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Steric effects of the 2-(diphenylphosphino)pyridine bridging ligand in the synthesis of binuclear palladium(II) complexes

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Abstract

Treatment of $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ (Ph_2PPy = 2-(diphenylphosphino)pyridine) with *cis*-$[Pd(^tBuNC)_2Cl_2]$ in dichloromethane affords the mixed isocyanide–tertiary phosphine complex *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$, in which the Ph_2PPy is a monodentate *P*-donor, and $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$. The steric effects of the Ph_2PPy bridging ligand in determining the reaction course is discussed. The complex *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ was crystallographically characterized: $P2_1/n$, $a = 15.143(2)$, $b = 9.527(1)$, $c = 17.517(4)$ Å, $\beta = 113.96(1)°$, $V = 2309.4(7)$ Å^3, $Z = 4$. The final R value was 0.044, $R_w = 0.046$ for the 3078 reflections with $I > 3\sigma(I)$.

1. Introduction

The reaction of a metal complex with coordinatively unsaturated species or with complexes containing labile ligands provides an easy route to binuclear complexes in which two metal atoms are surrounded by a binucleating ligand [1,2]. By this synthetic route we prepared new rhodium–rhodium, rhodium–palladium, rhodium–iridium and platinum–platinum binuclear complexes containing 2-(diphenylphosphine)pyridine (Ph_2PPy), a short-bite binucleating ligand [3–7]. However, the attempt to synthesize new heterobimetallic compounds was sometimes frustrated and only the transfer of the Ph_2PPy from one metal to another was achieved. For example, starting from the square-planar rhodium(I) complex $[Rh(COD)(Ph_2PPy)Cl]$ (COD = cyclooctadiene), in which the Ph_2PPy is a monodentate *P*-donor, we obtained the tetranuclear Rh^{II}–Pd^I complex $[\{(^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)\}_2]$ and the binuclear complex $[(COD)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}Cl)PdCl_2]$ (containing the Ph_2PPy *N*-bonded to the rhodium atom) from reactions with *cis*-$[Pd(^tBuNC)_2Cl_2]$ and with $[Pd(COD)Cl_2]$, respectively. However, the mononuclear complexes $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ and *cis*-$[Pd(DMSO)(Ph_2PPy)Cl_2]$ (DMSO = dimethylsulfoxide) together with $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$, have been obtained from the reactions of $[Rh(COD)(Ph_2PPy)Cl]$ with $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$ and *cis*-$[Pd(DMSO)_2Cl_2]$, respectively. The change in the bonding mode of the Ph_2PPy to Rh from P-bonded (as in $[Rh(COD)(Ph_2PPy)Cl]$) to *N*-bonded, as in $[\{(^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)\}_2]$ and $[(COD)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}Cl)PdCl_2]$, has been explained by the steric requirements of the Ph_2PPy when bridging.

In this paper we report on the effort to synthesize unsymmetrical palladium(II)–palladium(II) complexes containing the Ph_2PPy bridging ligand and the crystal and molecular structure of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$.

2. Results and discussion

2.1. *Reaction of* $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ *with cis*-$[Pd(^tBuNC)_2Cl_2]$

We have reported [6] the synthesis of the palladium(II) allyl complex $[Pd\{CH_2C(CH_3)CH_2\}$-

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$(Ph_2PPy)Cl]$ by reacting $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$ with Ph_2PPy; the same compound has been obtained, together with $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$, from the reaction of $[Rh(COD)(Ph_2PPy)Cl]$ with $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$. We have attempted the preparation of unsymmetrical homobinuclear palladium(II) complexes using a bridge-assisted reaction in which the uncoordinated dipyridine nitrogen atom of $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ displaces one CN^tBu from *cis*-$[Pd(^tBuNC)_2Cl_2]$. Unexpectedly, the products are *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ and $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$. Formally the reaction implies transfer of the Ph_2PPy from the palladium(II) allyl to the palladium(II) isocyanide and appears to be similar to that of *cis*-$[Pd(^tBuNC)_2Cl_2]$ with tertiary phosphines [8].

