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Dichlorido{2-[(3,5-diphenyl-1*H*-pyrazol-1-yl-κN^2)methyl]pyridine-κN}palladium(II)

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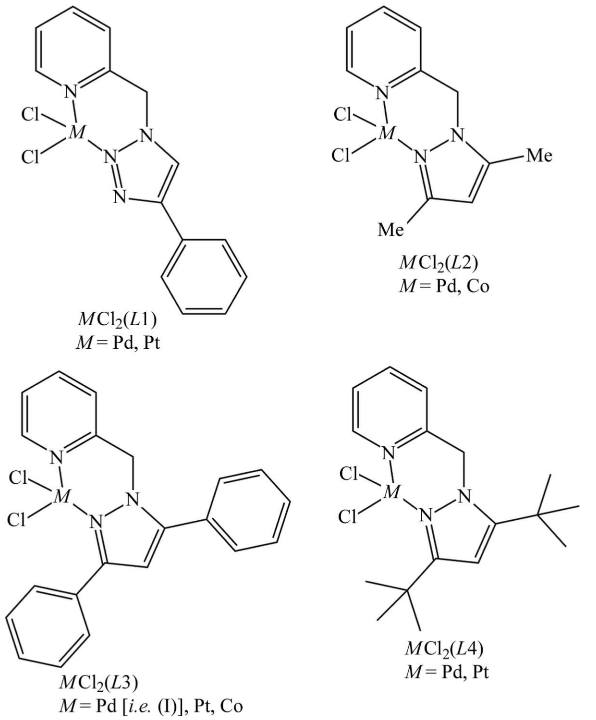
The title compound, [$PdCl_2(C_{21}H_{17}N_3)$], is a member of a sequence of Pd, Pt and Co dichloride complexes bearing polysubstituted (pyrazol-1-ylmethyl)pyridine ligands. It is shown that there is a correlation between the steric bulkiness of the bidentate (pyrazol-1-ylmethyl)pyridine ligands and the Pd—$N_{pyrazole}$ distances, *i.e.* the larger the ligand, the longer the bond. In contrast, no trend is observed between the steric properties of the ligand and the Pd—$N_{pyridine}$ bond lengths.

Comment

(Pyrazol-1-ylmethyl)pyridine ligands have been used to prepare platinum(II) and gold(III) complexes that were investigated as potential anticancer agents (Segapelo *et al.*, 2009). (Pyrazol-1-ylmethyl)pyridine palladium(II) complexes with 3,5-dimethyl- and 3,5-di-*tert*-butyl- substitutents have also been investigated as catalysts for ethylene polymerization reactions (House *et al.*, 1986; Mohlala *et al.*, 2005; Ojwach *et al.*, 2007, 2009). In the course of this experimental work, the palladium 3,5-diphenyl- analogue, namely dichlorido{2-[(3,5-diphenyl-1*H*-pyrazol-1-yl-κN^2)methyl]pyridine-κN}palladium(II), (I), was synthesized.

Compound (I) (Fig. 1) has a slightly distorted square-planar geometry, with a bidentate ligand bite angle of 87.04 (4)°. The six-membered heterocycle is in the boat conformation which is common for metal compounds with this family of ligands (Ojwach *et al.*, 2009). The geometric parameters (Table 1) agree well with those of the 3,5-dimethyl- and 3,5-*tert*-butyl-analogues, as well as with those of {2-[(4-phenyl-1*H*-1,2,3-triazol-4-yl)methyl]pyridine}palladium(II) chloride (Ojwach *et al.*, 2009; Kilpin & Crowley, 2010).

It has been established in previous work with similar compounds that the metal–N_{pz} distance (pz is pyrazole) is dependent on the steric size of the pz ligand and its ability to shield the metal coordination sphere (Ojwach *et al.*, 2009). There is a correlation between the shielding ability and the metal–N_{pz} distance. The shielding is expressed by the percentage of the metal coordination sphere blocked by the ligand from molecular attack. Tables 2 and 3 compile the data of the shielding percentage (Guzei & Wendt, 2006) and the metal–N_{pz} distance for (I), literature data and other related compounds in the Cambridge Structural Database (see Scheme; Allen, 2002) (Ojwach *et al.*, 2009; Segapelo *et al.*, 2009; Balamurugan *et al.*, 2004; Benade *et al.*, 2011; Kilpin & Crowley, 2010; Allen, 2002).



