Electronic Supplementary Information for Dalton Transactions

Synthetic and Structural Studies on Amine Coordination to Pd-*N*-Heterocyclic Carbene Complexes

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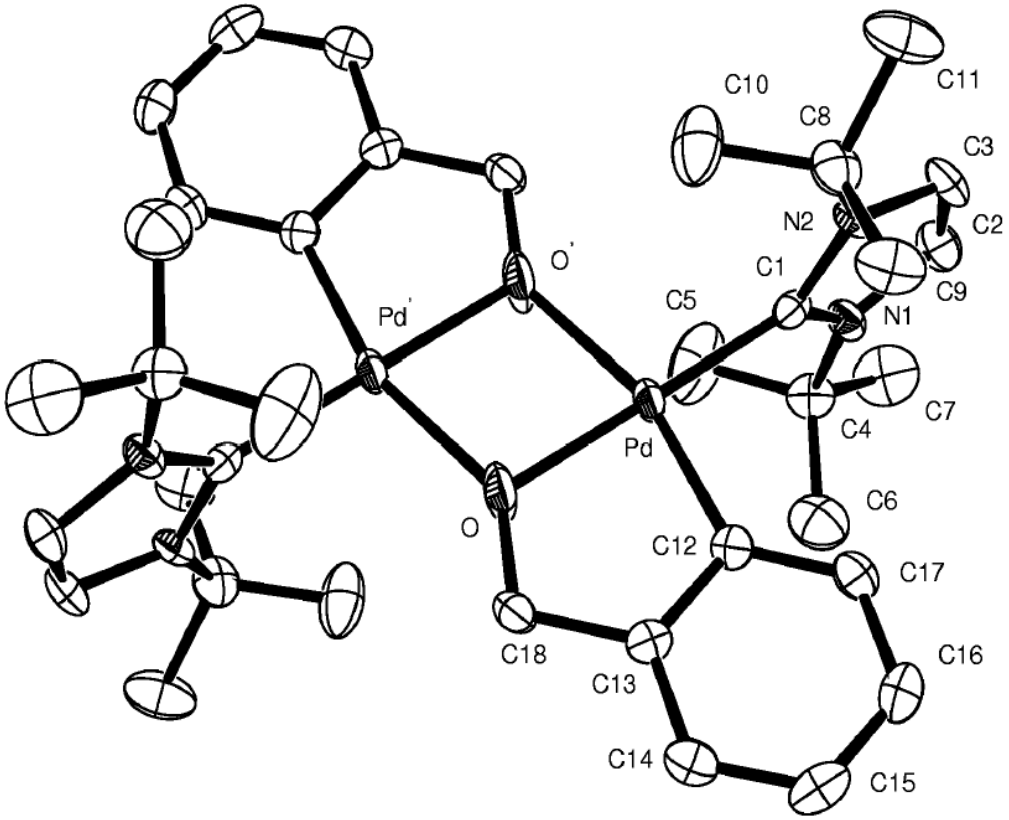

Table 1. Crystal data and structure refinement for [{Pd(C3H2N2tBu2)(C6H4CH2O)}2].2(C6D6).

Identification code	aug1002	
Empirical formula	C36 H52 N4 O2 Pd2 . 2(C6 D6)	
Formula weight	953.8	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (No.14)	
Unit cell dimensions	a = 11.8296(4) Å	α= 90°.
	b = 16.5642(6) Å	β= 116.119(1)°.
	c = 12.7733(5) Å	γ = 90°.
Volume	2247.31(14) $Å^3$	
Z	2	
Density (calculated)	1.39 Mg/m^3	
Absorption coefficient	0.84 mm^{-1}	
F(000)	976	
Crystal size	0.05 x 0.05 x 0.02 mm^3	
Theta range for data collection	3.76 to 22.98°.	
Index ranges	-12<=h<=12, -18<=k<=13, -13<=l<=13	

Reflections collected	9508
Independent reflections	3073 [R(int) = 0.077]
Reflections with I>2sigma(I)	2397
Completeness to theta = 22.98°	98.8 %
Tmax. and Tmin.	1.011 and 0.879
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3073 / 0 / 253
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.042, wR2 = 0.085
R indices (all data)	R1 = 0.065, wR2 = 0.092
Largest diff. peak and hole	0.42 and -0.46 e.$Å^{-3}$