It is very likely that the reaction of $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ with *cis*-$[Pd(^tBuNC)_2Cl_2]$ occurs with initial liberation of CN^tBu and formation of the binuclear intermediate species $[\{CH_2C(CH_3)CH_2\}ClPd(\mu\text{-}Ph_2PPy)Pd(^tBuNC)Cl_2]$, in which the Pd–P bond is retained. In this intermediate rotation around the Pd–P bond may be hindered. Because of the rigidity of Ph_2PPy, steric interactions between the allyl ligand and the phenyl groups promote breaking of the Pd–P bond and formation of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ together with $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$.

Bridging coordination of Ph_2PPy requires ligands with little steric demands *cis* to the P atom. A-frame bimetallic complexes containing "head-to-tail" Ph_2PPy have been synthesized only when CO, halogenides or $CNCH_3$ are the terminal ligands *cis* to phosphorus [9]. The $^{31}P\{^1H\}$ NMR spectrum of the *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ shows a singlet at δ 24.5 ppm indicating that the Ph_2PPy is monodentate and P-bonded [6]. Subsequently to Pd–P breaking, rearrangement of Ph_2PPy-Pd from N-bonding to P-bonding occurs. Drago *et al.* [10] showed that the enthalpy value for the formation of the Pd–P bond is higher than that of a Pd–N bond in the bridge-cleavage reaction of $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$ by pyridine and PPh_3. This is general.

The reaction of *cis*-$[Pd(^tBuNC)_2Cl_2]$ with $[Rh(COD)(Ph_2PPy)Cl]$ proceeds differently and affords nearly quantitatively the tetranuclear complex, $[\{(^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)\}_2]$ whose structure has been established by single crystal X-ray diffraction [6].

The reaction proceeds by formation of the transient species $[(COD)ClRh(\mu\text{-}Ph_2PPy)Pd(^tBuNC)Cl_2]$ whose binuclear structure is disrupted to give *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ and $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$, as a consequence of steric interactions between the COD and the phenyl groups of the P-bonded bridging Ph_2PPy. In this case, the reaction proceeds further, splitting the chloro-bridge of $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$ by the uncoordinated pyridine nitrogen atom of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ to give the intermediate $[(COD)ClRh(\mu\text{-}Ph_2PPy)Pd(^tBuNC)Cl_2]$ in which the steric interactions are reduced.

The final product results from the displacement of the COD by the isocyanide initially coordinated to palladium(II), and subsequent oxidative addition of a Pd–Cl bond across to the rhodium with formation of the Rh–Pd bond. The reaction clearly indicates the importance of the steric requirements of the terminal ligands in stabilizing binuclear species containing bridging Ph_2PPy.

The pathway proposed for these reactions have been further confirmed [11] starting from $[Rh(COD)(Ph_2PPyOMe)Cl]$, in which the $Ph_2PPyOMe$ is η^1 and P-bonded ($Ph_2PPyOMe$ = 2-(diphenylphosphino)-6-methoxypyridine). In this case, because the steric requirements of $Ph_2PPyOMe$ are greater than those of Ph_2PPy, only transfer of $Ph_2PPyOMe$ from rhodium to palladium was observed, and *cis*-$[Pd(^tBuNC)(Ph_2PPyOMe)Cl_2]$ and $[\{Pd(Ph_2PPyOMe)Cl(\mu\text{-}Cl)\}_2]$ are the products of the reactions of $[Rh(COD)(Ph_2PPyOMe)Cl]$ with *cis*-$[Pd(^tBuNC)_2Cl_2]$ and $[Pd(COD)Cl_2]$, respectively.

The initial reaction steps of the reaction between *cis*-$[Pd(^tBuNC)_2Cl_2]$ and $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ are very similar to those suggested for the reaction of *cis*-$[Pd(^tBuNC)_2Cl_2]$ with $[Rh(COD)(Ph_2PPy)Cl]$. The reactions of chloro-bridge splitting of $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$ by the uncoordinated pyridine nitrogen atom of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ to give a binuclear complex does not occur. This seems to be the result of the steric demands of the bridging Ph_2PPy; in fact it has been ascertained [10] that $[\{Pd[CH_2C(CH_3)CH_2]Cl\}_2]$ reacts with pyridine to give $[Pd\{CH_2C(CH_3)CH_2\}(py)Cl]$.

