

New palladium complexes with phosphino- and phosphinitopyridine ligands

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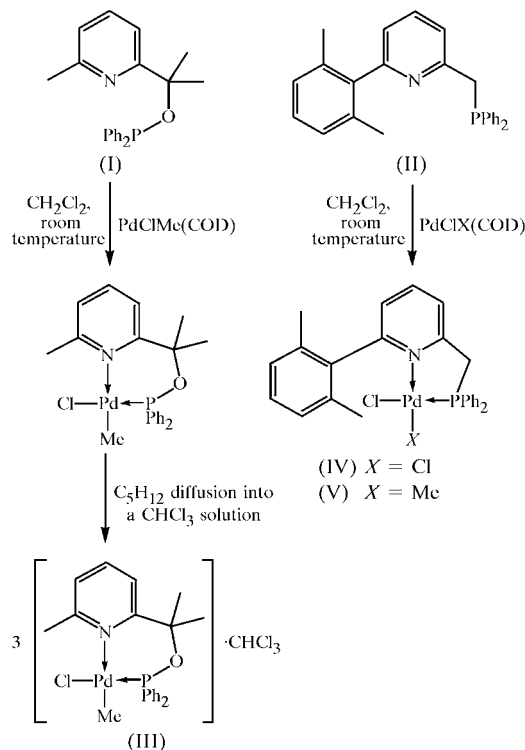
Three new palladium complexes containing a difunctional *P,N*-chelate, namely tris(chloro{[1-methyl-1-(6-methyl-2-pyridyl)ethoxy]diphenylphosphine- κ^2N,P }methylpalladium(II) chloroform solvate, $3[\text{Pd}(\text{CH}_3)\text{Cl}(\text{C}_{21}\text{H}_{22}\text{NOP})]\cdot\text{CHCl}_3$, (III), dichloro[2-(2,6-dimethylphenyl)-6-(diphenylphosphinomethyl)pyridine- κ^2N,P]palladium(II), $[\text{PdCl}_2(\text{C}_{26}\text{H}_{24}\text{NP})]$, (IV), and chloro[2-(2,6-dimethylphenyl)-6-(diphenylphosphinomethyl)pyridine- κ^2N,P]methylpalladium(II), $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{C}_{26}\text{H}_{24}\text{NP})]$, (V), are reported. Geometric data and the conformations of the ligands around the metal centers, as well as slight distortions of the Pd coordination environments from idealized square-planar geometry, are discussed and compared with the situations in related compounds. Non-conventional hydrogen-bond interactions ($\text{C}-\text{H}\cdots\text{Cl}$) have been found in all three complexes. Compound (III) is the first six-membered chloro-methyl-phosphinite *P,N*-type Pd^{II} complex to be structurally characterized.

Comment

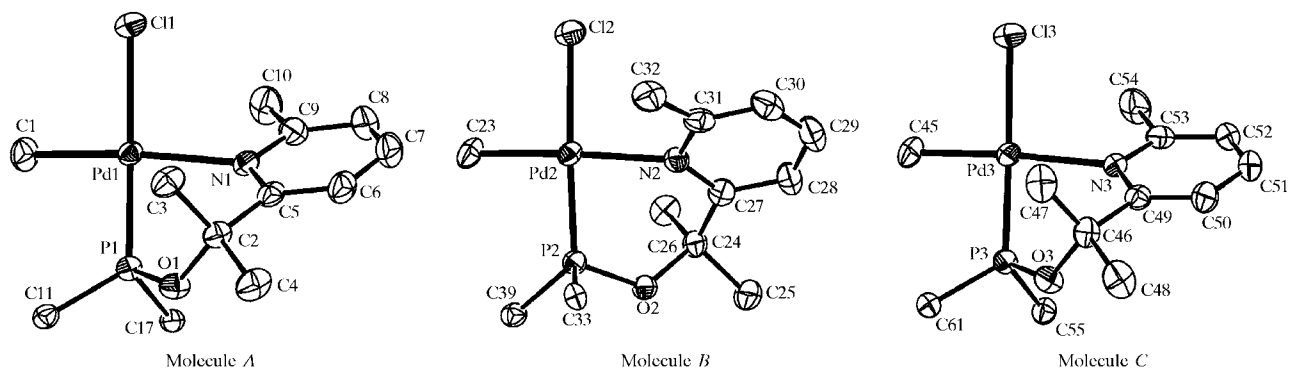
Ligands containing at least two chemically different donor functions and able to chelate a metal center are of considerable interest since they provide a way to influence selectively the bonding and/or reactivity of the other ligands, in particular those in *trans* positions (Braunstein & Naud, 2001). This concept has been successfully applied to ligands containing a *P,O*- or a *P,N*-donor set (Braunstein & Naud, 2001; Slone *et al.*, 1999).

