

CHAPTER III

**C-H BOND ACTIVATION: ISOLATION,
CHARACTERIZATION AND REACTIVITY OF
CYCLOPALLADATES WITH C, N, S DONOR SET**

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ABSTRACT:

At room temperature palladium (II) smoothly activates the C-H bond of naphthyl groups present in (HL) in ethanol medium. Palladium(II) can activate both C(2)-H and C(8)-H bonds of 1-naphthylazo moiety resulting in formation of two isomeric cyclometallates of types (A) and (B) respectively. Both types of isomers have been isolated in pure form. The characterization of isomers (A) and (B) have been done on the basis of microanalytical and spectral (IR, Electronic, NMR, FAB mass) data. The structures of both (2A) and (2B) have been determined by X-ray diffraction method. Both the compounds are cyclopalladated species having Pd-C(naphthyl) bond. The compound (2A) contains Pd-C bond at C(2) of naphthyl ring and the bond distance is 1.994(5)Å. Cyclometallation occurs at C(8) of naphthyl ring with bond distance 2.026(4)Å in compound (2B). Photochemical conversion of (B) → (A) in dichloromethane solution has been observed. At room temperature *m*-chloro-perbenzoic acid selectively insert oxygen atom into Pd-C(2) bond of compound (A) but it fails to react with isomer (B).

Part of the work published in proceedings Indian Academy of Sciences, Chemical Science, II, 397 (2000).

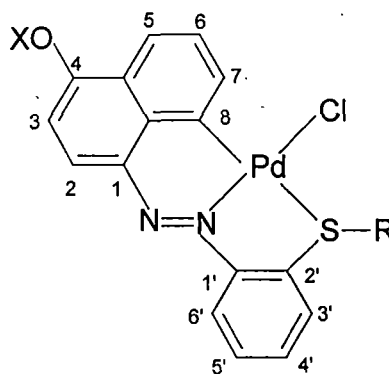
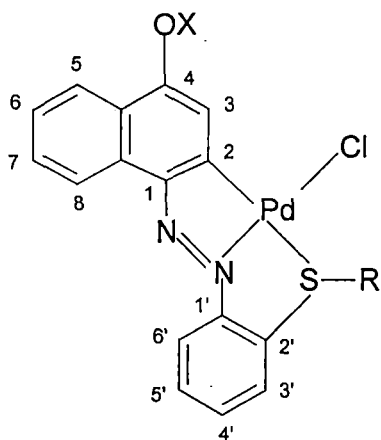
III.1 INTRODUCTION

The success of selective C(naphthyl)-H bond activation by ruthenium prompted us to explore the area of C(naphthyl)-H bond activation by palladium(II). Our objective is to isolate the cyclopalladates produced by C(naphthyl)-H bond activation followed by their structural characterization. A limited number of cyclometallates containing palladium(II)-C(naphthyl) bonds are reported [1-16] in the literature. Here we have used azo group and neutral thioether function as primary and auxiliary donor centres respectively for C-H bond activation of naphthyl moiety. Preliminary studies of the photochemical behaviour and the reactivity pattern of the palladated carbon have also been undertaken.

III.2 RESULTS AND DISCUSSION

III.2.1 SYNTHESIS

A group of 2'-alkylthiophenylazo-1-naphthalenes (**HL**⁴, **HL**⁶ & **HL**⁷) undergo cyclometallation with sodium tetrachloropalladate in ethanol medium at room temperature and produce isomeric mixtures of [PdLCl]. The separation of the mixture into isomer **A** (blue) and isomer **B** (pink) has been done by chromatography.



| | <u>R</u> | <u>X</u> |
|-------------|-------------------------|----------------|
| 1A : | $-\text{CH}_2\text{Ph}$ | $-\text{H}$ |
| 2A : | $-\text{CH}_2\text{Ph}$ | $-\text{CH}_3$ |
| 3A : | $-\text{CH}_3$ | $-\text{CH}_3$ |

| | <u>R</u> | <u>X</u> |
|-------------|-------------------------|----------------|
| 1B : | $-\text{CH}_2\text{Ph}$ | $-\text{H}$ |
| 2B : | $-\text{CH}_2\text{Ph}$ | $-\text{CH}_3$ |
| 3B : | $-\text{CH}_3$ | $-\text{CH}_3$ |