2.2. *Crystal and molecular structure of cis-*$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$

The structure of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ is depicted in Fig. 1 together with the atomic number scheme; in Fig. 2 a space filling diagram of the molecule is shown. The atomic coordinates for non-hydrogen atoms are given in Table 1; selected bond distances and angles are given in Table 2. The crystal structure of *cis*-$[Pd(^tBuNC)(Ph_2PPy)Cl_2]$ consists of mononuclear molecules, with no unusual intermolecular contacts. The palladium atom is in a nearly square planar configuration; the coordination around the Pd involves the Cl(1) and Cl(2) atoms, the phosphorus of Ph_2PPy and the isocyanide C(19) carbon atom; the chloride atoms are *cis*. The difference between the Pd–Cl(1) [2.349(2) Å] and Pd–Cl(2) [2.300(2) Å] bond distances of 0.049 Å is the result of the higher *trans* labilizing

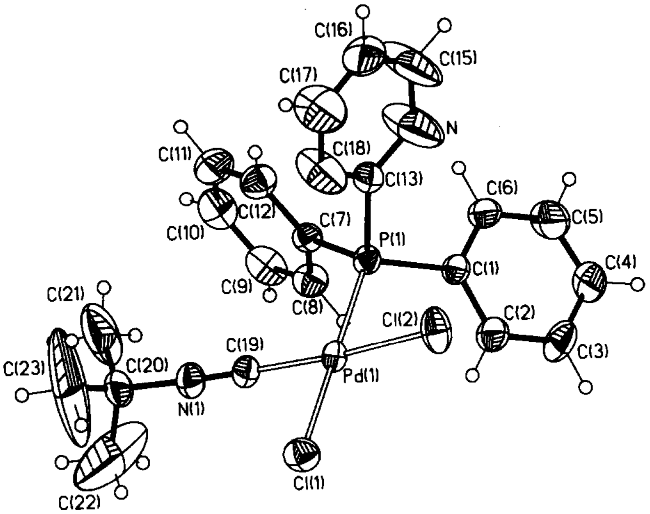

Fig. 1. View of the molecular structure of the complex *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] with the atomic numbering scheme.

TABLE 1. Fractional atomic coordinates

Atom	*x*	*y*	*z*
Pd(1)	0.37741(3)	0.03229(5)	0.03222(3)
P(1)	0.3406(1)	−0.1014(2)	0.12092(9)
Cl(1)	0.4098(1)	0.1746(2)	−0.0628(1)
Cl(2)	0.2390(1)	−0.0591(2)	−0.0695(1)
N(1)	0.5470(4)	0.1816(6)	0.1683(3)
C(1)	0.3348(4)	−0.2892(6)	0.0979(3)
C(2)	0.3628(5)	−0.3388(7)	0.0378(4)
C(3)	0.3582(6)	−0.4817(8)	0.0214(4)
C(4)	0.3230(6)	−0.5698(7)	0.0633(5)
C(5)	0.2983(7)	−0.5166(8)	0.1236(6)
C(6)	0.3029(5)	−0.3778(7)	0.1399(5)
C(7)	0.4234(4)	−0.0914(6)	0.2311(3)
C(8)	0.5110(5)	−0.1599(7)	0.2575(4)
C(9)	0.5755(5)	−0.1541(8)	0.3395(5)
C(10)	0.5537(6)	−0.0764(9)	0.3964(4)
C(11)	0.4671(6)	−0.0071(9)	0.3704(4)
C(12)	0.4027(5)	−0.0137(8)	0.2878(4)
C(13)	0.2237(4)	−0.0501(7)	0.1188(4)
N	0.1660(7)	−0.1394(9)	0.1301(8)
C(15)	0.0784(9)	−0.091(1)	0.128(1)
C(16)	0.0526(6)	0.038(1)	0.1166(6)
C(17)	0.1110(8)	0.125(1)	0.1053(9)
C(18)	0.1980(7)	0.0830(9)	0.1055(9)
C(19)	0.4863(4)	0.1195(6)	0.1197(3)
C(20)	0.6223(5)	0.2633(9)	0.2323(4)
C(21)	0.6305(9)	0.234(1)	0.3115(5)
C(22)	0.7075(7)	0.250(2)	0.2248(8)
C(23)	0.599(1)	0.404(1)	0.2151(8)