$MCl_2(L1)$
M = Pd, Pt

$MCl_2(L2)$
M = Pd, Co

$MCl_2(L3)$
M = Pd [*i.e.* (I)], Pt, Co

$MCl_2(L4)$
M = Pd, Pt

The 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine ligand ($L1$), with only one phenyl substituent on the triazole ring, is the least sterically demanding among the ligands in Table 2 (Kilpin & Crowley, 2010). Therefore it shields the metal coordination sphere in $PdCl_2(L1)$ and $PtCl_2(L1)$ to the least extent, resulting in the shortest metal–N_{pz} distance. This trend continues for the Pd and Pt complexes with the 3,5-dimethylpyrazole ($L2$), 3,5-diphenylpyrazole ($L3$) and 3,5-di-*tert*-butylpyrazole ($L4$) ligands. Interestingly, the cobalt analogues do not adhere to this trend. While the $L2$ analogue shields a smaller percentage of the metal than the $L3$ analogue, it is $CoCl_2(L2)$ that has a longer metal–N_{pz} distance than $CoCl_2(L3)$ (Balamurugan *et al.*, 2004; Benade *et al.*, 2011). Steric effects alone cannot explain the latter observations for a metal with different electronic properties; thus, electronic effects must contribute to the solid-state geometry of the Co complexes.

The metal–N_{py} distances (py is pyridine) for the Pd, Pt and Co compounds are presented in Table 4. There are no consistent trends found between the ligand shielding percentage and this distance. Table 5 tabulates the ligand folding angle along the metal–methylene C atom. The folding angle is defined as a dihedral angle between two planes defined by

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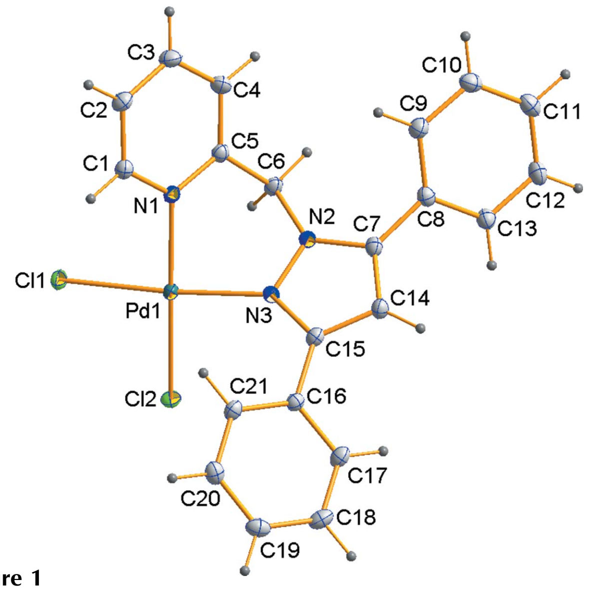

Figure 1
The molecular structure of the title Pd complex, (I). Displacement ellipsoids are drawn at the 50% probability level.

four atoms, *viz*. the metal and a chain of three atoms connected to it; in (I), the planes are defined as Pd1/N1/C5/C6 and Pd1/N3/N2/C6. Overall the folding angles are fairly similar for the Pd and Pt analogues except for the triazoles. The average folding angle in Pd and Pt complexes with pyrazole ligands is 62.4 (18)°. The triazole folding angles in Pd and Pt complexes have a significantly lower average of 52.10 (4)°. The pyrazole ligands with Co as the metal also have a significantly lower folding angle [a 54 (2)° average] than with Pd or Pt as the metal. For comparison, the folding angle in the C_{2v} symmetrical boat conformation cyclohexane is 126.9°.

