Novel (Methyl)- and (Acetyl)palladium Complexes Containing Bis(pyrazolyl)borate Ligands – Dynamic Equilibrium between η^2 and η^1 Forms for the Complex Bp*(Me)(PCy_3)Pd [Bp* = dihydridobis(3,5-dimethylpyrazolyl)borate]

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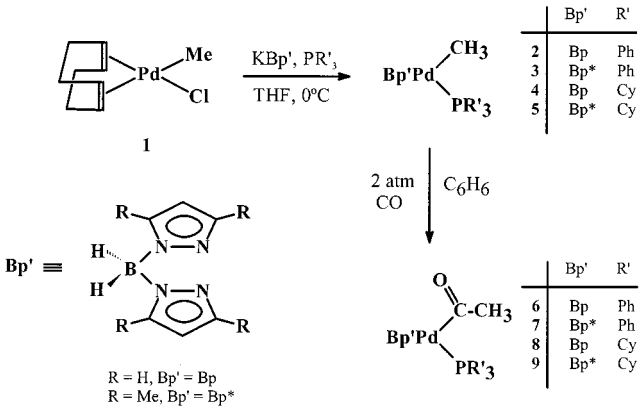
A series of (methyl)palladium complexes of general formula Bp′Pd(CH_3)(L) [Bp′ = Bp = dihydridobis(pyrazolyl)borate; Bp′ = Bp* = dihydridobis(3,5-dimethylpyrazolyl)borate, L = phosphane] has been synthesised. The interaction of these alkyl complexes with carbon monoxide produces the acetyl derivatives Bp′Pd(C(O)Me)(L), one of the members of this series, BpPd[C(O)Me](PPh_3), being structurally characterised by X-ray diffraction studies.

Introduction

After Brookhart's discovery of (diimine)nickel and -palladium complexes as highly efficient catalysts for olefin polymerisation,[1] the synthesis of new alkyl complexes of group-10 metals has emerged. The number of such complexes reported in the recent literature is considerable, but the catalytic capabilities towards polymerisation seem to be restricted to cationic compounds containing few, selected nitrogen-based ligands such as the above-mentioned diimine ligand.[1–3] Recently, Grubbs and co-workers have reported several neutral (aryl)(salicylaldimininato)nickel(II) complexes which act as good olefin polymerisation catalysts.[4] On the other hand, although there exist an important number of palladium complexes containing poly(pyrazolyl)borate ligands,[5] few examples of simple (alkyl)palladium(II) species have been reported.[6] The synthesis of (methyl)palladium complexes containing tris- and tetrakis-(pyrazolyl)borate has been described,[5] but, to our knowledge, there is no report on the synthesis of the analogous bis(pyrazolyl)borate derivatives. With the aim of preparing new Pd complexes bearing nitrogen donor ligands as possible olefin polymerisation catalysts, in this contribution we describe the synthesis, characterisation and chemical behaviour of several complexes of general formula Bp′Pd(Me)(PR'_3) as well as their corresponding acyl derivatives (Scheme 1).



Scheme 1

Results and Discussion

Synthesis of the Alkyl Complexes

When 1 equivalent of the KBp′ (Bp′ = Bp or Bp*) salt is added to cold (0 °C) THF solutions of Pd(Me)Cl(cod) (**1**) and PR'_3 (R′= Ph, Cy), a ligand exchange reaction takes place as shown in Scheme 1. After work up, white microcrystalline compounds **2–5** (see Table 1) are isolated in good yields. Some of these complexes are not very stable in solution at room temperature, so temperature control becomes crucial during their synthesis reactions as well as during the work up of their crystallisation solutions.

The NMR data of **2–4** are in accordance with a square-planar environment around the palladium atom, assuming that both pyrazolyl rings are bound to the metal centre. The resonances in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra are well

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Table 1. Microanalyses and IR data for compounds **2–9**

