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Cyclometallation of phenylhydrazones of ketones. Crystal and molecular structure of $[PdCl\{C_6H_4C(C_6H_5)=NNH(C_6H_4\text{-}4\text{-}Cl)\}(PPh_3)_2]$

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Abstract

The reaction of phenylhydrazones $C_6H_5C(R)=NNH(C_6H_4\text{-}4\text{-}Cl)$ (R = Me, Ph, or $PhCH_2$) with $PdCl_2$, in ethanol for 3 days at room temperature and posterior addition of PPh_3, leads to the *endo* five-membered cyclometallated derivatives $[\overline{PdCl\{C_6H_4C(R)=N}NH(C_6H_4\text{-}4\text{-}Cl)\}(PPh_3)]$. In contrast, from $2,4,6\text{-}(CH_3)_3C_6H_2C(CH_3)=NNH\{C_6H_3\text{-}2,4\text{-}(NO_2)_2\}$ and palladium acetate, in refluxing acetic acid, the *exo* five-membered metallocycle $[\overline{PdCl\{2,4\text{-}(NO_2)_2C_6H_2NHN}=C(CH_3)C_6H_2\text{-}2,4,6\text{-}(CH_3)_3\}\text{-}(PPh_3)]$ is obtained.

$[PdCl\{C_6H_4C(C_6H_5)=NNH(C_6H_4\text{-}4\text{-}Cl)\}(PPh_3)_2]$ crystallizes in the triclinic space group $P1$, with $a = 20.107(4)$, $b = 12.678(3)$, $c = 12.547(3)$ Å, $\alpha = 114.71(2)$, $\beta = 90.72(3)$, $\gamma = 115.01(3)°$ and $Z = 2$; $R_w = 0.059$ for 7417 reflections. The palladium atom shows a strong interaction with the imine nitrogen atom, the Pd–N distance being 2.860 Å.

Introduction

Cyclopalladation reactions have been widely studied [1] to obtain new organometallic compounds by activation of C–H bonds, as well as for their applications in organic synthesis. Their reactions with CO, alkynes, alkenes, etc., have led to new pathways for the synthesis of carbocyclic and heterocyclic compounds [2].

Unlike *N*-donors such as amines, imines and azobenzenes, little attention has been paid to hydrazones. The cyclopalladation of some hydrazones such as acetophenone- and benzophenone-*N*-phenylhydrazones, by direct reaction with

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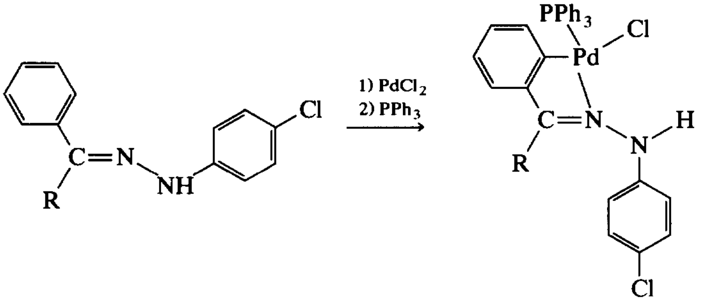
palladium salts have been reported [3]. Pfeffer *et al.* [4], obtained acetophenone cyclometallated derivatives by a different method, that involves reaction of acetophenone and the complex $[PdCl_2(H_2NNHPh)_2]$. There is also one report on the cyclopalladation of the acetylhydrazone of acetylferrocene [5]. In all cases the compounds obtained are *endo* (the metallocycle contains a double bond C=N) five-membered derivatives. Natile *et al.* have studied the cyclopalladation of the methylphenylhydrazone of pinacolone [6]. Depending on the experimental conditions, the metallation of the CMe group or of the tert-butyl group is achieved, with formation, in both cases, of *endo* metallocycles. The metallation of the phenyl group, which would give *exo* five-membered derivatives containing $Pd-C_{aromatic}$ bonds, has not been observed. Some cyclopalladated compounds in which the hydrazone is tridentate by coordination of a third atom, of nitrogen or oxygen, have also been reported [7].

Following our studies on the cyclopalladation of benzalazines and imines [8], we report here the preparation of metallocycle derivatives of arylketone phenylhydrazones. When bulky substituents are present in the carbonyl carbon atom, the formation of *exo* derivatives is achieved.