III.2.2 SPECTRAL PROPERTIES

(a) IR spectra:

The infrared spectral data of the cyclopalladates are given in the Table III.1. The IR spectra of (2A) and (2B) are shown in the Figures III.1 and III.2 respectively as representative cases. All the cyclopalladates (1A-3B) show absorption in the range of $1446\text{-}1462\text{ cm}^{-1}$ due to the presence of N=N fragment [17].

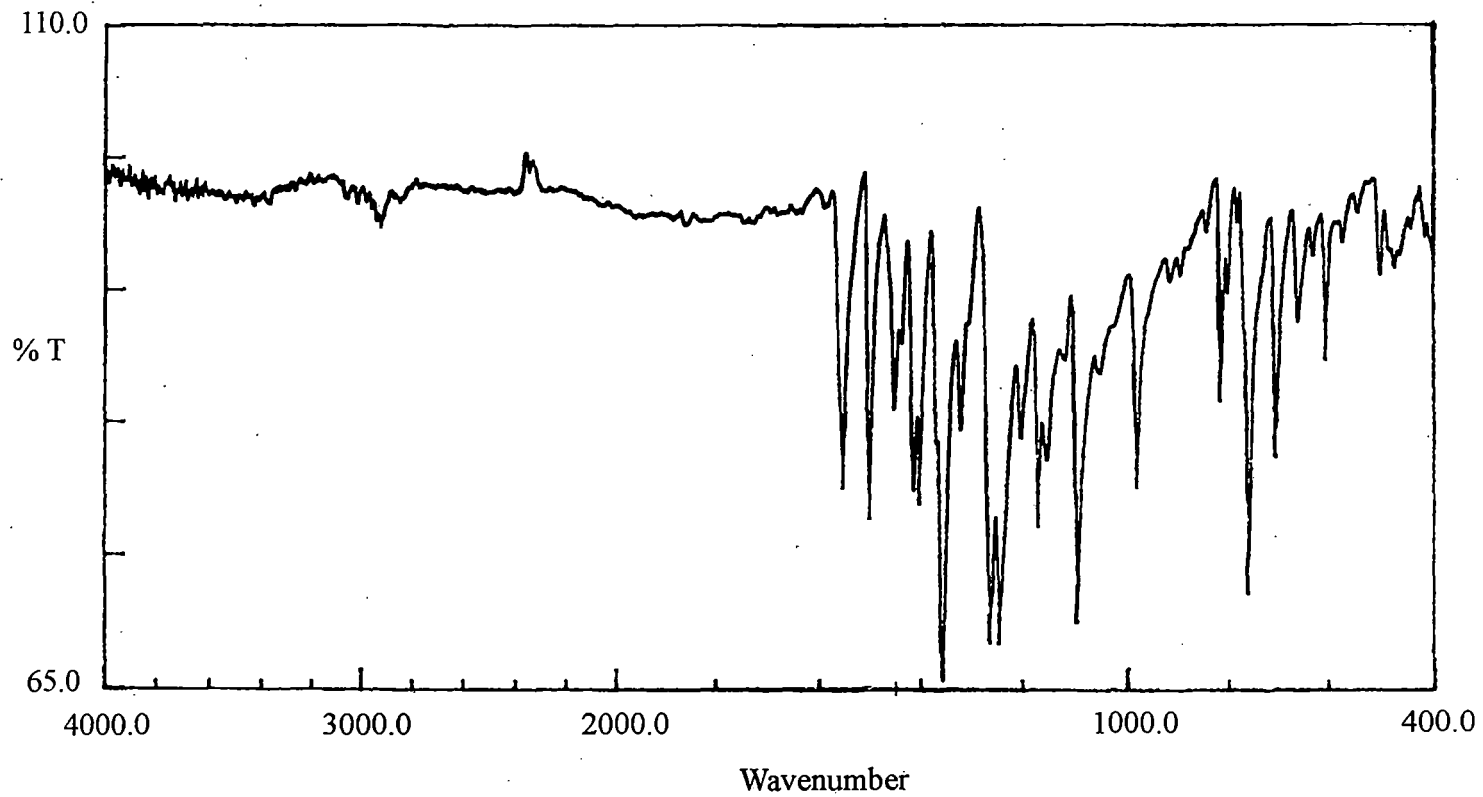


FIG. III. 1. INFRARED SPECTRUM OF $[Pd(L^6)Cl](2A)$ IN KBr DISC.

