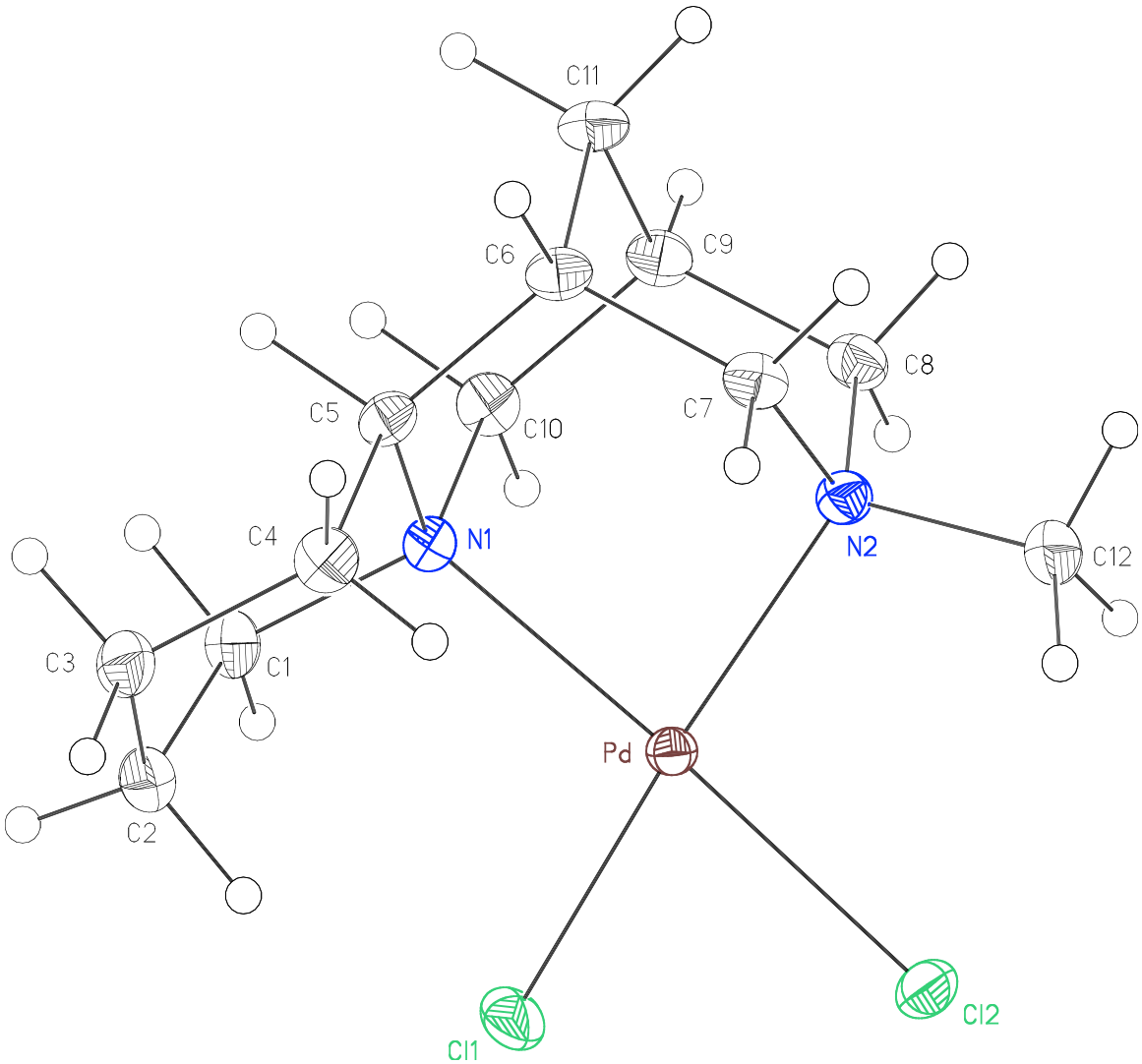


Figure A3.1.3 Unit cell of Pd(N-Me Diamine)Cl_2 (**269**).

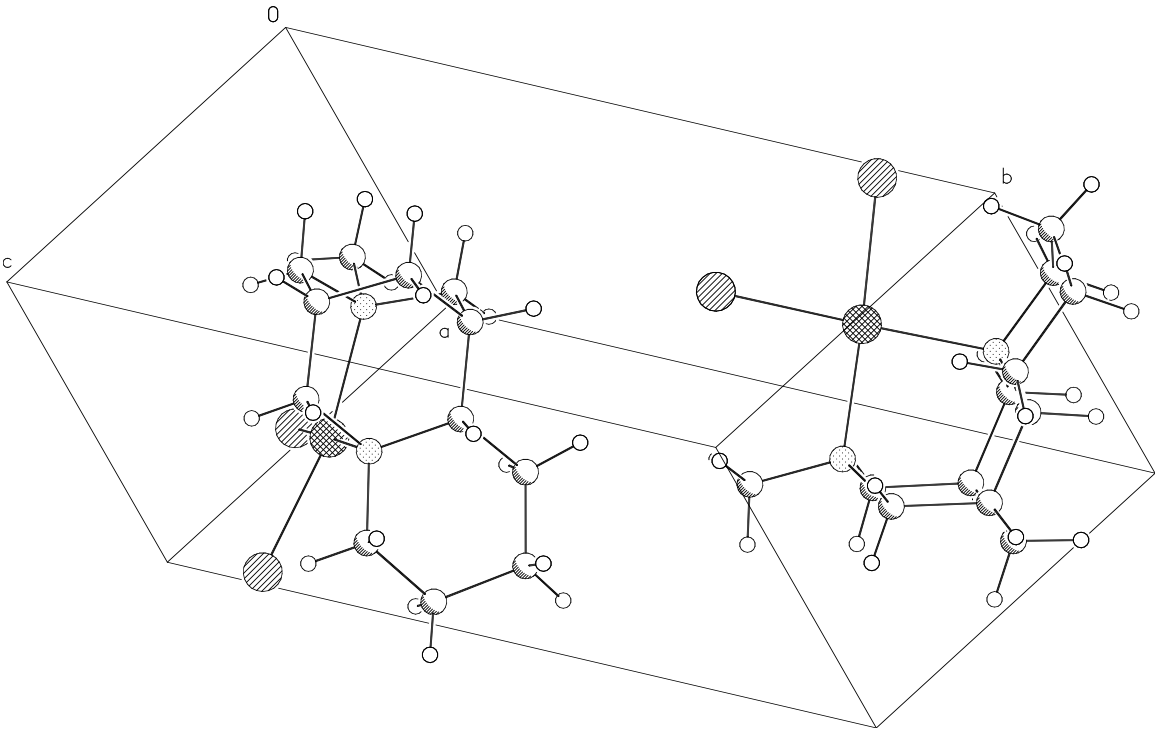


Figure A3.1.4 Stereo view of unit cell of Pd(N-Me Diamine)Cl_2 (**269**).

