Pergamon

PII: S0277–5387(98)00216–2

Polyhedron Vol. 17, No. 23–24, pp. 4109–4114, 1998

0277–5387/98 \$19.00+0.00

Studies on some reactions of cyclopalladated azobenzenes with N,O-chelators

K. Bag, T. K. Misra and C. Sinha*

Department of Chemistry, The University of Burdwan, Burdwan 713104, India

(Received 16 January 1998; accepted 25 May 1998)

Abstract—The synthesis and characterization of new planar mixed chelates of the type [Pd(A)(N,O)] (A = *ortho*-metallated azobenzene or its substituted derivatives, A_1 to A_5, N,O = 2-picolinato (pic), quinaldato (qnd), 8-quinolinolato (q) and 2-methyl-5-sulphonic-8-quinolinolato (msq)) are achieved by splitting the halogeno-bridge in $[Pd_2(A)_2Cl_2]$ by aqueous $AgNO_3$ solution followed by the addition of N,O-chelator. $[Pd(A_2)(N,O)]$ occurs as isomer $[Pd(A_3)(N,O)]$ and the composition have been established using ^1H NMR data. The complex composition is supported by elemental analyses and IR data. Cyclic voltammetric studies suggest two successive redox responses correspond to azo reduction. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: cyclopalladated; mixed chelates; N,O-donor; spectral studies; electrochemistry.

INTRODUCTION

Cyclopalladated compounds of transition metals have attracted a great deal of attention in recent times [1–8]. Many reviews concerning their synthesis and reactivities appear in literature [9–14]. We have extensively studied the cyclopalladation reactions of many substituted azobenzenes and Schiff bases [15–19]. Azobenzene becomes palladated at the azo-nitrogen and *ortho*-carbon atom and produces bridged dimeric species [20–22]. The bridge splitting reactions of the dimer with neutral ligands such as tertiary phosphines [23–25], pyridines [26] and anionic ligands such as acetylacetonate [27], arylazooximate [28] gave large number of planar mixed organopalladium complexes. In the present paper we report a further new type (**2**) of mixed cyclopalladated complexes of azobenzenes with (N,O)-chelators. We have chosen monoanionic N,O-chelator: picolinic acid (Hpic), quinaldic acid (Hqnd), 8-quinolinol (Hq) and its derivative 2-methyl-5-sulphonic-8-quinolinol (Hmsq) (H stands for the phenolic hydrogen) as the capping ligand. They form five membered chelate ring with cyclopalladated Pd(C,N) fragment (**1**).

RESULTS AND DISCUSSION

The complex (**2**) is abbreviated as Pd(A)(N,O) where A represents the azobenzenes. A_1 to A_5 are the specific abbreviations of the ligand A depending on substituents and binding mode as set out in Scheme 1.

The chloro-bridged cyclopalladated azobenzenes $[Pd_2(A)_2Cl_2]$ in acetone were treated with aqueous $AgNO_3$ and refluxed for a few hours. To the filtrate (N,O)-chelators were added in equivalent amount (1:1 mole ratio). The picolinato [Pd(A)(pic)], quinaldato [Pd(A)(qnd)] and 8-quinolinolato [Pd(A)(q)] and [Pd(A)(msq)] derivatives were precipitated as orange solid. The complexes are non-electrolytic in nature and suggest covalent binding of the chelators. The composition of the complexes are supported by elemental analyses data (Table 1).

The complexes display spectral characteristics corresponding to $\nu(N{=}N)$ at 1360–1385 cm^{-1}. The assignment of all bands has not been attempted. However, a comparison of the spectra with those of the respective chloro-bridged dimers and of free (N,O)-chelator affords useful information. Picolinato [Pd(A)(pic)] and quinaldato [Pd(A)(qnd)] derivatives exhibit strong stretching due to $\nu_{as}(COO)$ and $\nu_s(COO)$ at $\sim$1650 and 1340 cm^{-1} respectively which appears in the free ligand at 1720 cm^{-1}. The difference in stret-

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* Author to whom correspondence should be addressed.