Phosphinito- and phosphinopyridine ligands find widespread applications in the coordination chemistry of transition metals (Newkome, 1993, and references therein; Chen *et al.*, 2003a) and in homogeneous catalysis (Agbossou *et al.*, 1998, and references therein; Espinet & Soulantica, 1999, and references therein; Bianchini & Meli, 2002, and references therein; Chen *et al.*, 2003b; Braunstein, 2004, and references

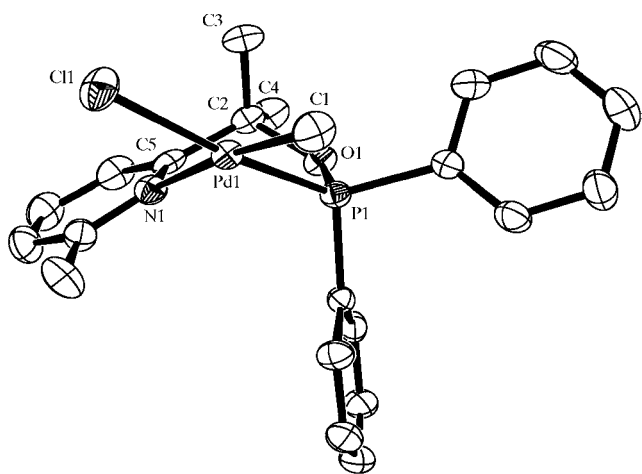
therein; Speiser *et al.*, 2004, 2004a,b). We have recently reported the synthesis of the ligands [1-methyl-1-(6-methyl-2-pyridyl)ethoxy]diphenylphosphine, (I) (Speiser *et al.*, 2004), and 2-(2,6-dimethylphenyl)-6-(diphenylphosphinomethyl)pyridine, (II) (Speiser *et al.*, 2004a), and investigated the catalytic properties of their $[\text{NiCl}_2(\text{P,N})]$ complexes (*P,N* = *P,N*-chelating ligand) for ethylene oligomerization. Owing to the paramagnetism of these Ni^{II} compounds, it was felt desirable to prepare analogous Pd^{II} complexes amenable to NMR studies in solution. For comparison, we have selected complexes of the type $[\text{PdCl}_2(\text{P,N})]$, for which the Pd–Cl distances should provide direct evidence of the respective *trans* influences of the *P*- and *N*-donor functions, and of the type $[\text{PdCl}(\text{CH}_3)(\text{P,N})]$, since the stoichiometric or catalytic insertion of small molecules (such as CO or olefins) into the Pd– CH_3 σ bond is very much influenced by the nature of the donor group situated in the *trans* position. The new Pd complexes (III)–(V) have been synthesized, and their structural features are analyzed and, in the case of (III), compared with the Ni analog (Speiser *et al.*, 2004).



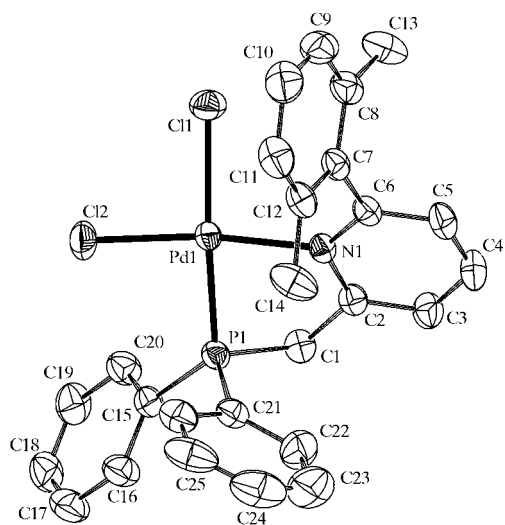
Despite the relevance of Pd complexes featuring these types of *P,N*-donor ligands in the catalytic alternating copolymerization of olefins and CO, as well as in other C–C coupling reactions, (III) is the first six-membered chloro-methyl-phosphinite *P,N*-type palladium(II) complex to be structurally characterized. Other groups have reported six-membered chloro-methyl-Pd complexes with iminophosphine (van den Beuken *et al.*, 1998; Song *et al.*, 2002; Reddy *et al.*, 2002; Spek, 2003) and 1-(dimethylamino)-8-(diphenylphosphino)naphthalene ligands (Dekker *et al.*, 1992). Recently, Chen *et al.* (2003b) reported the first structurally characterized five-membered chloro-methyl-phosphinopyridine-based Pd^{II} complex. Other five-membered chloro-methyl complexes