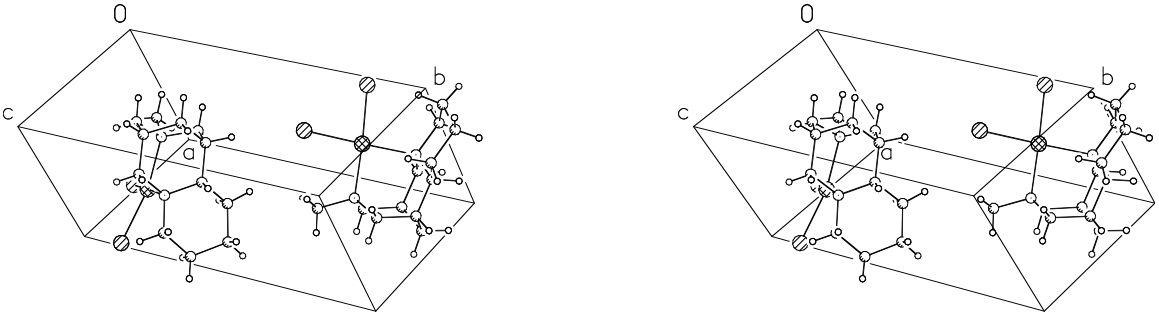


Table A3.1.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for DCE03 (CCDC 274539). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd	4607(1)	7707(1)	1579(1)	12(1)
Cl(1)	2190(1)	7345(1)	-1278(1)	22(1)
Cl(2)	3137(1)	6436(1)	2738(1)	19(1)
N(1)	5775(2)	8934(1)	560(2)	13(1)
N(2)	7149(2)	7812(1)	4004(2)	14(1)
C(1)	4413(3)	9321(1)	-1293(3)	18(1)
C(2)	2473(3)	9778(1)	-1170(3)	20(1)
C(3)	2876(3)	10580(1)	318(3)	19(1)
C(4)	4301(3)	10173(1)	2169(3)	18(1)
C(5)	6231(3)	9805(1)	1889(2)	14(1)
C(6)	7912(3)	9599(1)	3719(2)	16(1)
C(7)	7432(3)	8795(1)	4916(3)	16(1)
C(8)	8913(3)	7580(1)	3341(2)	16(1)
C(9)	9359(3)	8386(1)	2135(3)	16(1)
C(10)	7675(3)	8583(1)	284(2)	16(1)
C(11)	9824(3)	9335(1)	3284(3)	18(1)
C(12)	7154(3)	7080(2)	5468(3)	21(1)

Table A3.1.3 Selected bond lengths [Å] and angles [°] for DCE03 (CCDC 274539).

Pd-N(2)	2.1038(14)	N(2)-Pd-N(1)	86.67(6)
Pd-N(1)	2.1116(14)	N(2)-Pd-Cl(1)	168.14(4)
Pd-Cl(1)	2.3197(4)	N(1)-Pd-Cl(1)	94.80(4)
Pd-Cl(2)	2.3262(4)	N(2)-Pd-Cl(2)	94.52(4)
		N(1)-Pd-Cl(2)	175.64(4)
		Cl(1)-Pd-Cl(2)	84.895(18)

Table A3.1.4 Bond lengths [Å] and angles [°] for DCE03 (CCDC 274539).

Pd-N(2)	2.1038(14)	C(5)-N(1)-C(1)	105.84(13)
Pd-N(1)	2.1116(14)	C(10)-N(1)-Pd	105.60(10)
Pd-Cl(1)	2.3197(4)	C(5)-N(1)-Pd	113.60(10)
Pd-Cl(2)	2.3262(4)	C(1)-N(1)-Pd	114.10(11)
N(1)-C(10)	1.495(2)	C(7)-N(2)-C(12)	106.97(14)
N(1)-C(5)	1.517(2)	C(7)-N(2)-C(8)	109.88(14)
N(1)-C(1)	1.508(2)	C(12)-N(2)-C(8)	107.55(14)
N(2)-C(7)	1.487(2)	C(7)-N(2)-Pd	114.23(11)
N(2)-C(12)	1.487(2)	C(12)-N(2)-Pd	113.32(12)
N(2)-C(8)	1.512(2)	C(8)-N(2)-Pd	104.69(10)
C(1)-C(2)	1.529(3)	N(1)-C(1)-C(2)	113.28(15)
C(1)-H(1A)	0.97(3)	N(1)-C(1)-H(1A)	106.5(18)
C(1)-H(1B)	0.97(3)	C(2)-C(1)-H(1A)	111.6(19)
C(2)-C(3)	1.523(3)	N(1)-C(1)-H(1B)	105.4(19)
C(2)-H(2A)	0.99(3)	C(2)-C(1)-H(1B)	111(2)
C(2)-H(2B)	0.93(3)	H(1A)-C(1)-H(1B)	108(3)
C(3)-C(4)	1.531(3)	C(1)-C(2)-C(3)	112.36(17)
C(3)-H(3A)	0.95(4)	C(1)-C(2)-H(2A)	105.6(18)
C(3)-H(3B)	0.94(3)	C(3)-C(2)-H(2A)	110.7(18)
C(4)-C(5)	1.523(2)	C(1)-C(2)-H(2B)	106.4(19)
C(4)-H(4A)	0.87(3)	C(3)-C(2)-H(2B)	110.4(18)
C(4)-H(4B)	0.96(3)	H(2A)-C(2)-H(2B)	111(3)
C(5)-C(6)	1.521(3)	C(4)-C(3)-C(2)	108.78(15)
C(5)-H(5)	1.06(2)	C(4)-C(3)-H(3A)	106(2)
C(6)-C(11)	1.525(3)	C(2)-C(3)-H(3A)	110(2)
C(6)-C(7)	1.524(3)	C(4)-C(3)-H(3B)	111.6(19)
C(6)-H(6)	1.02(3)	C(2)-C(3)-H(3B)	109.2(19)
C(7)-H(7A)	0.92(3)	H(3A)-C(3)-H(3B)	111(3)
C(7)-H(7B)	0.88(3)	C(3)-C(4)-C(5)	109.87(16)
C(8)-C(9)	1.521(3)	C(3)-C(4)-H(4A)	115(2)
C(8)-H(8A)	0.83(3)	C(5)-C(4)-H(4A)	102(2)
C(8)-H(8B)	0.91(3)	C(3)-C(4)-H(4B)	115.5(18)
C(9)-C(10)	1.530(3)	C(5)-C(4)-H(4B)	107(2)
C(9)-C(11)	1.529(3)	H(4A)-C(4)-H(4B)	106(3)
C(9)-H(9)	0.87(3)	N(1)-C(5)-C(6)	112.95(13)
C(10)-H(10A)	1.01(3)	N(1)-C(5)-C(4)	110.01(14)
C(10)-H(10B)	0.92(3)	C(6)-C(5)-C(4)	113.45(15)
C(11)-H(11A)	0.96(3)	N(1)-C(5)-H(5)	105.4(13)
C(11)-H(11B)	1.04(3)	C(6)-C(5)-H(5)	108.9(14)
C(12)-H(12A)	0.94(3)	C(4)-C(5)-H(5)	105.5(14)
C(12)-H(12B)	0.94(3)	C(5)-C(6)-C(11)	109.03(15)
C(12)-H(12C)	1.10(3)	C(5)-C(6)-C(7)	114.36(14)
		C(11)-C(6)-C(7)	109.79(15)
N(2)-Pd-N(1)	86.67(6)	C(5)-C(6)-H(6)	105.3(16)
N(2)-Pd-Cl(1)	168.14(4)	C(11)-C(6)-H(6)	112.0(17)
N(1)-Pd-Cl(1)	94.80(4)	C(7)-C(6)-H(6)	106.3(16)
N(2)-Pd-Cl(2)	94.52(4)	N(2)-C(7)-C(6)	113.18(14)
N(1)-Pd-Cl(2)	175.64(4)	N(2)-C(7)-H(7A)	107(2)
Cl(1)-Pd-Cl(2)	84.895(18)	C(6)-C(7)-H(7A)	111(2)
C(10)-N(1)-C(5)	109.60(13)	N(2)-C(7)-H(7B)	107.6(19)
C(10)-N(1)-C(1)	107.97(13)	C(6)-C(7)-H(7B)	112.5(19)