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for aug1002. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	-47(1)	-511(1)	1035(1)	25(1)
O	1093(4)	289(3)	774(3)	66(2)
N(1)	-2109(4)	-1179(3)	1581(3)	23(1)
N(2)	-1108(4)	-2139(2)	1191(3)	21(1)
C(1)	-1138(4)	-1319(3)	1292(4)	20(1)
C(2)	-2636(5)	-1897(4)	1689(5)	34(1)
C(3)	-2013(5)	-2493(4)	1453(5)	35(1)
C(4)	-2608(5)	-368(3)	1725(4)	28(1)
C(5)	-2996(7)	98(4)	603(6)	62(2)
C(6)	-1586(6)	70(4)	2748(5)	46(2)
C(7)	-3717(5)	-491(4)	1992(5)	53(2)
C(8)	-185(5)	-2627(3)	946(5)	31(1)
C(9)	1039(5)	-2670(4)	2054(5)	39(2)
C(10)	23(6)	-2247(4)	-39(5)	50(2)
C(11)	-721(6)	-3470(4)	564(6)	48(2)
C(12)	1245(4)	-446(3)	2671(4)	21(1)
C(13)	2185(4)	125(3)	2811(4)	22(1)
C(14)	3168(5)	275(3)	3917(4)	26(1)
C(15)	3222(5)	-136(4)	4885(4)	34(2)
C(16)	2304(5)	-691(3)	4757(4)	31(1)
C(17)	1329(5)	-839(3)	3664(4)	26(1)
C(18)	2141(5)	543(3)	1752(4)	28(1)
C(19)	-4713(7)	-2129(5)	-1826(9)	74(2)
C(20)	-5008(6)	-2775(5)	-1328(6)	68(2)
C(21)	-5818(6)	-3349(4)	-1991(6)	51(2)
C(22)	-6371(6)	-3290(4)	-3162(6)	53(2)
C(23)	-6108(8)	-2653(7)	-3684(7)	71(2)
C(24)	-5280(9)	-2059(5)	-3009(11)	82(3)

Table 3. Bond lengths [Å] and angles [°] for aug1002.

Pd-C(12)	1.976(5)
Pd-C(1)	1.985(5)
Pd-O	2.020(4)
Pd-O'	2.118(3)
O-C(18)	1.383(6)
N(1)-C(1)	1.372(6)
N(1)-C(2)	1.376(7)
N(1)-C(4)	1.512(7)
N(2)-C(1)	1.367(6)
N(2)-C(3)	1.385(6)
N(2)-C(8)	1.498(6)
C(2)-C(3)	1.342(8)
C(4)-C(7)	1.508(7)
C(4)-C(5)	1.510(8)
C(4)-C(6)	1.517(7)
C(8)-C(9)	1.517(7)
C(8)-C(10)	1.520(7)
C(8)-C(11)	1.522(8)
C(12)-C(17)	1.389(7)
C(12)-C(13)	1.410(7)
C(13)-C(14)	1.401(7)
C(13)-C(18)	1.501(7)
C(14)-C(15)	1.389(7)
C(15)-C(16)	1.376(8)
C(16)-C(17)	1.386(7)
C(19)-C(24)	1.362(12)
C(19)-C(20)	1.367(11)
C(20)-C(21)	1.350(9)
C(21)-C(22)	1.346(9)
C(22)-C(23)	1.356(11)
C(23)-C(24)	1.389(12)
C(12)-Pd-C(1)	96.8(2)
C(12)-Pd-O	83.0(2)
C(1)-Pd-O	178.6(2)
C(12)-Pd-O'	162.3(2)

