Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Synthesis and reactivity of alkyl palladium *N*-heterocyclic carbene complexes

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GENERAL EXPERIMENTAL

All glassware was oven-dried prior to use.

Air sensitive compounds were manipulated using standard Schlenk line techniques or in an inert atmosphere provided by a glove box.

Schlenk line manipulations involved the use of oven-dried glassware or glassware that had been flame dried *in vacuo*. Glassware was repeatedly evacuated and purged with dry argon.

Glove box manipulations were performed in a Mbraun or a Miller Howe glove box under an atmosphere of catalytically dried and deoxygenated dinitrogen.

Alkyl halides were purchased from commercial sources (Lancaster and Aldrich) degassed prior to use and vacuum transferred over 4 Å molecular sieves. Amines were distilled at reduced pressure. The imidazolium salts 1,3-bis(*t*-butyl) imidazolium chloride and 1,3-bis(2,6-di*iso*propylphenyl) imidazolium chloride, palladium(COD)(chloride)$_2$ and neopentyl lithium were prepared according to literature procedures.
Solvents were purified by pre-drying over sodium wire, followed by heating at reflux over a suitable drying agent in a solvent still under an atmosphere of dinitrogen. The collected solvent was degassed and stored in an ampoule under argon.

Solvent	Drying Agent	Stored Over
THF	Potassium	4 Å molecular sieves
Toluene	Sodium	Potassium mirror
Pentane	Potassium	Potassium mirror
Diethyl ether	Sodium/potassium alloy	Potassium mirror
Chloroform	Calcium hydride	4 Å molecular sieves

NMR solvents were purified by refluxing over a suitable drying agent, then vacuum transferred to an ampoule and stored under dinitrogen in a glove box.

EXPERIMENTAL PROCEDURES

Synthesis of (neopentyl)(Cl)Pd(1,5-COD) complex (1)

$Pd(COD)Cl_2$ (0.3 g; 1.05 mmol) was placed in a Schlenk tube and dried under vacuum for an hour before use. It was then suspended in 20 ml of Et_2O, cooled to -75°C and neopentyl lithium (0.09 g ; 1 eq) in 5 ml of Et_2O added dropwise *via* cannula. The dark reaction mixture was stirred at -75°C for an hour, and allowed to gradually warm up to room temperature with stirring over a further 3 hours. The mixture was filtered through flamed-dried Celite, and the orange-yellow filtrate was dried under vacuum affording complex **1** in 48% yield (0.175 g; 0.5 mmol). Recrystallization of the product was achieved from cold pentane (-20°C) after 3 days.

^{1}H NMR (d_1-chloroform): 5.89 ppm (q; 2H; $CH_2C\underline{H}=C\underline{H}CH_2$, $J_{(H-H)}$ = 15 Hz); 5.15 ppm (q; 2H; $CH_2C\underline{H}=C\underline{H}CH_2$, $J_{(H-H)}$ = 12 Hz); 2.58 ppm (m; 4H); 2.43 ppm (m; 4H); 2.22 ppm (s; 2H); 1.12 ppm (s; 9H). **^{13}C NMR** (d_6-benzene): 125.1 ppm (CH=CH), 99.9 ppm (CH=CH), 35.8 ppm ($\underline{C}(CH_3)_3$), 33.4 ppm (CH_3), 30.6 ppm (CH_2), 27.0 ppm (CH_2- CH_2). **MS (ES):** *m/z* 285 (M^+ - Cl). **Elemental analysis**: Anal. Calc'd. for $C_{13}H_{23}ClPd$: C: 46.61, H: 7.17; Found C: 46.50, H: 7.07.

Synthesis of *trans*-(neopentyl)Pd(Cl)(I^{t}Bu) dimer (2)

(neopentyl)Pd(Cl)(1,5-COD), **1**, (0.175 g; 0.5 mmol) was dissolved in 15 mL of THF, cooled to 0°C and I^{t}Bu (0.09 g, 1 eq) in 5 mL of THF added *via* cannula. The reaction was stirred at 0°C for 30 min, after that time a very fine grey solid ($ItBuH^+Cl^-$) precipitated. It was left to settle and filtered by cannula filtration to afford a dark orange solution. The solvent was removed under reduced pressure, and the solid residue washed with pentane (2 x 10 mL) and with Et_2O (15 mL) yielding the desired complex as a white powder. A further batch of product was obtained by concentrating the Et_2O and pentane washings until precipitation was observed. The mixture was kept at RT for 12 hours to achieve complete precipitation of **2**, which was isolated by decantation Dimer **2** was obtained in 75% yield (0.375 mmol; 0.147 g). Crystals suitable for X-Ray diffraction were growth from Et_2O at -20°C.

^{1}H NMR(d_6-benzene): 6.51 ppm (s; 2H); 1.99 ppm (s; 18H); 1.86 ppm (s; 2H); 1.37 ppm (s; 9H). **^{13}C NMR**(d_6-benzene): 170.4 ppm (Pd-$C_{(carbene)}$); 118.7 ppm (NCH=CHN); 59.2 ppm ($\underline{C}(CH_3)_{(t\text{-Butyl})}$); 34.5 ppm ($\underline{C}(CH_3)_{(neopentyl)}$); 32.8 ppm ($CH_{3(neopentyl)}$); 32.3 ppm ($CH_{3(t\text{-Butyl})}$); 31.0 ppm ($CH_{2(neopentyl)}$). **MS (EI):** *m/z* 502 (M^+ - Cl, $CH_2(CCH_3)_3$ and I^{t}Bu), 465 (M^+ - 2Cl, $CH_2(CCH_3)_3$ and I^{t}Bu), 322 (M^+ - 2Cl, $2CH_2(CCH_3)_3$ and I^{t}Bu). **Elemental analysis**: Anal. Calc'd. for $C_{16}H_{31}N_2ClPd$: C: 48.87, H: 7.89, N: 7.12. Found: C: 48.73, H: 7.78, N: 7.07.