Complex	Microanalyses [found (calcd.)] C	H	N	IR (nujol) [cm^{-1}] ν(B–H)	ν(C–N)	ν(CO)
BpPd (CH_3)(PPh_3) (**2**)	55.8 (56.6)	5.0 (4.9)	9.7 (10.6)	2250–2450	1530	
BpPd (CH_3)(PCy_3) (**3**)	54.1 (54.7)	7.4 (8.1)	9.9 (10.2)	2290–2480	1510	
Bp*Pd (CH_3)(PPh_3) (**4**)	59.1 (59.4)	5.6 (5.8)	9.0 (9.5)	2250–2490	1550	
Bp*Pd (CH_3)(PCy_3) (**5**)	58.2 (57.6)	9.0 (8.7)	10.0 (9.3)	2295–2480	1534	
BpPd ($COCH_3$)(PPh_3) (**6**)	56.0 (55.9)	5.0 (4.7)	10.0 (10.0)	2200–2428	1510	1681
BpPd ($COCH_3$)(PCy_3) (**7**)	54.1 (54.1)	7.4 (7.6)	9.8 (9.7)	2295–2429	1495	1683
Bp*Pd ($COCH_3$)(PPh_3) (**8**)	58.6 (58.6)	5.7 (5.5)	8.9 (9.1)	2200–2448	1537	1679
Bp*Pd ($COCH_3$)(PCy_3) (**9**)	56.6 (56.9)	8.0 (8.2)	8.7 (8.8)	2443–2200	1538	1677

Table 2. ^{1}H- and ^{31}P-NMR data for compounds **2–5**

Compound	^{1}H (values of *J* in Hz) PdCH_3[a]	Bp′[b] C*H*(pz)	Me(pz)	P*R*$_3$	^{31}P{^{1}H}
BpPd (CH_3)(PPh_3) (**2**)[c]	0.84 (d) (2.4)	7.68 (d) (2) 6.28 (d) (2) 6.01 t (2) 5.66 t (2)		7.60 (m) (6 H) 6.94 (m) (9 H)	39.2 (s)
BpPd (CH_3)(PCy_3) (**3**)[c]	0.81 (d) (2.5)	5.99 (m) 7.39 (d) (2) 7.56 (d) (2) 7.63 (m) 7.68 (d) (2)		2.2–0.7 (m) (33 H)	37.5 (s)
Bp*Pd (CH_3)(PPh_3) (**4**)[c]	0.78 (d) (4.3)	5.66 (s) 5.45 (s)	2.39 2.38 2.26 1.53	7.65 (m) (6 H) 6.95 (m) (9 H)	37.1 (s)
Bp*Pd (CH_3)(PCy_3) (**5**)[d]	0.79 (d) (3.1)	5.66 (br s)	2.11 2.32	2.2–0.8 (m) (33 H)	33.9 (s)

[a] *J*(HP) in parentheses. – [b] *J*(HH) in parentheses. – [c] In C_6D_6. – [d] In CD_2Cl_2.

Table 3. ^{13}C{^{1}H}-NMR data for compounds **2–5**

Compound[a]	PdCH_3	^{13}C{^{1}H}[b] Bp′ C(pz)	CH_3(pz)	P*R*$_3$
BpPd (CH_3)(PPh_3) (**2**)	–2.43 (6)	139.9 (s) 138.3 (s) 135.4 (s) 135.0 (s) 104.5 (br s) 103.9 (s)		134.7 (d) (12) 131.3 (d) (49) 129.9 (d) (2) 128.0 (d) (11)
BpPd (CH_3)(PCy_3) (**3**)	–4.6 (d) (7)	139.9 (s) 137.6 (d) (2) 135.2 (s) 134.0 (d) (2.5) 104.2 (d) (2.5) 104.1 (s)		33.6–26.4 (m)
Bp*Pd (CH_3)(PPh_3) (**4**)	–2.6 (d) (8)	105.2 (s) 104.5 (d) (3) 147.0 (d) (2.6) 146.7 (s) 144.4 (s) 143.4 (d) (2.9)	13.9 (s) 13.3 (s) 12.8 (s) 12.7 (s)	134.5 (d) (12) 132.2 (d) (49) 129.9 (d) (2.3) 128.1 (d) (11)
Bp*Pd (CH_3)(PCy_3) (**5**)	–9.86 (d) (8)	104.8 (s) 146.0 (br s) 143.1 (br s)	12.8 (s) 12.6 (s) 11.8 (br s)	35–26 (m)

[a] In C_6D_6. – [b] *J*(CP), in Hz, in parentheses.

defined (see Table 2 and Table 3). For instance, the proton signals of the Pd–CH_3 groups in the ^{13}C{^{1}H}-NMR spectra range from δ = –9.9 to δ = –2.4, each resonance splitting into a sharp doublet. The values of J_{CP} coupling constants are small (J_{CP} = 6–8 Hz), in agreement with a mutually *cis* distribution of the alkyl and phosphane ligands. The pyrazolyl rings are inequivalent since two sets of signals are observed in the ^{1}H- and ^{13}C{^{13}H}-NMR spectra. In contrast,

the ^{1}H-NMR spectrum of **5** at room temperature consists of one broad resonance for the C*H* protons (δ = 5.66) and two broad singlets for the methyl protons of the two pyrazolyl rings (δ = 2.1 and 2.3, respectively). At low temperature, –30 °C, the low-field resonance splits into two peaks centred at δ = 5.67 and 5.65, corresponding to two inequivalent C*H* protons (see Figure 1 for the VT experiment).