Results and discussion

The action of $PdCl_2$ on the hydrazones $C_6H_5C(R)=NNH(C_6H_4\text{-}4\text{-}Cl)$ [R = Me (**1a**), Ph (**1b**) or $PhCH_2$ (**1c**)] was examined at room temperature, in ethanol for 3 days. The chloro-bridged dimeric compounds formed were treated with PPh_3 (1 : 1) in order to obtain more soluble monomeric derivatives (**2**) (eq. 1).



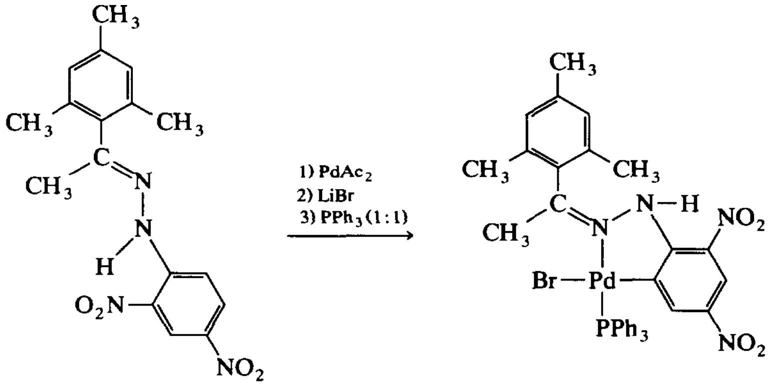
(1)

1a, R = CH_3;
1b, R = Ph;
1c, R = $PhCH_2$

2a, b, c

These hydrazones might form *endo* or *exo* five-membered metallocycles, but in fact only *endo* derivatives were obtained, consistent with previous work [3]. Only the *endo* five-membered compound is formed with the hydrazone **1c**, which might have given an *endo* six-membered compound by metallation of the benzyl ring.

Very different results were obtained with $2,4,6\text{-}(CH_3)_3C_6H_2C(C_6H_5)=NNH\{2',4'\text{-}(NO_2)_2C_6H_3\}$, **1d**. This can give *endo* six-membered derivatives by metallation of the *ortho* methyl substituent, or *exo* five-membered derivatives by metallation of *ortho* aromatic carbon atoms of the phenylhydrazine ring. In the same conditions as before (ethanol at room temperature for 3 days) no reaction was observed and the hydrazone was almost quantitatively recovered. Under more drastic conditions, the reaction with $PdAc_2$ in refluxing acetic acid gave only the *exo* five-membered metallocycle.



1d **2d** (2)

The other hydrazones studied (**1,a,b,c**) decomposed under these drastic conditions (refluxing acetic acid), and no cyclometallated compound was detected.

The formation of the *exo* metallocycle **2d** is unexpected, because mesitylbenzylidenamines gave *endo* six-membered compounds containing Pd–C benzyl bonds, under similar conditions [9]. In addition, the metallated phenylhydrazine ring contains two electron-withdrawing (NO_2) substituents, that hinder the electrophilic attack of the Pd^{II}, this being the accepted mechanism for the palladation of *N*-donor ligands [1].

Nevertheless, the formation of **2d** can be explained by the following arguments. In order for C–H bond activation to occur, coplanar interaction with the coordination plane of the metal is needed [1]. The mesityl and methyl substituents at the carbonyl carbon atom prevent the adoption of the planar conformation with the imine moiety, and the activation of the *ortho* methyl group does not occur. On the other hand, the intramolecular hydrogen bond between the *ortho* NO_2 substituent of the phenylhydrazine ring and the hydrazine NH group (see below) favours the planarity of phenylhydrazine ring and the imine moiety, which promotes the metallation of this ring.

As with the imine derivatives, the *exo* metallocycle formed has the hydrazone ligand in the *Z* form [8b]. Thus, *E*–*Z* isomerization occurs during the cyclometallation process, in order to decrease the steric repulsion between the phenylhydrazine ring and the "PdX" moiety. If the metallation could take place without isomerization of the ligand, the *exo* cyclopalladated derivative formed would have the mesityl ring and the "PdX" group on the same side of the imine C=N bond.

In no case has interaction of the palladium atom with an amine nitrogen atom been detected, not even with hydrazone **1d**, that has the imine nitrogen shielded by very bulky groups such as methyl and mesityl. The fact that the coordination of the amine nitrogen atom would give *endo* six- or seven-membered derivatives or *exo* four-membered derivatives does not favour this type of coordination.