C(1)-Pd-O’	100.8(2)
O-Pd-O’	79.5(2)
C(18)-O-Pd	116.7(3)
C(18)-O-Pd’	142.5(3)
Pd-O-Pd’	100.5(2)
C(1)-N(1)-C(2)	110.6(4)
C(1)-N(1)-C(4)	126.9(4)
C(2)-N(1)-C(4)	122.5(4)
C(1)-N(2)-C(3)	110.0(4)
C(1)-N(2)-C(8)	127.4(4)
C(3)-N(2)-C(8)	122.3(4)
N(2)-C(1)-N(1)	104.6(4)
N(2)-C(1)-Pd	127.5(3)
N(1)-C(1)-Pd	127.9(4)
C(3)-C(2)-N(1)	107.2(4)
C(2)-C(3)-N(2)	107.6(5)
C(7)-C(4)-C(5)	110.7(5)
C(7)-C(4)-N(1)	109.4(4)
C(5)-C(4)-N(1)	108.1(4)
C(7)-C(4)-C(6)	108.2(5)
C(5)-C(4)-C(6)	111.5(5)
N(1)-C(4)-C(6)	108.9(4)
N(2)-C(8)-C(9)	108.3(4)
N(2)-C(8)-C(10)	110.4(4)
C(9)-C(8)-C(10)	110.8(5)
N(2)-C(8)-C(11)	108.8(4)
C(9)-C(8)-C(11)	110.3(5)
C(10)-C(8)-C(11)	108.1(5)
C(17)-C(12)-C(13)	117.5(4)
C(17)-C(12)-Pd	130.7(4)
C(13)-C(12)-Pd	111.7(3)
C(14)-C(13)-C(12)	120.4(4)
C(14)-C(13)-C(18)	120.7(5)
C(12)-C(13)-C(18)	118.9(4)
C(15)-C(14)-C(13)	120.1(5)
C(16)-C(15)-C(14)	119.8(5)
C(15)-C(16)-C(17)	120.0(5)
C(16)-C(17)-C(12)	122.1(5)

O-C(18)-C(13)	109.5(4)
C(24)-C(19)-C(20)	118.7(8)
C(21)-C(20)-C(19)	121.0(7)
C(22)-C(21)-C(20)	120.7(6)
C(21)-C(22)-C(23)	119.8(7)
C(22)-C(23)-C(24)	119.9(7)
C(19)-C(24)-C(23)	119.7(7)

Symmetry transformations used to generate equivalent atoms:

‘ -x,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for aug1002. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd	25(1)	26(1)	21(1)	5(1)	8(1)	-11(1)
O	61(3)	89(4)	25(2)	20(2)	-3(2)	-58(3)
N(1)	19(2)	21(3)	26(2)	2(2)	7(2)	-4(2)
N(2)	20(2)	14(2)	25(2)	-2(2)	8(2)	-4(2)
C(1)	23(3)	21(3)	15(3)	0(2)	8(2)	3(2)
C(2)	28(3)	41(4)	40(3)	-2(3)	21(3)	-16(3)
C(3)	42(4)	23(3)	43(3)	-1(3)	22(3)	-16(3)
C(4)	23(3)	30(4)	33(3)	-4(3)	13(2)	3(2)
C(5)	81(5)	61(5)	51(4)	26(4)	36(4)	45(4)
C(6)	49(4)	39(4)	56(4)	-10(3)	29(3)	0(3)
C(7)	37(4)	64(5)	59(4)	-8(4)	23(3)	7(4)
C(8)	35(3)	22(3)	38(3)	2(3)	19(2)	6(3)
C(9)	26(3)	36(4)	48(4)	-7(3)	11(3)	2(3)
C(10)	76(5)	42(4)	55(4)	13(3)	50(4)	20(4)
C(11)	44(4)	24(4)	68(4)	-16(3)	17(3)	1(3)
C(12)	19(3)	23(3)	24(3)	-1(2)	12(2)	1(2)
C(13)	21(3)	21(3)	22(3)	-1(2)	8(2)	4(2)
C(14)	16(3)	25(3)	34(3)	-3(2)	9(2)	1(2)
C(15)	30(3)	47(4)	22(3)	-5(3)	7(2)	7(3)
C(16)	35(3)	34(4)	26(3)	8(3)	15(2)	8(3)
C(17)	23(3)	25(3)	32(3)	1(2)	13(2)	-4(2)
C(18)	29(3)	22(3)	26(3)	1(3)	6(2)	-9(3)
C(19)	61(5)	47(5)	126(8)	-9(5)	51(5)	-21(4)
C(20)	57(5)	88(6)	56(5)	-7(4)	23(4)	-22(5)
C(21)	51(4)	33(4)	71(5)	15(4)	30(4)	0(3)
C(22)	44(4)	46(5)	66(5)	-9(4)	24(4)	7(3)
C(23)	59(5)	104(8)	59(5)	21(5)	34(4)	47(5)
C(24)	78(6)	61(6)	146(9)	60(6)	85(6)	34(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for aug1002.