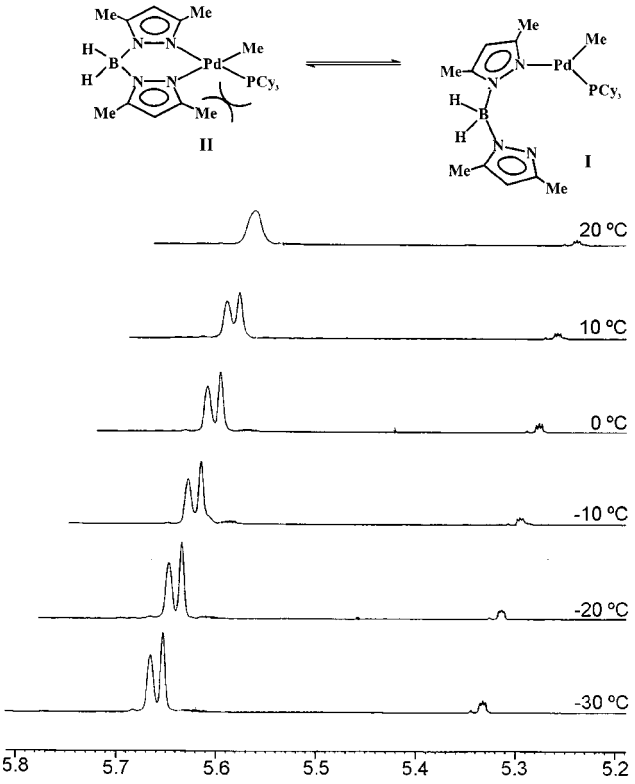

Figure 1. Variable-temperature ^{1}H-NMR spectra (CD_2Cl_2, 400 MHz) of **5** and proposed mechanism for the observed fluxionality

A phosphane exchange process cannot be responsible of the observed fluxionality, based of the following: (i) when PCy_3 is added to a solution of complex **5** in CD_2Cl_2 at room temperature, no change is observed for the resonances observed in the ^{1}H-NMR spectrum of **5**; (ii) the J_{HP} coupling constant for the methyl group remains unchanged through studied the temperature range, clearly confirming the strength of the Pd–P bond.

A possible alternative explanation for the fluxional process would invoke dissociation and re-association of one pyrazolyl ring to the Pd centre. This would be the result of steric repulsions between the methyl groups and the bulky PCy_3. Subsequently, an equilibrium between the η^2-Bp* species and an η^1-Bp* species might occur (Figure 1). Furthermore, the absence of any band in the 2100–1900 cm^{-1} range in the IR spectrum of **5** (see Table 1) indicates that no agostic interactions exist between the palladium centre and any of the B–H bonds,[7,8] making the species **I** the more reasonable proposition. An example of a process similar to the one represented in Figure 1 has been recently reported for the Rh^I complex [Rh(CO)($PMePh_2$)$_2$-($Tp^{Me2,4-Cl}$)] containing a bulky η^2-Tp ligand.[9] Etienne et al. concluded that steric effects were undoubtedly responsible of the observed structure. In addition, Ni^{II} complexes containing bulky poly(pyrazolyl)borate ligands coordinated in an η^1- fashion [e. g., Tp*t*BuNi(C_6H_5)(PMe_3)$_2$] have been described.[10,11] In the case of **5**, the existence of a 14-electron species, similar to that of structure **I**, has been proposed an intermediate in insertion-type reactions.[12] More information can be extracted from the NMR study shown in Figure 1. The calculated value of $\Delta G^{\neq}$ [13] of ca. 59.1 kJ mol^{-1} compares well with those values reported by Espinet and co-workers,[14] 45–60 kJ mol^{-1}, for exchange of pyridine groups in palladium complexes containing $P(CH_2CH_2Py)_nPh_{3-n}$ ligands.