Synthesis of the *cis*-(neopentyl)Pd(Cl)(IPr) dimer (3)

The synthesis of dimer **3** was conducted by following the same experimental procedure adopted for the synthesis of dimer **2**, with the exception that subsequent to the addition of IPr (0.145 g, 1 eq) no precipitate was observed. The reaction solution was stirred at RT and the solvent removed under vacuum affording a yellow oil. Pentane (15 mL) was added and few seconds later a white solid precipitated. The solid was isolated by decanting the solution *via* thin cannula, and washing the precipitate with cold pentane (3 x 5 ml). The product was obtained as a white-grey powder in 80% yield. Crystals suitable for X-Ray diffraction were growth from Et_2O at -20°C.

^{1}H NMR(d_1-chloroform): 7.52 ppm; (t; 2H; $J_{(H-H)}$= 8 MHz); 7.36 ppm (d; 4H; $J_{(H-H)}$= 16 Hz); 7.13 ppm (s; 2H); 2.66 ppm (septet; 4H; $J_{(H-H)}$= 12 MHz); 2.29 ppm (s; 2H); 1.44 ppm (d; 12H; $J_{(H-H)}$= 8 Hz); 1.17 ppm (d; 12H; $J_{(H-H)}$= 8 Hz); 0.73 ppm (s; 9H). **^{13}C NMR**(d_1-chloroform): 187.8 ppm (Pd-$C_{(carbene)}$); 146.5 ($C_{(aryl)}$); 134.6 ppm ($C_{(aryl)}$); 130.7 ppm ($CH_{(aryl)}$); 125.6 ppm ($CH_{(aryl)}$); 124.6 ppm (NCH=CHN); 31.8 ppm ($\underline{C}H(CH_3)_2$); 31.2 ppm ($\underline{C}(CH_3)_3$); 29.0 ppm ($CH(\underline{C}H_3)_2$); 26.6 ppm ($CH(\underline{C}H_3)_2$); 26.1 ppm ($CH_{2(neopentyl)}$); 23.6 ppm ($C(\underline{C}H)_3$). **MS (ES):** 996 (M^+ - Aryl and $CH(CH_3)_2$), 960 (M^+ - Aryl, $CH(CH_3)_2$ and Cl), 600 ($M^+_{(monomer)}$). **Elemental analysis**: Anal. Calc'd. for $C_{32}H_{47}N_2ClPd$: C: 64.12, H: 7.84, N: 4.67. Found C: 64.25, H: 7.74, N: 4.51.

Synthesis of (neopentyl)Pd(I^{t}Bu)(ITMe)(Cl) complex (4) on NMR scale

Dimer **2** (0.05g; 0.06 mmol) was weighed in a glove box, and placed in a Young's tap NMR tube. ITMe (2 eq; 0.015 g) was added, followed by the C_6D_6 (0.6 ml). A ^{1}H NMR, recorded few minute after the starting of the reaction, showed that only the desired product was present in solution. The solvent was removed under vacuum to afford pure **4**.

^{1}H NMR(d_6-benzene): 6.73 ppm (s; 2H); 3.82 ppm (s; 6H); 2.07 ppm (s; 18H); 1.76 ppm (s; 6H); 0.96 ppm (s; 9H). **^{13}C NMR**(d_6-benzene): 184.7 ppm (Pd-$C_{(carbene)}$); 181.0 ppm (Pd-$C_{(carbene)}$); 124.0 ppm (C=C); 118.1 ppm (CH_2=CH_2); 58.8 ppm ($\underline{C}(CH_3)_{(t\text{-Butyl})}$); 35.4 ppm ($\underline{C}(CH_3)_{3(neopentyl)}$); 34.4 ppm ($CH_{2(neopentyl)}$); 33.6 ppm ($CH_{3(t\text{-Butyl})}$); 32.9 ppm ($CH_{3(neopentyl)}$), 26.4 ppm (N-$CH_3$); 8.8 ppm ($\underline{C}H_3C$=$C\underline{C}H_3$). **Elemental analysis**: Anal. Calc'd. for $C_{23}H_{41}N_4Cl$: C: 53.40, H: 7.93, N:10.83. Found C; 53.56, H: 8.09, N:10.77.

Synthesis of (neopentyl)Pd(I^{t}Bu)(PPh_3)(Cl) complex (5)

Dimer **2** (0.12g; 0.153 mmol) and *tri*-phenylphosphine (2 eq; 0.08 g) placed in a Schlenk tube and THF (10 ml) added. The yellow reaction solution was stirred at RT for 2 hours- after 1 hour a colour change was observed from yellow to orange. The solvent was removed under vacuum, and

the orange residue washed with pentane (3 x 5 ml) giving **5** in 75% yield (0.15 g; 0.23 mmol). Crystals suitable for X-Ray analysis were grown in toluene at -20^{o}C.