	x	y	z	U(eq)
H(2)	-3313	-1959	1892	41
H(3)	-2166	-3055	1464	42
H(5A)	-3654	-200	-39	93
H(5B)	-2265	168	441	93
H(5C)	-3319	628	678	93
H(6A)	-1358	-247	3460	69
H(6B)	-1897	600	2840	69
H(6C)	-844	138	2603	69
H(7A)	-3449	-795	2720	79
H(7B)	-4375	-793	1354	79
H(7C)	-4049	35	2074	79
H(9A)	1377	-2124	2285	58
H(9B)	1647	-3000	1916	58
H(9C)	882	-2913	2677	58
H(10A)	365	-1702	188	75
H(10B)	-780	-2219	-742	75
H(10C)	619	-2576	-197	75
H(11A)	-1506	-3433	-156	73
H(11B)	-890	-3719	1177	73
H(11C)	-112	-3799	426	73
H(14)	3800	659	4004	31
H(15)	3889	-34	5634	41
H(16)	2340	-974	5418	37
H(17)	699	-1220	3592	32
H(18A)	2103	1135	1841	33
H(18B)	2913	418	1664	33
H(19)	-4123	-1736	-1355	89
H(20)	-4638	-2822	-503	81
H(21)	-5998	-3798	-1628	61
H(22)	-6945	-3695	-3621	63
H(23)	-6490	-2613	-4510	85
H(24)	-5109	-1605	-3372	98

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 Least-squares planes (x,y,z in crystal coordinates) and deviations
from them
 (* indicates atom used to define plane)

  2.9499 (0.0279) x - 0.8294 (0.0402) y + 9.6895 (0.0202) z = 1.0149
(0.0109)

 *   -0.0076 (0.0028)  N1
 *   -0.0106 (0.0028)  N2
 *    0.0111 (0.0026)  C1
 *    0.0011 (0.0031)  C2
 *    0.0060 (0.0031)  C3
      0.0161 (0.0079)  Pd
     -0.0825 (0.0081)  C4
      0.0648 (0.0082)  C8

 Rms deviation of fitted atoms =   0.0081


 - 7.5917 (0.0190) x + 12.3309 (0.0188) y + 5.7227 (0.0153) z =
0.0027 (0.0003)

 Angle to previous plane (with approximate esd) = 88.91 ( 0.16 )

 *   -0.0252 (0.0029)  C1
 *    0.0305 (0.0035)  C12
 *   -0.0339 (0.0039)  O
 *    0.0286 (0.0032)  O_$1
     -0.0057 (0.0019)  Pd

 Rms deviation of fitted atoms =   0.0297


 - 7.4169 (0.0344) x + 12.4682 (0.0280) y + 5.8283 (0.0156) z =
0.0000 (0.0000)

 Angle to previous plane (with approximate esd) =  1.35 ( 0.37 )

 *    0.0000 (0.0000)  Pd
 *    0.0000 (0.0000)  O
 *    0.0000 (0.0000)  Pd_$1
 *    0.0000 (0.0000)  O_$1

 Rms deviation of fitted atoms =   0.0000


  8.0089 (0.0181) x - 11.9464 (0.0238) y - 5.4883 (0.0235) z = 0.0597
(0.0090)

 Angle to previous plane (with approximate esd) =  4.60 ( 0.39 )