The dependence of the stability of Pd–N bonds on the basicity of the *N*-donor atoms found in *N*-benzylidenamine derivatives [8b], can be applied to these hydrazone derivatives. Thus, an excess of PPh_3 breaks the Pd–N bond in the

Table 1

Analytical data and melting points

Compound	Analysis (found (calc.) (%))			M.p. (°C) [a]
	C	H	N	
2a	59.2 (59.31)	4.2 (4.17)	4.2 (4.32)	205–208
4a	49.9 (50.21)	6.7 (6.76)	4.4 (4.50)	144–148
2b	62.6 (62.58)	4.6 (4.08)	3.5 (3.94)	204–206
3b	67.7 (67.94)	4.5 (4.52)	2.9 (2.88)	169–171
2c	63.0 (63.03)	4.2 (4.28)	3.8 (3.87)	200–204
4c	54.8 (55.06)	6.5 (6.59)	3.7 (4.01)	145–148
2d	53.2 (53.21)	4.0 (4.05)	7.1 (7.09)	224–228
3d	60.5 (60.49)	4.4 (4.47)	5.2 (5.32)	200–204

[a] With decomposition.

benzophenone derivative **2b** and in the *exo* metallocycle **2d**, and compounds $[Pd(C{-}N)X(PPh_3)_2]$ (**3b,d**) are formed. In contrast, in the cyclometallated compounds of the more basic hydrazones **2a** and **2c**, containing alkyl substituents, an excess of PPh_3 does not break the Pd–N bond. The more basic and less bulky PEt_3 gives, even with the derivatives of hydrazones **1a** and **1c**, compounds with two phosphines $[PdX(C{-}N)(PEt_3)_2]$ **4**. Compounds **3** lose one molecule of PPh_3 giving compounds **2**, when they are eluted with a mixture of $CHCl_3$ and MeOH (100:1) from silica gel.

Characterization

All the new compounds obtained are air stable and yellow or orange. They are quite soluble in chloroform and dichloromethane and slightly soluble in ethanol and diethylether. The analytical data and decomposition temperatures are shown in Table 1. The IR spectra show bands typical of coordinated phosphines and hydrazones.

The proton and ^{31}P NMR spectra of compounds **2** and **4**, and of the free hydrazones are reported in Table 2. The assignment of the aromatic signals is conclusive evidence of the palladation position (*endo* or *exo*). The aromatic proton signals of the metallated ring in compounds **2**, which contain the Pd–N bond, are shifted to high fields; this must be caused by a phosphine phenyl ring, consistent with a *cis* arrangement of the phosphine and the metallated ring and thus a *trans* disposition of phosphorus and nitrogen atoms. The ^{31}P chemical shifts of compounds **2** (41–43 ppm) are consistent with this *trans* arrangement. Similarly, compounds **3** (21–23 ppm) have *trans* phosphines.

The signal assigned to the methine CH_3 group in the cyclometallated compound **2d** is shifted to low field compared to the free ligand. This shift can be explained by the paramagnetic anisotropy of the palladium atom and indicates a close approach between the metal and the methyl group, suggesting a *Z* form for the ligand, as has been found for similar exocyclic derivatives of imines [8b,10]. The signal assigned to the NH proton in cyclometallated derivatives **2a,b,c** also appears low-field shifted, showing that the ligand adopts a conformation in which the NH group is close to palladium in order to minimize the steric repulsions.

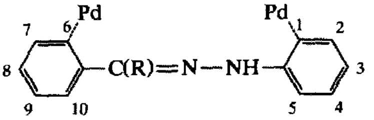
It has been shown by X-ray structure determination that there is an intramolecular hydrogen bond between the *ortho* nitro and the NH groups in hydrazones