^{1}H NMR(d_6-benzene): 8.00-7.94 ppm (m; 5H); 7.16-7.03 ppm (m: 10H); 6.67 ppm (s; 2H); 1.96 ppm (s; 18H); 1.52 ppm (s; 2H); 0.73 ppm (s; 9H). **^{31}P NMR**: 27.37 ppm. **^{13}C NMR**(d_6-benzene): 176.0 ppm (Pd-$C_{(carbene)}$); 135.9 ppm ($CH_{(aryl)}$), 135.7 ppm ($CH_{(aryl)}$), 134.0 ppm ($CH_{(aryl)}$), 133. 5 ppm ($CH_{(aryl)}$), 129.7 ppm ($CH_{(aryl)}$), 128.7 ppm ($CH_{(aryl)}$), 128.7 ppm ($C_{(aryl)}$), 128.5 ppm ($C_{(aryl)}$), 119.6 ppm (HC=CH); 59.9 ppm ($\underline{C}(CH_3)_{(t\text{-Butyl})}$); 34.7 ppm ($CH_{3(neopentyl)}$), 33.1 ppm ($CH_{2(neopentyl)}$); 32.8 ppm ($CH_{3(t\text{-Butyl})}$); 32.5 ppm ($CH_{3(neopentyl)}$). **MS (ES):** *m/z* 655 (M^+), 399 (M^+ - PPh_3).

Synthesis of (neopentyl)Pd(I^{t}Bu)(amine)chloride complexes (6 and 7)

Dimer **2** (0.08 g; 0.18 mmol) was placed in a Schlenk tube, and dissolved in toluene (10 mL). The amine (morpholine: 3.0 eq; 27.0 μL or hexylamine: 3.0 eq ; 38.0 μL) was added *via* microlitre syringe, and the reaction solution stirred at RT for an hour. After that time the solvent and the excess of amine were removed under reduced pressure. The residue was washed with pentane and dried under vacuum to afford, respectively, 84% (0.145 g) and 75% (0.132 g) yields of the palladium-amine adducts **6** and **7**.

(neopentyl)Pd(I^{t}Bu)(morpholine)chloride complex (6)

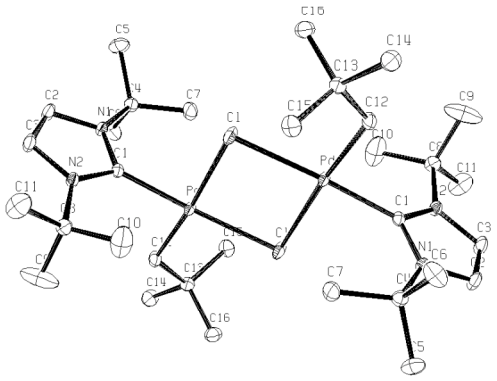
^{1}H NMR (d_1-chloroform): 7.12 ppm (s; 2H); 3.83 ppm (bd; 2H; $J_{(H-H)}$= 12 Hz); 3.74 ppm (b s; 1H); 3.46 ppm (broad quartet; 4H; $J_{(H-H)}$= 16 Hz); 2.91 ppm (b d; 2H; $J_{(H-H)}$= 12 Hz); 2.01 ppm (s; 18H); 1.00 ppm (s; 2H); 0.79 ppm (s; 9H). **^{13}C NMR** (d_1-chloroform): 167.5 ppm ($C_{(carbene)}$); 119.4 ppm (NCH=CHN); 77.2 ppm ($CH_{2(morpholine)}$); 68.4 ppm ($\underline{C}(CH_3)_{(t\text{-Butyl})}$); 59.0 ppm ($\underline{C}(CH_3)_{3(neopentyl)}$); 48.1 ppm ($CH_{2(morpholine)}$); 34.5 ppm ($CH_{2(neopentyl)}$); 32.4 ppm ($CH_{3(t\text{-Butyl})}$); 32.1 ppm ($CH_{3(neopentyl)}$). **Elemental analysis**: Anal. Calc'd. for $C_{20}H_{40}N_3OClPd$ C: 50.0, H: 8.33, N: 8.75. Found C: 49.90, H: 8.24; N: 8.86.

Pd(I^{t}Bu)(hexylamine)(neopentyl)chloride complex (7)

^{1}H NMR (d_1-chloroform): 7.14 ppm (s; 2H); 2.30 ppm (broad t; 2H; NH_2; $J_{(H-H)}$= 12 Hz); 1.98 ppm (s; 18H); 1.46 ppm (broad q; 2H; $J_{(H-H)}$= 8 Hz); 1.32 ppm (s; 2H); 1.25 ppm (m; 6H); 0.87 ppm (m; 3H); 0.85 ppm (s; 9H). **^{13}C NMR** (d_1-chloroform): 171.3 ppm (Pd-$C_{(carbene)}$); 119.4 ppm (NCH=CHN); 59.3 ppm ($\underline{C}(CH_3)_{(t\text{-Butyl})}$); 44.3 ppm ($\underline{C}(CH_3)_{3(neopentyl)}$); 34.8 ppm ($CH_{2(neopentyl)}$); 33.3 ppm ($CH_{3(neopentyl)}$); 32.4 ppm ($CH_{3(t\text{-Butyl})}$); 31.9 ppm ($CH_2$); 30.9 ppm ($CH_2$); 23.0 ppm

(CH_2); 14.4 ppm (CH_3). **MS (ES):** *m/z* 397 (M+ **-** hexylamine). **Elemental analysis**: Anal. Calc'd. for $C_{22}H_{44}N_3PdCl$: C: 53.45, H: 8.90, N: 8.50. Found C: 53.34, H: 9.10, N: 8.66.

CRYSTALLOGRAPHIC DATA



2

Table 1. Crystal data and structure refinement for [{(I^{t}Bu)Pd(neopentyl)Cl}2].