Figure 1

The *P,N*-chelate conformations of molecules *A–C* in (III), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. H atoms and CH groups of phenyl rings have been omitted for clarity.


Figure 2

A view of the roof-like conformation formed by the ligand folding along the Pd1...C2 hinge in the structure of molecule *A* of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.


Figure 3

A view of (IV), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

containing 2-(2-pyridyl)phosphaalkenes (van der Sluis *et al.*, 1997), 2-(2-pyridyl)phospholes (Sauthier *et al.*, 2002), imino-phosphines (Coleman *et al.*, 2001; Reddy *et al.*, 2001, 2002; Doherty *et al.*, 2002; Daugulis & Brookhart, 2002) and phosphinoxazoline (Apfelbacher *et al.*, 2003) *P,N*-donor ligands have also been reported.

The structure of (III) shows that the asymmetric unit contains three very similar but crystallographically different molecules (*A–C*), together with a chloroform solvent molecule. Although the geometric data are as expected for the three molecules (Table 1), examination reveals (Fig. 1) that the *P,N*-chelate in molecules *A* and *C* has approximately the same conformation, whereas in *B* the pyridine ring has a different orientation with respect to the Pd–N axis. This is confirmed by the torsion-angle values, which are similar for *A* and *C* [Cl1–Pd1–N1–C9 = $-55.9(3)^\circ$ and Cl3–Pd3–N3–C53 = $-61.6(3)^\circ$, respectively], whereas for *B* the Cl2–Pd2–N2–C31 angle is $51.3(3)^\circ$. The symmetry-equivalent asymmetric units contain enantiomers of molecules *A*, *B* and *C* with opposite torsion angles.

Analysis of molecule *A* shows a folding of the ligand along the Pd1...C2 hinge, creating a roof-like conformation, which generates a niche limited by a phenyl group (Fig. 2). This conformation is similar to the [NiCl₂(*P,N*)] analog (Speiser *et al.*, 2004) for which the Ni coordination geometry was slightly distorted square planar. The Pd atom is almost in the mean plane passing through atoms Cl1, C1, N1 and P1 [the deviation of the Pd atom is 0.0390(3) Å], and the sum of the bond angles around the Pd atom is 360.56°. Although the distance from the metal atom to the corresponding plane in the analogous Ni complex [0.03(1) Å] is similar to that for Pd, the sum of the bond angles around the Ni center is larger (365.22°), indicating a slight distortion toward tetrahedral for the Ni coordination (Speiser *et al.*, 2004). Molecules *B* and *C* are almost identical to *A* and therefore will not be discussed further.

In the ligands of complexes (IV) (Fig. 3) and (V) (Fig. 4), the geometric data (Tables 2 and 3) are similar and in the expected ranges; the only marked difference between these two structures concerns the Pd–N distance, which is larger in (V) [2.286(3) Å] than in (IV) [2.098(2) Å]. The aromatic

substituent at the 6-position is oriented nearly perpendicular to the pyridine ring, as evidenced by the N1—C6—C7—C12 torsion angles [70.3 (3)° for (IV) and 78.9 (4)° for (V)].

In (IV), the Pd—Cl bond distance *trans* to the P atom is longer than that *trans* to the N atom, which is consistent with the respective *trans* influences of the *P*- and *N*-donor atoms (Hartley, 1973). The methyl group in (III) and (V) is *cis* to the P atom, which is in agreement with the fact that the donor groups with the largest *trans* influence avoid being mutually *trans* to one another. This is consistent with complexes of the type [Pd(CH₃)Cl(*P,N*)] (Apfelbacher *et al.*, 2003; Chen *et al.*, 2003*b*; Coleman *et al.*, 2001; Daugulis & Brookhart, 2002).