Table 2

^{1}H and ^{31}P NMR data

Compound	^{1}H [a]		^{31}P [b]
	Aromatic, NH	Aliphatic	
1a	8.0–7.26 (br m, H arom., NH)	2.62 (s, MeC=N)	
2a	9.02 (d, $^{4}J(HP) = 2.8$, NH)	2.34 (s, MeC=N)	41.37
	7.87–7.16 (br m, H_1, H_2, H_4, H_5, PPh_3)		
	6.98 (t, $^{3}J(HH) = 9.1$, H_9)		
	6.74 (d, $^{3}J(HH) = 9.1$, H_{10})		
	6.58 (t, $^{3}J(HH) = 9.0$, H_8)		
	6.48 (t, $^{3}J(HH) = 9.0$, $^{4}J(HP) = 9.0$, H_7)		
4a	7.5–6.9 (br m, H arom., NH)	2.48 (s, MeC=N)	9.05
		1.59 (m, CH_2)	
		0.98 (m, CH_3)	
1b	7.60–6.90 (br m, H arom., NH)		
2b	8.82 (d, $^{4}J(HP) = 3.15$, NH)		41.39
	7.80–7.26 (br m, H_1, H_2, H_4, H_5, PPh_3, PhC=N)		
	6.9–6.4 (br m, H_7, H_8, H_9, H_{10})		
1c	7.78–7.0 (br m, CH_2Ph, NH)	4.13 (s, CH_2Ph)	
2c	9.0 (d, $^{4}J(HP) = 2.82$, NH)	4.11 (s, CH_2Ph)	41.11
	7.8–7.2 (br m, H_1, H_2, H_4, H_5, PPh_3, CH_2Ph)		
	6.9–6.4 (br m, H_7, H_8, H_9, H_{10})		
4c	7.5–6.9 (br m, H arom.)	4.40 (s, CH_2Ph)	9.34
		1.56 (m, CH_2)	
		0.96 (m, CH_3)	
1d	10.72 (s, NH)	2.35 (s, Me_6, Me_{10})	
	9.06 (d, $^{4}J(HH) = 2.3$, H_4)	2.15 (s, Me_8, MeC=N)	
	8.33 (dd, $^{3}J(HH) = 9$, $^{4}J(HH) = 2.3$, H_2)		
	8.05 (d, $^{3}J(HH) = 9$, H_1)		
	7.02 (s, H_7, H_9)		
2d	10.75 (m, NH)	3.03 (s, MeC=N)	41.87
	8.58 (d, $^{4}J(HH) = 3.6$, H_4)	2.37 (s, Me_8)	
	7.9–7.3 (br m, H_2, PPh_3)	2.23 (Me_6)	
	7.06 (s, H_7, H_9)		

[a] In $CDCl_3$; chemical shifts in ppm with respect to internal $SiMe_4$; coupling constants in Hz; numbering thus:



[b] In $CHCl_3$; chemical shift (ppm) with respect to 85% H_3PO_4.

derived from 2,4-dinitrophenylhydrazines [11]. In these compounds, the signal assigned to the NH group appears strongly shifted to low fields ($\delta = 10.5–11.5$ ppm). The chemical shift of the NH protons suggests such hydrogen bonding in the metallated derivatives of the hydrazone **1d**.

In compounds **4**, the methyl signals of PEt_3 appear as quintuplets, which is characteristic of a *trans* arrangement between the phosphines, due to so-called "virtual coupling".

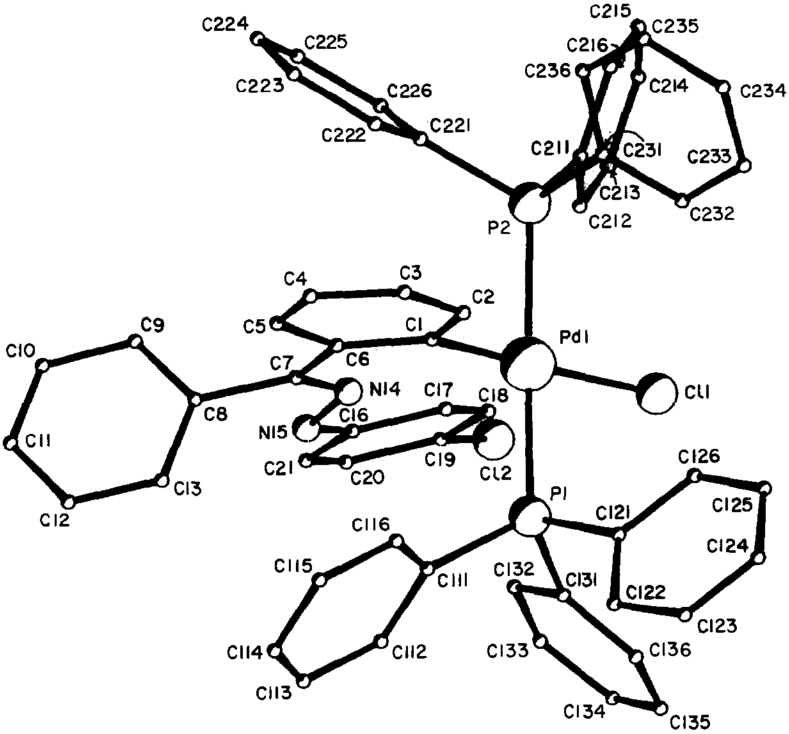


Fig. 1. Molecular structure of [PdCl{C$_6$H$_4$C(C$_6$H$_5$)=NNH(C$_6$H$_4$-4-Cl)}(PPh$_3$)$_2$].

