Journal of Organometallic Chemistry, 456 (1993) 287-291

JOM 23589

Studies on interactions of isocyanide with transition metal complexes

XXXVI *. Spontaneous successive insertion of isocyanide into palladium-carbon σ-bond

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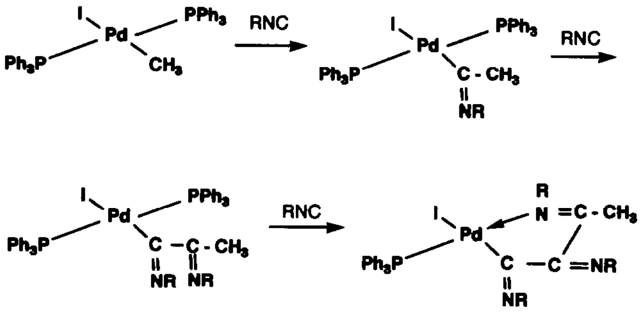
(Received December 25, 1992; in revised form February 5, 1993)

Abstract

Reaction of *trans*-Pd$(PPh_3)_2I(CH_3)$ (**1a**) with 2,6-xylyl isocyanide in a 1:1 molar ratio led to a spontaneous insertion of isocyanides into a Pd-C bond to give the tris-imino insertion product **2a**. The structure was determined by an X-ray analysis. The crystals are triclinic with space group $P1$ ($a = 14.638(9)$, $b = 15.662(7)$, $c = 7.895(3)$ Å, $\alpha = 85.06(6)$, $\beta = 82.84(4)$, $\gamma = 102.4(4)°$, and $Z = 2$; $R = 0.066$ for 2076 independent reflections with $F_0 > 5\sigma(F_0)$. The tris-imino group acts as a bidentate ligand through C- and N-coordinations. The 2-methyl-1-naphthyl complex, *trans*-Pd$(PPh_3)Br(2\text{-}CH_3C_{10}H_9)$ reacted with 2,6-xylyl isocyanide to give a bis-imino complex containing μ_2-Br bridging ligands. Using *p*-nitrophenyl isocyanide, the reaction produced a mono-imino compound. Reaction of **2a** with $CuCl_2$ gave a mixed metal complex, in which the copper(II) atom is coordinated to two neighbouring imino-nitrogens.

1. Introduction

Insertion reactions are of fundamental importance in organometallic chemistry [1] and we have been studying the insertion of isocyanide. Isocyanides have been found to insert stepwise into metal-carbon bonds (Scheme 1) [2] and such stepwise-multiple insertions have often been observed in alkyl isocyanide. Recently the reaction of $(CO)_5Mn(CH_2C_6H_4\text{-}p\text{-}X)$ with *p*-tolyl isocyanide gave the products of double insertion, $(CO)_4Mn[C(=N\text{-}p\text{-toly)}C(=N\text{-}p\text{-tolyl})CH_2C_6H_4\text{-}p\text{-}X]$ and no mono-imino complex was isolated [3]. Selective double-insertion of isocyanides into just one of the two metal-carbon bonds of the μ-ethynediyl complexes has been reported [4]. We have examined the reactivity of *ortho*-substituted phenyl isocyanide to alkyl or phenyl palladium complexes and found the spontaneous triple-insertion of isocyanides. In this paper we describe the spontaneous triple insertion of sterically bulky isocyanide.



Scheme 1. Insertion reaction of isocyanide into palladium-carbon bond.

2. Results and discussion

The reaction of *trans*-Pd$(PPh_3)_2I(CH_3)$ (**1a**) with 2,6-xylyl isocyanide in a 1:1 molar ratio at ice-cool

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* For Part 35, see T. Tanase, T. Horiuchi, Y. Yamamoto and K. Kobayashi, *J. Organomet. Chem.*, *440* (1992) 1.