 *    0.0045 (0.0035)  C12
 *   -0.0021 (0.0036)  C13
 *   -0.0008 (0.0036)  C14
 *    0.0014 (0.0038)  C15
 *    0.0011 (0.0038)  C16
 *   -0.0040 (0.0036)  C17
      0.0445 (0.0085)  C18
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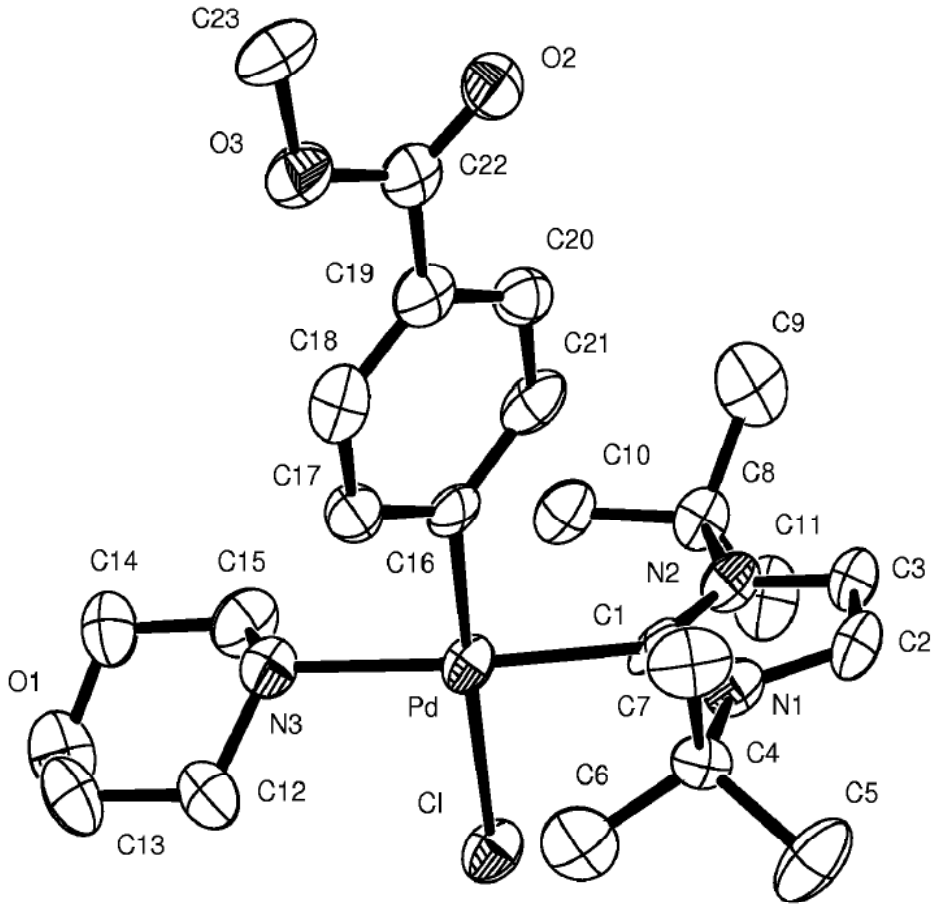

Rms deviation of fitted atoms = 0.0027

Table 1. Crystal data and structure refinement .

Identification code	may2906	
Empirical formula	C23 H36 Cl N3 O3 Pd	
Formula weight	544.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/a$ (No.14)	
Unit cell dimensions	a = 13.4010(16) Å	α= 90°.
	b = 13.4541(10) Å	β= 111.894(4)°.
	c = 14.9057(18) Å	γ = 90°.
Volume	2493.6(5) $Å^3$	
Z	4	
Density (calculated)	1.45 Mg/m^3	
Absorption coefficient	0.88 mm^{-1}	

F(000)	1128
Crystal size	0.10 x 0.10 x 0.01 mm^3
Theta range for data collection	3.50 to 22.93°.
Index ranges	-14<=h<=13, -14<=k<=13, -15<=l<=16
Reflections collected	9369
Independent reflections	3310 [R(int) = 0.105]
Reflections with I>2sigma(I)	2435
Completeness to theta = 22.93°	96.1 %
Tmax. and Tmin.	0.996 and 0.672
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3310 / 0 / 281
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.087, wR2 = 0.211
R indices (all data)	R1 = 0.123, wR2 = 0.237
Largest diff. peak and hole	2.95 and -0.92 e.$Å^{-3}$ (near Pd)

The crystal used was a small , very thin, plate cut from an inter-grown mass. It was not completely single but could be indexed. The diffraction was weak and limited in extent.