H(7A)-C(7)-H(7B)	105(3)	N(1)-C(10)-H(10B)	105.8(18)
N(2)-C(8)-C(9)	113.43(14)	C(9)-C(10)-H(10B)	112.2(17)
N(2)-C(8)-H(8A)	108(2)	H(10A)-C(10)-H(10B)	107(2)
C(9)-C(8)-H(8A)	108.2(19)	C(6)-C(11)-C(9)	106.27(14)
N(2)-C(8)-H(8B)	108.9(16)	C(6)-C(11)-H(11A)	112.8(18)
C(9)-C(8)-H(8B)	107.4(17)	C(9)-C(11)-H(11A)	110.4(18)
H(8A)-C(8)-H(8B)	111(3)	C(6)-C(11)-H(11B)	107.7(17)
C(8)-C(9)-C(10)	115.02(15)	C(9)-C(11)-H(11B)	111.7(16)
C(8)-C(9)-C(11)	108.50(15)	H(11A)-C(11)-H(11B)	108(3)
C(10)-C(9)-C(11)	109.15(15)	N(2)-C(12)-H(12A)	106.9(16)
C(8)-C(9)-H(9)	104.9(17)	N(2)-C(12)-H(12B)	110.7(17)
C(10)-C(9)-H(9)	106.0(17)	H(12A)-C(12)-H(12B)	109(2)
C(11)-C(9)-H(9)	113.3(18)	N(2)-C(12)-H(12C)	113.3(15)
N(1)-C(10)-C(9)	112.86(14)	H(12A)-C(12)-H(12C)	113(2)
N(1)-C(10)-H(10A)	110.0(18)	H(12B)-C(12)-H(12C)	105(2)
C(9)-C(10)-H(10A)	108.8(18)		

Table A3.1.5 Anisotropic displacement parameters ($Å^2$ x 10^4) for DCE03 (CCDC 274539). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2*a^2*U^{11}$ + ... + 2h*k*a*b*U^{12}]

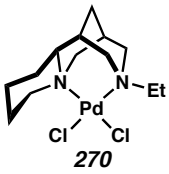
	U^{11}	U^{22}	U^{33}	U^{23}	$U^{13\ 13}$	U^{12}
Pd	104(1)	108(1)	131(1)	-6(1)	32(1)	-3(1)
Cl(1)	202(2)	164(2)	215(2)	-19(1)	-45(2)	-12(1)
Cl(2)	158(2)	149(2)	265(2)	25(1)	87(2)	-11(1)
N(1)	133(5)	121(5)	128(5)	-3(3)	53(4)	3(3)
N(2)	131(4)	164(8)	137(5)	10(4)	44(4)	-14(4)
C(1)	200(7)	178(7)	149(7)	25(5)	55(6)	14(5)
C(2)	183(7)	170(7)	211(8)	31(5)	30(6)	17(5)
C(3)	185(7)	147(6)	244(8)	26(5)	69(6)	29(5)
C(4)	172(7)	166(6)	211(8)	-10(5)	95(6)	27(5)
C(5)	153(6)	118(5)	164(6)	-16(4)	68(5)	-14(4)
C(6)	146(6)	158(6)	167(7)	-45(5)	59(5)	-27(4)
C(7)	148(6)	191(7)	128(6)	-33(5)	48(5)	-10(5)
C(8)	123(5)	174(10)	179(6)	-1(5)	39(4)	14(4)
C(9)	125(6)	197(7)	186(7)	-13(5)	73(5)	6(4)
C(10)	161(6)	195(7)	157(7)	-8(5)	89(5)	15(5)
C(11)	127(6)	197(7)	223(8)	-30(5)	65(6)	-34(5)
C(12)	186(8)	233(8)	190(8)	62(6)	37(6)	-7(6)

Table A3.1.6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for DCE03 (CCDC 274539).

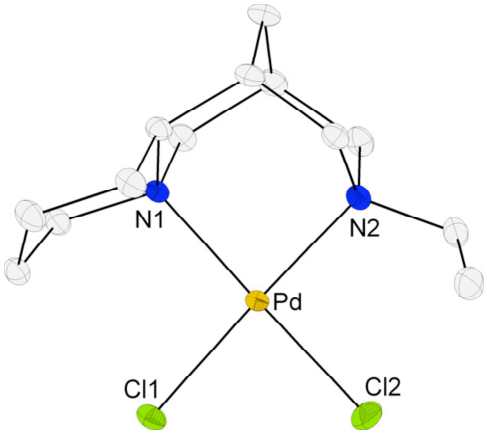
	x	y	z	U_{iso}
H(1A)	4140(50)	8770(20)	-2160(40)	23(7)
H(1B)	5210(50)	9800(30)	-1690(40)	30(9)
H(2A)	1700(50)	9230(20)	-860(40)	25(8)
H(2B)	1800(50)	10040(20)	-2350(40)	23(7)
H(3A)	3570(60)	11120(30)	-10(50)	43(10)
H(3B)	1650(50)	10790(20)	440(40)	24(7)
H(4A)	3880(50)	9650(20)	2580(40)	21(7)
H(4B)	4690(50)	10630(20)	3190(40)	21(7)
H(5)	6690(40)	10374(18)	1170(30)	8(5)
H(6)	8070(40)	10230(20)	4480(40)	17(6)
H(7A)	8450(50)	8730(20)	6050(40)	27(8)
H(7B)	6350(50)	8930(20)	5210(40)	18(7)
H(8A)	8660(40)	7070(20)	2710(40)	17(6)
H(8B)	10040(40)	7500(20)	4360(40)	16(6)
H(9)	10370(40)	8168(19)	1830(30)	11(6)
H(10A)	8170(50)	9080(20)	-460(40)	23(7)
H(10B)	7330(40)	8026(19)	-450(40)	16(6)
H(11A)	10960(50)	9240(20)	4390(40)	21(7)
H(11B)	10140(50)	9910(20)	2520(40)	18(7)
H(12A)	8380(40)	7152(19)	6440(30)	11(6)
H(12B)	7080(50)	6440(20)	4990(40)	15(7)
H(12C)	5840(50)	7140(20)	5950(40)	26(8)

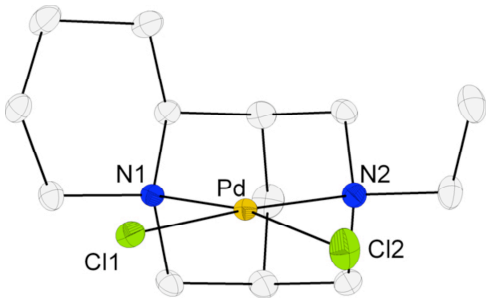
A3.2 Pd(N-Et Diamine)Cl_2 (270)

Figure A3.2.1 Pd(N-Et Diamine)Cl_2 (**270**).[2]



270





Select bond lengths (Å) and angles (°)			
Pd–N1	2.1294(16)	N1–Pd–N2	86.90(6)°
Pd–N2	2.1114(16)	Cl1–Pd–Cl2	83.73(2)°
Pd–Cl1	2.3254(5)	N2–Pd–Cl1	176.22(5)°
Pd–Cl2	2.3116(5)	N1–Pd–Cl2	171.22(4)°
		N1–Pd–Cl1	95.33(4)°
		N2–Pd–Cl2	93.61(5)°
		Σ ∠	707.01°

[2] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 274867.

Table A3.2.1 Crystal data and structure refinement for DCE02 (CCDC 274867).

