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Regioselectivity in metallation reactions of 2-(2′-naphthyl)pyridine: 1′- versus 3′-reactivity in mercuration and palladation reactions. Crystal structure of chloro(pyridine)[2-(2′-pyridinyl)naphthyl-C^3,N]palladium ☆

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Abstract

Regioselectivity is found to vary with the reagent in cyclometallation reactions of 2-(2′-naphthyl)pyridine. Mercuration produces a mixture of 1′- and 3′-naphthyl metallated species with the 1′-substituted material as the major product. Palladation results in clean 3′-naphthyl metallation, as confirmed by the crystal structure of the pyridine derivative chloro(pyridine)[2-(2′-pyridinyl)naphthyl-C^3,N]palladium.

Keywords: Mercury; Palladium; Cyclometallation; Crystal structure

1. Introduction

N,*N*-Donor ligands such as 2,2′-bipyridyl and 1,10-phenanthroline have been shown to suppress double-bond cleavage in ruthenium-catalysed oxidation reactions of olefins and hence promote useful epoxidations [1,2]. Attempts to carry out this reaction enantioselectively by using chiral *N*,*N*-ligands have so far met with limited success [3,4]. Ligands based on 1,2-di(2′-pyridyl)benzene (**1**) and in particular the isoquinoline **2** are possible candidates for use in these asymmetric transformations. During work directed towards the synthesis of **2** and related compounds, we required a metallated derivative of 2-(2′-naphthyl)pyridine (**3**) that could be used directly or indirectly in the formation of the critical naphthyl–isoquinoline bond. As there are precedents for cyclometallation [5] of 2-phenylpyridine with mercury [6] and palladium [7], we examined the applicability of these reactions to the functionalization of 2-(2′-naphthyl)pyridine. We report here that the use of mercury(II) trifluoroacetate results in the desired mercuration of the 1′-naphthyl position whereas directed palladation leads to exclusive 3′-substitution. Directed lithiation [8] and magnesiation [9] are found not to be effective strategies.

2. Results and discussion

We find that 2-(2′-naphthyl)pyridine (**3**) is most conveniently prepared using the Suzuki boronic acid coupling reaction [10]. 2-Naphthylboronic acid (obtained in quantitative yield from 2-bromonaphthalene via lithium–halogen exchange followed by $B(OMe)_3$ quench and acid hydrolysis) couples with 2-bromopyridine in the presence of $Pd(PPh_3)_4$ and $Ba(OH)_2 \cdot 8H_2O$ in aqueous DME in 60–70% yield. To aid in the identification of the metallated products, the proton NMR spectrum of **3** was investigated in some detail, and fully assigned with the aid of ^1H:^1H COSY techniques. The 1′-naphthyl proton is clearly visible in both $CDCl_3$ (δ_H 8.41) and DMSO-D_6 (δ_H 8.67) coupled to H-(C3′) ($J_{1',3'}$ = 1.6–1.7 Hz). The 3′-naphthyl proton can also be seen, coupled to H-(Cl′) and H-(C4′) with coupling constants of 1.6 Hz ($J_{3',1'}$) and 8.8 Hz ($J_{3',4'}$), respectively, in $CDCl_3$.

☆ The organometallic complexes reported here are named according to the IUPAC system of nomenclature; thus the precedence of the naphthyl and pyridyl functions exchanges upon metallation. Within this paper, primed hydrogens (H′) always refer to the naphthyl ring protons to facilitate comparison of the ^1H NMR spectra of the metallated and free ligands.