Identification code	jul1005	
Empirical formula	C32 H62 Cl2 N4 Pd2	
Formula weight	786.56	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (No.14)	
Unit cell dimensions	a = 11.1540(3) Å	α= 90°.
	b = 9.7982(2) Å	β= 107.560(1)°.
	c = 17.5999(4) Å	γ = 90°.
Volume	1833.85(7) Å^3	
Z	2	
Density (calculated)	1.42 Mg/m^3	
Absorption coefficient	1.15 mm^{-1}	
F(000)	816	
Crystal size	0.10 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.52 to 26.03°.	
Index ranges	-13<=h<=13, -11<=k<=12, -21<=l<=21	
Reflections collected	26967	
Independent reflections	3596 [R(int) = 0.066]	
Reflections with I>2sigma(I)	3084	
Completeness to theta = 26.03°	99.7 %	
Tmax. and Tmin.	0.967 and 0.833	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3596 / 0 / 181
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.031, wR2 = 0.061
R indices (all data)	R1 = 0.041, wR2 = 0.064
Largest diff. peak and hole	0.54 and -0.40 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 jul1005. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	6329(1)	5875(1)	5700(1)	17(1)
Cl	5386(1)	3656(1)	5585(1)	28(1)
N(1)	7722(2)	8339(2)	5369(1)	19(1)
N(2)	6472(2)	8883(2)	6056(1)	20(1)
C(1)	6894(3)	7795(3)	5719(2)	17(1)
C(2)	7817(3)	9739(3)	5500(2)	28(1)
C(3)	7048(3)	10068(3)	5919(2)	28(1)
C(4)	8505(3)	7628(3)	4926(2)	22(1)
C(5)	8567(3)	8537(4)	4234(2)	36(1)
C(6)	9816(3)	7417(4)	5501(2)	39(1)
C(7)	7947(3)	6275(3)	4576(2)	34(1)
C(8)	5586(3)	8885(3)	6559(2)	24(1)
C(9)	6367(4)	8695(6)	7414(2)	76(2)
C(10)	4581(4)	7810(4)	6292(3)	68(1)
C(11)	4931(4)	10258(4)	6467(3)	50(1)
C(12)	7822(3)	5619(3)	6730(2)	26(1)
C(13)	8487(3)	4241(3)	6955(2)	22(1)
C(14)	9788(3)	4532(3)	7555(2)	32(1)
C(15)	8704(3)	3492(3)	6245(2)	30(1)
C(16)	7768(3)	3327(3)	7369(2)	31(1)

Table 3. Bond lengths [Å] and angles [°] for jul1005.

Pd-C(1)	1.980(3)
Pd-C(12)	2.075(3)
Pd-Cl	2.3975(7)
Pd-Cl'	2.5252(7)
N(1)-C(1)	1.364(4)
N(1)-C(2)	1.389(4)
N(1)-C(4)	1.506(4)
N(2)-C(1)	1.371(3)
N(2)-C(3)	1.383(4)
N(2)-C(8)	1.513(4)
C(2)-C(3)	1.328(4)
C(4)-C(7)	1.515(4)
C(4)-C(6)	1.520(4)
C(4)-C(5)	1.527(4)
C(8)-C(9)	1.505(5)
C(8)-C(10)	1.507(5)
C(8)-C(11)	1.516(4)
C(12)-C(13)	1.534(4)
C(13)-C(16)	1.526(4)
C(13)-C(15)	1.530(4)
C(13)-C(14)	1.542(4)
C(1)-Pd-C(12)	86.14(11)
C(1)-Pd-Cl	172.76(8)
C(12)-Pd-Cl	100.36(8)
C(1)-Pd-Cl'	89.64(8)
C(12)-Pd-Cl'	175.28(9)
Cl-Pd-Cl'	83.98(2)
Pd-Cl-Pd'	96.02(2)
C(1)-N(1)-C(2)	109.9(2)
C(1)-N(1)-C(4)	129.1(2)
C(2)-N(1)-C(4)	121.0(2)
C(1)-N(2)-C(3)	109.8(2)
C(1)-N(2)-C(8)	128.6(2)

C(3)-N(2)-C(8)	121.5(2)
N(1)-C(1)-N(2)	105.0(2)
N(1)-C(1)-Pd	128.2(2)
N(2)-C(1)-Pd	126.7(2)
C(3)-C(2)-N(1)	107.5(3)
C(2)-C(3)-N(2)	107.8(3)
N(1)-C(4)-C(7)	112.6(2)
N(1)-C(4)-C(6)	108.1(2)
C(7)-C(4)-C(6)	110.3(3)
N(1)-C(4)-C(5)	108.4(2)
C(7)-C(4)-C(5)	107.3(3)
C(6)-C(4)-C(5)	110.1(3)
C(9)-C(8)-C(10)	112.2(4)
C(9)-C(8)-N(2)	107.5(3)
C(10)-C(8)-N(2)	111.9(3)
C(9)-C(8)-C(11)	109.4(3)
C(10)-C(8)-C(11)	107.3(3)
N(2)-C(8)-C(11)	108.5(2)
C(13)-C(12)-Pd	122.01(19)
C(16)-C(13)-C(15)	110.1(2)
C(16)-C(13)-C(12)	110.9(2)
C(15)-C(13)-C(12)	113.3(2)
C(16)-C(13)-C(14)	107.7(2)
C(15)-C(13)-C(14)	107.5(2)
C(12)-C(13)-C(14)	107.2(2)