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temperature occurred chemoselectively to give reddish brown crystals as the only main product, formulated as $Pd(2,6\text{-}Me_2C_6H_3NC)_4I(CH_3)$ (**2a**) (Table 1). A monomolecular insertion product of isocyanide was not obtained. Similar reactions were carried out in 1:4 or 1:7 ratio of **1a** and 2,6-xylyl isocyanide, and the complex **2a** was isolated as the only product. The infrared spectrum showed three characteristic bands at 2175, 1630, 1580 cm^{-1}, the first band is assigned to the terminal isocyanide, the latter, to the C=N double bond. The ^1H NMR spectrum showed five singlets due to the methyl groups at δ 1.72, 2.14, 2.19, 2.27_9 and 2.28_2 consisting of a 2:2:2:1:2 ratio. In the ^1H NMR spectra of a mixture of **2a** and 2,6-xylyl isocyanide, the peak at δ 2.14 showed a ligand exchange with free isocyanide and then was assigned to the terminal isocyanide, the peak at δ 2.27_9 to the methyl group, and other ones, to the *o*-methyl groups of inserted isocyanides. These spectroscopic data suggested multiple insertion of isocyanides into a palladium–methyl bond.

In an attempt to confirm the structure, an X-ray analysis was undertaken (Fig. 1 and Table 2). The molecule is square planar. The tris-imino group, formed by insertion of three isocyanide molecules into a Pd–CH_3 bond, acts as a bidentate ligand through σ- and N-coordination. The five-membered ring, [PdC(2)C(3)C(4)N(4)] has an envelope conformation. The torsion angle of N(2)–C(2)–C(3)–N(3) is 36°. This torsional structure is assumed to represent a step in the formation of the helical structure in asymmetric polymerization of isocyanide [5]. The bond angles of C(2)–Pd–N(4) and C(1)–Pd–I are 80.3(9)° and 87.2(7)°, respectively, compared with those (av. 79.9(5)° and av. 87.5(5)°) in $NiCl(^tBuNC)[(C{=}N^tBu)_2(C(CH_3){=}N^tBu)]$ (**3**) (Table 2) [6]. Two other bond angles are greater than 90°. The Pd–C(1), Pd–C(2), and Pd–N(4) bond distances are 1.93(3), 2.03(2), and 2.08(2) Å, respectively. These bond distances are longer than the corresponding distances in **3**, due to difference of bond radii between palladium and nickel atoms.

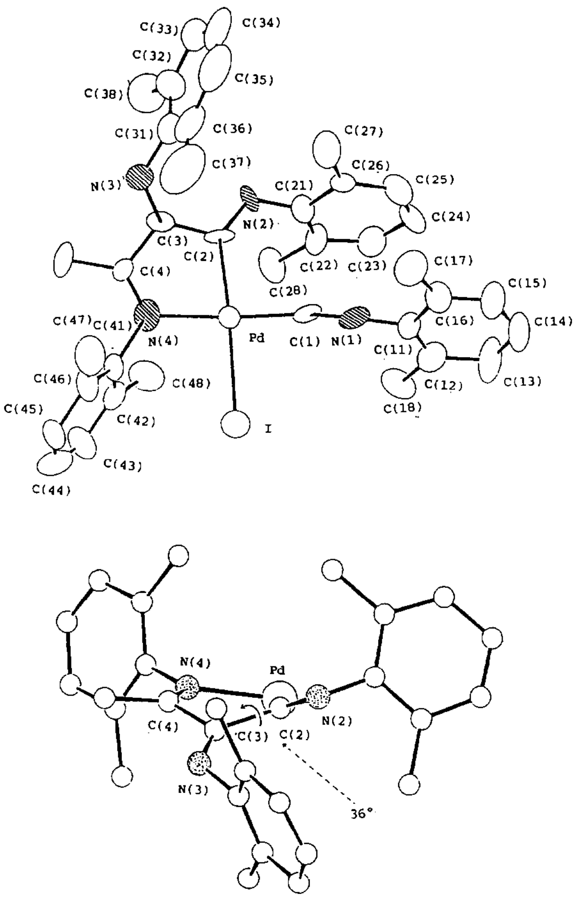


Fig. 1. Structure of the triple-isocyanide insertion complex **2a**.

The similar tris-iminoacyl complex (**2b**) was also obtained as the only product by using 2,4,6-mesityl isocyanide. The complex, $Pd(PPh_3)_2Br(Ph)$ reacted with 2,6-xylyl or 2,4,6-mesityl isocyanide to give tris-iminoacyl complexes (**2c**, **2d**) as the only isolated product.