In the *L*3 analogues for Pd [*i.e.* (I)] and Pt, the phenyl rings form angles with the pyrazole ring of 48.35 (5) and 34.97 (6)° for the former, and 48.97 (8) and 36.04 (9)° for the latter. In recently published work, in the compound 1,2-[bis(3,5-diphenylpyrazol-1-yl)methyl]benzene, the phenyl rings form angles of 15.9 (6), 48.48 (4), 17.62 (6) and 44.13 (3)° with the planes of the pyrazole rings (Spencer *et al.*, 2012). In each of four pairs of dihedral angles, one is close to 48°, whereas the second is either around 35° of in the vicinity of 16°. We attribute differences in the latter to electronic and intrinsic packing effects. We note that frequently large changes in dihedral angles are associated with only small molecular energy changes.

In metal compounds of Pd and Pt with analogues of the bidentate (pyrazol-1-ylmethyl)pyridine ligand and (triazol-4-ylmethyl)pyridine ligands, the larger the ligand (resulting in a greater shielding percentage of the metal) the longer is the metal–N_{pz} bond length. An equivalent trend was not observed in Co (pyrazol-1-ylmethyl)pyridine analogues. No obvious trend was observed for the metal–N_{py} distances.

Experimental

A mixture of 2-[(3,5-diphenylpyrazol-1-yl)methyl]pyridine (0.29 g, 0.93 mmol) and $[PdCl_2(NCMe)_2]$ (0.24 g, 0.93 mmol) dissolved in dichloromethane (15 ml) was stirred for 6 h. The solvent was removed *in vacuo* to give an analytically pure yellow powder of the title compound (yield 0.21 g, 46%). Crystals of the product were obtained by slow evaporation from a solution used to run the NMR spectrum of the product. ^{1}H NMR (CDCl$_3$): δ 9.23 (*d*, 1H, py, $^3J_{HH}$ = 5.4 Hz), 8.26 (*m*, 2H, py), 7.92 (*d*, 1H, py, $^3J_{HH}$ = 7.2 Hz), 7.53 (*m*, 10H, Phpz), 6.53 (*d*, 1H, CH$_2$–, $^3J_{HH}$ = 17.4 Hz), 5.45 (*d*, 1H, CH$_2$–, $^3J_{HH}$ = 15.0 Hz). Analysis calculated for $C_{21}H_{17}Cl_2N_3Pd\cdot0.25CHCl_3$: C 49.22, H 3.35, N 8.10%; found: C 49.14, H 3.21, N 7.75%.

Table 1
Selected geometric parameters (Å, °).

Pd1—N1	2.0317 (11)	Pd1—Cl1	2.2848 (3)
Pd1—N3	2.0381 (11)	Pd1—Cl2	2.2906 (4)
N1—Pd1—N3	87.04 (4)	N1—Pd1—Cl2	176.44 (3)
N1—Pd1—Cl1	88.95 (3)	N3—Pd1—Cl2	93.08 (3)
N3—Pd1—Cl1	175.55 (3)	Cl1—Pd1—Cl2	90.808 (12)

Table 2
Shielding percentage of metal centre by the bidentate ligand (%).

Ligand	Substituents on the bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	36.0	36.4	
*L*2	3,5-Dimethylpyrazole	38.9		38.6
*L*3	3,5-Diphenylpyrazole	42.4	42.7	41.8
*L*4	3,5-Di-*tert*-butylpyrazole	43.9	44.5	

Table 3
Metal–N_{pz} distances (Å).

Ligand	Substituents on the bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	2.012 (3)	2.000 (3)	
*L*2	3,5-Dimethylpyrazole	2.034 (3)		2.0503 (19)
*L*3	3,5-Diphenylpyrazole	2.0381 (11)	2.0193 (16)	2.023 (4)
*L*4	3,5-Di-*tert*-butylpyrazole	2.060 (3)	2.041 (4)	

Table 4
Metal–N_{py} distances (Å).

Ligand	Substituents on the bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	2.067 (3)	2.052 (3)	
*L*2	3,5-Dimethylpyrazole	2.048 (3)		2.0609 (19)
*L*3	3,5-Diphenylpyrazole	2.0317 (11)	2.0220 (17)	2.048 (4)
*L*4	3,5-Di-*tert*-butylpyrazole	2.037 (3)	2.012 (4)	

Table 5
Ligand folding angle (°).