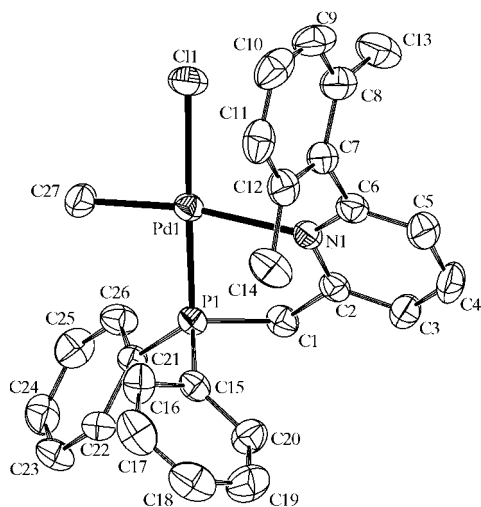


Figure 4

A view of (V), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

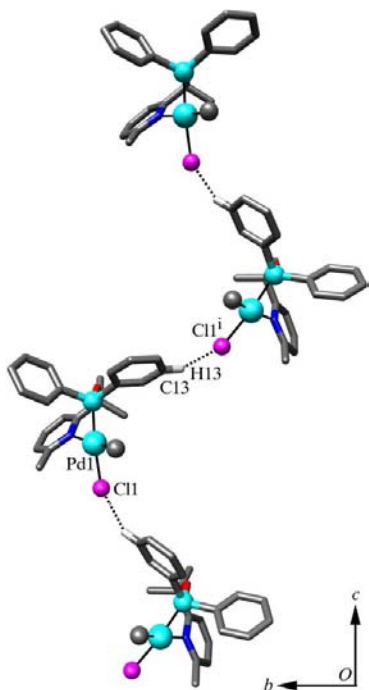


Figure 5

Part of the crystal structure of (III), showing the C—H...Cl interactions (viewed down the *a* axis). (The symmetry code is as in Table 4.)

The *P,N*-chelate bite angle [81.74 (5)° for (IV) and 78.92 (8)° for (V)] is in accordance with that of other five-membered *P,N*-chelates [82.5 (2)°; Perera *et al.*, 1995]. As

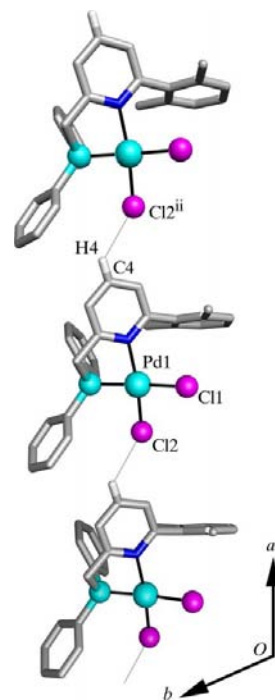


Figure 6

Part of the crystal structure of (IV), showing the C—H...Cl interactions (viewed down the *c* axis). (The symmetry code is as in Table 4.)

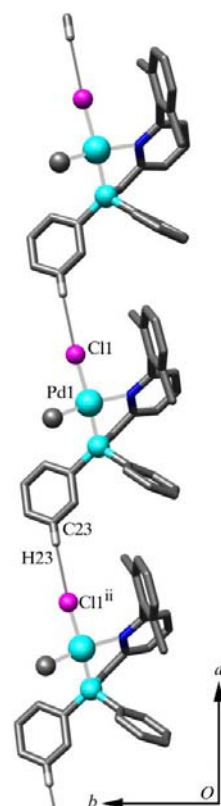


Figure 7

Part of the crystal structure of (V), showing the C—H...Cl interaction (viewed down the *c* axis). (The symmetry code is as in Table 4.)

expected, on increasing in size from this five-membered chelate ring to a six-membered ring as in (III), the chelate bite angle increases by 4–5° [84.03 (8)° for molecule *A* in (III)].