Empirical formula	$C_{13}H_{24}N_2Cl_2Pd \bullet CHCl_3$
Formula weight	505.01
Crystallization Solvent	Chloroform/heptane
Crystal Habit	Fragment
Crystal size	0.33 x 0.23 x 0.03 mm^3
Crystal color	Orange

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 11657 reflections used in lattice determination	2.34 to 44.83°
Unit cell dimensions	a = 9.0343(3) Å b = 11.9016(4) Å β = 109.1540(10)° c = 9.2290(4) Å
Volume	937.39(6) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.789 Mg/m^3
F(000)	508
Data collection program	Bruker SMART v5.630
θ range for data collection	2.34 to 47.35°
Completeness to θ = 47.35°	94.5 %
Index ranges	$-18 \le h \le 18$, $-24 \le k \le 24$, $-18 \le l \le 16$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	29263
Independent reflections	14853 [R_{int}= 0.0447]
Absorption coefficient	1.700 mm^{-1}
Absorption correction	Face-indexed and (SADABS)
Max. and min. transmission	0.93080 (1.000000) and 0.61310 (0.877919)

Structure Solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	14853 / 1 / 299
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.076
Final R indices [I>2σ(I), 12280 reflections]	R1 = 0.0374, *w*R2 = 0.0699
R indices (all data)	R1 = 0.0532, *w*R2 = 0.0753
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Anomalous dispersion
Absolute structure parameter	-0.005(16)
Largest diff. peak and hole	1.688 and -1.015 e.$Å^{-3}$

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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

Figure A3.2.2 Pd(N-Et Diamine)Cl_2 (**270**).

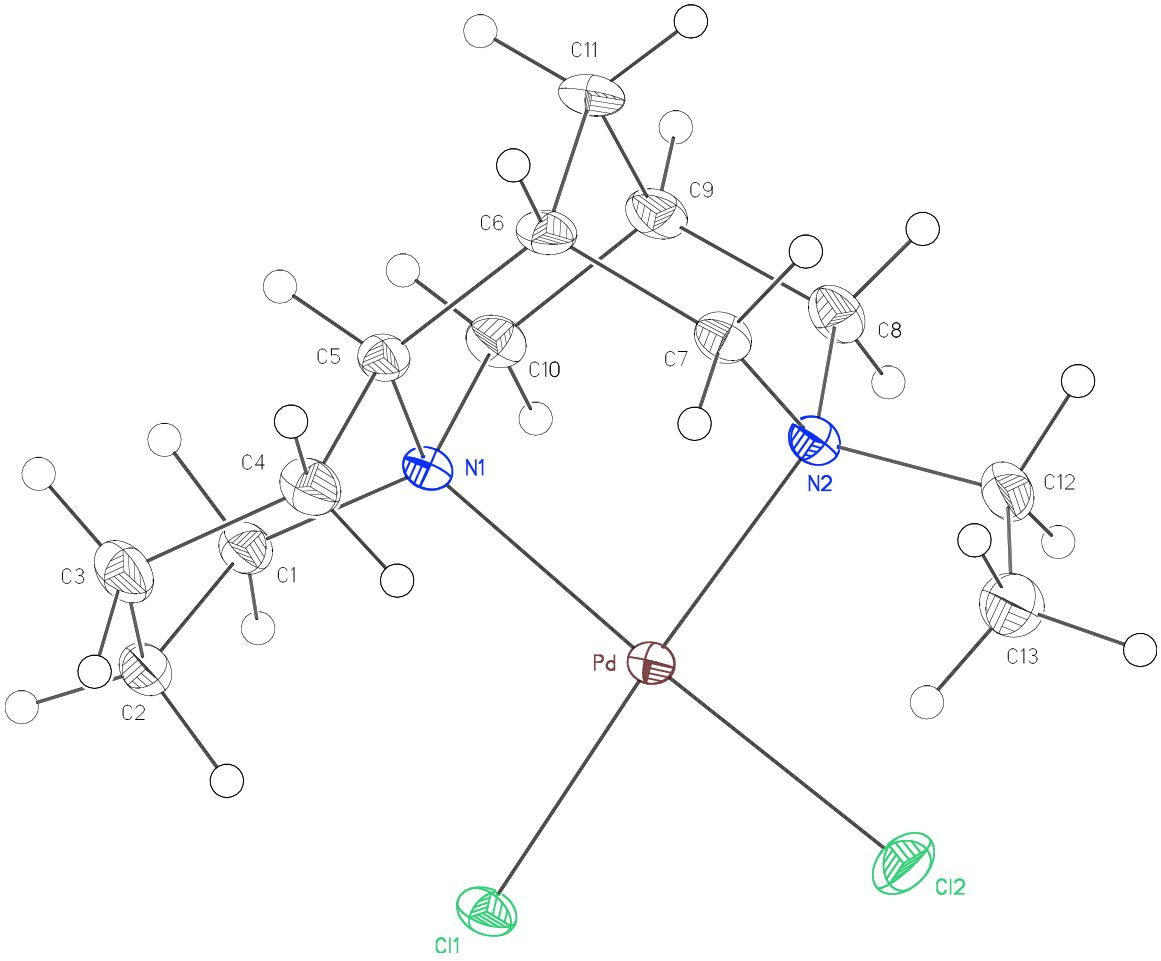


Figure A3.2.3 Unit cell of Pd(N-Et Diamine)Cl_2 (**270**).

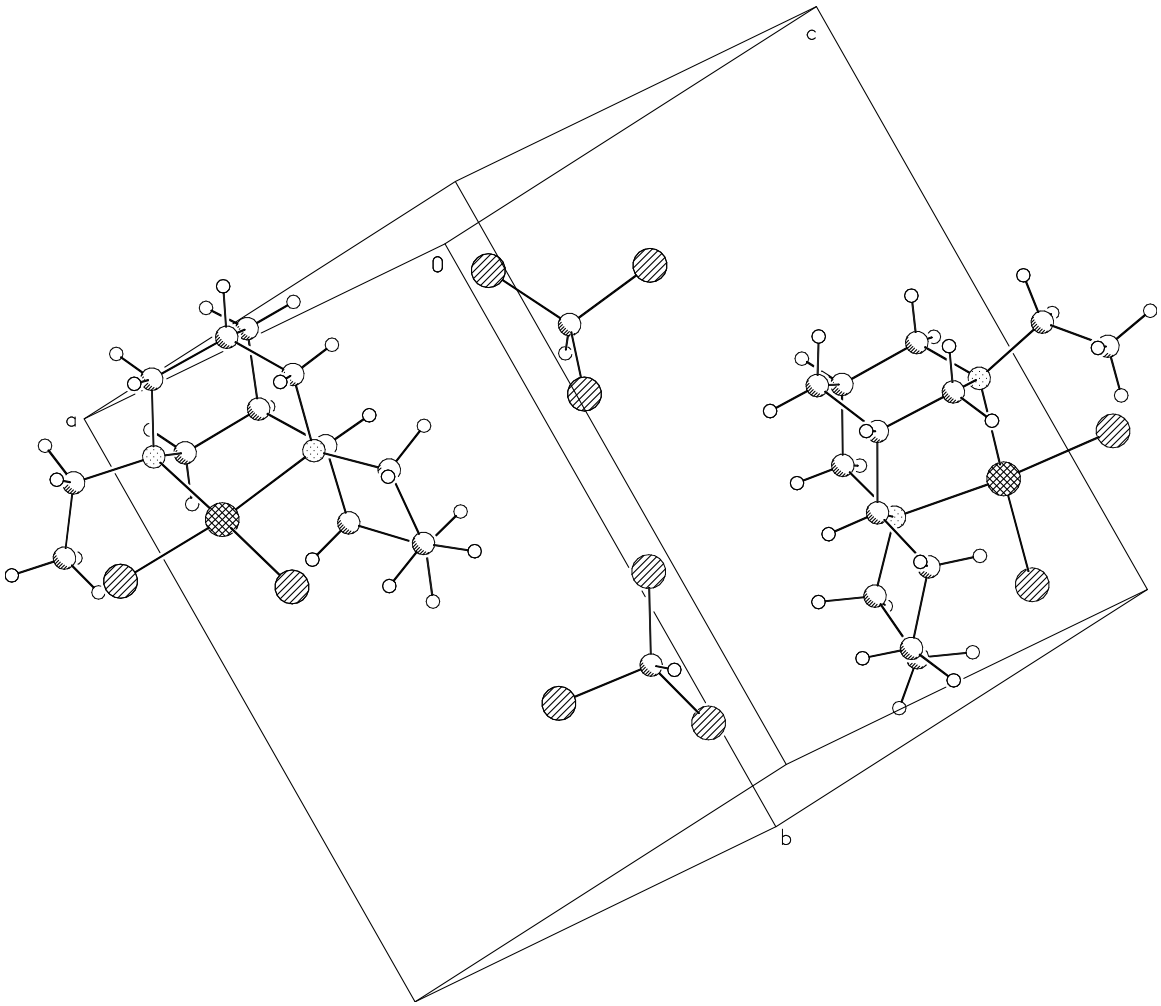


Figure A3.2.4 Stereo view of unit cell of Pd(N-Et Diamine)Cl_2 (**270**).