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for may2906. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	1971(1)	845(1)	8660(1)	32(1)
Cl	2281(3)	-580(2)	9745(2)	42(1)
O(1)	1149(8)	1934(8)	11423(7)	55(3)
O(2)	1109(7)	4483(7)	5023(7)	43(2)
O(3)	1827(7)	5407(7)	6358(7)	45(2)
N(1)	2959(8)	-147(8)	7351(8)	35(3)
N(2)	1297(8)	-559(8)	6969(8)	37(3)
N(3)	1662(8)	1761(8)	9709(8)	36(3)
C(1)	2098(10)	-9(8)	7628(9)	33(3)
C(2)	2690(10)	-734(9)	6543(10)	39(3)
C(3)	1646(10)	-1001(9)	6300(10)	35(3)
C(4)	4065(9)	315(10)	7788(9)	33(3)
C(5)	4890(11)	-464(11)	7742(14)	61(5)
C(6)	4340(10)	580(13)	8842(11)	55(4)
C(7)	4126(11)	1212(11)	7198(11)	53(4)
C(8)	148(10)	-746(9)	6886(9)	34(3)
C(9)	-575(11)	-505(13)	5875(11)	56(4)
C(10)	-188(10)	-120(10)	7569(10)	43(3)
C(11)	77(12)	-1846(10)	7101(12)	54(4)
C(12)	2468(12)	1704(9)	10691(9)	43(3)
C(13)	2153(12)	2267(12)	11430(10)	51(4)
C(14)	363(13)	2069(12)	10504(11)	52(4)
C(15)	603(11)	1486(11)	9746(11)	49(4)
C(16)	1791(9)	2005(9)	7755(9)	31(3)
C(17)	2282(10)	2917(9)	8153(10)	38(3)
C(18)	2182(10)	3745(10)	7544(11)	41(3)
C(19)	1627(11)	3684(10)	6556(10)	39(3)
C(20)	1162(10)	2783(10)	6172(10)	38(3)
C(21)	1245(10)	1977(9)	6774(11)	40(3)
C(22)	1480(10)	4539(10)	5892(10)	35(3)
C(23)	1629(12)	6271(10)	5753(12)	51(4)

Table 3. Bond lengths [Å] and angles [°] for may2906.

Pd-C(1)	1.977(12)
Pd-C(16)	2.018(12)
Pd-N(3)	2.149(10)
Pd-Cl	2.442(3)
O(1)-C(14)	1.395(18)
O(1)-C(13)	1.415(17)
O(2)-C(22)	1.204(15)
O(3)-C(22)	1.349(16)
O(3)-C(23)	1.435(16)
N(1)-C(2)	1.372(16)
N(1)-C(1)	1.374(15)
N(1)-C(4)	1.513(15)
N(2)-C(1)	1.371(16)
N(2)-C(3)	1.383(16)
N(2)-C(8)	1.519(15)
N(3)-C(12)	1.461(17)
N(3)-C(15)	1.487(16)
C(2)-C(3)	1.356(18)
C(4)-C(7)	1.515(18)
C(4)-C(6)	1.516(19)
C(4)-C(5)	1.543(18)
C(8)-C(9)	1.49(2)
C(8)-C(10)	1.514(18)
C(8)-C(11)	1.524(18)
C(12)-C(13)	1.520(19)
C(14)-C(15)	1.51(2)
C(16)-C(21)	1.370(18)
C(16)-C(17)	1.414(18)
C(17)-C(18)	1.411(19)
C(18)-C(19)	1.383(19)
C(19)-C(20)	1.385(19)
C(19)-C(22)	1.482(19)
C(20)-C(21)	1.385(18)

C(1)-Pd-C(16)	87.3(5)
C(1)-Pd-N(3)	174.3(4)
C(16)-Pd-N(3)	92.0(4)
C(1)-Pd-Cl	90.9(4)