Symmetry transformations used to generate equivalent atoms: ‘ -x+1,-y+1,-z+1

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

 - 8.8710 (0.0046) x + 2.8374 (0.0062) y + 13.1592 (0.0086) z = 3.5649
(0.0064)

 *    0.0442 (0.0010)  Cl
 *   -0.0483 (0.0011)  Cl_$1
 *    0.0574 (0.0014)  C1
 *   -0.0532 (0.0013)  C12
     -0.0117 (0.0012)  Pd

 Rms deviation of fitted atoms =   0.0510


  5.6980 (0.0138) x - 1.4166 (0.0145) y + 11.5070 (0.0190) z = 9.4009
(0.0151)

 Angle to previous plane (with approximate esd) = 89.82 ( 0.08 )

 *    0.0039 (0.0016)  C1
 *    0.0027 (0.0018)  C2
 *   -0.0002 (0.0019)  C3
 *   -0.0040 (0.0017)  N1
 *   -0.0022 (0.0017)  N2

 Rms deviation of fitted atoms =   0.0030
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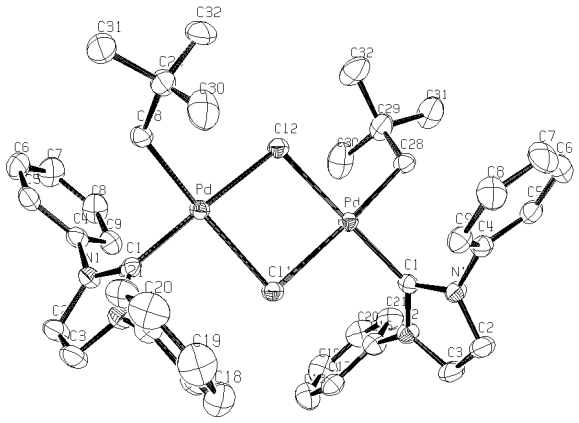


3

Table 1. Crystal data and structure refinement for [{(IPr)Pd(neopentyl)Cl}2] . 2(Et_2O).

Identification code	mar606
Empirical formula	C64 H94 Cl2 N4 Pd2 . 2(C4 H10 O)
Formula weight	1351.37
Temperature	173(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c (No.15)	
Unit cell dimensions	a = 22.4708(6) Å	α= 90°.
	b = 17.9840(7) Å	β= 106.288(2)°.
	c = 19.0590(5) Å	γ = 90°.
Volume	7392.9(4) $Å^3$	
Z	4	
Density (calculated)	1.21 Mg/m^3	
Absorption coefficient	0.60 mm^{-1}	
F(000)	2864	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.40 to 26.01°.	
Index ranges	-27<=h<=27, -22<=k<=15, -23<=l<=23	
Reflections collected	24839	
Independent reflections	7207 [R(int) = 0.070]	
Reflections with I>2sigma(I)	5451	
Completeness to theta = 26.01°	99.0 %	
Tmax. and Tmin.	0.924 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7207 / 0 / 371	
Goodness-of-fit on F^2	0.774	
Final R indices [I>2sigma(I)]	R1 = 0.043, wR2 = 0.104	
R indices (all data)	R1 = 0.068, wR2 = 0.124	
Largest diff. peak and hole	0.95 and -0.83 $e.Å^{-3}$	

The molecule lies on a crystallographic 2-gold axis.

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 mar606. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	710(1)	6211(1)	2209(1)	20(1)
Cl(1)	0	7148(1)	2500	25(1)
Cl(2)	0	5362(1)	2500	28(1)
N(1)	1048(1)	7064(2)	1060(2)	24(1)
N(2)	1506(1)	7572(2)	2090(2)	25(1)
C(1)	1164(2)	6957(2)	1797(2)	21(1)
C(2)	1286(2)	7734(2)	904(2)	33(1)
C(3)	1574(2)	8048(2)	1544(2)	34(1)
C(4)	763(2)	6533(2)	496(2)	25(1)
C(5)	1154(2)	6076(2)	221(2)	31(1)
C(6)	876(2)	5603(3)	-348(2)	40(1)
C(7)	240(2)	5579(3)	-640(2)	44(1)
C(8)	-134(2)	6031(3)	-363(2)	41(1)
C(9)	117(2)	6526(2)	214(2)	30(1)
C(10)	1860(2)	6106(2)	507(2)	38(1)
C(11)	2160(2)	5340(3)	598(3)	50(1)
C(12)	2134(2)	6574(3)	2(3)	55(1)
C(13)	-300(2)	7046(2)	481(2)	34(1)
C(14)	-850(2)	6640(3)	634(3)	47(1)
C(15)	-517(2)	7678(3)	-74(3)	56(1)
C(16)	1824(2)	7717(2)	2852(2)	28(1)
C(17)	1595(2)	8280(2)	3216(2)	29(1)
C(18)	1940(2)	8457(3)	3926(2)	41(1)
C(19)	2488(2)	8089(3)	4253(3)	51(1)
C(20)	2702(2)	7550(3)	3886(2)	46(1)
C(21)	2388(2)	7350(2)	3169(2)	36(1)
C(22)	1006(2)	8714(2)	2872(2)	33(1)
C(23)	597(2)	8783(2)	3395(2)	40(1)
C(24)	1161(2)	9489(3)	2632(3)	46(1)
C(25)	2670(2)	6801(3)	2751(3)	45(1)
C(26)	2970(2)	7185(3)	2224(3)	63(2)

C(27)	3152(2)	6285(3)	3250(4)	68(2)
C(28)	1263(2)	5388(2)	1984(2)	25(1)
C(29)	1563(2)	4836(3)	2605(2)	39(1)
C(30)	1732(2)	5231(3)	3347(2)	55(1)
C(31)	2164(2)	4547(3)	2467(3)	54(1)
C(32)	1151(2)	4163(3)	2619(3)	60(2)
O	793(3)	8595(2)	-699(2)	90(2)
C(33)	692(7)	9353(4)	-631(6)	164(5)
C(34)	1027(7)	9624(5)	107(6)	187(6)
C(35)	494(4)	8297(4)	-1395(4)	96(2)
C(36)	633(4)	7504(4)	-1413(3)	90(2)

Table 3. Bond lengths [Å] and angles [°] for mar606.