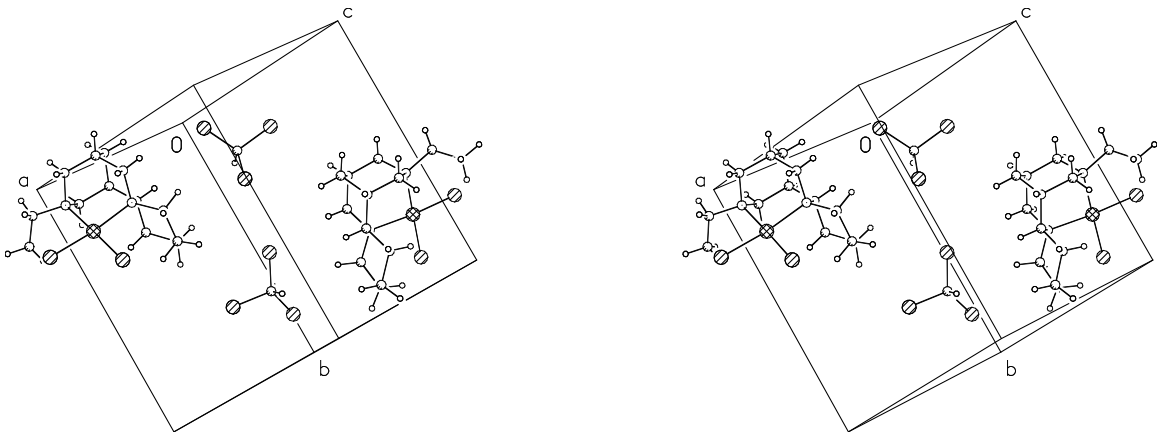


Table A3.2.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for DCE02 (CCDC 274867). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd	-502(1)	7416(1)	7945(1)	11(1)
Cl(1)	-1611(1)	8902(1)	6313(1)	16(1)
Cl(2)	-2765(1)	7533(1)	8586(1)	25(1)
N(1)	1376(2)	7154(1)	7068(2)	11(1)
N(2)	359(2)	6015(1)	9376(2)	14(1)
C(1)	1487(2)	7997(2)	5899(2)	16(1)
C(2)	2061(2)	9155(2)	6567(3)	17(1)
C(3)	3579(2)	9095(2)	7934(3)	21(1)
C(4)	3431(2)	8198(2)	9058(3)	18(1)
C(5)	2985(2)	7074(2)	8246(2)	14(1)
C(6)	3144(2)	6060(2)	9299(2)	16(1)
C(7)	2074(2)	6097(2)	10273(2)	15(1)
C(8)	66(3)	5041(2)	8277(3)	17(1)
C(9)	1135(3)	5041(2)	7299(3)	17(1)
C(10)	941(2)	6055(2)	6231(2)	16(1)
C(11)	2840(3)	4977(2)	8351(3)	20(1)
C(12)	-472(3)	5756(2)	10498(3)	19(1)
C(13)	-169(3)	6607(2)	11797(3)	24(1)
Cl(3)	4429(1)	6076(1)	4377(1)	23(1)
Cl(4)	6571(1)	7160(1)	3071(1)	22(1)
Cl(5)	4005(1)	8432(1)	3477(1)	23(1)
C(14)	5387(2)	7339(2)	4248(2)	17(1)

Table A3.2.3 Selected bond lengths [Å] and angles [°] for DCE02 (CCDC 274867).

Pd-N(2)	2.1114(16)	N(2)-Pd-N(1)	86.90(6)
Pd-N(1)	2.1294(16)	N(2)-Pd-Cl(2)	93.61(5)
Pd-Cl(2)	2.3116(5)	N(1)-Pd-Cl(2)	171.22(4)
Pd-Cl(1)	2.3254(5)	N(2)-Pd-Cl(1)	176.22(5)
		N(1)-Pd-Cl(1)	95.33(4)
		Cl(2)-Pd-Cl(1)	83.73(2)

Table A3.2.4 Bond lengths [Å] and angles [°] for DCE02 (CCDC 274867).

Pd-N(2)	2.1114(16)	N(2)-Pd-Cl(2)	93.61(5)
Pd-N(1)	2.1294(16)	N(1)-Pd-Cl(2)	171.22(4)
Pd-Cl(2)	2.3116(5)	N(2)-Pd-Cl(1)	176.22(5)
Pd-Cl(1)	2.3254(5)	N(1)-Pd-Cl(1)	95.33(4)
N(1)-C(1)	1.500(2)	Cl(2)-Pd-Cl(1)	83.73(2)
N(1)-C(10)	1.505(2)	C(1)-N(1)-C(10)	106.28(15)
N(1)-C(5)	1.505(2)	C(1)-N(1)-C(5)	106.58(14)
N(2)-C(12)	1.497(3)	C(10)-N(1)-C(5)	110.07(14)
N(2)-C(7)	1.501(2)	C(1)-N(1)-Pd	115.17(11)
N(2)-C(8)	1.505(2)	C(10)-N(1)-Pd	102.45(11)
C(1)-C(2)	1.530(3)	C(5)-N(1)-Pd	115.83(12)
C(1)-H(1A)	0.99(4)	C(12)-N(2)-C(7)	107.03(16)
C(1)-H(1B)	1.01(3)	C(12)-N(2)-C(8)	106.85(15)
C(2)-C(3)	1.531(3)	C(7)-N(2)-C(8)	110.09(15)
C(2)-H(2A)	0.98(4)	C(12)-N(2)-Pd	115.45(12)
C(2)-H(2B)	1.01(3)	C(7)-N(2)-Pd	113.31(11)
C(3)-C(4)	1.524(3)	C(8)-N(2)-Pd	103.87(12)
C(3)-H(3A)	1.04(4)	N(1)-C(1)-C(2)	113.96(17)
C(3)-H(3B)	0.93(4)	N(1)-C(1)-H(1A)	114(2)
C(4)-C(5)	1.522(3)	C(2)-C(1)-H(1A)	105(2)
C(4)-H(4A)	0.89(4)	N(1)-C(1)-H(1B)	107.1(18)
C(4)-H(4B)	0.94(4)	C(2)-C(1)-H(1B)	111.0(19)
C(5)-C(6)	1.527(3)	H(1A)-C(1)-H(1B)	106(3)
C(5)-H(5)	0.94(3)	C(1)-C(2)-C(3)	112.56(16)
C(6)-C(7)	1.521(3)	C(1)-C(2)-H(2A)	111(2)
C(6)-C(11)	1.531(3)	C(3)-C(2)-H(2A)	109(3)
C(6)-H(6)	0.94(4)	C(1)-C(2)-H(2B)	107.5(19)
C(7)-H(7A)	0.93(3)	C(3)-C(2)-H(2B)	105.6(18)
C(7)-H(7B)	0.99(3)	H(2A)-C(2)-H(2B)	111(3)
C(8)-C(9)	1.523(3)	C(4)-C(3)-C(2)	109.83(16)
C(8)-H(8A)	0.92(4)	C(4)-C(3)-H(3A)	105(2)
C(8)-H(8B)	0.91(5)	C(2)-C(3)-H(3A)	108(2)
C(9)-C(11)	1.530(3)	C(4)-C(3)-H(3B)	107(3)
C(9)-C(10)	1.531(3)	C(2)-C(3)-H(3B)	111(2)
C(9)-H(9)	0.97(3)	H(3A)-C(3)-H(3B)	116(3)
C(10)-H(10A)	0.87(4)	C(5)-C(4)-C(3)	110.40(19)
C(10)-H(10B)	0.94(3)	C(5)-C(4)-H(4A)	109(2)
C(11)-H(11A)	0.93(4)	C(3)-C(4)-H(4A)	108(2)
C(11)-H(11B)	0.95(4)	C(5)-C(4)-H(4B)	111(2)
C(12)-C(13)	1.525(3)	C(3)-C(4)-H(4B)	110(2)
C(12)-H(12A)	0.95(4)	H(4A)-C(4)-H(4B)	108(3)
C(12)-H(12B)	0.90(3)	N(1)-C(5)-C(4)	109.69(14)
C(13)-H(13A)	0.98(4)	N(1)-C(5)-C(6)	112.15(14)
C(13)-H(13B)	0.98(4)	C(4)-C(5)-C(6)	115.27(17)
C(13)-H(13C)	0.93(5)	N(1)-C(5)-H(5)	102(2)
Cl(3)-C(14)	1.758(2)	C(4)-C(5)-H(5)	106(2)
Cl(4)-C(14)	1.7694(19)	C(6)-C(5)-H(5)	111(2)
Cl(5)-C(14)	1.781(2)	C(7)-C(6)-C(5)	114.08(15)
C(14)-H(14)	0.92(3)	C(7)-C(6)-C(11)	109.43(16)
		C(5)-C(6)-C(11)	109.85(17)
N(2)-Pd-N(1)	86.90(6)	C(7)-C(6)-H(6)	105(2)