effect of PPh_2Py compared to ^{t}BuNC. The square planar coordination angles P(1)–Pd–C(19) [93.9(2)°], P(1)–Pd–Cl(2) [85.3(1)°]; Cl(2)–Pd–Cl(1) [93.2(1)°] and Cl(1)–Pd–C(19) [87.5(2)°]. The maximum deviations from the mean Cl(2)Cl(1)P(1)C(19) coordination plane are −0.087(7) Å for C(19), and 0.007(2) Å for Cl(1); the Pd atom is 0.038(1) Å away from this plane. To minimize the repulsive contact of one methyl group of ^{t}BuNC with the phenyl ring of Ph_2PPy, the Pd(1)–C(19)–N(1) and C(19)–N(1)–C(20) angles deviate slightly from linearity (174.1°(6) and 177.6°(7), respectively). The Pd–P(1)–C(7) angle [116.4(2)°] is larger than that expected for tetrahedral coordination at a phosphorus atom. The separation between the C(21) methyl carbon atom and the centroid of the C(7) ··· C(12) phenyl ring is of 3.69(2) Å. The space filling diagram of Fig. 2 shows that the Ph_2PPy ligand is obliged to assume its conformation to avoid steric interaction of the phenyl rings with Cl(2) [Cl(2) ··· C(1) 3.472(6) Å; Cl(2) ··· C(2) 3.360(7) Å; Cl(2) ··· C(13) 3.399(8) Å; Cl(2) ··· C(18) 3.63(1) Å].

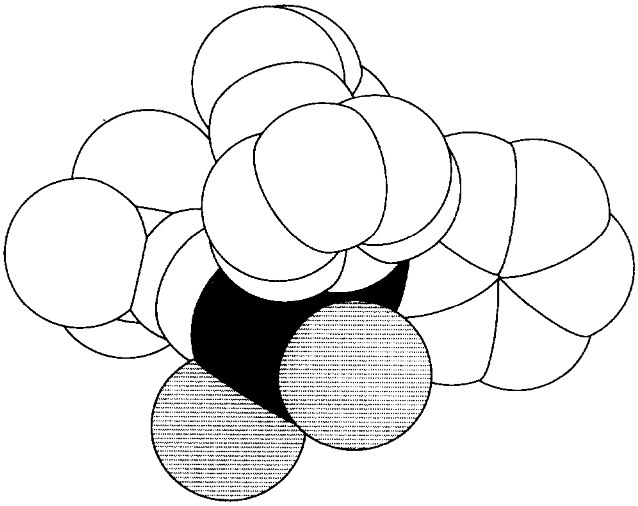

Fig. 2. Computer generated space-filling model of the *cis*-[Pd(^{t}BuNC)(Ph_2PPy)Cl_2] molecule.

The Pd–P(1) [12] and Pd–C(19) [13] bond distances of 2.247 (2) Å and 1.925 (5) Å lie within the range reported for related complexes.

3. Experimental details

Established methods were used to prepare the compounds *cis*-[Pd(^{t}BuNC)$_2$$Cl_2$] [14], [Pd{$CH_2C(CH_3)$-$CH_2$}($Ph_2PPy$)Cl] [15] and Ph_2PPy [16]. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under purified dinitrogen. IR spectra were obtained as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^{1}H, and ^{31}P NMR spectra were recorded on a Bruker WP80-SY or on a Varian Gemini-300 spectrometers.

^{1}H NMR spectra were referenced to internal tetramethylsilane, and ^{31}P spectra to external 85% H_3PO_4. Elemental analyses were performed by

Malissa-Reuter Mikroanalytishes Laboratorium, Elbach, Germany and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

3.1. *Reaction of* $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ *with cis*-$[Pd({}^tBuNC)_2Cl_2]$