Pd-C(1)	1.977(4)
Pd-C(28)	2.053(4)
Pd-Cl(2)	2.3832(9)
Pd-Cl(1)	2.4887(9)
N(1)-C(1)	1.369(4)
N(1)-C(2)	1.383(5)
N(1)-C(4)	1.446(5)
N(2)-C(1)	1.373(5)
N(2)-C(3)	1.388(5)
N(2)-C(16)	1.452(4)
C(2)-C(3)	1.336(5)
C(4)-C(9)	1.399(5)
C(4)-C(5)	1.407(6)
C(5)-C(6)	1.383(6)
C(5)-C(10)	1.526(6)
C(6)-C(7)	1.382(6)
C(7)-C(8)	1.376(6)
C(8)-C(9)	1.404(6)
C(9)-C(13)	1.509(6)
C(10)-C(11)	1.521(6)
C(10)-C(12)	1.532(6)
C(13)-C(14)	1.532(6)
C(13)-C(15)	1.536(6)
C(16)-C(21)	1.405(5)
C(16)-C(17)	1.405(6)
C(17)-C(18)	1.394(5)
C(17)-C(22)	1.517(6)
C(18)-C(19)	1.382(7)
C(19)-C(20)	1.361(7)
C(20)-C(21)	1.398(6)
C(21)-C(25)	1.515(6)
C(22)-C(24)	1.538(6)
C(22)-C(23)	1.539(6)
C(25)-C(26)	1.525(7)

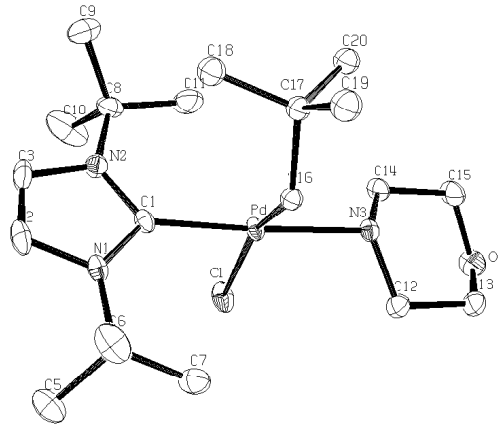
C(25)-C(27)	1.537(7)
C(28)-C(29)	1.546(5)
C(29)-C(32)	1.527(7)
C(29)-C(30)	1.532(7)
C(29)-C(31)	1.538(6)
O-C(33)	1.394(9)
O-C(35)	1.413(8)
C(33)-C(34)	1.479(13)
C(35)-C(36)	1.464(10)

C(1)-Pd-C(28)	89.81(14)
C(1)-Pd-Cl(2)	168.82(10)
C(28)-Pd-Cl(2)	94.03(11)
C(1)-Pd-Cl(1)	93.65(10)
C(28)-Pd-Cl(1)	176.49(10)
Cl(2)-Pd-Cl(1)	82.46(3)
Pd-Cl(1)-Pd’	94.71(4)
Pd-Cl(2)-Pd’	100.37(5)
C(1)-N(1)-C(2)	111.6(3)
C(1)-N(1)-C(4)	126.0(3)
C(2)-N(1)-C(4)	122.2(3)
C(1)-N(2)-C(3)	111.0(3)
C(1)-N(2)-C(16)	127.9(3)
C(3)-N(2)-C(16)	120.8(3)
N(1)-C(1)-N(2)	103.2(3)
N(1)-C(1)-Pd	122.1(2)
N(2)-C(1)-Pd	132.6(3)
C(3)-C(2)-N(1)	106.9(3)
C(2)-C(3)-N(2)	107.3(3)
C(9)-C(4)-C(5)	122.8(3)
C(9)-C(4)-N(1)	119.1(3)
C(5)-C(4)-N(1)	117.9(3)
C(6)-C(5)-C(4)	117.3(4)
C(6)-C(5)-C(10)	119.8(4)
C(4)-C(5)-C(10)	122.8(3)
C(7)-C(6)-C(5)	121.6(4)