C(5)-C(6)-H(6)	110(2)	H(10A)-C(10)-H(10B)	112(3)
C(11)-C(6)-H(6)	109(2)	C(9)-C(11)-C(6)	105.96(15)
N(2)-C(7)-C(6)	114.39(16)	C(9)-C(11)-H(11A)	109(3)
N(2)-C(7)-H(7A)	110(2)	C(6)-C(11)-H(11A)	107(2)
C(6)-C(7)-H(7A)	107.1(19)	C(9)-C(11)-H(11B)	109(2)
N(2)-C(7)-H(7B)	110.3(18)	C(6)-C(11)-H(11B)	109(2)
C(6)-C(7)-H(7B)	109.5(18)	H(11A)-C(11)-H(11B)	116(3)
H(7A)-C(7)-H(7B)	105(2)	N(2)-C(12)-C(13)	113.94(18)
N(2)-C(8)-C(9)	113.15(15)	N(2)-C(12)-H(12A)	109(2)
N(2)-C(8)-H(8A)	108(2)	C(13)-C(12)-H(12A)	108(2)
C(9)-C(8)-H(8A)	114(2)	N(2)-C(12)-H(12B)	102.9(17)
N(2)-C(8)-H(8B)	105(3)	C(13)-C(12)-H(12B)	117.9(17)
C(9)-C(8)-H(8B)	109(3)	H(12A)-C(12)-H(12B)	104(3)
H(8A)-C(8)-H(8B)	108(4)	C(12)-C(13)-H(13A)	117(2)
C(8)-C(9)-C(11)	109.05(18)	C(12)-C(13)-H(13B)	109(2)
C(8)-C(9)-C(10)	114.87(16)	H(13A)-C(13)-H(13B)	106(3)
C(11)-C(9)-C(10)	109.07(17)	C(12)-C(13)-H(13C)	109(2)
C(8)-C(9)-H(9)	112(2)	H(13A)-C(13)-H(13C)	105(3)
C(11)-C(9)-H(9)	105(2)	H(13B)-C(13)-H(13C)	112(3)
C(10)-C(9)-H(9)	106.2(19)	Cl(3)-C(14)-Cl(4)	110.45(12)
N(1)-C(10)-C(9)	113.56(16)	Cl(3)-C(14)-Cl(5)	110.80(10)
N(1)-C(10)-H(10A)	108(2)	Cl(4)-C(14)-Cl(5)	109.16(11)
C(9)-C(10)-H(10A)	107(2)	Cl(3)-C(14)-H(14)	113.4(17)
N(1)-C(10)-H(10B)	106(2)	Cl(4)-C(14)-H(14)	110.2(16)
C(9)-C(10)-H(10B)	110(2)	Cl(5)-C(14)-H(14)	102.5(17)

Table A3.2.5 Anisotropic displacement parameters ($Å^2$ x 10^4) for DCE02 (CCDC 274867). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2*a^2*U^{11} + ... + 2h*k*a*b*U^{12}]$

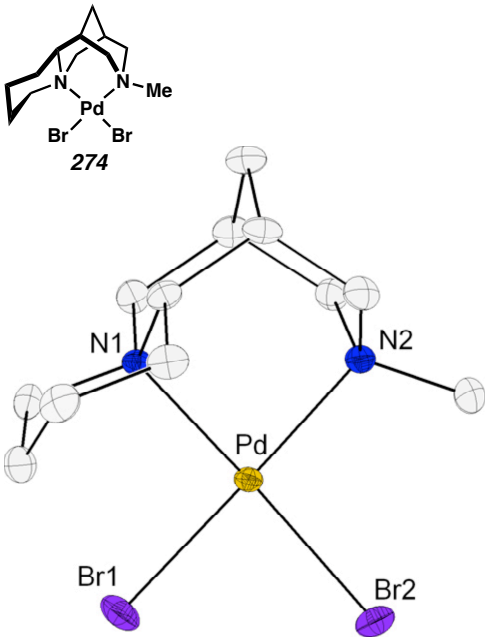
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd	103(1)	96(1)	111(1)	-4(1)	24(1)	5(1)
Cl(1)	136(2)	127(1)	184(2)	24(1)	7(1)	15(1)
Cl(2)	167(2)	337(3)	288(2)	91(2)	120(2)	80(2)
N(1)	127(5)	93(4)	115(6)	-1(4)	30(4)	7(3)
N(2)	159(6)	113(5)	135(7)	3(5)	46(5)	3(4)
C(1)	187(7)	144(6)	154(8)	22(6)	63(6)	17(5)
C(2)	166(7)	131(6)	210(9)	28(6)	60(6)	-1(5)
C(3)	177(7)	151(6)	274(11)	34(7)	31(7)	-34(6)
C(4)	152(7)	151(6)	214(9)	2(6)	15(6)	-18(5)
C(5)	110(5)	133(5)	153(7)	19(5)	22(5)	11(4)
C(6)	132(6)	140(6)	180(8)	19(6)	20(5)	39(5)
C(7)	168(6)	140(6)	125(7)	7(6)	25(5)	11(5)
C(8)	222(8)	113(6)	176(9)	-22(6)	60(6)	-32(5)
C(9)	242(8)	109(6)	166(8)	-28(6)	72(6)	12(5)
C(10)	226(8)	129(6)	124(7)	-23(6)	56(6)	10(5)
C(11)	226(8)	117(6)	253(10)	6(6)	88(7)	60(6)
C(12)	254(9)	156(6)	200(9)	33(7)	112(7)	3(6)
C(13)	348(11)	225(8)	206(10)	19(8)	153(9)	40(8)
Cl(3)	244(2)	163(2)	285(3)	30(2)	92(2)	-26(2)
Cl(4)	218(2)	203(2)	264(2)	-37(2)	117(2)	-5(1)
Cl(5)	248(2)	166(2)	289(3)	18(2)	123(2)	30(2)
C(14)	168(5)	154(7)	180(7)	-12(7)	62(5)	-19(6)