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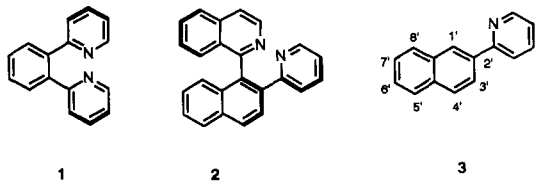

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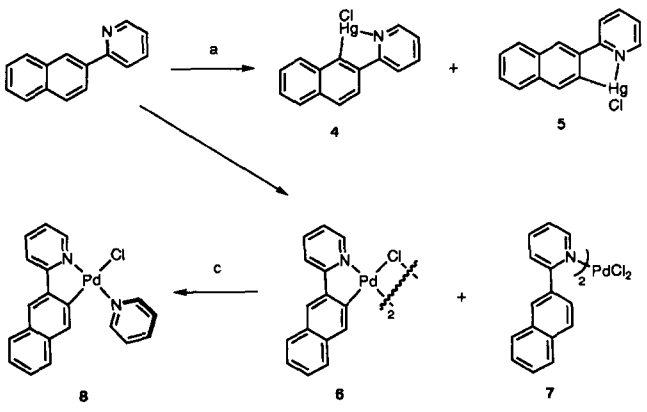
Attempts to metallate 2-(2′-naphthyl)pyridine using lithium or magnesium reagents were unsuccessful. No reaction was observed with either LDA at −30 or 0°C or with DA_2Mg [11] at room temperature. Reaction with t-BuLi at −78°C led to nucleophilic attack at the 1′-naphthyl position, as indicated by ^{1}H NMR spectrum of the crude product mixture.

2.1. Mercuration reactions

Initial mercuration reactions were carried out by use of mercury(II) acetate in absolute ethanol under reflux for 48 h followed by addition of LiCl. These conditions led to a 20–40% conversion of **3** into a mixture of chloro[2-(2′-pyridinyl)naphthyl-C^1,N]mercury (**4**) and its isomeric C^3-mercurated complex (**5**) (Scheme 1). The mixture is typically isolated with a regioisomeric ratio of 1.6:1 in favour of **4**. The ratio of the two regioisomers is conveniently determined by ^{1}H NMR spectroscopy as the 1′-naphthyl proton in **5** is clearly visible and well separated from other signals. Polymercuration was not encountered in these reactions although prolonged reaction times (> 60 h) led to complicated mixtures; the latter effect originates in the high tendency of arylmercury species to undergo metal migration, resulting in statistical mixtures of all possible regioisomers [12]. Shorter reaction times result in a lower yields but a higher proportion of **4**.

The more reactive electrophile mercury(II) trifluoroacetate [13] under similar conditions gives higher yields of the mercurated products **4**–**5** (60%) after 24 h



Scheme 1. Reaction conditions a: (i) $Hg(OAc)_2$ [or $Hg(O_2CCF_3)_2$], (ii) LiCl. b: $Li_2[PdCl_4]$-NaOAc. c: C_5H_5N.

and also a regiochemical distribution that is shifted in favour of 1′-substitution (2.2:1 ratio of **4**:**5**), as determined by ^{1}H NMR spectroscopy. Addition of base (2,6-dichloropyridine, chosen because it is deactivated towards electrophilic substitution and sterically hindered, preventing coordination with the mercury) causes an increase in the rate of mercuration of **3** but a decrease in the regioselectivity (a **4**:**5** ratio of 1.5:1 results). No significant effect on the total conversion of **3** is observed.

The chloromercurated products **4**–**5** are only sparingly soluble in chlorinated solvents and completely insoluble in diethyl ether, toluene and light petroleum. Their solid-state structure probably consists of dimeric or oligomeric units with bridging chlorides [14], which must be broken up before the material will dissolve. This is supported by the fact that strongly coordinating, basic ethers such as THF or DME will dissolve the product, and after recrystallization from hot DME, pure chloro[2-(2′-pyridinyl)naphthyl-C^1,N]mercury (**4**) is obtained in 33% yield based on 2-(2′-naphthyl)pyridine. All attempts to grow crystals suitable for X-ray analysis were unsuccessful, however, as the product favours a fern-like microneedle habit.