The reactions of the methyl- or phenyl complex with bulky isocyanides such as $2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC$ or $2,4,6\text{-}t\text{-}Bu_3C_6H_2NC$ led to recovery of the starting complex even at 60°, due to the steric bulk of the

TABLE 1. Reaction of $Pd(PPh_3)_2(R')(X)$ with RNC

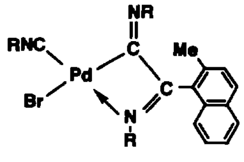
R	R'(X)	complex		[RNC]/[(1)] [a]	Yield(%) [b]
Xyl	CH_3(I)	$Pd(XylNC)_4(CH_3)I$	**2a**	1	25
Xyl	CH_3(I)			4	37
Xyl	CH_3(I)			7	25
Mes	CH_3(I)	$Pd(MesNC)_4(CH_3)I$	**2b**	1	14
Mes	CH_3(I)			4	24
Xyl	Ph(I)	$Pd(XylNC)_4(Ph)I$	**2c**	4	85
Mes	Ph(I)	$Pd(MesNC)_4(Ph)I$	**2d**	4	84
Xyl	Nap*(Br) [c]	$Pd(XylNC)_3(Nap^*)Br$	**2e**	4	50
$p\text{-}NO_2C_6H_4$	Ph(Br)	$Pd(PPh_3)_2(p\text{-}NO_2C_6H_4)(Ph)Br$	**2f**	1	65

[a] Molar ratio. [b] Based on the starting palladium complex. [c] Nap* = 2-methyl-1-naphthyl.

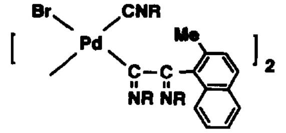
TABLE 2. Selective bond distances (Å) and angles (deg) for complex **2a**

Bond distances			
Pd–I	2.694(3)	Pd–N(4)	2.08(2)
Pd–C(1)	1.93(3)	Pd–C(2)	2.03(2)
N(1)–C(1)	1.15(3)	N(1)–C(11)	1.38(3)
N(2)–C(2)	1.28(3)	N(2)–C(21)	1.37(3)
N(3)–C(3)	1.23(3)	N(3)–C(31)	1.43(4)
N(4)–C(4)	1.24(3)	N(4)–C(41)	1.47(3)
C(2)–C(3)	1.54(3)	C(3)–C(4)	1.5(3)
C(4)–C(5)	1.51(4)		
Bond angles			
I–Pd–N(4)	96.7(5)	I–Pd–C(1)	87.2(7)
I–Pd–C(2)	176.8(7)	N(4)–Pd–C(1)	175.8(8)
N(4)–Pd–C(2)	80.3(9)	C(1)–Pd–C(2)	95.8(10)
C(1)–N(1)–C(11)	174(2)	C(2)–N(2)–C(21)	122(2)
C(3)–N(3)–C(31)	125(2)	Pd–N(4)–C(4)	119(2)
Pd–N(4)–C(41)	122(1)	C(4)–N(4)–C(41)	119(2)
Pd–C(1)–N(1)	172(2)	Pd–C(2)–N(2)	135(2)
Pd–C(2)–C(3)	106(1)	N(2)–C(2)–C(3)	119(2)
N(3)–C(3)–C(2)	130(2)	N(3)–C(3)–C(4)	118(2)
C(2)–C(3)–C(4)	112(2)	N(4)–C(4)–C(3)	113(2)
N(4)–C(4)–C(5)	128(2)	C(3)–C(4)–C(5)	119(2)

isocyanides. The bulky 2-methyl-naphthyl complex, *trans*-Pd(PPh$_3$)$_2$Br(2-CH$_3$C$_{10}$H$_6$) reacted with 2,6-xylyl isocyanide to give yellow crystals, formulated as Pd(2,6-Me$_2$C$_6$H$_4$NC)$_3$Br(2-CH$_3$C$_{10}$H$_6$). The infrared spectrum showed the presence of terminal and inserted isocyanide groups (**2e**). The ^{1}H NMR spectrum showed the presence of three methyl groups at δ 2.08, 2.16 and 2.90 consisting of a relative intensity of a 4:2:1 ratio. The last one is assigned to methyl protons of the naphthyl group and other bands, to *o*-methyl protons of the terminal and inserted isocyanide molecules. Only two signals were observed for three kinds of isocyanide groups, probably due to an accidental degeneracy of the chemical shifts. Based on the spectroscopic data and the structural results of known insertion-products [1], two possible structures (**A** and **B**) are considered as follows:



(A)



(B)

If the complex has a bridged structure (**B**), the reaction of the complex with Lewis bases will lead to cleavage of halogen bridges. However, since such a reaction recovered the starting materials, it is considered that the complex has the **A** structure.