Table 1. Microanalytical[a] and UV–VIS spectral data[b]

Complex	Elemental			UV–VIS spectral data λ_{max} (nm) ($10^{-3}\varepsilon$, $dm^3\,mol^{-1}\,cm^{-1}$)
	C(%)	H(%)	N(%)	
[Pd(A_1)(pic)]	52.7 (52.8)	3.0 (3.2)	10.4 (10.3)	478(3980)[c], 448(3360), 382(7000)
[Pd(A_2)(pic)]	54.0 (53.9)	3.4 (3.5)	9.9 (9.9)	480(4220)[c], 450(4340), 385(7890)
[Pd(A_4)(pic)]	55.0 (54.9)	3.9 (3.9)	9.5 (9.6)	483(4600)[c], 454(5320), 387(9810)
[Pd(A_5)(pic)]	45.1 (45.2)	2.3 (2.3)	8.7 (8.8)	485(5840)[c], 452(5080), 385(8940)
[Pd(A_1)(qnd)]	57.8 (57.5)	3.3 (3.3)	9.2 (9.1)	480(3060)[c], 450(3640), 383(7850)
[Pd(A_2)(qnd)]	58.1 (58.3)	3.5 (3.6)	9.0 (8.9)	485(5430)[c], 450(6340), 380(9560)
[Pd(A_4)(qnd)]	59.2 (59.1)	3.9 (3.9)	8.7 (8.6)	484(7245)[c], 454(8580), 387(16520)
[Pd(A_5)(qnd)]	49.8 (50.0)	2.6 (2.5)	7.8 (8.0)	485(6460)[c], 452(8540), 385(10360)
[Pd(A_1)(q)]	58.5 (58.4)	3.4 (3.5)	9.6 (9.7)	484(3280)[c], 451(4020), 386(8240)
[Pd(A_2)(q)]	59.2 (59.3)	3.9 (3.8)	9.5 (9.4)	480(4230)[c], 450(5226), 380(9370)
[Pd(A_4)(q)]	60.2 (60.1)	4.0 (4.1)	9.0 (9.1)	483(5280)[c], 454(6140), 387(11620)
[Pd(A_5)(q)]	50.3 (50.4)	2.5 (2.6)	8.5 (8.4)	484(4650)[c], 452(5840), 380(9240)
[Pd(A_1)(msq)]	50.1 (50.3)	3.3 (3.2)	8.2 (8.0)	488(4480)[c], 448(5660), 385(8450)
[Pd(A_2)(msq)]	51.3 (51.2)	3.6 (3.5)	7.9 (7.8)	486(5030)[c], 450(6890), 380(9460)
[Pd(A_4)(msq)]	52.2 (52.0)	3.9 (3.8)	7.4 (7.6)	482(4940)[c], 454(6330), 385(8020)
[Pd(A_5)(msq)]	44.2 (44.4)	2.3 (2.5)	7.3 (7.1)	485(4780)[c], 450(6260), 380(7940)

[a] Calculated values are in parentheses.

[b] In $CHCl_3$ except [Pd(A)(msq)] derivatives, those are recorded in DMSO.

[c] Shoulder.

ching frequency ($\Delta\nu = 290\,cm^{-1}$) suggests unidentate carboxylato coordination [29, 30, 31]. Additional bands are observed at 860–840, 720–700 and 680–660 cm^{-1} and support the coordinated picolinate ion. Similarly quinolinolato [Pd(A)(q)] and [Pd(A)(msq)] exhibit two characteristic band at 1560–1580 and 1490–1505 cm^{-1} along with ring deformation at $\sim 400\,cm^{-1}$ supporting the presence of N,O-chelator in the cyclopalladated moiety. All the complexes exhibit stretching at 520–530 and 350–380 cm^{-1} corresponding to ν(Pd–O) and ν(Pd–N), respectively.

The solution electronic spectra of the complexes were recorded in $CHCl_3$ and the transitions are assigned on the basis of reported literature [18–22, 28]. The transition around 500 nm is assigned to charge transfer transition in the metallated fragment [20–22, 28] and the higher energy transitions are referred to intraligand charge transfer transitions.