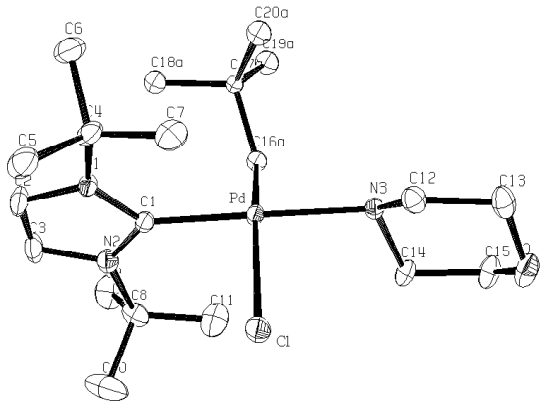
C(8)-C(7)-C(6)	120.0(4)
C(7)-C(8)-C(9)	121.4(4)
C(4)-C(9)-C(8)	116.8(4)
C(4)-C(9)-C(13)	122.7(3)
C(8)-C(9)-C(13)	120.4(4)
C(11)-C(10)-C(5)	113.0(4)
C(11)-C(10)-C(12)	109.0(4)
C(5)-C(10)-C(12)	110.9(4)
C(9)-C(13)-C(14)	112.2(4)
C(9)-C(13)-C(15)	109.5(4)
C(14)-C(13)-C(15)	111.5(4)
C(21)-C(16)-C(17)	122.5(3)
C(21)-C(16)-N(2)	118.5(4)
C(17)-C(16)-N(2)	118.5(3)
C(18)-C(17)-C(16)	117.5(4)
C(18)-C(17)-C(22)	118.9(4)
C(16)-C(17)-C(22)	123.6(3)
C(19)-C(18)-C(17)	120.8(4)
C(20)-C(19)-C(18)	120.5(4)
C(19)-C(20)-C(21)	122.1(4)
C(20)-C(21)-C(16)	116.5(4)
C(20)-C(21)-C(25)	120.7(4)
C(16)-C(21)-C(25)	122.6(4)
C(17)-C(22)-C(24)	110.6(3)
C(17)-C(22)-C(23)	111.6(4)
C(24)-C(22)-C(23)	110.2(4)
C(21)-C(25)-C(26)	112.2(4)
C(21)-C(25)-C(27)	113.2(4)
C(26)-C(25)-C(27)	108.4(4)
C(29)-C(28)-Pd	117.6(3)
C(32)-C(29)-C(30)	110.2(4)
C(32)-C(29)-C(31)	107.5(4)
C(30)-C(29)-C(31)	108.2(4)
C(32)-C(29)-C(28)	112.7(4)
C(30)-C(29)-C(28)	110.5(4)
C(31)-C(29)-C(28)	107.6(3)

C(33)-O-C(35)	114.2(6)
O-C(33)-C(34)	111.0(8)
O-C(35)-C(36)	110.0(6)

Symmetry transformations used to generate equivalent atoms: ‘ -x,y,-z+1/2



6



6a

Table 1. Crystal data and structure refinement for (neopentyl)Pd(I^{t}Bu)(morpholine)chloride

Identification code	oct406	
Empirical formula	C20 H40 Cl N3 O Pd	
Formula weight	480.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$ (No.14)	
Unit cell dimensions	a = 9.6642(3) Å	α= 90°.
	b = 23.1895(5) Å	β= 95.324(1)°.
	c = 10.4673(3) Å	γ = 90°.
Volume	2335.69(11) Å^3	
Z	4	
Density (calculated)	1.37 Mg/m^3	
Absorption coefficient	0.92 mm^{-1}	
F(000)	1008	

Crystal size	0.25 x 0.02 x 0.02 mm^3
Theta range for data collection	3.49 to 26.01°.
Index ranges	-11<=h<=11, -28<=k<=28, -12<=l<=11
Reflections collected	21525
Independent reflections	4570 [R(int) = 0.073]
Reflections with I>2sigma(I)	3366
Completeness to theta = 26.01°	99.6 %
Tmax. and Tmin.	0.9978 and 0.8610
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4570 / 10 / 243
Goodness-of-fit on F^2	0.821
Final R indices [I>2sigma(I)]	R1 = 0.046, wR2 = 0.108
R indices (all data)	R1 = 0.077, wR2 = 0.129
Largest diff. peak and hole	0.90 and -0.50 e.$Å^{-3}$ (near Pd)

The neopentyl group is disordered over two resolved orientations which were included with isotropic C atoms and restrained to have similar geometries.

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 oct406. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	2175(1)	1891(1)	8345(1)	24(1)
Cl	1061(2)	2377(1)	6401(1)	40(1)
O	3808(5)	3875(2)	8609(4)	44(1)
N(1)	1476(4)	710(2)	7197(4)	29(1)
N(2)	-197(5)	1036(2)	8244(4)	31(1)
N(3)	3268(4)	2656(2)	8934(4)	25(1)
C(1)	1097(5)	1179(2)	7885(4)	26(1)
C(2)	465(7)	282(2)	7206(6)	45(2)
C(3)	-554(7)	488(2)	7824(6)	43(2)
C(4)	2702(6)	620(2)	6448(5)	35(1)
C(5)	2159(7)	407(3)	5111(6)	49(2)
C(6)	3641(7)	159(3)	7122(6)	50(2)
C(7)	3513(6)	1171(3)	6285(6)	44(1)
C(8)	-1239(6)	1394(3)	8897(5)	37(1)
C(9)	-1685(8)	1050(3)	10036(7)	59(2)
C(10)	-2470(8)	1510(4)	7914(7)	80(3)
C(11)	-676(7)	1973(3)	9370(7)	52(2)
C(12)	4139(6)	2880(2)	7948(5)	34(1)
C(13)	4806(6)	3455(2)	8351(5)	40(1)
C(14)	2312(6)	3118(2)	9280(5)	31(1)
C(15)	3055(7)	3678(2)	9633(6)	42(1)
C(16)	3575(6)	1443(3)	9594(6)	24(2)a
C(17)	3309(7)	1294(3)	10993(7)	28(2)a
C(18)	2213(7)	818(3)	11006(7)	36(2)a
C(19)	4691(8)	1049(3)	11640(8)	42(2)a
C(20)	2918(7)	1817(3)	11733(7)	34(2)a
C(16A)	2423(18)	1626(7)	10279(18)	25(5)b
C(17A)	3458(17)	1142(7)	10765(16)	19(5)b
C(18A)	2730(20)	558(8)	10550(20)	31(5)b
C(19A)	3740(20)	1222(9)	12234(16)	38(6)b
C(20A)	4797(19)	1167(9)	10160(20)	36(6)b

occupancy: a 0.76 , b 0.24

Table 3. Bond lengths [Å] and angles [°] for oct406.