Ligand	Substituents on the bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	52.07	52.12	
*L*2	3,5-Dimethylpyrazole	63.50 (13)		55.13 (8)
*L*3	3,5-Diphenylpyrazole	62.04 (5)	61.50 (8)	52.15
*L*4	3,5-Di-*tert*-butylpyrazole	60.18 (29)	64.93 (17)	

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Crystal data

$[PdCl_2(C_{21}H_{17}N_3)]$
$M_r = 488.68$
Monoclinic, $P2_1/n$
$a = 12.1226\ (10)$ Å
$b = 14.6299\ (12)$ Å
$c = 12.258\ (1)$ Å
$\beta = 116.862\ (1)°$
$V = 1939.4\ (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.24$ mm^{-1}
$T = 105$ K
$0.50 \times 0.32 \times 0.24$ mm

Data collection

Bruker CCD-1000 area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.575$, $T_{max} = 0.755$
26141 measured reflections
4815 independent reflections
4638 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.050$
$S = 1.05$
4815 reflections
244 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

All H atoms were placed in idealized positions and refined as riding with appropriate displacement parameters [$U_{iso}(H) = 1.2U_{eq}$(parent)]. Default effective X—H distances for $T = 105$ K were Csp^2—H = 0.95 Å and Csp^3—H = 0.99 Å.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*, *publCIF* (Westrip, 2010) and *modiCIFer* (Guzei, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3079). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C**68**, m317–m319   [doi:10.1107/S0108270112043119]

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Dichlorido{2-[(3,5-diphenyl-1H-pyrazol-1-yl- κN<ι>^{2})methyl]pyridine-κN}palladium(II)

Crystal data

$[PdCl_2(C_{21}H_{17}N_3)]$
M_r = 488.68
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 12.1226 (10) Å
b = 14.6299 (12) Å
c = 12.258 (1) Å
β = 116.862 (1)°
V = 1939.4 (3) Å^3
Z = 4

$F(000)$ = 976
D_x = 1.674 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 6759 reflections
θ = 2.3–28.3°
μ = 1.24 mm^{-1}
T = 105 K
Block, orange
0.50 × 0.32 × 0.24 mm

Data collection

Bruker CCD-1000 area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
0.30° ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.575, T_{max} = 0.755

26141 measured reflections
4815 independent reflections
4638 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.3°, θ_{min} = 2.0°
$h = -16 \rightarrow 16$
$k = -19 \rightarrow 19$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.050
S = 1.05
4815 reflections
244 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.2359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Pd1	0.683785 (8)	0.080530 (6)	0.528942 (8)	0.01059 (4)
Cl1	0.49395 (3)	0.14882 (2)	0.43695 (3)	0.01617 (7)
Cl2	0.69038 (3)	0.07176 (2)	0.34540 (3)	0.01573 (7)
N1	0.68232 (10)	0.09629 (8)	0.69295 (10)	0.0126 (2)
N2	0.93246 (11)	0.06958 (7)	0.72770 (11)	0.0136 (2)
N3	0.85548 (10)	0.02498 (8)	0.62306 (10)	0.0130 (2)
C1	0.58389 (13)	0.07388 (9)	0.71018 (13)	0.0147 (2)
H1	0.5151	0.0449	0.6459	0.018*
C2	0.58038 (13)	0.09201 (9)	0.81962 (13)	0.0173 (3)
H2	0.5102	0.0752	0.8303	0.021*
C3	0.68009 (13)	0.13482 (10)	0.91297 (13)	0.0195 (3)
H3	0.6785	0.1493	0.9878	0.023*
C4	0.78310 (13)	0.15634 (9)	0.89553 (13)	0.0177 (3)
H4	0.8532	0.1849	0.9588	0.021*
C5	0.78181 (12)	0.13563 (9)	0.78487 (12)	0.0137 (2)
C6	0.88994 (12)	0.15469 (9)	0.75856 (12)	0.0143 (2)
H6A	0.8646	0.1983	0.6896	0.017*
H6B	0.9582	0.1827	0.8312	0.017*
C7	1.04486 (12)	0.02823 (9)	0.78236 (12)	0.0145 (2)
C8	1.14894 (12)	0.06141 (9)	0.89556 (12)	0.0153 (2)
C9	1.13559 (14)	0.08301 (9)	0.99996 (14)	0.0183 (3)
H9	1.0568	0.0783	0.9986	0.022*
C10	1.23782 (14)	0.11145 (10)	1.10624 (13)	0.0201 (3)
H10	1.2286	0.1260	1.1772	0.024*
C11	1.35308 (13)	0.11847 (10)	1.10837 (13)	0.0199 (3)
H11	1.4227	0.1376	1.1809	0.024*
C12	1.36664 (13)	0.09757 (10)	1.00465 (13)	0.0198 (3)
H12	1.4454	0.1031	1.0062	0.024*
C13	1.26537 (13)	0.06854 (10)	0.89814 (13)	0.0170 (3)
H13	1.2753	0.0537	0.8276	0.020*
C14	1.03930 (12)	−0.04562 (9)	0.71005 (12)	0.0157 (2)
H14	1.1039	−0.0878	0.7239	0.019*
C15	0.91971 (12)	−0.04642 (9)	0.61202 (12)	0.0137 (2)
C16	0.86762 (12)	−0.11326 (9)	0.51164 (12)	0.0132 (2)
C17	0.94438 (13)	−0.15154 (9)	0.46607 (13)	0.0168 (3)