For asymmetrical azobenzene (A_2/A_3) the cyclopalladated complex occurs as a mixture of isomers but in no case they are separated by chromatography. Because of bad solubility of the chloro-bridged species in common organic solvents direct isomer assessment by ^1H NMR is not easily achieved [32]. Different other methods [33, 34] like gas chromatographic analysis of the products obtained by exhaustive carbonylation of the dimer had been used. The ^1H NMR spectral technique had been employed in a limited area [28] for the product analysis obtained by bridge splitting reactions using PPh_3, arylazooximes etc. We are also using ^1H NMR technique for the assessment of isomer population (Table 2). For symmetrical azobenzenes (A_1, A_4, A_5) no such isomerism is observed. The bridge splitting reaction followed by chelation using N,O-chelator may produce, in principle, two geometric isomers (B and C) for symmetrical and four isomers for asymmetrical azobenzenes, respectively. The isomers could not be isolated by chromatography on silica gel or alumina. There are many bridge splitting reactions [23–27] of cyclopalladated azobenzenes, Schiff bases with pyridines or phosphines where the base occupies *trans*-position to azo/azomethine-N. 2-Picolinic acid is also used as bridge splitter in a cyclopalladated α-naphthylethylamine where heterocyclic-N occupies *trans* to amine nitrogen. This may provide a guide to consider single isomer (B) from the symmetrical azobenzenes and two isomers from asymmetrical azobenzene.

The ^1H NMR spectra of free ligands and the cyclopalladated complexes of symmetrical azobenzenes are the guide lines to the signal assignment. In cases, where the metallation of both substituted and unsubstituted rings occurs, the population of the isomer having metallation in the substituted ring is higher, in line with the electrophilic nature of the palladation reaction. Symmetrical azobenzenes yield single mixed chelate complex which is supported by two Me signals of [Pd(A_4)(N,O)] in ^1H NMR spectra, in line with the electrophilic nature of the palladation reaction. Asymmetrical ligand in [Pd(A_2)(N,O)] gives closely spaced δ_{Me} signal. Originally cyclopalladated complex exists in two isomeric forms and at least two mixed chelates will appear in the product. The observed ratio of [Pd(A_2)(N,O)]:[Pd(A_3)(N,O)] is 3:2. The results are in agreement with those obtained by the bridge splitting reaction using PPh_3 and pyridine.

Table 2. ^{1}H NMR data of complexes in [Pd(A)(N,O)]