Pd-C(1)	1.988(5)
Pd-C(16)	2.072(6)
Pd-C(16A)	2.109(18)
Pd-N(3)	2.126(4)
Pd-Cl	2.4821(13)
O-C(13)	1.413(7)
O-C(15)	1.425(7)
N(1)-C(1)	1.373(6)
N(1)-C(2)	1.393(7)
N(1)-C(4)	1.495(7)
N(2)-C(3)	1.378(7)
N(2)-C(1)	1.379(7)
N(2)-C(8)	1.517(7)
N(3)-C(14)	1.482(6)
N(3)-C(12)	1.485(6)
C(2)-C(3)	1.317(9)
C(4)-C(7)	1.516(8)
C(4)-C(5)	1.530(8)
C(4)-C(6)	1.531(7)
C(8)-C(11)	1.515(8)
C(8)-C(10)	1.522(8)
C(8)-C(9)	1.529(8)
C(12)-C(13)	1.525(7)
C(14)-C(15)	1.514(7)
C(16)-C(17)	1.549(9)
C(17)-C(20)	1.507(10)
C(17)-C(18)	1.530(9)
C(17)-C(19)	1.548(10)
C(16A)-C(17A)	1.556(16)
C(17A)-C(20A)	1.492(17)
C(17A)-C(18A)	1.535(17)
C(17A)-C(19A)	1.548(17)
C(1)-Pd-C(16)	91.9(2)

C(1)-Pd-C(16A)	90.0(5)
C(16)-Pd-C(16A)	40.4(5)
C(1)-Pd-N(3)	176.70(18)
C(16)-Pd-N(3)	87.6(2)
C(16A)-Pd-N(3)	87.5(5)
C(1)-Pd-Cl	90.03(14)
C(16)-Pd-Cl	162.41(18)
C(16A)-Pd-Cl	157.2(5)
N(3)-Pd-Cl	91.45(11)
C(13)-O-C(15)	109.2(4)
C(1)-N(1)-C(2)	109.8(4)
C(1)-N(1)-C(4)	130.4(4)
C(2)-N(1)-C(4)	119.7(4)
C(3)-N(2)-C(1)	110.0(5)
C(3)-N(2)-C(8)	119.4(5)
C(1)-N(2)-C(8)	130.4(4)
C(14)-N(3)-C(12)	108.9(4)
C(14)-N(3)-Pd	111.7(3)
C(12)-N(3)-Pd	112.9(3)
N(1)-C(1)-N(2)	104.2(4)
N(1)-C(1)-Pd	128.7(4)
N(2)-C(1)-Pd	127.0(4)
C(3)-C(2)-N(1)	107.6(5)
C(2)-C(3)-N(2)	108.3(5)
N(1)-C(4)-C(7)	112.7(4)
N(1)-C(4)-C(5)	107.6(5)
C(7)-C(4)-C(5)	107.8(5)
N(1)-C(4)-C(6)	108.6(5)
C(7)-C(4)-C(6)	110.5(5)
C(5)-C(4)-C(6)	109.5(4)
C(11)-C(8)-N(2)	113.5(5)
C(11)-C(8)-C(10)	107.4(6)
N(2)-C(8)-C(10)	107.6(5)
C(11)-C(8)-C(9)	109.0(5)
N(2)-C(8)-C(9)	108.3(5)
C(10)-C(8)-C(9)	111.1(6)

N(3)-C(12)-C(13)	111.5(4)
O-C(13)-C(12)	112.1(5)
N(3)-C(14)-C(15)	112.9(4)
O-C(15)-C(14)	110.8(4)
C(17)-C(16)-Pd	123.5(4)
C(20)-C(17)-C(18)	111.7(6)
C(20)-C(17)-C(19)	108.5(6)
C(18)-C(17)-C(19)	107.6(6)
C(20)-C(17)-C(16)	112.2(6)
C(18)-C(17)-C(16)	110.2(6)
C(19)-C(17)-C(16)	106.4(6)
C(17A)-C(16A)-Pd	122.4(12)
C(20A)-C(17A)-C(18A)	112.2(15)
C(20A)-C(17A)-C(19A)	109.6(14)
C(18A)-C(17A)-C(19A)	106.7(14)
C(20A)-C(17A)-C(16A)	113.0(14)
C(18A)-C(17A)-C(16A)	108.3(13)
C(19A)-C(17A)-C(16A)	106.7(14)

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

- 7.7844 (0.0076) x + 7.1305 (0.0354) y + 6.0622 (0.0090) z = 4.7487 (0.0108)

*	0.0179	(0.0011)	C1
*	0.0004	(0.0000)	Cl
*	0.0167	(0.0010)	N3
*	-0.0350	(0.0022)	Pd
	-0.6869	(0.0074)	C16_a
	0.7554	(0.0185)	C16A_b

Rms deviation of fitted atoms = 0.0214

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N3-H3X	0.93	2.67	160	3.559	Cl [x+1/2, -y+1/2, z+1/2]