Although no classical intermolecular hydrogen bonds were detected in (III)–(V), significant non-conventional C–H···Cl hydrogen bonds are present and these constitute structure-directing elements. Compound (III) has an interaction involving the Cl atom on the Pd metal center of molecule *A* and a phenyl H atom of a neighboring *A* molecule (C13–H13···Cl1ⁱ; all symmetry codes as in Table 4; Fig. 5). Another interaction of this type is observed between the H atom of the chloroform solvent molecule and the Cl atom from the palladium metal center of molecule *B* (C67–H67···Cl2ⁱⁱ). Furthermore, molecules *A* and *C* have an intramolecular interaction between a phenyl H atom and the O atom adjacent to the P atom (C22–H22···O1 and C66–H66···O3), and finally in molecule *B* an interaction involves the H atoms of the pyridine methyl group and the Pd-bound Cl atom (C32–H32···Cl2). In (IV), an interaction exists between a Pd-bound Cl atom and a pyridine H atom (C4–H4···Cl2ⁱⁱ) (Fig. 6). A similar interaction occurs in (V) involving a phenyl H atom

(C23–H23···Cl1ⁱⁱ; Fig. 7). In both cases, these interactions result in infinite one-dimensional chains of molecules along (100).

From a packing viewpoint, the crystal structure of (III) can be described in term of pseudo-slabs stacked along (001). These slabs, interconnected by van der Waals contacts, are constituted by a succession of *A*, *B* and *C* moieties, as defined above (Fig. 1), with chloroform solvent molecules located between these slabs (Fig. 8). For (IV) and (V) (Fig. 9), the *bc* and *ac* projections show that the molecular moieties are placed along pseudo-slabs, with these slabs connected *via* van der Waals contacts, but specifically through the organic part of the corresponding molecules.

Experimental

All solvents were dried and distilled under N₂ using common techniques unless otherwise stated. [Pd(CH₃)Cl(COD)] and [PdCl₂(COD)] (COD is 1,5-cyclooctadiene, C₈H₁₂) were prepared according to literature methods (Rulke *et al.*, 1993; Ladipo & Anderson, 1994; Chatt *et al.*, 1957), as were ligands (I) and (II) (Speiser *et al.*, 2004, 2004a). Compound (III) was synthesized by the addition of solid [Pd(CH₃)Cl(COD)] (0.391 g, 1.475 mmol) to a solution of (I) (0.545 g, 1.623 mmol) in CH₂Cl₂ (20 ml); the resulting yellow mixture was stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and the white residue was washed with diethyl ether (2 × 10 ml) and pentane (1 × 10 ml). The product was dried under vacuum overnight, and (III) was obtained as a white solid. Crystals of (III) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CHCl₃ solution of (III) (yield 0.442 g, 0.897 mmol, 61%). Compound (IV) was obtained using a procedure similar to that described for (III), using (II) (0.615 g, 1.612 mmol) and [PdCl₂(COD)] (0.460 g, 1.612 mmol), and was obtained as a yellow–white solid. Crystals of (IV) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of (IV) (yield 0.595 g, 1.064 mmol, 66%). Compound (V) was obtained using a procedure similar to that described above for the preparation of (III), using (II) (0.588 g, 1.541 mmol) and [Pd(CH₃)Cl(COD)] (0.408 g, 1.541 mmol), and was obtained as a yellow–white solid. Crystals of (V) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of this complex (yield 0.463 g, 0.859 mmol, 56%).

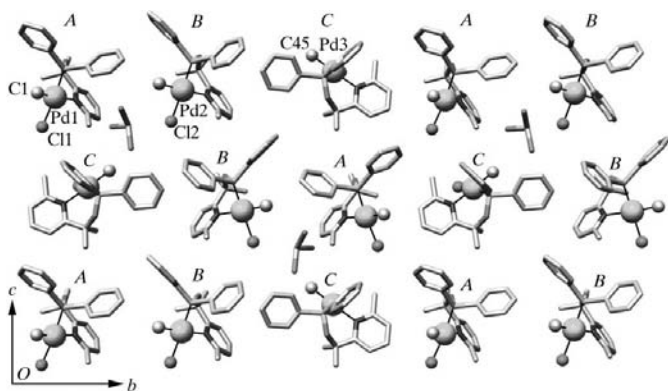


Figure 8
A view of the packing for complex (III) (viewed down the *a* axis).