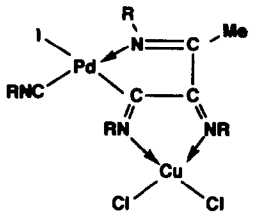
Previously we reported that the insertion reaction of the methyl palladium(II) complex, *trans*-Pd(PPh$_3$)$_2$I(CH$_3$) with cyclohexyl isocyanide proceeded stepwise to give a triple insertion product [2a]. In the present reactions, selective and spontaneous triple-insertions into the methyl or phenyl palladium complex of *ortho*-substituted phenyl isocyanide were observed. A similar selective multiple-insertion has been noted in reactions of μ-ethynediyl complexes of palladium(II) with isocyanides, such as phenyl, 4-nitrophenyl, and 2,6-xylyl isocyanide [4].

The dependence of reactivity on the isocyanide is not necessarily due to steric constraints, because the reaction of phenyl complex with 4-nitrophenyl isocyanide gave the mono-imino compound, *trans*-Pd(PPh$_3$)$_2$I[C(=NC$_6$H$_4$-4-NO$_2$)Ph]. The insertion reaction was controlled by delicate electronic and steric balances between alkyl (and/or aryl) and incoming isocyanide. There is no information on their origin yet.

It is due to the great stability of the five-membered chelate structure of the compound **2a–2d** that further insertion did not occur. This is confirmed by the fact that treatment of **2a** with carbon monoxide (50 kg cm^{-2}) at 50°C led to a recovery of the chelate complex.

2.1. *Reaction of 2 with copper(II) chloride*

It was well known that Schiff's bases and oximes coordinated to various metals. Bis-iminoacyl metal complexes reacted with metal halides such as those of iron, cobalt, nickel, copper and zinc to give mixed-metal complexes [7].



Reactions of **2a** with metal halides were carried out. When copper(II) chloride was added to a solution of **2a** in CH$_2$Cl$_2$, the colour changed from reddish brown to dark brown, from which brown crystals of **3**, formulated as [PdCu(2,6-Me$_2$C$_6$H$_4$NC)$_4$(CH$_3$)ICl$_2$] were isolated. The infrared spectrum of **3** appeared at 2190, 1670, 1640, and 1590 cm^{-1}. The terminal ν(N≡C) band shifted to higher energy than that of the starting compound **2a**, suggesting coordination of imino-nitrogen to copper atom. In the electronic spectrum, the lowest energy band red-shifted by *ca.* 80 nm. These spectroscopic data suggest that the compound **3** has a mixed-metal structure in which α- and β-imino-nitrogens are coordinated to the copper atom.

Cobalt(II) chloride reacted with compound **2a**, but an isolated compound was not obtained. The cyclic voltammogram of **3** showed two irreversible reductive

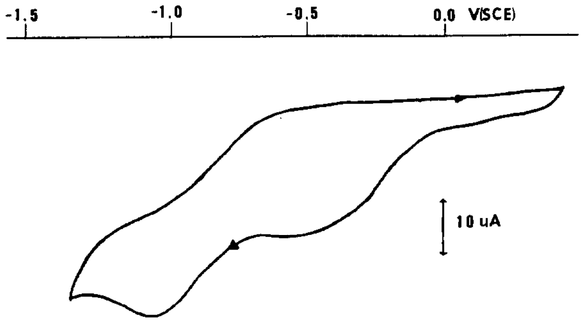


Fig. 2. Cyclic voltammogram of the palladium-copper complex 3. Concentration: *ca.* 1.0 mM solution/0.1 M [^{n}Bu$_4$N][ClO$_4$]-MeCN; scan rate: 0.2 V/s; working electrode: Pt chip electrode.

waves at −0.47 and −1.07 V (*vs.* SCE) (Fig. 2). Since the CV of compound **2a** did not appear at about −0.5 V and that of the model compound, [CuCl$_2$(HC=N(2,6-Me$_2$C$_6$H$_3$)$_2$] showed a quasi-reversible redox wave at −0.44 V (SCE), the reductive wave at −0.47 V is assignable to that of copper(II) ($Cu^{II} \rightarrow Cu^0$), and the wave at −1.07 V, to that of palladium(II) atom ($Pd^{II} \rightarrow Pd^0$). It has been known that reductive potentials of this type of palladium complexes and of those related to it often appeared in a similar region.