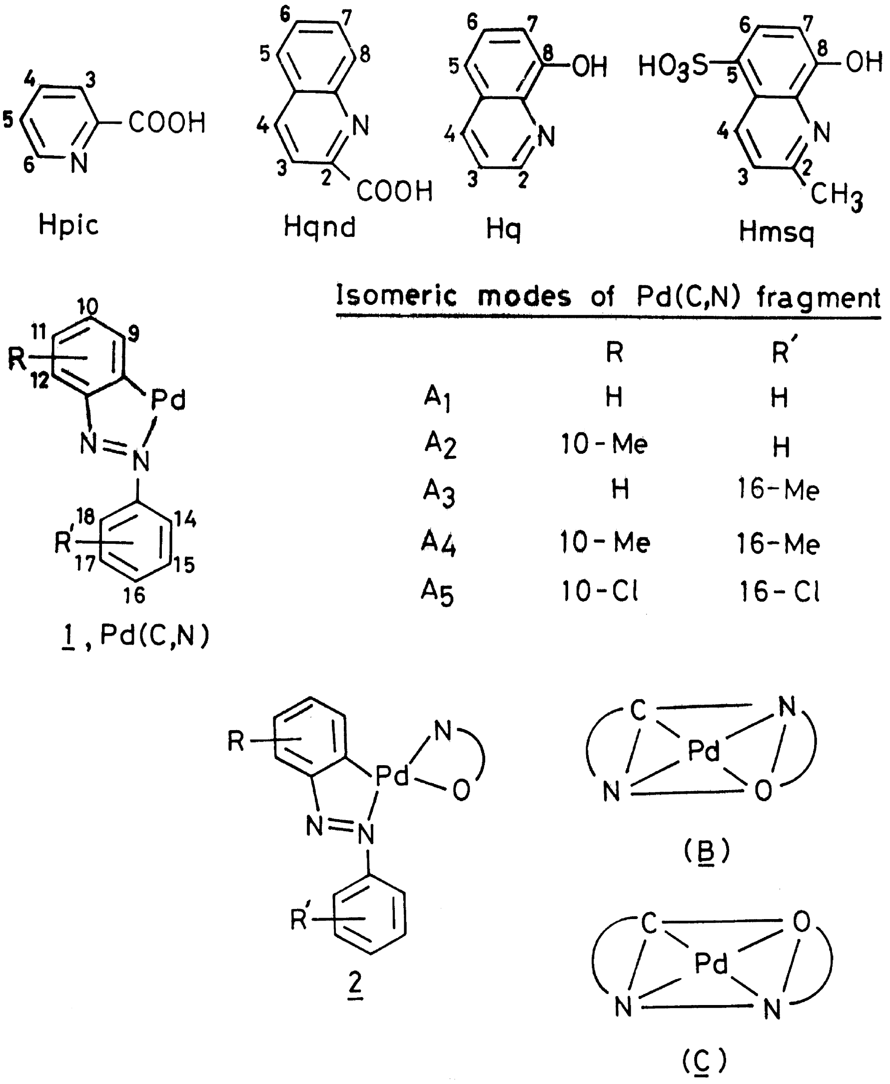
Complex	δ (ppm)													
	2-H[a]	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H	11-H	12-H[a]	14, 18-H	15, 17-H	Me
[Pd(A_1)(pic)]	–	8.65[a]	8.08[b]	7.90[b]	8.25[a]	–	–	7.64[a]	7.36[a]	7.36[b]	7.8	7.89	7.58[c]	
[Pd(A_2)(pic)]	–	8.63[a]	8.03[b]	7.86[b]	8.23[a]	–	–	7.48[d]	–	7.09[a]	7.62	7.80	7.49[c]	2.44[e]
[Pd(A_4)(pic)]	–	8.61[a]	8.00[b]	7.85[b]	8.27[a]	–	–	7.44[d]	–	7.04[a]	7.63	7.7	7.26[a]	2.52, 2.4
[Pd(A_5)(pic)]	–	8.68[a]	8.04[b]	7.88[b]	8.25[a]	–	–	7.77[d]	–	7.58[a]	7.89	7.96	7.68[a]	
[Pd(A_1)(qnd)	–	8.78[a]	8.55[b]	8.08[c]	7.81[c]	7.81[c]	8.48[a]	7.67[a]	7.39[b]	7.39[b]	7.84	7.96	7.63[c]	
[Pd(A_2)(qnd)	–	8.70[a]	8.50[b]	8.08[c]	7.81[c]	7.81[c]	8.52[a]	7.47[d]	–	7.08[a]	7.59	7.82	7.54[c]	2.45[e]
[Pd(A_4)(qnd)	–	8.70[a]	8.51[b]	8.09[c]	7.79[c]	7.79[c]	8.50[a]	7.48[d]	–	7.07[a]	7.66	7.75	7.31[a]	2.48, 2.4
[Pd(A_5)(qnd)	–	8.84[a]	8.61[b]	8.13[c]	7.84[c]	7.84[c]	8.52[a]	7.81[d]	–	7.61[a]	7.93	8.0	7.73[a]	
[Pd(A_1)(q)	8.94	8.12[b]	8.42[c]	7.69[c]	7.83[c]	7.60[a]	–	7.58[a]	7.33[b]	7.33[b]	7.75	7.8	7.51[c]	
[Pd(A_2)(q)	8.92	8.11[b]	8.34[c]	7.70[c]	7.81[c]	7.60[a]	–	7.40[d]	–	7.09[a]	7.64	7.74	7.45[c]	2.50
[Pd(A_4)(q)	8.90	8.08[b]	8.36[c]	7.65[c]	7.80[c]	7.56[a]	–	7.37[d]	–	7.02[a]	7.6	7.65	7.21[a]	2.50, 2.3
[Pd(A_5)(q)	8.95	8.10[b]	8.45[c]	7.72[c]	7.87[c]	7.64[a]	–	7.79[d]	–	7.55[a]	7.85	7.91	7.65[a]	
[Pd(A_1)(msq)[g]	–	7.83[a]	8.34[a]	–	8.05[a]	7.72[a]	–	7.50[a]	7.26[b]	7.26[b]	7.7	7.74	7.46[c]	2.84[f]
[Pd(A_2)(msq)[g]	–	7.80[a]	8.33[a]	–	8.03[a]	7.71[a]	–	7.30[d]	–	6.97[a]	7.58	7.68	7.42[c]	2.84[f], 2.5
[Pd(A_4)(msq)[g,h]	–	7.80[a]	8.30[a]	–	8.01[a]	7.69[a]	–	7.31[d]	–	7.00[a]	7.56	7.6	7.17[a]	2.82[f], 2.51

[a] Doublet.
[b] Triplet.
[c] Multiplet.
[d] Singlet.
[e] Isomeric δ_{Me}, 2.38 ppm.
[f] δ_{Me} of msq.
[g] Solvent: $CDCl_3$, except [Pd(A)(msq)] where DMSO-d_6 is used.
[h] The concentration of [Pd(A_5)(msq)] is very low to get well defined ^{1}H NMR in DMSO-d_6.