H17	1.0296	−0.1358	0.5015	0.020*
C18	0.89541 (14)	−0.21269 (9)	0.36864 (13)	0.0186 (3)
H18	0.9475	−0.2385	0.3376	0.022*
C19	0.77100 (14)	−0.23637 (9)	0.31639 (12)	0.0182 (3)
H19	0.7376	−0.2766	0.2483	0.022*
C20	0.69582 (12)	−0.20081 (9)	0.36438 (12)	0.0170 (3)
H20	0.6113	−0.2183	0.3305	0.020*
C21	0.74385 (12)	−0.13964 (9)	0.46188 (12)	0.0152 (2)
H21	0.6922	−0.1158	0.4946	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.00982 (6)	0.01110 (6)	0.01107 (6)	0.00066 (3)	0.00492 (4)	−0.00010 (3)
Cl1	0.01324 (14)	0.01939 (15)	0.01563 (14)	0.00494 (11)	0.00629 (11)	0.00276 (11)
Cl2	0.01638 (15)	0.01883 (15)	0.01406 (14)	0.00034 (11)	0.00871 (12)	0.00063 (11)
N1	0.0125 (5)	0.0117 (5)	0.0142 (5)	0.0009 (4)	0.0066 (4)	−0.0005 (4)
N2	0.0121 (5)	0.0140 (5)	0.0144 (5)	−0.0003 (4)	0.0055 (4)	−0.0024 (4)
N3	0.0117 (5)	0.0138 (5)	0.0130 (5)	−0.0007 (4)	0.0050 (4)	−0.0018 (4)
C1	0.0132 (6)	0.0143 (6)	0.0161 (6)	0.0002 (4)	0.0063 (5)	0.0002 (4)
C2	0.0179 (6)	0.0181 (6)	0.0196 (7)	0.0002 (5)	0.0116 (5)	0.0004 (5)
C3	0.0229 (7)	0.0218 (7)	0.0172 (6)	−0.0005 (5)	0.0121 (5)	−0.0033 (5)
C4	0.0180 (6)	0.0182 (6)	0.0161 (6)	−0.0011 (5)	0.0071 (5)	−0.0043 (5)
C5	0.0133 (6)	0.0121 (5)	0.0159 (6)	0.0011 (4)	0.0068 (5)	−0.0006 (5)
C6	0.0139 (6)	0.0122 (6)	0.0175 (6)	−0.0005 (4)	0.0077 (5)	−0.0026 (4)
C7	0.0119 (5)	0.0164 (6)	0.0154 (6)	0.0003 (5)	0.0064 (5)	0.0014 (5)
C8	0.0139 (6)	0.0148 (6)	0.0154 (6)	0.0007 (5)	0.0051 (5)	0.0009 (5)
C9	0.0161 (7)	0.0202 (7)	0.0191 (7)	0.0000 (5)	0.0085 (6)	0.0000 (5)
C10	0.0231 (7)	0.0206 (7)	0.0152 (6)	0.0007 (5)	0.0074 (5)	−0.0013 (5)
C11	0.0195 (6)	0.0178 (6)	0.0164 (6)	−0.0013 (5)	0.0027 (5)	−0.0003 (5)
C12	0.0134 (6)	0.0229 (7)	0.0199 (7)	−0.0021 (5)	0.0048 (5)	0.0010 (5)
C13	0.0150 (6)	0.0194 (6)	0.0158 (6)	0.0001 (5)	0.0063 (5)	0.0014 (5)
C14	0.0131 (6)	0.0157 (6)	0.0176 (6)	0.0020 (5)	0.0064 (5)	0.0006 (5)
C15	0.0134 (6)	0.0133 (6)	0.0159 (6)	0.0006 (5)	0.0080 (5)	0.0006 (5)
C16	0.0141 (6)	0.0123 (6)	0.0138 (6)	0.0010 (4)	0.0067 (5)	0.0007 (4)
C17	0.0158 (6)	0.0161 (6)	0.0214 (6)	0.0003 (5)	0.0110 (5)	0.0003 (5)
C18	0.0241 (7)	0.0159 (6)	0.0222 (7)	0.0015 (5)	0.0162 (6)	−0.0002 (5)
C19	0.0252 (7)	0.0134 (6)	0.0160 (6)	−0.0007 (5)	0.0093 (5)	−0.0006 (5)
C20	0.0157 (6)	0.0135 (6)	0.0189 (6)	−0.0002 (5)	0.0052 (5)	0.0014 (5)
C21	0.0148 (6)	0.0135 (6)	0.0187 (6)	0.0018 (5)	0.0089 (5)	0.0005 (5)