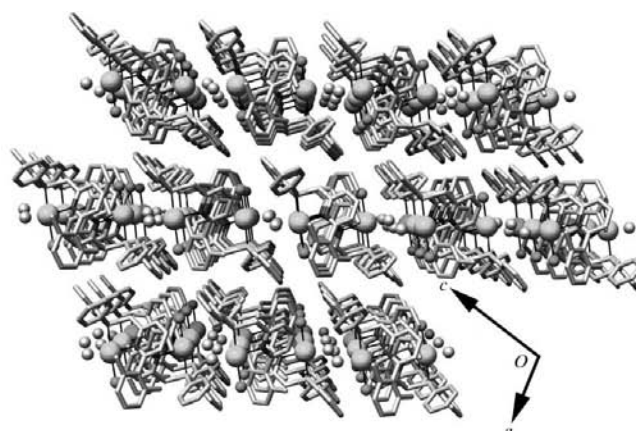
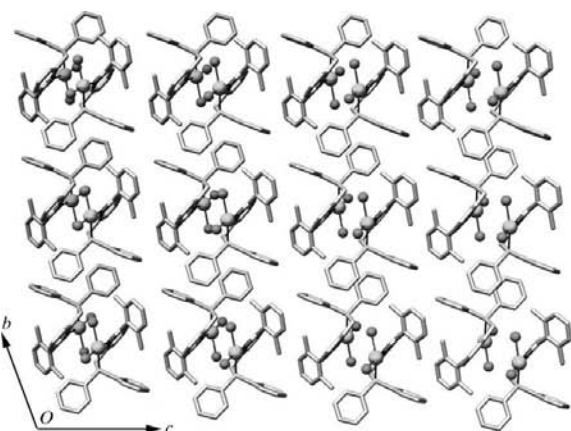


Figure 9
A view of the packing for complexes (IV) (left; viewed down the *a* axis) and (V) (right; viewed down the *b* axis).

Compound (III)

Crystal data

3[Pd(CH₃)Cl(C₂₁H₂₂NOP)]·CHCl₃
M_r = 1596.12
 Monoclinic, *P*₂₁/*c*
a = 14.628 (1) Å
b = 28.573 (5) Å
c = 17.324 (2) Å
 β = 106.39 (5)°
V = 6947 (2) Å³
Z = 4

D_x = 1.526 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 53191 reflections
 θ = 1.0–30.0°
 μ = 1.11 mm⁻¹
T = 173 (2) K
 Prism, yellow
 0.13 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 58356 measured reflections
 20304 independent reflections
 13997 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.067
 θ_{max} = 30.0°
h = -20 → 20
k = -40 → 37
l = -20 → 24

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.059
wR(*F*²) = 0.123
S = 1.09
 20304 reflections
 766 parameters

H-atom parameters constrained
w = 1/[σ²(*F*_o²) + (0.05*P*)²]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.69 e Å⁻³
 Δρ_{min} = -0.88 e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (III).

Pd1—Cl1	2.3838 (10)	Pd3—Cl3	2.3929 (12)
Pd1—P1	2.1650 (9)	Pd3—P3	2.1725 (13)
Pd1—N1	2.205 (3)	Pd3—N3	2.200 (3)
Pd1—C1	2.038 (4)	Pd3—C45	2.034 (4)
Pd2—Cl2	2.4047 (10)	P1—O1	1.611 (2)
Pd2—P2	2.1717 (10)	P2—O2	1.608 (2)
Pd2—N2	2.193 (3)	P3—O3	1.617 (2)
Pd2—C23	2.050 (4)		
C1—Pd1—P1	91.45 (12)	C23—Pd2—Cl2	88.48 (12)
C1—Pd1—N1	173.65 (14)	P2—Pd2—Cl2	175.46 (4)
P1—Pd1—N1	84.03 (8)	N2—Pd2—Cl2	94.50 (8)
C1—Pd1—Cl1	90.20 (12)	C45—Pd3—P3	91.45 (12)
P1—Pd1—Cl1	172.09 (4)	C45—Pd3—N3	174.34 (14)
N1—Pd1—Cl1	94.87 (8)	P3—Pd3—N3	84.71 (8)
C23—Pd2—P2	93.23 (12)	C45—Pd3—Cl3	90.38 (12)
C23—Pd2—N2	176.97 (13)	P3—Pd3—Cl3	168.49 (4)
P2—Pd2—N2	83.76 (8)	N3—Pd3—Cl3	94.21 (9)

Compound (IV)