Reaction of 2–5 with Olefin and/or CO

Our main interest in the study of these complexes was their possible application as catalysts in olefin polymerisation and/or CO/olefin copolymerisation processes. Previously, there had been examples described of the use of cationic (methyl)palladium(II) complexes for the polymerisation of ethylene and α-olefins.[1] Unfortunately, in our case, attempts to polymerise ethylene with the neutral complexes **2–5** yielded no polyethylene, even under ethylene pressure (2 atm) and the presence of phosphane scavengers like $B(C_6F_5)_3$.[15]

On the other hand, since Sen's report of palladium(II) catalysts for the CO–olefin copolymerisation reaction,[16,17] and later, Drent and co-workers' report of the perfectly alternating copolymerisation of such substrates,[18,19] the synthesis and study of new (alkyl)palladium compounds containing P–P or N–N ligands have been developed.[20,21,22] We have also tested our Bp′Pd(Me)(L) complexes as catalysts in such processes, but again, no polymer formation was observed and only the CO insertion products, Bp′Pd(COMe)(PR'_3) (**6–9**) were obtained (Scheme 1), even under CO and olefin pressure or heating conditions. These acyl derivatives **6–9** can be prepared by exposure of a solution of the corresponding alkyl complex under CO pressure (2 atm).

Spectroscopic data of the complexes **6–9** have unambiguously revealed the presence of the acyl function. Thus, the intense absorbances observed at ca. 1680 cm^{-1} in their IR spectra are attributed to ν(COR) (Table 1). In addition, in the $^{13}C\{^1H\}$-NMR spectra, the quaternary carbon atoms of the acyl moiety resonate as doublets within the range δ = 231.1–234.6 (see Table 4). Both pyrazolyl rings are inequivalent as inferred from the well-defined resonances observed in the $^{13}C\{^1H\}$-NMR spectra (see Table 5). In contrast to the observations for the other acyl derivatives, and in agreement with its alkyl precursor, complex **9**, Bp* Pd(COMe)(PCy_3) appears to also be fluxional.

A single-crystal X-ray diffraction study has been carried out on the compound BpPd(COMe)(PPh_3) (**6**). An ORTEP[22] perspective view of the molecule is depicted in Figure 2. Selected bond lengths and angles are shown in Table 6. Compound **6** has a similar geometry around the

Table 4. ^{1}H- and ^{31}P{^{1}H}-NMR data for compounds **6–9**

Compound[a]	^{1}H[b] PdCOC*H*$_3$	Bp′ C*H* (pz)	Me (pz)	P*R*$_3$	^{31}P{^{1}H}
BpPd ($COCH_3$)(PPh_3) (**6**)	1.98 (s)	7.71 (d) (2) 7.51 (d) (2) 7.42 (d) (2) 7.38 (d) (2) 6.18 (t) (2) 5.72 (t) (2)		7.74 (m) 7.50 (m) 7.45 (m)	26.7 (s)
BpPd ($COCH_3$)(PCy_3) (**7**)	2.28 (s)	7.54 (br s) 7.28 (br s) 6.11 (br s)		1.16–2.0 (m)	30.7 (s)
Bp*Pd ($COCH_3$)(PPh_3) (**8**)	2.20 (s)	5.73 (s) 5.35 (s)	2.35 (br s) 1.75 (s) 1.31 (s)	7.72 (m) 7.49 (m) 7.43 (m)	24.7 s
Bp*Pd ($COCH_3$)(PCy_3) (**9**)	2.29 (s)	5.64 (br s)	2.34 (br s) 2.21 (br s)	1.0–2.2 (m)	27.5 (s)

[a] In C_6D_6. – [b] *J*(HH), in Hz, in parentheses.

Table 5. ^{13}C{^{1}H}-NMR data for compounds **6–9**

Compound[a]	^{13}C{^{1}H} Pd–CO*C*H$_3$[b]	Bp′ *C* (pz)	Me (pz)	*C*O	P*R*$_3$[b]
BpPd ($COCH_3$)(PPh_3) (**6**)	37.9 d (20)	140.8 (s) 140.0 (s) 135.6 (s) 135.5 (s) 104.7 (s) 104.3 (s)		234.2 (s)	134.8 (d) (12) 131.4 (d) (2) 130.7 (s) 128.9 (d) (11)
BpPd ($COCH_3$)(PCy_3) (**7**)	39.1 (d) (14)	140.7 (s) 139.5 (s) 135.9 (s) 134.9 (s) 104.5 (s) 104.4 (s)		234.6 (s)	26.7 (s) 27.9 (d) (10) 30.1 (s) 34.9 (d) (21)
Bp*Pd ($COCH_3$)(PPh_3) (**8**)	37.2 (d) (16)	148.3 (s) 148.1 (s) 144.5 (s) 144.2 (s) 105.1 (s) 104.7 (s)	13.8 (s) 13.5 (s) 12.9 (s) 12.7 (s)	233.5 (s)	134.9 (d) (12) 130.9 (d) (2) 130.5 (s) 128.7 (d) (11)
Bp*Pd ($COCH_3$)(PCy_3) (**9**)	38.4 (d) (14)	146.9 (br s) 143.9 (br s) 104.9 (br s)	14.3 (br s) 12.6 (br s)	231.1 (s)	27.8 d (10) 29.9 d (20) 26.3 (s) 35.1 d (20)

[a] In C_6D_6. – [b] *J*(CP) in parentheses.