2.2. Palladation reactions

Directed palladation is well known and normally takes place at the site of highest electron density [15]. A survey of the literature suggests that 1′-palladation should be expected, but reaction of 2-(2′-naphthyl) pyridine with Li_2PdCl_4 in MeOH results in a 71% yield of dichlorobis[2-(2′-pyridyl)naphthyl-C^3,N]dipalladium (**6**) as a very insoluble yellow powder. The unpalladated complex $[PdCl_2(\mathbf{3})_2]$ (**7**) initially remains in solution but is deposited on standing as dark red–brown crystals, complicating the work-up. This problem is overcome by the addition of NaOAc to the reaction mixture, which results in the exclusive formation of the palladated dimer **6** in 93% yield. The dimer **6** is probably a mixture of *cis*- and *trans*-isomers, but the ^{1}H NMR spectra of **6** proved very broad and uninformative, preventing confirmation of this hypothesis. Additionally, the low solubility of the product **6** precludes recrystallization, so analytically pure material could not be obtained. We sought to overcome these problems by preparing a pyridine derivative of **6** by simple halide bridge cleavage.

When the palladium complex **6** is suspended in CH_2Cl_2 and treated with one equivalent of pyridine, the chloride bridges of the dimer are cleaved and the complex chloro(pyridine)[2-(2′-pyridinyl)naphthyl-C^3,N] palladium (**8**) is formed. A mutually *trans* arrangement of the two nitrogen donors is suggested by the pronounced low-frequency shift of the 1′-naphthyl hydro-

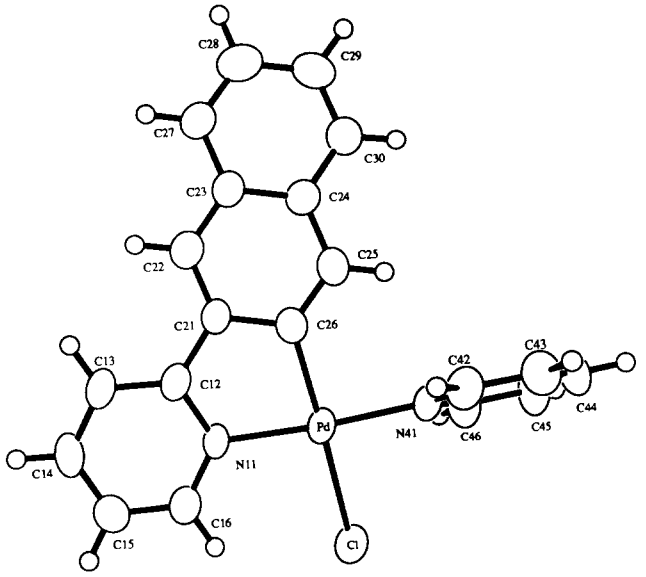


Fig. 1. Molecular structure of **8** together with numbering scheme.

gen (δ_H 6.53) in **8** compared with the free ligand **3** (δ_H 8.41). Such behaviour is best explained by the close proximity of a pyridyl ring current in a *trans-N,N* complex. The ^{1}H NMR spectrum of crude **8** also reveals the presence of a small second set of signals very similar to those from **8**, presumably belonging to the isomeric complex in which the two nitrogen donors are mutually *cis*, formed in trace amounts during the cleavage of the dimer **6**. The low yield of this by-product prevents its isolation but the presence of a small amount of an *cis-N,N*-isomer is not unexpected in view of the similar *trans* influences of the chloride and pyridyl ligands. Such an arrangement has been suggested recently for a close analogue of our complex, i.e. [PdCl(3-$C_{10}H_6CH_2NMe_2$-2)(C_5H_5N)] [16]. We note in passing, however, that the ^{1}H NMR spectrum reported for this complex [δ_H 6.36, H-C(1′)] also strongly indicates a *trans-N,N* arrangement analogous to that in **8**.