The heterocyclic ring protons appear in general at the downfield region relative to arylazo protons. The proton numbering pattern is shown in Scheme 1. The signals are assigned on the basis of spin–spin interaction and change therein on substitution. In picolinato derivatives the most downfield doublet is 3-H ($\sim$8.6 ppm) followed by 6-H ($\sim$8.2 ppm) signal. The protons 4-H and 5-H appear relatively at upfield position $\sim$8.0 and 7.8 ppm respectively. The quinaldato derivatives [Pd(A)(qnd)] similarly exhibit resonances in downfield region for 3-H to 8-H at 8.7 to 7.8 ppm. 8-Quinolinolato complexes [Pd(A)(q)] exhibit 2-H signal at most downfield region ($\sim$8.9 ppm); the pyridinic ring protons appear in downfield region (2-H to 4-H, 8.9 to 8.4 ppm) and phenolic ring protons appear at relatively upfield region (5-H to 7-H, $\sim$7.6 to 7.8 ppm). Arylazo ring protons appear relatively in upfield position (7.0 to 7.7 ppm) and the signal position is highly sensitive to the substituent in the aryl ring. In A_2/A_3, A_4 and A_5 singlet resonance is due to 9-H proton. Metallated ring protons appear in more downfield region than non-metallated ring ones. Other ring protons appear at usual position and the signal movement is in accordance with the electronic effect of the substituents [35].

Electrochemistry

Cyclic voltammetric data were collected under N_2 environment using glassy carbon working electrode in acetonitrile versus saturated calomel electrode (SCE) in presence of tetrabutylammonium perchlorate (TBAP). The iR compensation was applied internally in the instrument. All the complexes display two redox responses and the data are collected in Table 3. The peak potentials are nearly invariant with scan rate (50–500 $\mathrm{mV\,s^{-1}}$) and the cathodic peak current (i_{pc}) is proportional to $v^{1/2}$ and i_{pa}/i_{pc} lies at 0.9–1.02 suggesting reversibility of the redox process. The current height measurement shows one-electron redox type and the peak-to-peak separation (ΔE_p) suggests quasireversible character of the couples. Palladium(II) reduction in mixed complexes of cyclopalladated azobenzenes were reported at very high potential and a two-electron quasireversible reduction process followed by chemical reaction [28]. In the present series of complexes the couples are one-electron reduction type at relatively lower value and stable on repetitive cyclic operation. This excludes the metal reduction. Ligand reduction is believed to occur primarily at the azo-function who can accommodate up to two electrons [28] at the LUMO. The coulometric experiment for the first couple confirms one-electron reduction at the azo-centre. The experiment was performed in one case [Pd(A_1)(q)] at -1.4 V vs SCE in MeCN and coulomb count ($\eta = Q/Q' = 0.94$ where Q and Q' are observed and calculated coulomb) suggests just one-electron reduction. On reduction the solution colour has changed from orange red to brown red



Isomeric modes of Pd(C,N) fragment

	R	R′
A_1	H	H
A_2	10-Me	H
A_3	H	16-Me
A_4	10-Me	16-Me
A_5	10-Cl	16-Cl

Scheme 1.

and in the UV–VIS spectra the shoulder at 484 nm is eliminated while new band appears at 510 nm. The ESR spectra of the reduced product shows interesting behaviour; at room temperature a broad signal is observed at $g = 2.005$ with peak-to-peak separation 45 G. The spectrum at liquid-nitrogen temperature (77 K) shows hyperfine splitting pattern. Detail investigation is under scrutiny. The observation supports the literature report [36, 37] and suggests that the first reduction is believed to occur at the azo-function of the ligand. The effect of the substitution on reduction potential data again supports the assignment. Change of substituents (*para*-to-azo group in aryl ring) in the metallated ring brings about in increasing cathodic shift of $E_{1/2}$ in the order $Cl > H > Me$ as expected from Hammett relation [38]. The second couple ($E_{1/2}{}^2$) varies irregularly and does not confirm to the second step reduction, of azo-function. The reduction of heterocyclic coligand is not ruled out which may need comparatively higher energy to accommodate electrons at the antibonding orbital. There may be a certain degree of involvement of coligand π^*-orbital in conjunction with azo-antibonding orbital.†

EXPERIMENTAL

The solvents used in the reactions were of reagent grade and were dried by reported procedures [15, 16]. 2-Picolinic acid (Hpic), quinaldic acid (Hqnd) (Fluka), 2-methyl-5-sulfonic-8-quinolinol (Hmsq) (Aldrich) and 8-quinolinol (BDH) were recrystallized before use from ethanol–water (2:1, v/v). Palladium chloride was

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† One of the Referees has suggested in this manner.