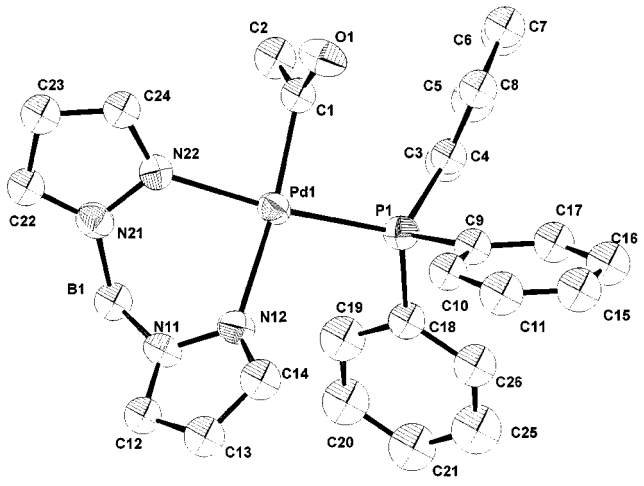

Figure 2. Molecular structure for **6**

Table 6. Selected bond lengths (Å) and angles (°) for compound **6**

Pd(1)–P(1)	2.278(3)	N(12)–Pd(1)–N(22)	87.5(3)
Pd(1)–N(12)	2.189(7)	N(12)–Pd(1)–C(1)	171.0(3)
Pd(1)–N(22)	2.107(7)	N(22)–Pd(1)–C(1)	86.1(3)
Pd(1)–C(1)	1.973(8)	P(1)–Pd(1)–N(12)	100.3(2)
		P(1)–Pd(1)–N(22)	169.4(2)
		P(1)–Pd(1)–C(1)	86.9(2)

metal centre as other palladium poly(pyrazolyl)borate complexes.[5] The molecule of **6** presents a distorted square-planar geometry in the solid state, with the values of the angles P(1)–Pd(1)–N(22) [169.4(2)°] and N(12)–Pd(1)–C(1) [171.0(3)°] slightly deviated from the ideal of 180°. The Pd–N(12) and Pd–N(22) distances [2.189(7) and 2.107(7) Å, respectively] are also in the range of those reported, for instance, in the related compound Bp*Pd(CH_2SiMe_3)(PMe_3)

[2.123(5) and 2.098(4) Å].[6] Finally, the palladium–carbon bond length found in compound **6** [1.973(8) Å] is within the range reported for the related (acyl)palladium bidentate nitrogen donor complexes [for example, 1.952(5) Å for (bpy)($MeOCC_7H_{10}COC_7H_{10}CO$)PdI[21]].

Experimental Section

All preparations were carried out using standard Schlenk techniques under nitrogen using freshly distilled and degassed solvents. Potassium bis(pyrazolyl)borates[23] and the complex (COD)-(CH_3)PdCl[24] were prepared according to literature procedures. PCy_3 and PPh_3 were purchased and used without further purification. – Infrared spectra were recorded with a Perkin–Elmer spectrophotometer, model 884. – ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker DRX400 spectrometer, chemical shifts being referred to TMS. – ^{31}P-NMR spectra were obtained with the same spectrometer using 85% aqueous H_3PO_4 as the standard. – Microanalyses were carried out by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain).

Synthesis of the Alkyl Derivatives Bp′(CH_3)(PR'_3)Pd [Bp′= Bp, R′ = Ph (2), Cy (3); Bp′= Bp*, R′ = Ph (4), Cy (5)]: (COD)-(CH_3)PdCl (0.5 mmol, 128 mg) was dissolved in THF (40 mL) and the corresponding phosphane ligand (0.5 mmol) was added. To the resulting solution, cooled at 0 °C, 1 equiv. of KBp′ was added and the mixture was stirred for 2 h. The solvent was removed under vacuum and the residue was extracted with THF/petroleum ether (1:1). Complexes Bp′(CH_3)(PR_3)Pd were isolated as microcrystalline white solids upon cooling of these solutions to –20 °C (75–90% yield).