Single-crystal X-ray analysis of **8** (major isomer) reveals the structure shown in Fig. 1. Final positional parameters for **8** are given in Table 1 and selected bond lengths and angles in Table 2. The molecule is essentially planar except for the pyridine ligand, which is rotated by 70° with respect to the central Cl–N–C–N plane. The pyridylnaphthalene ligand is fairly flat, the pyridine ring being bent by only 4° away from the naphthalene fragment. Since we carried out these experiments, similar regioselectivity has been observed for the palladation of 2-[(dimethylamino)methyl]naphthalene by Valk et al. [16], who reported the structure of the derivative [Pd{BH(pz)$_3$}(3-$C_{10}H_6CH_2NMe_2$-2)] (**9**). Despite their different constitutions, complexes **8** and **9** show very similar coordination geometries about palladium if one neglects the obvious substitution of a pyrazolylborate for the chloride and pyridine ligands in

Table 1
Positional parameters for **8**

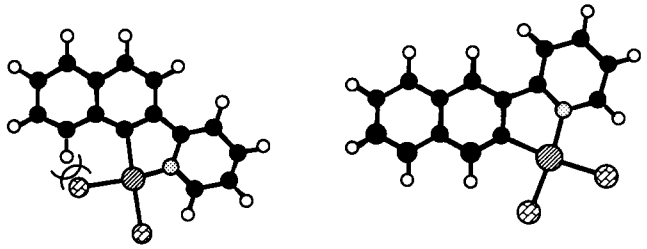
Atom	x	y	z
Pd	0.09480(6)	0.05160(3)	0.21246(3)
Cl	0.3212(2)	0.1375(1)	0.1668(1)
N(11)	0.1378(6)	−0.0348(2)	0.1021(3)
N(41)	0.0450(6)	0.1275(3)	0.3355(4)
C(12)	0.0238(7)	−0.0946(3)	0.0948(4)
C(13)	0.0493(7)	−0.1582(3)	0.0251(4)
C(14)	0.1896(8)	−0.1610(4)	−0.0329(4)
C(15)	0.3034(8)	−0.1010(4)	−0.0235(5)
C(16)	0.2736(8)	−0.0377(3)	0.0436(5)
C(21)	−0.1151(7)	−0.0839(3)	0.1630(4)
C(22)	−0.2504(8)	−0.1335(3)	0.1622(4)
C(23)	−0.3842(8)	−0.1193(3)	0.2271(4)
C(24)	−0.3776(7)	−0.0501(4)	0.2945(4)
C(25)	−0.2353(8)	0.0003(3)	0.2951(5)
C(26)	−0.1054(7)	−0.0146(3)	0.2322(4)
C(27)	−0.5253(8)	−0.1698(4)	0.2283(5)
C(28)	−0.6547(8)	−0.1533(4)	0.2902(5)
C(29)	−0.6495(8)	−0.0854(4)	0.3569(5)
C(30)	−0.5164(8)	−0.0341(3)	0.3584(5)
C(42)	0.0732(8)	0.1064(4)	0.4375(5)
C(43)	0.0443(8)	0.1569(4)	0.5206(5)
C(44)	−0.0178(8)	0.2319(4)	0.4998(5)
C(45)	−0.0446(9)	0.2549(4)	0.3953(5)
C(46)	−0.0107(9)	0.2016(4)	0.3149(5)

8. For example, the Pd–C bond lengths are identical within experimental error (1.982(6) Å in **8**; 1.987(2) Å, average of two independent molecules in **9**), as are the C–Pd–$N_{chelate}$ angles (81.7(2)° in **8**; 81.76(9)° average in **9**). However, the Pd–$N_{chelate}$ distances do differ slightly (Pd–N(11) 2.041 Å in **8**; Pd–NMe_2 2.084(2) Å average in **9**) owing to the different natures of the two nitrogen chelate donor atoms.

Fig. 2 shows molecular models of the two possible regioisomeric palladation products, the chloride bridges being represented by two chlorine atoms. The model for 1′-substitution (Fig. 2(A)) clearly shows the unfavourable interaction between H-(C8) and the chloride