Geometric parameters (Å, º)

Pd1—N1	2.0317 (11)	C8—C13	1.4013 (19)
Pd1—N3	2.0381 (11)	C9—C10	1.395 (2)
Pd1—Cl1	2.2848 (3)	C9—H9	0.9500
Pd1—Cl2	2.2906 (4)	C10—C11	1.389 (2)
N1—C1	1.3429 (18)	C10—H10	0.9500
N1—C5	1.3518 (17)	C11—C12	1.388 (2)
N2—C7	1.3589 (17)	C11—H11	0.9500

N2—N3	1.3638 (15)	C12—C13	1.394 (2)
N2—C6	1.4613 (16)	C12—H12	0.9500
N3—C15	1.3457 (17)	C13—H13	0.9500
C1—C2	1.3869 (19)	C14—C15	1.4041 (18)
C1—H1	0.9500	C14—H14	0.9500
C2—C3	1.383 (2)	C15—C16	1.4721 (18)
C2—H2	0.9500	C16—C21	1.3946 (18)
C3—C4	1.395 (2)	C16—C17	1.4004 (18)
C3—H3	0.9500	C17—C18	1.3923 (19)
C4—C5	1.3830 (18)	C17—H17	0.9500
C4—H4	0.9500	C18—C19	1.390 (2)
C5—C6	1.5107 (18)	C18—H18	0.9500
C6—H6A	0.9900	C19—C20	1.390 (2)
C6—H6B	0.9900	C19—H19	0.9500
C7—C14	1.3797 (19)	C20—C21	1.3926 (19)
C7—C8	1.4734 (18)	C20—H20	0.9500
C8—C9	1.397 (2)	C21—H21	0.9500