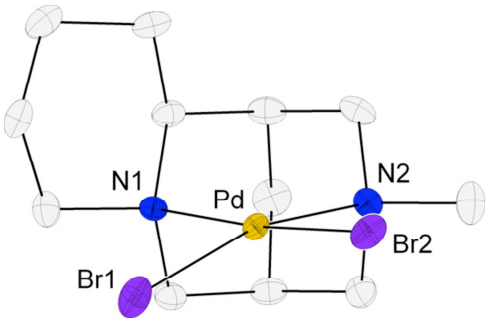
Table A3.2.6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for DCE02 (CCDC 274867).

	x	y	z	U_{iso}
H(1A)	480(50)	8140(30)	5080(40)	26(9)
H(1B)	2210(40)	7670(30)	5370(30)	19(8)
H(2A)	2230(50)	9650(30)	5800(50)	36(11)
H(2B)	1250(40)	9470(30)	6980(30)	13(7)
H(3A)	3710(50)	9850(30)	8530(40)	28(9)
H(3B)	4420(50)	8890(40)	7620(40)	34(10)
H(4A)	4350(50)	8130(30)	9790(50)	31(10)
H(4B)	2700(50)	8420(30)	9530(40)	26(9)
H(5)	3620(40)	6990(30)	7620(40)	26(9)
H(6)	4160(50)	6040(30)	10010(40)	28(9)
H(7A)	2360(40)	5510(20)	10960(40)	11(7)
H(7B)	2290(40)	6790(20)	10910(30)	11(7)
H(8A)	-980(50)	5030(30)	7720(40)	28(9)
H(8B)	270(50)	4420(40)	8880(50)	39(11)
H(9)	980(40)	4380(30)	6650(40)	14(7)
H(10A)	1560(40)	5950(30)	5690(40)	24(8)
H(10B)	-110(40)	6120(30)	5610(40)	18(8)
H(11A)	2950(50)	4380(30)	9030(40)	31(10)
H(11B)	3510(40)	4970(30)	7740(40)	22(8)
H(12A)	-150(50)	5040(30)	10940(50)	29(10)
H(12B)	-1460(30)	5650(20)	9890(30)	5(6)
H(13A)	890(40)	6620(30)	12550(40)	21(8)
H(13B)	-870(50)	6450(40)	12390(50)	34(10)
H(13C)	-310(40)	7320(40)	11380(40)	36(10)
H(14)	5980(30)	7630(20)	5190(30)	7(6)

A3.3 Pd(N-Me Diamine)Br_2 (274)

Figure A3.3.1 Pd(N-Me Diamine)Br_2 (**274**).[3,4]





Select bond lengths (Å) and angles (°)			
Pd–N1	2.126(2)	N1–Pd–N2	86.46(8)°
Pd–N2	2.117(2)	Br1–Pd–Br2	84.449(12)°
Pd–Br1	2.4463(3)	N2–Pd–Br1	165.81(6)°
Pd–Br2	2.4513(3)	N1–Pd–Br2	174.56(6)°
		N1–Pd–Br1	95.17(6)°
		N2–Pd–Br2	95.24(6)°
		Σ ∠	701.69°

[3] The numbering in Figure A3.3.1 differs from that in the X-ray crystallographic report.

[4] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 639648.

Table A3.3.1 Crystal data and structure refinement for DCE04 (CCDC 639648).

Empirical formula	$C_{12}H_{22}N_2Br_2Pd$
Formula weight	460.54
Crystallization Solvent	Chloroform/hexanes
Crystal Habit	Fragment
Crystal size	0.36 x 0.12 x 0.08 mm^3
Crystal color	Brown

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 13773 reflections used in lattice determination	2.84 to 42.48°
Unit cell dimensions	a = 7.0987(2) Å b = 13.9562(3) Å β = 107.4540(10)° c = 7.5296(2) Å
Volume	711.62(3) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	2.149 Mg/m^3
F(000)	448
Data collection program	Bruker SMART v5.630
θ range for data collection	2.84 to 42.48°
Completeness to θ = 42.48°	94.4 %
Index ranges	$-13 \le h \le 13$, $-26 \le k \le 26$, $-14 \le l \le 14$
Data collection scan type	ω scans at 9 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	23293
Independent reflections	8669 [R_{int}= 0.0533]
Absorption coefficient	6.900 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7480 and 0.2324

Structure Solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8669 / 1 / 155
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	0.991
Final R indices [I>2σ(I), 7491 reflections]	R1 = 0.0348, *w*R2 = 0.0686
R indices (all data)	R1 = 0.0445, *w*R2 = 0.0719
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.039(5)
Largest diff. peak and hole	2.583 and -0.963 e.$Å^{-3}$

Special Refinement Details

All difference Fourier peaks larger than one electron lie within 1Å of either Pd or Br.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) 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 $F^2 > 2\sigma(F^2)$ 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.

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

Figure A3.3.2 Pd(N-Me Diamine)Br_2 (**274**).