Crystal structure of [PdCl{C$_6$H$_4$C(C$_6$H$_5$)=NNH(C$_6$H$_4$-4-Cl)}(PPh$_3$)$_2$]

The crystal structure of **3b** has been determined (Fig. 1). Selected bond lengths and bond angles are listed in Table 3, and atomic coordinates in Table 4.

The molecular structure consists of discrete molecules separated by van der Waals distances. The palladium atom is coordinated to C(1), P(1), P(2) and C(1), and shows a significant interaction with N(14). The Pd, P(1), P(2) and C(1) atoms are not coplanar, the largest deviation from the mean plane reaching 0.16 Å for the palladium atom. The angles between adjacent atoms in the coordination sphere lie in the range 86.0° for C(1)PdP(2) to 94.6° for P(2)PdCl(1). The two phosphine molecules adopt a *trans* arrangement with an angle P(1)–Pd–P(2) of 169.7°. The metallated phenyl ring [C(1)–C(6)] forms a dihedral angle of 86.43° with the coordination plane. The Pd–ligand distances are similar to those found in analogous palladated compounds. The Pd–N(14) distance of 2.860 Å is shorter than the sum of the van der Waals radii (*ca.* 3.1 Å), but is longer than the value found in compounds with a Pd–N bond (*ca.* 2.0 Å), suggesting a significant Pd- - -N interaction. The pentacoordination of palladium in metallated derivatives of *N*-donor ligands has been reported before. In compounds with *endo* structures derived from Schiff bases, [PdCl(*p*-ClC$_6$H$_3$CH=N)(PEt$_3$)$_2$]$_2$ [13] and [PdBr(C$_6$H$_4$CH=NC$_6$H$_5$)(PPh$_3$)$_2$] [12b], the palladium atom is coordinated to the imine nitrogen atom with Pd–N distances of 2.710 and 2.743 Å, respectively. In the hydrazone derivative [PdCl(C$_6$H$_4$C(CH$_3$)=NNHC$_6$H$_5$)(PEt$_3$)$_2$] [12a] there is an interaction between the palladium and one of the hydrogen atoms of the methyl