N1—Pd1—N3	87.04 (4)	C13—C8—C7	118.10 (12)
N1—Pd1—Cl1	88.95 (3)	C10—C9—C8	120.07 (13)
N3—Pd1—Cl1	175.55 (3)	C10—C9—H9	120.0
N1—Pd1—Cl2	176.44 (3)	C8—C9—H9	120.0
N3—Pd1—Cl2	93.08 (3)	C11—C10—C9	120.06 (13)
Cl1—Pd1—Cl2	90.808 (12)	C11—C10—H10	120.0
C1—N1—C5	119.63 (12)	C9—C10—H10	120.0
C1—N1—Pd1	122.24 (9)	C12—C11—C10	120.06 (13)
C5—N1—Pd1	118.02 (9)	C12—C11—H11	120.0
C7—N2—N3	111.00 (11)	C10—C11—H11	120.0
C7—N2—C6	130.09 (11)	C11—C12—C13	120.42 (13)
N3—N2—C6	118.66 (11)	C11—C12—H12	119.8
C15—N3—N2	106.55 (10)	C13—C12—H12	119.8
C15—N3—Pd1	137.90 (9)	C12—C13—C8	119.71 (13)
N2—N3—Pd1	115.56 (8)	C12—C13—H13	120.1
N1—C1—C2	121.54 (13)	C8—C13—H13	120.1
N1—C1—H1	119.2	C7—C14—C15	106.75 (11)
C2—C1—H1	119.2	C7—C14—H14	126.6
C3—C2—C1	119.31 (13)	C15—C14—H14	126.6
C3—C2—H2	120.3	N3—C15—C14	109.15 (11)
C1—C2—H2	120.3	N3—C15—C16	123.40 (11)
C2—C3—C4	118.93 (13)	C14—C15—C16	127.44 (12)
C2—C3—H3	120.5	C21—C16—C17	119.50 (12)
C4—C3—H3	120.5	C21—C16—C15	121.32 (11)
C5—C4—C3	119.12 (13)	C17—C16—C15	119.18 (12)
C5—C4—H4	120.4	C18—C17—C16	119.76 (13)
C3—C4—H4	120.4	C18—C17—H17	120.1
N1—C5—C4	121.42 (12)	C16—C17—H17	120.1
N1—C5—C6	115.73 (11)	C19—C18—C17	120.58 (13)
C4—C5—C6	122.86 (12)	C19—C18—H18	119.7
N2—C6—C5	109.85 (10)	C17—C18—H18	119.7

N2—C6—H6A	109.7
C5—C6—H6A	109.7
N2—C6—H6B	109.7
C5—C6—H6B	109.7
H6A—C6—H6B	108.2
N2—C7—C14	106.55 (11)
N2—C7—C8	123.98 (12)
C14—C7—C8	129.45 (12)
C9—C8—C13	119.67 (13)
C9—C8—C7	122.20 (12)
C18—C19—C20	119.61 (13)
C18—C19—H19	120.2
C20—C19—H19	120.2
C19—C20—C21	120.26 (13)
C19—C20—H20	119.9
C21—C20—H20	119.9
C20—C21—C16	120.21 (12)
C20—C21—H21	119.9
C16—C21—H21	119.9