A dichloromethane solution (20 ml) of $[Pd\{CH_2C(CH_3)CH_2\}(Ph_2PPy)Cl]$ (0.161 g, 0.349 mmol) was added to a $[Pd({}^tBuNC)_2Cl_2]$ (0.120 g, 0.349 mmol) solution (20 ml) in the same solvent. The reaction mixture was stirred for about 1 h; during this time the solution changed from orange to pale yellow. The solvent was evaporated off at reduced pressure; the solid residue was treated several times with small portions of benzene. The resulting extract affords the $[\{Pd\{CH_2C(CH_3)CH_2\}Cl]_2]$ (0.059 g, 0.151 mmol, yield 86.8%). The residue gives *cis*-$[Pd({}^tBuNC)(Ph_2PPy)Cl_2]$ (0.158 g, 0.302 mmol, yield 86.5%) by recrystallization from dichloromethane/diethyl ether (1 : 2). Anal. Found: C, 50.32; H, 4.46; N, 5.21; Cl, 13.32. $C_{22}H_{23}Cl_2N_2PPd$ calcd.: C, 50.46; H, 4.43; N, 5.35; Cl, 13.54%. IR (CsI, Nujol): ν(CN) 2228, ν(PdCl) 339, 294 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.77 (*o*-H py); 1.14 (s, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.5 (s).

TABLE 2. Bond distances (Å) and angles (°)

Distances			
Pd(1)–P(1)	2.247(2)	C(8)–C(9)	1.371(9)
Pd(1)–Cl(1)	2.349(2)	C(9)–C(10)	1.38(1)
Pd(1)–Cl(2)	2.300(2)	C(10)–C(11)	1.37(1)
Pd(1)–C(19)	1.925(5)	C(11)–C(12)	1.379(9)
P(1)–C(1)	1.828(6)	C(13)–N	1.29(1)
P(1)–C(7)	1.828(5)	C(13)–C(18)	1.32(1)
P(1)–C(13)	1.821(7)	N–C(15)	1.39(2)
N(1)–C(19)	1.133(7)	C(15–C(16)	1.28(2)
N(1)–C(20)	1.458(8)	C(16)–C(17)	1.28(2)
C(1)–C(2)	1.37(1)	C(17)–C(18)	1.37(2)
C(1)–C(6)	1.33(1)	C(20)–C(21)	1.37(1)
C(2)–C(3)	1.39(1)	C(20)–C(22)	1.35(2)
C(3)–C(4)	1.36(1)	C(20)–C(23)	1.39(1)
C(4)–C(5)	1.35(2)	C(7)–C(8)	1.380(9)
C(7)–C(12)	1.37(1)	C(5)–C(6)	1.35(1)
Angles			
Cl(2)–Pd(1)–C(19)	175.2(2)	C(8)–C(7)–C(12)	118.9(6)
Cl(1)–Pd(1)–C(19)	87.5(2)	C(7)–C(8)–C(9)	120.7(7)
Cl(1)–Pd(1)–Cl(2)	93.2(1)	C(8)–C(9)–C(10)	119.9(7)
P(1)–Pd(1)–C(19)	93.9(2)	C(9)–C(10)–C(11)	119.6(7)
P(1)–Pd(1)–Cl(2)	85.3(1)	C(10)–C(11)–C(12)	120.1(8)
P(1)–Pd(1)–Cl(1)	177.9(1)	C(7)–C(12)–C(11)	120.7(7)
Pd(1)–P(1)–C(13)	110.2(2)	P(1)–C(13)–C(18)	118.5(6)
Pd(1)–P(1)–C(7)	116.4(2)	P(1)–C(13)–N	122.2(6)
Pd(1)–P(1)–C(1)	113.9(2)	N–C(13)–C(18)	119.3(9)
C(7)–P(1)–C(13)	104.6(3)	C(13)–N–C(15)	118.2(9)
C(1)–P(1)–C(13)	107.4(3)	N–C(15)–C(16)	123.6(1.3)
C(1)–P(1)–C(7)	103.6(3)	C(15)–C(16)–C(17)	116.9(1.2)
C(19)–N(1)–C(20)	177.6(7)	C(16)–C(17)–C(18)	122.5(1.0)
P(1)–C(1)–C(6)	119.6(5)	C(13)–C(18)–C(17)	119.5(9)
P(1)–C(1)–C(2)	120.4(5)	Pd(1)–C(19)–N(1)	174.1(6)
C(2)–C(1)–C(6)	120.0(6)	N(1)–C(20)–C(23)	107.5(8)
C(1)–C(2)–C(3)	119.6(7)	N(1)–C(20)–C(22)	110.7(8)
C(2)–C(3)–C(4)	119.5(7)	N(1)–C(20)–C(21)	112.9(8)
C(3)–C(4)–C(5)	118.9(7)	C(22)–C(20)–C(23)	103.6(1.1)
C(4)–C(5)–C(6)	121.7(9)	C(21)–C(20)–C(23)	109.3(9)
C(1)–C(6)–C(5)	120.2(8)	C(21)–C(20)–C(22)	112.3(9)
P(1)–C(7)–C(12)	122.1(5)	P(1)–C(7)–C(8)	118.9(5)