Table 3

Selected bond distances (Å) and angles (°) for **4b**

Cl(1)- - -Pd(1)	2.426(2)	C(8)- - -C(7)	1.518(8)
P(1)- - -Pd(1)	2.355(2)	N(14)- - -C(7)	1.301(7)
P(2)- - -Pd(1)	2.370(2)	C(9)- - -C(8)	1.400(15)
C(1)- - -Pd(1)	2.026(5)	C(13)- - -C(8)	1.382(10)
C(111)- - -P(1)	1.857(5)	C(10)- - -C(9)	1.402(11)
C(121)- - -P(1)	1.836(8)	C(11)- - -C(10)	1.346(15)
C(131)- - -P(1)	1.840(8)	C(12)- - -C(11)	1.363(15)
C(211)- - -P(2)	1.844(5)	C(13)- - -C(12)	1.398(9)
C(221)- - -P(2)	1.860(9)	N(15)- - -N(14)	1.379(8)
C(231)- - -P(2)	1.819(7)	C(16)- - -N(15)	1.391(7)
C(2)- - -C(1)	1.389(10)	C(17)- - -C(16)	1.411(8)
C(6)- - -C(1)	1.405(9)	C(21)- - -C(16)	1.383(11)
C(3)- - -C(2)	1.390(9)	C(18)- - -C(17)	1.349(8)
C(4)- - -C(3)	1.393(14)	C(19)- - -C(18)	1.390(12)
C(5)- - -C(4)	1.370(11)	C(20)- - -C(19)	1.423(12)
C(6)- - -C(5)	1.416(8)	Cl(2)- - -C(19)	1.731(7)
C(7)- - -C(6)	1.467(10)	C(21)- - -C(20)	1.364(10)
P(1)–Pd(1)–Cl(1)	90.3(1)	C(7)–C(6)–C(1)	123.3(5)
P(2)–Pd(1)–Cl(1)	94.6(1)	C(7)–C(6)–C(5)	118.3(6)
P(2)–Pd(1)–P(1)	169.7(1)	C(8)–C(7)–C(6)	119.9(5)
C(1)–Pd(1)–Cl(1)	172.3(2)	N(14)–C(7)–C(6)	119.8(5)
C(1)–Pd(1)–P(1)	87.9(2)	N(14)–C(7)–C(8)	120.3(6)
C(1)–Pd(1)–P(2)	86.0(2)	C(9)–C(8)–C(7)	120.0(6)
C(111)–P(1)–Pd(1)	120.8(3)	C(13)–C(8)–C(7)	120.3(8)
C(121)–P(1)–Pd(1)	111.3(3)	C(13)–C(8)–C(9)	119.4(6)
C(121)–P(1)–C(111)	102.4(3)	C(10)–C(9)–C(8)	118.0(9)
C(131)–P(1)–Pd(1)	111.6(2)	C(11)–C(10)–C(9)	122.0(12)
C(131)–P(1)–C(111)	105.2(3)	C(12)–C(11)–C(10)	120.3(8)
C(131)–P(1)–C(121)	103.7(4)	C(13)–C(12)–C(11)	119.9(7)
C(211)–P(2)–Pd(1)	119.8(3)	C(12)–C(13)–C(8)	120.3(8)
C(221)–P(2)–Pd(1)	118.9(2)	N(15)–N(14)–C(7)	116.4(5)
C(221)–P(2)–C(211)	100.8(3)	C(16)–N(15)–N(14)	120.2(5)
C(231)–P(2)–Pd(1)	108.0(3)	C(17)–C(16)–N(15)	123.4(6)
C(231)–P(2)–C(211)	102.1(3)	C(21)–C(16)–N(15)	119.0(5)
C(231)–P(2)–C(221)	105.4(4)	C(21)–C(16)–C(17)	117.6(5)
C(2)–C(1)–Pd(1)	116.8(5)	C(18)–C(17)–C(16)	121.8(7)
C(6)–C(1)–Pd(1)	124.3(5)	C(19)–C(18)–C(17)	119.9(6)
C(6)–C(1)–C(2)	118.9(5)	C(20)–C(19)–C(18)	119.6(6)
C(3)–C(2)–C(1)	122.2(7)	Cl(2)–C(19)–C(18)	120.2(6)
C(4)–C(3)–C(2)	118.9(7)	Cl(2)–C(19)–C(20)	120.0(7)
C(5)–C(4)–C(3)	120.0(6)	C(21)–C(20)–C(19)	118.7(8)
C(6)–C(5)–C(4)	121.6(7)	C(20)–C(21)–C(16)	122.2(7)
C(5)–C(6)–C(1)	118.4(6)		

group because the molecule has rotated around the C–C bond of $C_6H_5{-}C(CH_3){=}N$ moiety, and the imine nitrogen atom is distant from the metal.

The crystal structure of **1b** has not been determined, but the molecular structure of the analogous *p*-nitrophenylhydrazone of benzophenone is known[11]. The angles and bond distances of the metallated *p*-chloro-compound are very similar to those of the free *p*-nitrophenylhydrazone. The hydrazone moiety C(6)C(7)N(14) and N(15) remains planar and is nearly coplanar with the metallated phenyl ring

Table 4

Fractional atomic coordinates ($\times 10^4$; Pd $\times 10^5$) of **4b** ($B_{eq} = 8\pi^2/3\Sigma_{ij}U_{ij}a_i a_j \mathbf{a}_i \cdot \mathbf{a}_j$)