C(16)-Pd-Cl	176.9(3)
N(3)-Pd-Cl	90.0(3)
C(14)-O(1)-C(13)	109.5(11)
C(22)-O(3)-C(23)	115.4(11)
C(2)-N(1)-C(1)	111.5(10)
C(2)-N(1)-C(4)	120.6(10)
C(1)-N(1)-C(4)	127.8(10)
C(1)-N(2)-C(3)	111.3(10)
C(1)-N(2)-C(8)	130.3(10)
C(3)-N(2)-C(8)	118.3(10)
C(12)-N(3)-C(15)	108.0(10)
C(12)-N(3)-Pd	115.3(8)
C(15)-N(3)-Pd	109.3(8)
N(2)-C(1)-N(1)	103.4(10)
N(2)-C(1)-Pd	126.8(9)
N(1)-C(1)-Pd	129.6(9)
C(3)-C(2)-N(1)	107.1(11)
C(2)-C(3)-N(2)	106.6(11)
N(1)-C(4)-C(7)	109.5(10)
N(1)-C(4)-C(6)	111.3(9)
C(7)-C(4)-C(6)	111.7(12)
N(1)-C(4)-C(5)	107.8(10)
C(7)-C(4)-C(5)	108.7(11)
C(6)-C(4)-C(5)	107.8(12)
C(9)-C(8)-C(10)	108.3(11)
C(9)-C(8)-N(2)	107.7(10)
C(10)-C(8)-N(2)	113.5(10)
C(9)-C(8)-C(11)	110.8(12)
C(10)-C(8)-C(11)	110.0(11)
N(2)-C(8)-C(11)	106.5(10)
N(3)-C(12)-C(13)	113.5(12)
O(1)-C(13)-C(12)	110.9(11)
O(1)-C(14)-C(15)	112.0(13)
N(3)-C(15)-C(14)	111.9(12)
C(21)-C(16)-C(17)	116.8(11)
C(21)-C(16)-Pd	125.1(9)
C(17)-C(16)-Pd	118.0(9)
C(18)-C(17)-C(16)	119.8(12)

C(19)-C(18)-C(17)	121.5(12)
C(18)-C(19)-C(20)	118.2(12)
C(18)-C(19)-C(22)	123.4(13)
C(20)-C(19)-C(22)	118.4(13)
C(21)-C(20)-C(19)	120.1(13)
C(16)-C(21)-C(20)	123.5(12)
O(2)-C(22)-O(3)	122.2(12)
O(2)-C(22)-C(19)	124.6(12)
O(3)-C(22)-C(19)	113.2(12)

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 Least-squares planes (x,y,z in crystal coordinates) and deviations
from them
 (* indicates atom used to define plane)

 - 12.7729 (0.0209) x + 3.7327 (0.0639) y + 6.9670 (0.0666) z =
3.8617 (0.0526)

 *    0.0023 (0.0081)  C16
 *   -0.0074 (0.0086)  C17
 *    0.0053 (0.0087)  C18
 *    0.0019 (0.0085)  C19
 *   -0.0072 (0.0088)  C20
 *    0.0051 (0.0086)  C21

 Rms deviation of fitted atoms =   0.0053


  12.0760 (0.0221) x + 2.6137 (0.0404) y + 0.3522 (0.0519) z = 2.8842
(0.0437)

 Angle to previous plane (with approximate esd) = 40.69 ( 0.25 )

 *    0.0615 (0.0045)  Cl
 *   -0.0841 (0.0056)  C1
 *    0.0757 (0.0055)  C16
 *   -0.0750 (0.0051)  N3
 *    0.0219 (0.0041)  Pd

 Rms deviation of fitted atoms =   0.0673


  0.9319 (0.0817) x - 10.8558 (0.0495) y + 7.7267 (0.0809) z = 6.1079
(0.0483)

 Angle to previous plane (with approximate esd) = 82.34 ( 0.40 )

 *   -0.0082 (0.0070)  C1
 *   -0.0048 (0.0077)  C2
 *   -0.0005 (0.0076)  C3
 *    0.0081 (0.0074)  N1
 *    0.0054 (0.0073)  N2

 Rms deviation of fitted atoms =   0.0061
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