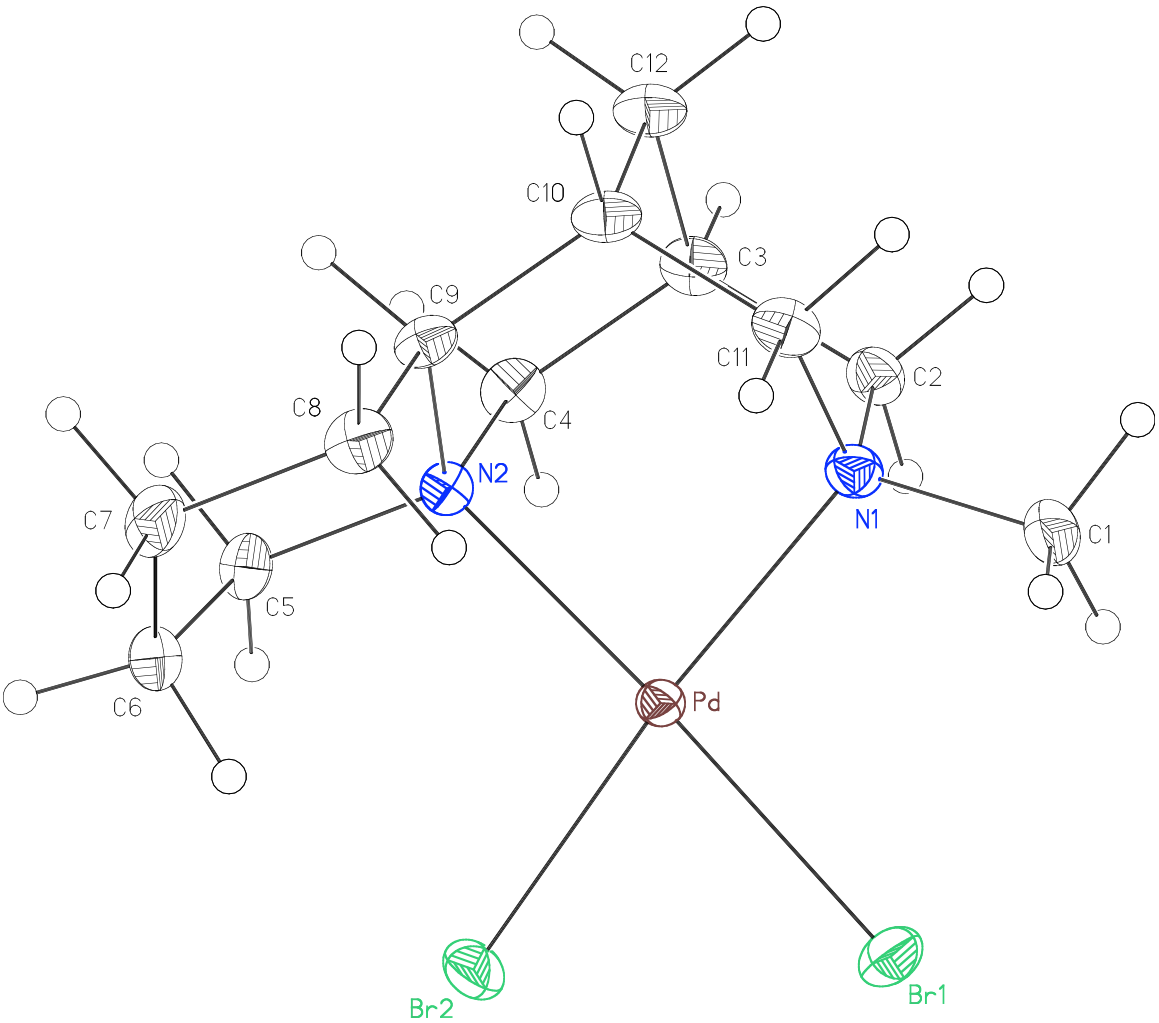


Table A3.3.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for DCE04 (CCDC 639648). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd	4434(1)	7358(1)	6449(1)	12(1)
Br(1)	2842(1)	6044(1)	7616(1)	20(1)
Br(2)	2121(1)	6941(1)	3422(1)	25(1)
N(1)	6883(3)	7466(2)	8877(3)	16(1)
N(2)	5599(3)	8584(2)	5468(3)	13(1)
C(1)	6893(4)	6742(2)	10329(4)	23(1)
C(2)	8636(4)	7247(2)	8200(3)	17(1)
C(3)	9104(4)	8050(2)	7009(4)	18(1)
C(4)	7496(4)	8248(2)	5183(4)	18(1)
C(5)	4314(4)	8974(2)	3645(4)	19(1)
C(6)	2377(4)	9409(2)	3784(4)	21(1)
C(7)	2732(5)	10167(2)	5296(4)	23(1)
C(8)	4074(4)	9759(2)	7107(4)	20(1)
C(9)	5998(4)	9417(2)	6811(4)	16(1)
C(10)	7627(4)	9213(2)	8624(4)	18(1)
C(11)	7135(4)	8421(2)	9805(4)	19(1)
C(12)	9530(4)	8964(2)	8174(4)	21(1)

Table A3.3.3 Selected bond lengths [Å] and angles [°] for DCE04 (CCDC 639648).

Pd-N(2)	2.126(2)	N(2)-Pd-N(1)	86.46(8)
Pd-N(1)	2.117(2)	N(2)-Pd-Br(2)	95.17(6)
Pd-Br(2)	2.4463(3)	N(1)-Pd-Br(2)	165.81(6)
Pd-Br(1)	2.4513(3)	N(2)-Pd-Br(1)	174.56(6)
		N(1)-Pd-Br(1)	95.24(6)
		Br(2)-Pd-Br(1)	84.449(12)

Table A3.3.4 Bond lengths [Å] and angles [°] for DCE04 (CCDC 639648).

Pd-N(2)	2.126(2)	C(11)-N(1)-C(2)	110.1(2)
Pd-N(1)	2.117(2)	C(1)-N(1)-C(2)	106.7(2)
Pd-Br(2)	2.4463(3)	C(11)-N(1)-Pd	114.87(16)
Pd-Br(1)	2.4513(3)	C(1)-N(1)-Pd	114.09(17)
N(1)-C(11)	1.490(3)	C(2)-N(1)-Pd	103.91(14)
N(1)-C(1)	1.487(4)	C(5)-N(2)-C(4)	107.84(19)
N(1)-C(2)	1.511(3)	C(5)-N(2)-C(9)	105.8(2)
N(2)-C(5)	1.504(3)	C(4)-N(2)-C(9)	109.9(2)
N(2)-C(4)	1.501(3)	C(5)-N(2)-Pd	114.59(16)
N(2)-C(9)	1.511(3)	C(4)-N(2)-Pd	104.94(16)
C(2)-C(3)	1.532(4)	C(9)-N(2)-Pd	113.69(15)
C(3)-C(12)	1.525(4)	N(1)-C(2)-C(3)	113.2(2)
C(3)-C(4)	1.526(4)	C(12)-C(3)-C(4)	109.4(2)
C(5)-C(6)	1.535(4)	C(12)-C(3)-C(2)	108.4(2)
C(6)-C(7)	1.519(4)	C(4)-C(3)-C(2)	115.1(2)
C(7)-C(8)	1.521(4)	N(2)-C(4)-C(3)	112.8(2)
C(8)-C(9)	1.525(4)	N(2)-C(5)-C(6)	113.0(2)
C(9)-C(10)	1.528(4)	C(7)-C(6)-C(5)	112.1(2)
C(10)-C(11)	1.524(4)	C(8)-C(7)-C(6)	109.3(2)
C(10)-C(12)	1.528(4)	C(7)-C(8)-C(9)	109.5(2)
		N(2)-C(9)-C(8)	110.0(2)
N(2)-Pd-N(1)	86.46(8)	N(2)-C(9)-C(10)	113.2(2)
N(2)-Pd-Br(2)	95.17(6)	C(8)-C(9)-C(10)	113.5(2)
N(1)-Pd-Br(2)	165.81(6)	C(11)-C(10)-C(12)	109.7(2)
N(2)-Pd-Br(1)	174.56(6)	C(11)-C(10)-C(9)	114.3(2)
N(1)-Pd-Br(1)	95.24(6)	C(12)-C(10)-C(9)	109.1(2)
Br(2)-Pd-Br(1)	84.449(12)	N(1)-C(11)-C(10)	113.1(2)
C(11)-N(1)-C(1)	106.8(2)	C(3)-C(12)-C(10)	106.4(2)

Table A3.3.5 Anisotropic displacement parameters ($Å^2$ x 10^4) for DCE04 (CCDC 639648). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2*a^2*U^{11}$ + ... + $2h*k*a*b*U^{12}$]

	U	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd	110(1)	111(1)	137(1)	-2(1)	27(1)	1(1)
Br(1)	175(1)	151(1)	305(1)	29(1)	103(1)	-6(1)
Br(2)	254(1)	174(1)	236(1)	-17(1)	-78(1)	-10(1)
N(1)	138(7)	183(10)	148(7)	4(7)	43(7)	-14(7)
N(2)	141(8)	135(8)	123(7)	-6(6)	52(7)	3(7)
C(1)	207(12)	280(13)	187(11)	76(10)	17(10)	-13(10)
C(2)	140(9)	188(11)	180(9)	6(8)	44(8)	15(8)
C(3)	133(9)	208(11)	212(11)	-20(9)	84(9)	13(8)
C(4)	186(10)	201(10)	179(10)	-14(9)	106(9)	11(9)
C(5)	224(12)	191(11)	163(10)	45(8)	61(9)	7(9)
C(6)	195(11)	178(11)	237(12)	49(9)	21(10)	24(9)
C(7)	225(12)	158(10)	316(14)	40(10)	89(12)	56(10)
C(8)	189(11)	160(10)	275(12)	-28(9)	100(10)	34(9)
C(9)	157(10)	121(9)	210(10)	-29(8)	89(9)	-8(8)
C(10)	176(10)	164(10)	198(10)	-66(8)	65(9)	-34(9)
C(11)	195(11)	221(11)	139(9)	-56(8)	52(9)	-12(9)
C(12)	148(10)	238(12)	259(13)	-22(10)	68(10)	-44(9)