	x	y	z	B_{eq}
Pd(1)	72765(2)	59518(4)	55535(4)	3.15(2)
Cl(1)	6298(1)	4662(2)	3714(2)	4.55(7)
P(1)	7539(1)	7892(2)	5440(2)	3.56(7)
P(2)	6959(1)	4181(2)	6001(2)	3.51(7)
C(111)	8456(3)	9403(6)	6263(6)	3.82(28)
C(112)	8968(4)	9904(7)	5623(7)	4.64(33)
C(113)	9658(4)	11068(7)	6281(9)	5.70(40)
C(114)	9831(4)	11709(7)	7499(9)	5.80(40)
C(115)	9334(4)	11212(7)	8106(8)	5.75(37)
C(116)	8650(4)	10076(6)	7488(7)	4.87(32)
C(121)	6856(4)	8475(6)	5998(6)	3.98(29)
C(122)	7020(4)	9767(7)	6432(7)	5.17(36)
C(123)	6467(5)	10131(9)	6814(8)	6.38(47)
C(124)	5769(5)	9222(10)	6760(8)	6.61(48)
C(125)	5598(4)	7921(10)	6307(8)	6.61(44)
C(126)	6134(4)	7523(8)	5923(7)	5.37(35)
C(131)	7428(4)	7605(6)	3869(6)	3.90(27)
C(132)	7808(5)	6969(7)	3151(7)	5.83(41)
C(133)	7706(6)	6667(8)	1951(8)	6.72(48)
C(134)	7228(6)	6903(9)	1434(8)	7.08(44)
C(135)	6855(5)	7571(9)	2153(8)	6.91(45)
C(136)	6955(4)	7898(7)	3352(7)	4.90(34)
C(211)	6475(3)	2472(6)	4775(6)	3.76(27)
C(212)	6572(5)	2189(7)	3618(7)	5.41(37)
C(213)	6274(5)	881(8)	2739(7)	6.20(42)
C(214)	5864(4)	−153(7)	2974(8)	5.36(37)
C(215)	5765(4)	124(7)	4111(8)	5.54(38)
C(216)	6064(4)	1444(6)	5026(7)	4.82(32)
C(221)	7718(4)	4141(7)	6820(6)	4.12(29)
C(222)	8049(4)	4997(8)	8028(7)	5.55(39)
C(223)	8608(5)	4919(10)	8610(9)	6.75(48)
C(224)	8838(5)	3981(11)	7985(11)	7.33(59)
C(225)	8555(5)	3194(9)	6810(10)	6.44(48)
C(226)	7982(4)	3250(8)	6204(8)	5.75(40)
C(231)	6280(3)	4196(6)	6945(6)	3.76(26)
C(232)	5726(4)	4480(7)	6647(7)	4.84(34)
C(233)	5163(4)	4458(9)	7302(8)	6.09(44)
C(234)	5183(5)	4232(9)	8256(9)	6.95(47)
C(235)	5728(5)	3960(9)	8590(8)	6.64(46)
C(236)	6281(4)	3916(8)	7913(7)	5.48(38)
C(1)	7994(3)	7102(6)	7201(5)	4.08(24)
C(2)	7686(4)	7515(6)	8183(6)	5.00(29)
C(3)	8118(5)	8291(7)	9359(6)	6.40(37)
C(4)	8881(5)	8636(8)	9562(6)	6.97(39)
C(5)	9200(4)	8257(8)	8607(6)	5.85(33)
C(6)	8768(3)	7485(6)	7403(6)	4.46(27)
C(7)	9157(3)	7162(6)	6428(5)	3.90(26)
C(8)	10013(3)	7816(6)	6706(6)	4.34(28)
C(9)	10385(4)	7091(9)	6674(11)	8.37(54)
C(10)	11175(5)	7723(10)	6896(12)	9.98(68)
C(11)	11573(4)	8984(8)	7119(9)	6.67(44)
C(12)	11213(4)	9682(7)	7114(7)	5.31(33)

Table 4 (continued)

	x	y	z	B_{eq}
C(13)	10427(3)	9098(6)	6902(6)	4.25(28)
N(14)	8769(3)	6365(5)	5321(5)	4.27(23)
N(15)	9176(3)	6193(6)	4445(5)	5.06(26)
C(16)	8816(3)	5200(6)	3270(6)	4.11(28)
C(17)	8025(4)	4441(6)	2863(6)	4.63(29)
C(18)	7694(4)	3474(7)	1720(6)	5.47(33)
C(19)	8135(5)	3239(8)	895(7)	6.51(40)
C(20)	8934(5)	3982(9)	1278(8)	7.17(45)
C(21)	9247(4)	4968(7)	2435(7)	5.64(36)
Cl(2)	7717(2)	1971(3)	−562(2)	11.80(16)
OW(1)	4426(3)	8344(4)	10038(4)	5.57(22)
OW(2)	4252(5)	2024(7)	391(5)	10.56(44)

(the dihedral angle is 7.63°). The two phenyl rings of the methine carbon atom form a dihedral angle of 101.79°, larger than in the hydrazone (70.4°), to minimize steric repulsions.

Experimental

NMR spectra were obtained on a Bruker WP 80SY (^{1}H, 80.13 MHz; ^{31}P, 32.8 MHz) spectrometer. IR spectra were recorded as KBr disks on a Perkin Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

Materials and synthesis

Solvents were dried and distilled before use. The hydrazones were obtained from the corresponding benzaldehydes and the appropriate hydrazines under standard conditions (refluxing ethanol) [14].