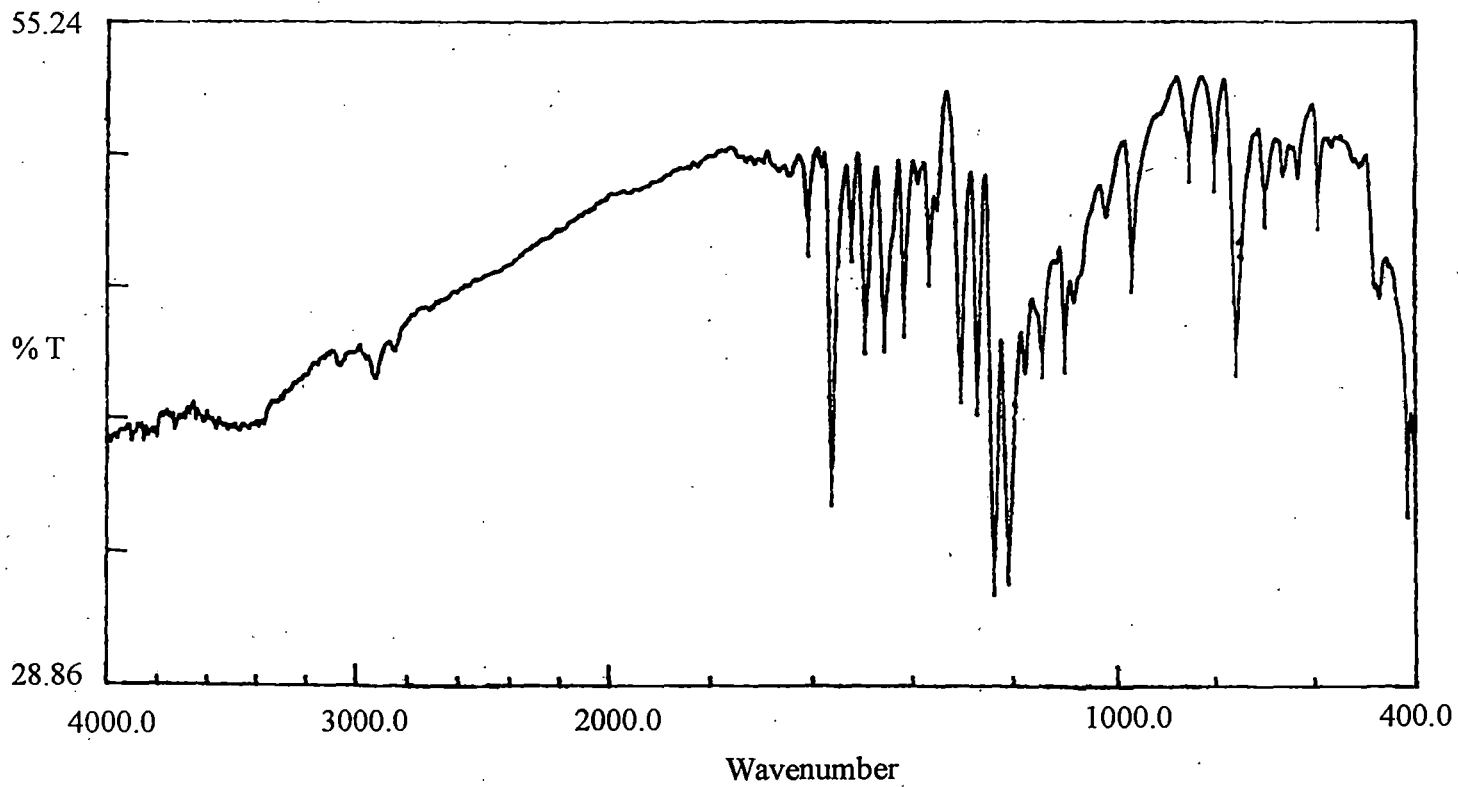


FIG. III. 2. INFRARED SPECTRUM OF [Pd(L⁹)Cl](2B) IN KBr DISC.