Table 3. Cyclic voltammetric data of [Pd(A)(N,O)] in acetonitrile at 298 K

Compound[a]	Reduction Potentials[b]	
	$-E_{1/2}^{1}(\Delta E_p)$	$-E_{1/2}^{2}(\Delta E_p)$
[Pd(A$_1$)(pic)]	1.055(100)	1.441(160)
[Pd(A$_2$)(pic)]	1.117(90)	1.514(140)
[Pd(A$_4$)(pic)]	1.15(80)	1.585(100)
[Pd(A$_5$)(pic)]	0.942(90)	1.365(140)
[Pd(A$_1$)(qnd)]	1.150(140)	1.384(180)
[Pd(A$_2$)(qnd)]	1.200(100)	1.435(140)
[Pd(A$_4$)(qnd)]	1.270(100)	1.545(130)
[Pd(A$_5$)(qnd)]	1.041(110)	1.309(150)
[Pd(A$_1$)(q)]	1.160(140)	1.550(120)
[Pd(A$_2$)(q)]	1.237(120)	1.644(140)
[Pd(A$_4$)(q)]	1.316(110)	1.805(160)
[Pd(A$_5$)(q)]	0.992(90)	1.276(120)
[Pd(A$_1$)(msq)]	1.105(80)	1.425(110)
[Pd(A$_2$)(msq)]	1.165(90)	1.500(120)
[Pd(A$_4$)(msq)]	1.214(120)	1.610(160)
[Pd(A$_5$)(msq)]	0.955(100)	1.376(120)

[a] Meaning of the symbols are as in the text.

[b] Potentials are 0.5 ($E_{pc}+E_{pa}$); E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively, unit in V and ΔE_p in mV (reference to SCE), scan rate 50 mV s^{-1}, solute concentration $\sim 10^{-3}$ M in MeCN, [NBu$_4$, ClO$_4$] is supporting electrolyte (0.1 M).

received from Arrora Matthey, Calcutta, India. Disodium tetrachloropalladate was prepared by reported procedure [15, 16]. Azobenzenes were synthesized by condensing nitroaromatics and aromatic amines in hot glacial acetic acid as reported earlier [20–22]. All other chemicals and solvents were reagent grade and were used as received.

IR spectra were recorded on Perkin Elmer 783 and 883 spectrophotometers. ^{1}H NMR data were collected from Bruker 300 MHz FT NMR spectrometer in CDCl$_3$. UV–VIS spectra were obtained using Shimadzu 160A spectrophotometer. Elemental analyses were obtained using Perkin Elmer 2400 CHNS/O analyser.

Synthesis of complexes

Complexes [Pd$_2$(A)$_2$Cl$_2$] were prepared according to reported methods [20–22, 28]. The mixed ligand complexes [Pd(A)(N,O)] were synthesized by a general procedure and representative case is detailed below.

2-(Picolinato)(7-phenylazophenyl-C^8,N)palladium(II), [Pd(A)(pic)]

To acetone solution (10 cm^3) of [Pd$_2$(A$_1$)$_2$Cl$_2$] (0.2 g, 0.31 mmol) was added aqueous AgNO$_3$ (0.11 g, 0.65 mmol) solution. The mixture was refluxed for 2 h. The precipitated AgCl was filtered at hot condition through G-4 sintered crucible. To this orange solution 2-picolinic acid (0.08 g, 0.65 mmol) in acetone (10 cm^3) was added dropwise with continuous stirring. The colour of the solution turned to orange-red and the precipitate appeared slowly on evaporation in air. The volume of the solution was reduced to half and the precipitate was filtered, washed with water, and recrystallized from chloroform–hexane via diffusion. The product was dried over CaCl$_2$. The yield was 70%.

The yield of other compounds varied between 65 and 80%.

Acknowledgements—Financial assistance from Department of Science and Technology, and University Grants Commission, New Delhi are thankfully acknowledged. One of the authors (K. B.) is indebted to Professor B. R. De, Department of Chemistry, Vidyasagar University, Midnapore for his help, T. K. M. thanks to the Council of Scientific and Industrial Research, New Delhi for giving him a fellowship.

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