Synthesis of the Acyl Derivatives (CH_3CO)Bp′(PR_3)Pd [Bp′= Bp, R′ = Ph (6), Cy (7); Bp′= Bp*, R′ = Ph (8), Cy (9)]: A typical preparation is the following: Synthesis of (MeCO)Bp*(PPh_3)Pd (**8**): Complex **4** (0.25 g, 0.43 mmol) was dissolved in dried THF (15 mL) and the resulting pale yellow solution was transferred to a pressure vessel which was charged with CO (2 atm). The reaction mixture was stirred for ca. 1 h affording a dark yellow solution. The solvent was pumped off and the crude residue investigated by NMR (C_6D_6), revealing that compound **8** was formed in almost quantitative yield. Crystallisation from petroleum ether/Et_2O (1:2) mixtures led to the isolation of complex **8** as pale yellow crystals of analytical purity (yield 75%).

Compounds **6**, **7**, **9** were obtained in a similar procedure in 65–70% yield after crystallisation. (MeCO)Bp(PPh_3)Pd (**6**) was crystallised from Et_2O/CH_2Cl_2 (1:1) mixtures; (MeCO)Bp(PCy_3)Pd (**7**) was crystallised from Et_2O solutions and (MeCO)Bp*(PCy_3)Pd (**7**) was purified by crystallisation from petroleum ether solutions.

Crystallography: A colourless crystal of $C_{26}H_{26}BN_4OPPd$ having approximate dimensions of 0.35 × 0.24 × 0.10 mm was mounted on a glass capillary and transferred to a Rigaku AFC6S diffractometer. Graphite-monochromated Mo-K_α radiation was used.

Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections. The system was determined to be orthorhombic, space group $P2_12_12_1$ (number 19, acentric). The data were collected using the ω/2θ scan method. The intensities of three standard reflections were measured after every 100 reflections to apply the decay correction. Lorentz-polarization and absorption correction (ψ-scan method) were also applied. A summary of experimental details is shown in Table 7.

Table 7. Summary of crystal data collection and structure analysis for complex **6**

Empirical formula	$C_{26}H_{26}BN_4OPPd$
Molecular mass	558.70
Crystal size [mm]	0.35 × 0.24 × 0.10
Colour, shape	colourless, plate
Cell measurements (25 refl.)	12.6 < 2θ < 15.5°
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (number 19)
Cell parameters	a = 13.849(6) Å
	b = 14.687(6) Å
	c = 12.202(5) Å
Volume	V = 2481(1) Å^3
Z	4
$\rho_{calcd.}$	1.495 g cm^{-3}
λ(Mo-K_α)	0.71069 A
μ(Mo-K_α)	8.26 cm^{-1}
F(000)	1136
Absorption correction	ψ-scan method
Transmision factors	0.715–1.000
Standards number, interval	3 refl., 100 refl.
Decay (%)	–1.00
Temperature	290(1) K
Scan method	ω/2θ
Scan Speed (ω)	4° min^{-1}
2θ interval	5° < 2θ < 50.1°
Measured reflections	2349
Unique reflections	2349
Observed reflections ($I > 3\sigma_I$)	1965
Number of parameters	172
Reflection/parameter ratio	11.42
Refinements	Full-matrix least squares on F
$R = (\|F_o\| - \|F_c\|)/\|F_o\|$	0.0434
R_w ($w = \sigma_F^2$) = $[(w(\|F_o\| - \|F_c\|)^2/wF_o^2)]^{1/2}$	0.0503
g.o.f.	1.727
Residuals peaks [e/Å^3]	+1.31, –0.53

The structure was solved by the Patterson method. The refinement was carried out on F by full-matrix least-squares methods. Pd, O and N atoms were anisotropically refined. The carbon atoms were isotropically refined, most of the hydrogen atoms (20) were included in difference Fourier and the remainder in idealised positions and were not refined. A set of 1965 observed reflections [$I > 3\ \sigma(I)$] and 172 variable parameters were used in the last cycles of refinements. The enantiomorph with slightly lower R, R_w and goodness of fit was selected. Final values of R = 0.0434 and R_w = 0.0503 were obtained. All calculations were carried out using the TEXSAN software package on a VAX 3520 computer at the "Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz". Crystallographic data have been deposited with the Cambridge Crystallographic Data Center: CCDC-135559. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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