Table 2
Selected bond lengths (Å) and angles (°) for **8**

Bond	Length	Bond	Length
Pd–Cl	2.414(2)	Pd–C(26)	1.982(6)
Pd–N(11)	2.041(4)	Pd–N(41)	2.052(4)
N(11)–C(12)	1.359(6)	C(12)–C(21)	1.452(7)
N(11)–C(16)	1.348(7)	C(21)–C(26)	1.447(7)
N(41)–C(42)	1.333(7)	C(25)–C(26)	1.364(7)
Atoms	**Angle**	**Atoms**	**Angle**
Cl–Pd–N(11)	96.0(1)	Cl–Pd–N(41)	89.3(1)
Cl–Pd–C(26)	172.6(2)	N(11)–Pd–N(41)	173.2(2)
N(11)–Pd–C(26)	81.7(2)	N(41)–Pd–C(26)	93.5(2)
Pd–(N11)–C(12)	115.6(5)	Pd–C(26)–C(21)	113.1(4)
Pd–N(11)–C(16)	124.4(4)	Pd–C(26)–C(25)	128.5(4)
Pd–N(41)–C(42)	121.7(4)	C(12)–C(21)–C(26)	115.5(4)
N(11)–C(12)–C(21)	114.0(5)	C(13)–C(12)–C(21)	127.1(5)



(A) (B)

Fig. 2. Ball-and-stick representations showing (A) 1'-palladation versus (B) 3'-palladation of 2-(2'-naphthyl)pyridine.

bridge atom. No such interaction is present in reaction coordinates leading to either 3'-palladation or mercuration at either site (owing to the linear mercury coordination geometry). Comparison of the two reactions reveals that electronic effects (relative electron density at C(1') and C(3')) are the dominant factors in mercuration whereas steric factors control the palladation reaction.

3. Experimental

Reactions involving air-or moisture-sensitive reagents were carried out under an atmosphere of dry nitrogen. Where appropriate, solvents were dried by standard procedures. Butyllithium, $B(OMe)_3$, 2-bromopyridine and mercury(II) trifluoroacetate were purchased from Aldrich. 2-Bromonaphthalene was supplied by Lancaster. The complex $Pd(PPh_3)_4$ was prepared by a published procedure [17]. The NMR spectra were recorded on Jeol-270 (270 MHz) or Bruker WH-400 (400 MHz) instruments. Chemical shifts are in ppm, coupling constants are in hertz and protons are numbered according to the carbon to which they are connected. For assignments of naphthylpyridine derivatives, primed hydrogens (H') refer to the naphthyl ring. IR spectra were recorded as KBr discs using a Perkin-Elmer 983 G instrument. Mass spectra were obtained with a Finnegan 1020 instrument operating under electron impact (EI) ionization or with a VG-ZAB instrument using fast atom bombardment (FAB). Elemental analyses were carried out with a Fisons EA 1108 machine.

3.1. 2-Naphthylboronic acid

A solution of ^nBuLi (1.6 M in hexanes, 100 cm^3, 0.16 mol) was added via a cannula to 2-bromonaphthalene (30 g, 0.14 mol) in dry THF (200 cm^3) at −78°C. The yellow suspension was stirred at this temperature for 30 min then $B(OMe)_3$ (26.6 cm^3, 29.1 g, 0.28 mol) in dry THF (150 cm^3) was added dropwise, with the temperature kept below −60°C. The resulting colourless solution was allowed to warm slowly to room temperature overnight, then 10 M HCl (ca. 300 cm^3) was added and the mixture stirred for a further 1 h under nitrogen. Water and Et_2O were added, and the aqueous layer was extracted several times with Et_2O. The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield a white solid (23.6 g, 98%), which was used in the coupling reaction without further purification. ^1H NMR (270 MHz, DMSO-d_6) δ_H 8.37 (s, 1 H, H1), 8.18 (s, 2 H, $B(OH)_2$), 7.95–7.83 (m, 4 H, ArH), 7.55–7.48 (m, 2 H, ArH).