Crystal data

[PdCl₂(C₂₆H₂₄NP)]
M_r = 558.73
 Triclinic, *P*₁
a = 10.151 (1) Å
b = 11.461 (1) Å
c = 12.106 (2) Å
 α = 95.40 (5)°
 β = 109.93 (5)°
 γ = 112.23 (5)°
V = 1184.7 (9) Å³

Z = 2
D_x = 1.566 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7840 reflections
 θ = 1.0–27.9°
 μ = 1.09 mm⁻¹
T = 173 (2) K
 Prism, yellow–orange
 0.13 × 0.10 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 14956 measured reflections
 5587 independent reflections
 4878 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.033
 θ_{max} = 27.8°
h = -13 → 13
k = -14 → 15
l = -15 → 15

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.078
S = 1.00
 5587 reflections
 280 parameters
 H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0331*P*)² + 0.3488*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.49 e Å⁻³
 Δρ_{min} = -0.80 e Å⁻³

Table 2

Selected geometric parameters (Å, °) for (IV).

Pd1—Cl1	2.3747 (12)	P1—C1	1.826 (3)
Pd1—Cl2	2.2749 (13)	N1—C2	1.369 (3)
Pd1—P1	2.2093 (11)	C1—C2	1.506 (3)
Pd1—N1	2.098 (2)		
N1—Pd1—P1	81.74 (5)	N1—Pd1—Cl1	96.05 (5)
N1—Pd1—Cl2	171.99 (5)	P1—Pd1—Cl1	167.92 (2)
P1—Pd1—Cl2	90.52 (3)	Cl2—Pd1—Cl1	91.95 (3)

Compound V

Crystal data

[Pd(CH₃)Cl(C₂₆H₂₄NP)]
M_r = 538.32
 Monoclinic, *P*₂₁/*n*
a = 11.507 (1) Å
b = 12.011 (2) Å
c = 17.490 (2) Å
 β = 99.92 (5)°
V = 2381.2 (6) Å³
Z = 4
D_x = 1.502 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 23164 reflections
 θ = 1.0–30.0°
 μ = 0.97 mm⁻¹
T = 173 (2) K
 Prism, yellow
 0.10 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 6838 measured reflections
 6837 independent reflections
 4250 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.045
 θ_{max} = 30.0°
h = -16 → 15
k = 0 → 16
l = 0 → 24

Table 3

Selected geometric parameters (Å, °) for V.

Pd1—Cl1	2.3681 (14)	P1—C1	1.823 (4)
Pd1—P1	2.189 (2)	N1—C2	1.356 (4)
Pd1—N1	2.286 (3)	C1—C2	1.510 (5)
Pd1—C27	2.042 (4)		
C27—Pd1—P1	91.64 (11)	C27—Pd1—Cl1	88.40 (11)
C27—Pd1—N1	170.52 (11)	P1—Pd1—Cl1	173.30 (4)
P1—Pd1—N1	78.92 (8)	N1—Pd1—Cl1	101.07 (8)

Table 4

Hydrogen-bond parameters (Å, °) for compounds (III)–(V).

Compound	<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
(III)	C13—H13...Cl1 ⁱ	0.95	2.74	3.630 (4)	156
	C22—H22...O1	0.95	2.56	2.975 (5)	107
	C32—H32...Cl2	0.98	2.68	3.449 (4)	136
	C66—H66...O3	0.95	2.53	2.909 (5)	104
	C67—H67...Cl2 ⁱⁱ	1.00	2.56	3.523 (4)	161
(IV)	C4—H4...Cl2 ⁱⁱ	0.95	2.73	3.410 (4)	130
(V)	C23—H23...Cl1 ⁱⁱ	0.95	2.83	3.750 (4)	164

Symmetry codes: (i) *x*, -*y* + 1/2, *z* - 1/2; (ii) *x* + 1, *y*, *z*.

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.055$$

$$wR(F^2) = 0.112$$

$$S = 0.91$$

6837 reflections

280 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2)]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.72 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.63 \text{ e } \text{Å}^{-3}$$

The rotational orientations of the methyl groups were refined using the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All H atoms were treated as riding, with C–H distances ranging from 0.95 to 1.00 Å and $U_{\text{iso}}(\text{H})$ values equal to 1.5 (methyl H atoms) or 1.2 (all other H atoms) times $U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1299). Services for accessing these data are described at the back of the journal.

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