3. Experimental section

Isocyanides [8] and Ph(PPh$_3$)$_2$X(CH$_3$) (**1a**) [2a] were prepared by literature methods, some with modification. Electronic and infrared spectra were recorded on JASCO A-100 and JASCO U-best 30 spectrometers, respectively. ^{1}H NMR spectra were measured on a JEOL GX-400 instrument. Cyclic voltammograms were measured by a potential scanning unit model 312. Electronic measurements were carried out in a 0.1 M solution of (^{n}Bu$_4$N)(ClO$_4$)-MeCN under an atmosphere of nitrogen after the solution was deaerated by bubbling with nitrogen. The reference electrode was a Ag/AgNO$_3$ (0.1 mol dm^{-3})-(^{n}Bu$_4$N)(ClO$_4$)/MeCN (0.1 mol dm^{-3}) system, whose potential was determined relative to SCE ($E = +0.375$ V *vs.* SCE). All reactions were carried out under an atmosphere of nitrogen.

3.1. *Reaction of trans-Pd(PPh$_3$)$_2$I(CH$_3$) (1a) with 2,6-xylyl isocyanide in a 1:1 ratio*

2,6-Xylyl isocyanide (0.034 g, 0.26 mmol) was added to a solution of *trans*-Pd(PPh$_3$)$_2$I(CH$_3$) (0.20 g, 0.26 mmol) in benzene (20 ml) at ice cool temperature. After stirring for 2 h at room temperature, the solvent was removed under reduced pressure, and the residue was chromatographed on deactivated alumina (containing 10% H$_2$O), using benzene as an eluant. The reddish brown band was collected, and the removal of the solvent and crystallization of the residue from benzene and hexane gave reddish brown crystals of **2a** (0.05 g, 25%). IR (Nujol): 2175 (N≡C), 1630, 1580 (C=N) cm^{-1}. Electronic spectra (C$_6$H$_6$): λ 342 (log ε 4.54) and 476 sh (3.67) nm. Found: C, 57.16; H, 5.00, N, 7.25. Calcd for C$_{37}$H$_{39}$N$_4$IPd: C, 57.49; H, 5.08; N, 7.25%. When the reaction of **1a** with 2,6-xylyl isocyanide was carried out in a 1:6 or 1:7 ratio, the similar compound **2a** was obtained. Other tris-iminoacyl complexes, Pd(2,4,6-Me$_3$C$_6$H$_2$NC)$_4$I(CH$_3$) (**2b**) and Pd(2,6-Me$_2$C$_6$H$_4$NC)$_4$-I(Ph) (**2c**) were prepared by a similar method to that described above. **2b**: IR (Nujol): 2175 (N≡C), 1630 1590 (C=N) cm^{-1}. Electronic spectrum (C$_6$H$_6$): λ 343 (4.02), 460sh (1.0) nm. Found: C, 59.27; H. 5.79; N, 6.48. Calcd for C$_{41}$H$_{47}$IPd: C, 59.27, H, 5.71; N, 6.48%. **2c**: IR (Nujol): 2180 (N≡C), 1625, 1580 (C=N) cm^{-1}. Electronic spectrum (C$_6$H$_6$): λ 343 (2.8), 464sh (0.2) nm. Found: C, 60.84; H, 5.10; N, 6.20. Calcd for C$_{42}$H$_{41}$N$_4$IPd: C, 60.41; H, 4.95; N, 6.71%.

3.2. *Reaction of trans-Pd(PPh$_3$)$_2$Br(2-methylnaphthyl) with 2,6-xylyl isocyanide in a 1:4 ratio*

A mixture of *trans*-Pd(PPh$_3$)$_2$Br(2-methylnaphthyl) (0.2 g, 0.23 mmol) and 2,6-xylyl isocyanide (0.13 g, 0.98 mmol) was stirred at room temperature. After 2 h, work-up as described above gave yellow crystals of **2e** (0.08 g, 50%). IR (Nujol): 2170 (N≡C), 1620 (C=N) cm^{-1}. Found: C, 63.54; H, 5.44; N, 5.55. Calcd for C$_{38}$H$_{36}$N$_3$BrPd: C, 63.30; H, 5.03; N, 5.83%.