TABLE 3. Crystal and refinement data

Formula	$C_{22}H_{23}N_2Cl_2PPd$
F.W.	523.72
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	15.143(2)
b, Å	9.527(1)
c, Å	17.517(4)
β, °	113.96(1)
V, Å^3	2309.4(7)
Z	4
Pcalcd, g cm^{-3}	1.466
Crystal size, mm	0.12×0.10×0.18
Orientations reflections, no., range (2θ),°	25, 15 < 2θ < 30
T, °C	23
μ, cm^{-1}	11.01
Radiation, Å	Mo Kα, λ = 0.71073
Monochromator	graphite crystal
Scan type	θ–2θ
Scan speed	variable
Scan range, °	1.2
Std. reflections	3 measd. after every 100 min
Data limits, °	3 < 2θ < 50
No. of data collected	5698
Obs. data	3078 $[I \geq 3\sigma(I)]$
No. of parameters refined	253
R [a]	0.044
R_w [b]	0.046
Quality-of -fit indicator [c]	1.68
Weighting scheme	$w = 1.0/(\sigma^2(F_o)+0.00037F_0^2)$
Largest shift esd. in final cycle	0.054
Largest peak, e Å^{-3}	0.71

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = n/(\sigma^2(F_o)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

3.2. *X-Ray data collection and structure refinement*

Suitable crystals of *cis*-$[Pd({}^tBuNC)(Ph_2PPy)Cl_2]$ were obtained from dichloromethane/diethyl ether (1:2) solution. Diffraction data were collected on a Siemens R3m/V automatic four-circle diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice parameters were obtained from least squares refinement of the setting angles of 25 reflections in the 15° < 2θ < 30° range. The complex crystallizes in the space group $P2_1/n$ with a = 15.143(2), b = 9.527(1), c = 17.517(4) Å, β = 113.96(1)°, V = 2309.4(7) Å^3, Z = 4. Information concerning the conditions of data collection and structure refinement is summarized in Table 3. A total of 5698 reflections were collected in the $3° < 2\theta < 54°$ range by ω–2θ scan; 5074 of them were unique ($R_{\text{int}} = 0.0116$) and 3078 were assumed as observed ($I < 3\sigma(I)$). Lorentz polarization corrections were applied to the intensity data, psi-scan absorption (max and min transmission = 0.914/0.845) corrections were applied. The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on F_o.

The N atom in the Ph_2PPy ligand was assigned to the appropriate six-membered ring (the one belonging with C13) on the basis of the isotropic thermal parameters and the bond lengths. The heteroatom was tested in each of the two possible positions in the appropriate ring and no difference in the R values was found. Attempts to resolve the statistical disorder by refining two separate six-membered rings failed, and therefore 50% occupancies were assigned to each. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter (0.06 Å^2). The final R value was 0.044, $R_w = 0.046$, GOF = 1.68. The weighting scheme used in the last refinement cycles was $w = 1.0/(\sigma^2(F_o) + 0.00037F_o^2)$.

Scattering factors for non-hydrogen atoms were taken from ref. 17 and for hydrogen atoms from ref. 18. Anomalous dispersion corrections for Pd and P atoms were taken from ref. 19.

All calculations were performed with the SHELX76 [20] and PARST [21] set of programs on the VAX-3400 computer at the Centro Interdipartimentale di servizi per la Diffrattometria a Raggi-X dell'università di Messina. Hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available from the authors as supplementary material.

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