3.2. 2-(2'-Naphthyl)pyridine (3)

To a stirred mixture of 2-bromopyridine (7.9 g, 50 mmol) and $Pd(PPh_3)_4$ (1.7 g 1.5 mmol) in DME (200 cm^3) were added, under a counterflow of dry nitrogen, 2-naphthylboronic acid (10.0 g, 60 mmol), water (100 cm^3) and $Ba(OH)_2 \cdot 8H_2O$ (23 g, 75 mmol). The mixture was heated under reflux (20 h) and the allowed to cool to room temperature, filtered through Celite, and the celite washed with water and CH_2Cl_2. The organic phase in the filtrate was separated, the aqueous layer extracted with CH_2Cl_2(2 × 200 cm^3) and the combined organic extracts were evaporated to leave a dark brown oil. This was dissolved in Et_2O (200 cm^3) and the solution washed with ca. 2 M HCl (5 × 100 cm^3). The aqueous layer was washed with Et_2O, made basic by the addition of NaOH pellets and extracted several times with CH_2Cl_2 (100 cm^3 portions). The dried ($MgSO_4$) solution was stirred for 20 min with activated charcoal and, after filtration, the solvent was removed to give a colourless oil, which solidified to a white, crystalline solid. The solid was warmed under vacuum to remove traces of pungent-smelling 2-bromopyridine. A yield of 6.66 g (65%) was obtained of material with physical properties in accord with published values [18]. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.67 (ddd, 1 H, $J_{6,3}$ = 0.94, $J_{6,4}$ = 1.8, $J_{6,5}$ = 4.8, H6), 8.41 (d, 1 H, $J_{1',3'}$ = 1.6, H1'), 8.06 (dd, 1 H, $J_{3',1'}$ = 1.6, $J_{3',4'}$ = 8.8, H3'), 7.90–7.85 (m, 1 H, H8'), 7.87 (d, 1 H, $J_{4',3'}$ = 8.8, H4'), 7.83–7.79 (m, 2 H, H3, H5'), 7.72 (dt, 1 H, $J_{4,6}$ = 1.8 $J_{4,3} \approx J_{4,5}$ = 7.5, H4), 7.45–7.41 (m, 2 H, H6', H7'), 7.19 (ddd, 1 H, $J_{5,3}$ = 1.1, $J_{5,6}$ = 4.8, $J_{5,4}$ = 7.5, H5); (400 MHz, DMSO-d_6) δ_H 8.72 (ddd, 1 H, $J_{6,3}$ = 1.0, $J_{6,4}$ = 1.8, $J_{6,5}$ = 4.7, H6), 8.67 (d, 1 H, $J_{1',3'}$ = 1.7, H1'), 8.27 (dd, 1 H, $J_{3',1'}$ = 1.7, $J_{3',4'}$ = 8.6, H3'), 8.14 (dt, 1 H, $J_{3,6} \approx J_{3,5}$ = 1.0, $J_{3,4}$ = 8.0, H3), 8.06–8.04 (m, 1 H, H5'/8'), 8.03 (d, 1 H, $J_{4',3'}$ = 8.6, H4'), 7.97–7.93 (m, 1 H, H8'/5'), 7.93 (ddd, 1 H, $J_{4,6}$ = 1.8, $J_{4,5}$ = 7.5, $J_{4,3}$ = 8.0, H4), 7.57 (m, 2 H, H6', H7'), 7.39 (ddd, 1 H, $J_{5,3}$ = 1.0, $J_{5,6}$ = 4.7, $J_{5,4}$ = 7.5, H5). IR 3050 w (C–H), 1587 m (C–N), 1475 m, 1435 w (C–C), 780 m, 740 s (C–H) cm^{-1}. Mass spectrum (EI) m/z 205 ($M^{+\cdot}$).

3.3. Mercuration of 2-(2'-naphthyl)pyridine

A stirred mixture of 2-(2'-naphthyl)pyridine (4.44 g, 22 mmol) and mercury(II) trifluoroacetate (9.23 g, 22