N3—Pd1—N1—C1	−134.67 (11)
Cl1—Pd1—N1—C1	47.24 (10)
Cl2—Pd1—N1—C1	133.3 (5)
N3—Pd1—N1—C5	49.19 (10)
Cl1—Pd1—N1—C5	−128.89 (9)
Cl2—Pd1—N1—C5	−42.8 (6)
C7—N2—N3—C15	0.71 (14)
C6—N2—N3—C15	175.58 (11)
C7—N2—N3—Pd1	−178.97 (9)
C6—N2—N3—Pd1	−4.11 (14)
N1—Pd1—N3—C15	137.04 (14)
Cl1—Pd1—N3—C15	162.6 (3)
Cl2—Pd1—N3—C15	−46.53 (13)
N1—Pd1—N3—N2	−43.41 (9)
Cl1—Pd1—N3—N2	−17.9 (5)
Cl2—Pd1—N3—N2	133.02 (9)
C5—N1—C1—C2	1.50 (19)
Pd1—N1—C1—C2	−174.58 (10)
N1—C1—C2—C3	0.5 (2)
C1—C2—C3—C4	−1.7 (2)
C2—C3—C4—C5	1.0 (2)
C1—N1—C5—C4	−2.25 (19)
Pd1—N1—C5—C4	173.99 (10)
C1—N1—C5—C6	177.53 (11)
Pd1—N1—C5—C6	−6.23 (15)
C3—C4—C5—N1	1.0 (2)
C3—C4—C5—C6	−178.79 (13)
C7—N2—C6—C5	−120.70 (14)
N3—N2—C6—C5	65.57 (15)
N1—C5—C6—N2	−58.74 (15)
C4—C5—C6—N2	121.04 (14)
N3—N2—C7—C14	−0.13 (15)
C6—N2—C7—C14	−174.25 (13)
N3—N2—C7—C8	178.58 (12)
C6—N2—C7—C8	4.5 (2)
N2—C7—C8—C9	49.9 (2)
C14—C7—C8—C9	−131.73 (16)
N2—C7—C8—C13	−132.06 (14)
C14—C7—C8—C13	46.3 (2)
C13—C8—C9—C10	0.0 (2)
C7—C8—C9—C10	177.98 (13)
C8—C9—C10—C11	0.1 (2)
C9—C10—C11—C12	0.3 (2)
C10—C11—C12—C13	−0.7 (2)
C11—C12—C13—C8	0.7 (2)
C9—C8—C13—C12	−0.3 (2)
C7—C8—C13—C12	−178.45 (13)
N2—C7—C14—C15	−0.48 (15)
C8—C7—C14—C15	−179.09 (13)
N2—N3—C15—C14	−1.00 (14)
Pd1—N3—C15—C14	178.58 (10)
N2—N3—C15—C16	178.44 (12)
Pd1—N3—C15—C16	−2.0 (2)
C7—C14—C15—N3	0.93 (15)
C7—C14—C15—C16	−178.48 (13)
N3—C15—C16—C21	−34.97 (19)
C14—C15—C16—C21	144.36 (14)
N3—C15—C16—C17	145.54 (13)
C14—C15—C16—C17	−35.1 (2)
C21—C16—C17—C18	2.5 (2)
C15—C16—C17—C18	−178.02 (12)
C16—C17—C18—C19	−0.2 (2)
C17—C18—C19—C20	−2.0 (2)
C18—C19—C20—C21	1.9 (2)
C19—C20—C21—C16	0.3 (2)
C17—C16—C21—C20	−2.55 (19)
C15—C16—C21—C20	177.96 (12)

Table 2. Shielding percentage of metal centre by the bidentate ligand (%)

Ligand	Substituents on bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	36.0	36.4	
*L*2	3,5-Dimethylpyrazole	38.9		38.6
*L*3	3,5-Diphenylpyrazole	42.4	42.7	41.8
*L*4	3,5-Di-*tert*-butylpyrazole	43.9	44.5	

Table 3. Metal–N_{pz} distances (Å)

Ligand	Substituents on bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	2.012 (3)	2.000 (3)	
*L*2	3,5-Dimethylpyrazole	2.034 (3)		2.0503 (19)
*L*3	3,5-Diphenylpyrazole	2.0381 (11)	2.0193 (16)	2.023 (4)
*L*4	3,5-Di-*tert*-butylpyrazole	2.060 (3)	2.041 (4)	

Table 4. Metal–N_{py} distances (Å)

Ligand	Substituents on bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	2.067 (3)	2.052 (3)	
*L*2	3,5-Dimethylpyrazole	2.048 (3)		2.0609 (19)
*L*3	3,5-Diphenylpyrazole	2.0317 (11)	2.0220 (17)	2.048 (4)
*L*4	3,5-Di-*tert*-butylpyrazole	2.037 (3)	2.012 (4)	

Table 5. Ligand folding angle (°)

Ligand	Substituents on bidentate ligand	Pd	Pt	Co
*L*1	4-Phenyl-1*H*-1,2,3-triazole	52.07	52.12	
*L*2	3,5-Dimethylpyrazole	63.50 (13)		55.13 (8)
*L*3	3,5-Diphenylpyrazole	62.04 (5)	61.50 (8)	52.15
*L*4	3,5-Di-*tert*-butylpyrazole	60.18 (29)	64.93 (17)	