[$\overline{PdCl\{C_6H_4C(R)=N}NH(4\text{-}ClC_6H_4)\}(PPh_3)$], R = Me, Ph, $PhCH_2$, ***(2a,b,c)****.* A stirred suspension of $PdCl_2$ (2 mmol, 0.35 g) in EtOH (30 ml) was treated with 2.2 mmol of the corresponding hydrazone for 3 days at room temperature. The precipitate was washed with ethanol and ether and used without further purification in the preparation of **2**. A stirred suspension of the precipitate (0.33 g) was treated with PPh_3 (0.75 mmol, 0.19 g) in refluxing acetone (30 ml) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was purified by column chromatography over SiO_2, with a mixture of $CHCl_3$ and MeOH (100 : 1) as eluant, to give compounds **2a,b,c** in 70% yield.

[$\overline{PdBr\{2,4\text{-}(NO_2)_2C_6H_2NHN}=C(CH_3)(2,4,6\text{-}CH_3C_6H_2)\}(PPh_3)$] ***(2d)****.* A stirred suspension of $Pd(AcO)_2$ (2 mmol, 0.45 g) in acetic acid (30 ml) was treated with 0.75 g (2.2 mmol) of hydrazone **1d** under reflux for 3 h. The precipitate was washed with ethanol and ether and used without further purification in the preparation of **2d**. A stirred suspension of the precipitate (0.38 g) was treated with PPh_3 (0.75 mmol, 0.19 g) and LiBr (0.75 mmol, 0.065 g) in refluxing acetone (30

ml) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was purified by column chromatography over SiO_2, with the $CHCl_3$–MeOH eluant, to give compound **2d** in 70% yield.

[PdX(C–N)(PPh$_3$)$_2$] (3b, X = Cl; 3d, X = Br). A stirred suspension of compound **2** (0.5 mmol) was treated with PPh_3 (0.75 mmol, 0.19 g) in refluxing acetone for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was washed with ether and recrystallized with $CHCl_3$ to give compounds **3b,d** in 90% yield.

*[PdCl{C$_6$H$_4$C(R)=NNH(4-ClC$_6$H$_4$)}(PEt$_3$)$_2$] (**4a,c**).* A stirred suspension of $PdCl_2$ (2 mmol, 0.35 g) in EtOH (30 ml) was treated with 2.2 mmol of hydrazone for 3 days at room temperature. The precipitate formed was washed with ethanol and ether and used without further purification in the preparation of **4**. A stirred suspension of the precipitate (0.33 g) was treated under nitrogen with PEt_3 (2 mmol, 0.24 g) in refluxing acetone (30 ml) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ethanol was recrystallized from $CHCl_3$–MeOH to afford compounds **4a,c** in 60–70% yield. Crystal data: $C_{55}H_{44}N_2P_2Cl_2Pd \cdot 2H_2O$. $F_w = 1008.26$, triclinic, $a = 20.107(4)$; $b = 12.678(3)$; $c = 12.547(3)$ Å; $\alpha = 114.71(2)$; $\beta = 90.71(3)$, $\gamma = 115.01(3)°$. $V = 2563(2)$ Å^3, $P1$, $D_x = 1.306$ g cm^{-3}, $Z = 2$, $F(000) = 1036.0$, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 5.65 cm^{-1}, 298 K.

Data collection. A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8 \leqslant \theta \leqslant 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-K_α radiation, using the ω-scan technique. 7423 reflections were measured in the range $2 \leqslant \theta \leqslant 25$, 7417 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, and significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Structure solution and refinement. The structure was solved by Patterson synthesis, using the SHELXS computer program [15] and refined by full-matrix least-squares method, with the SHELX76 computer program [16]. The function minimized was $\Sigma w[\,|F_o| - |F_c|\,]^2$, where $w = \sigma^{-2}(F_o)$. f, f' and f'' were taken from *International Tables of X-ray Crystallography* [17]. The position of 43 H atoms was located from a difference synthesis and refined with an overall isotropic temperature factor using a riding model. The final R factor was 0.059 ($R_w = 0.059$) for all observed reflections. The number of refined parameters was 630. Max. shift/esd = 0.1, max. and min. peaks in final difference synthesis were 0.4 and −0.4 e Å^{-3}, respectively.

Supplementary material available. Full tables of bond lengths and angles, hydrogen coordinates, thermal parameters, and structure factors are available from the authors.

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