mmol) in absolute ethanol (100 cm^3) was heated under reflux (24 h). A solution of LiCl (2 g, 44 mmol) in methanol (50 cm^3) was added, causing instant formation of a white precipitate that turned mauve very quickly. The mixture was stirred under reflux for a further 15 min, then cooled to room temperature, diluted with water (about 200 cm^3) and filtered. The precipitate was washed with water until the washings were colourless and once with Et_2O (50 cm^3). The residual grey solid was extracted repeatedly with CH_2Cl_2 and the combined extracts were dried over $MgSO_4$ and reduced to dryness on a rotary evaporator. The resulting white solid was dried under vacuum, yield 5.9 g (60%), shown by ^1H NMR to be a 2.2:1 mixture of 1'- and 3'-mercurated materials. Recrystallization from hot DME gave pure chloro[2-(2'-pyridinyl)naphthyl-C^1,N] mercury (**4**) as a white powder (3.0 g, 33%). ^1H NMR (270 MHz, $CDCl_3$) δ_H 8.69 (ddd, 1 H, $J_{6,5} = 1.0$, $J_{6,4} = 1.7$, $J_{6,5} = 4.9$, H6), 8.13 (d, 1 H, $J_{3',4'} = 8.9$, H3'), 8.09–8.05 (m, 2 H, H3, H5'), 7.93 (d, 1 H, $J_{4',3'} = 8.9$, H4'), 7.91–7.86, (m, 1 H, H8'), 7.88 (ddd, 1 H, $J_{4,6} = 1.7$, $J_{4,3} = 3.7$, $J_{4,5} = 7.6$, H4) 7.63–7.52 (m, 2H, H6', H7'), 7.44 (ddd, 1 H, $J_{5,3} = 1.0$, $J_{5,6} = 4.9$, $J_{5,4} = 7.6$, H5). IR 3020 w (C–H), 1583 m (C–N), 1467 m, 1429 m, 1270 m (C–C), 765 s, 783 s (C–H) cm^{-1}. Mass spectrum (EI) m/z 441 (Hg isotope pattern, $M^{+\cdot}$), 204 ($[M - HgCl]^{+\cdot}$). Calculated for $C_{15}H_{10}ClHgN$: C 40.92, H 2.29, N 3.18. Found: C 40.91, H 2.31, N 3.44%.

3.4. Dichlorobis[2-(2'-pyridyl)naphthyl-C^3,N]dipalladium (6)

A solution of Li_2PdCl_4 in methanol was prepared by heating $PdCl_2$ (1.78 g, 10 mmol) and LiCl (0.85 g, 20 mmol) in MeOH under nitrogen reflux for 90 min followed by filtration under nitrogen. To this was added a solution of NaOAc (0.82 g, 10 mmol) and 2-(2'-naphthyl)pyridine (2.05 g, 10 mmol) in hot methanol (100 cm^3) and the mixture was stirred at room temperature for 2 h. The yellow precipitate was filtered off and washed with water, ethanol and Et_2O before being dried under vacuum; yield 3.25 g (93%). ^1H NMR (270 MHz, DMSO-D_6) δ_H 9.37 (br, H6), 8.67–7.3 (br, m, all other Hs). IR 3025 w (C–H), 1610 s (C–N), 1480 s, 1409 m, 1130 m (C–C), 880 m, 775 s, 745 m (C–H) cm^{-1}. Mass spectrum (FAB) m/z 692 (Pd_2Cl_2 isotope pattern, $M^{+\cdot}$). Calculated for $C_{30}H_{20}Cl_2N_2Pd_2$: C 52.05, H 2.91, N 4.04. Found: C 51.10, H 2.71, N 3.73%.

In the absence of NaOAc, **6** is formed in 71% yield followed by subsequent crystallization of **7** from the mother liquors in ca. 20% yield. ^1H NMR (270 MHz, DMSO-d_6) δ_H 8.87 (dt, 1 H, $J_{6,5} = 5.1$, $J_{6,4}$ not resolved, H6), 8.40–8.35 (m, 2 H, ArH), 8.2–8.4 (m, 4 H, ArH), 7.53 (m, 1 H, ArH), 7.62 (m, 2 H, H6', H7'). IR 3010 w (C–H), 1605 s (C–N), 1530 s, 1455 m, 1385 m, 1225 m (C–C), 812 m, 780 s, 760 m (C–H) cm^{-1}. Mass spectrum (FAB) m/z 516 ($[M - Cl_2]^{+\cdot}$. No satisfactory analysis could be obtained.