3.3. *Reaction of trans-Pd(PPh$_3$)$_2$I(Ph) with p-nitrophenyl isocyanide*

A mixture of *trans*-Pd(PPh$_3$)$_2$(Ph)I (0.12 g, 0.14 mmol) and *p*-NO$_2$C$_6$H$_4$NC (0.028 g, 0.19 mmol) was stirred at room temperature and the solution changed from yellow-orange to brownish-orange. After 2 h, work-up as described above and crystallization from benzene-hexane gave brownish orange crystals of **2f** (0.092 mg, 65%). IR (Nujol): 1585 (C=N) cm^{-1}. Electronic spectrum (C$_6$H$_6$): λ 330 (7.36) nm. Found: C, 59.41; H, 3.75; N, 2.81. Calcd for C$_{49}$H$_{39}$N$_2$O$_2$P$_2$IPd: C, 59.82; H, 3.97; N, 2.85%.

3.4. *Reaction of 2a with CuCl$_2$*

A mixture of **2a** (0.10 g, 0.13 mmol) and CuCl$_2$ (0.21 g, 0.16 mmol) in CH$_2$Cl$_2$ (8 ml) was stirred at room temperature. The solution changed from reddish-brown to brown. After 2 h, removal of the solvent and crystallization of the residue from CH$_2$Cl$_2$ and ether gave brown crystals (0.02 g, 17%) of **3**, The complex contains 1/2CH$_2$Cl$_2$ as a solvated molecule. IR (Nujol): 2190

(N≡C), 1670, 1640, 1590 (C=N) cm^{-1}. Electronic spectrum (CH_2Cl_2): λ 346(6.0), 425sh (1.6) nm. Found: C, 47.22; H, 4.33; N, 5.58. Calcd for $C_{37.5}H_{40}N_4Cl_3ICuPd$: C, 47.41; H, 4.24; N, 5.90%.

3.5. *Reaction of 2a with carbon monoxide*

A benzene solution (20 ml) of **2a** (0.05 g) in a 100 ml autoclave was charged with carbon monoxide (50 kg/cm^2) and was kept stirring at 110°C. After 2 h, carbon monoxide was purged and the solvent was removed to dryness. The residue was identified as the starting compound **2a**.

3.6. *X-ray structure determination for complex 2a*

The preliminary data collection showed the crystal to be triclinic, with the space group $P1$. Crystal data. $C_{37}H_{39}N_4IPd$, M 773.1, $a = 14.638(9)$, $b = 15.662(7)$, $c = 7.805(3)$ Å, $\alpha = 85.06(3)$, $\beta = 82.84(4)$, $\gamma = 102.41(4)°$, $U = 1722$ Å^3, $Z = 2$, and $D_c = 1.503$ g cm^{-3}.

Data collection was with a Rigaku AFC-6 diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.7107$ Å) radiation with $3 < 2 < 60°$ and the ω ($\geq 30°$) and ω–2θ ($< 30°$) scan techniques with a scan rate 4°min^{-1}. Of 3500 reflections measured, 2076 [$F_o > 5\sigma(F_o)$] were used in the calculations. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient was $\mu = 1.44$ mm^{-1}, and an empirical absorption correction was made. The positions of the Pd and I atoms were determined with MULTAN 78 [9]. The other non-hydrogen atom positions were subsequently found from a series of Fourier difference maps [10]. Hydrogen atoms were placed in calculated positions (C–H for the methyl groups = 1.09 Å and C–H for the aromatic rings = 1.08 Å). All non-hydrogen atoms were refined anisotropically, using block-diagonal least-squares methods, minimizing $\Sigma w(F_o - |F_c|)$ and hydrogen atoms were refined isotropically. The final $R(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}\}$ values were 0.066 and 0.078 ($w = 1$) (number of variables refined = 428), respectively. A final Fourier difference map showed no residual peaks greater than 0.86 eÅ^{-3} around the palladium atom. Anomalous dispersion effects were included in the calculation of Fc by using $\Delta f'$ and $\Delta f''$. The atomic scattering factors for Pd, I, N and C were from ref. 11. The final atomic coordinates except those of hydrogen atoms are listed in Table 3.

4. Supplementary material available

Listings of anisotropic thermal parameters, atomic parameters of hydrogen atoms and bond distances and angles, and a table of structure factor amplitudes are available from the authors.

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