3.5. Chloro(pyridine)[2-(2'-pyridinyl)naphthyl-C^3, N]palladium (8)

Pyridine (22 μl, 0.29 mmol) was added to a stirred suspension of **6** (100 mg, 0.14 mmol) in CH_2Cl_2. The yellow solution was filtered to remove a small amount of insoluble material then evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2–hexane to yield yellow crystals (50 mg, 40%). ^1H NMR (270 MHz, $CDCl_3$) δ_H 9.56 (dd, 1 H, $J_{6,4} = 1.0$, $J_{6,5} = 5.7$, H6), 9.05 (m, 2 H, H2,2'-pyridine), 7.98 (s, 1 H, H4'), 7.93 (m, 1 H, H4-pyridine), 7.90–7.86 (m, 2 H, ArH), 7.81–7.76 (m, 1 H, ArH), 7.53 (m, 2 H, H3,3'-pyridine), 7.43–7.34 (m, 3 H, ArH), 7.23 (dt, 1 H, $J_{5,4} = 2.7$, $J_{5,6} = 5.7$, H5), 6.53 (s, 1 H, H1'). IR 3025 w (C–H), 1595 s, 1580 m (C–N), 1475 m, 1440 s, 1300 m (C–C), 825 m, 792 s, 745 s (C–H) cm^{-1}. Mass spectrum (FAB) m/z 424, 426 ($M^{+\cdot}$). Calculated for $C_{20}H_{15}ClN_2Pd$: C 56.48, H 3.55, N 6.58. Found: C 56.29, H 3.61, N 6.54%.

3.6. Crystal data for chloro(pyridine)[2-(2'-pyridinyl)naphthyl-C^3, N]palladium (8)

$PdClN_2C_{20}H_{15}$, pale yellow prismatic crystal, M_r 425 g mol^{-1}, monoclinic, space group $P2_1/a$ (No. 14), $Z = 4$, $a = 8.056(3)$, $b = 16.72(1)$, $c = 12.529(5)$ Å, $\beta = 92.88(3)°$, $V = 1686$ Å^3, $F(000)$ 848, $D_{calc} = 1.675$ g cm^{-3}, μ(Mo Kα) = 12.5 cm^{-1}, $F(000) = 848$, crystal dimensions $0.30 \times 0.30 \times 0.20$ mm, maximum/minimum transmission coefficients 0.82/1.00.

Data collection

Cell dimensions and space group data were obtained on a four-circle Rigaku AFC6s single-crystal diffractometer with graphite monochromated Mo Kα radiation. The $\omega - 2\theta$ scan technique was used at 296 K to record the intensities for all non-equivalent reflections for which $1° \leq 2\theta \leq 50.1°$. Scan widths were calculated as $(1.73 + 0.3 \tan\theta)$.

The intensities of three standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and for absorption [19]. A total of 3322 intensities were collected, of which 3093 were unique. These included 1925 with $F_o^2 \geq 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics [20]. These data were used in the final refinement of the structural parameters.

3.7. Structure determination

A three-dimensional Patterson function was used to determine the metal and chlorine positions, which phased

the data intensity data sufficiently well to permit location of the other non-hydrogen atoms from Fourier syntheses based ultimately on Zalkin's FORDAP program. Full-matrix least-squares refinement, based on F_o, was carried out using highly modified versions of the ORFLS program of Busing, Martin and Levy. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where. $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (0.03F_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count and Lp = Lorentz–polarization factor. Atomic scattering factors for non-hydrogen atoms were taken from Ref. [21] and those for hydrogen from Ref. [22]. The effects of anomalous dispersion were included using Cromer's values [23] for $\Delta f'$ and $\Delta f''$.

Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least squares and then held fixed. The model converged with $R = 3.1$, $R_w = 3.3\%$. $GOF = 1.90$, $n_{var} = 217$, maximum shift/error = 0.00. Tables of observed and calculated structure factors and thermal parameters are available. The principal programs used are contained in the TEXRAY set [24].

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