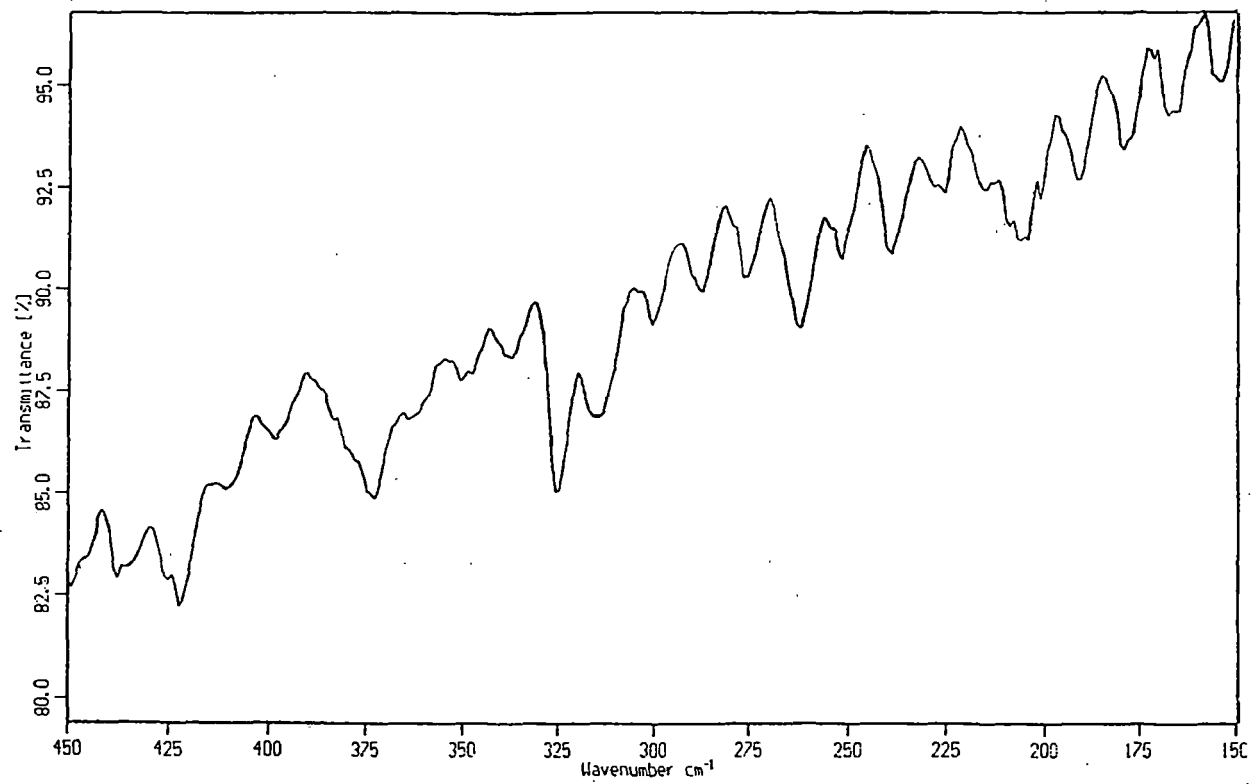


FIG. III. 3. FAR INFRARED SPECTRUM OF [Pd(L⁶)Cl](2A) IN KBr DISC.

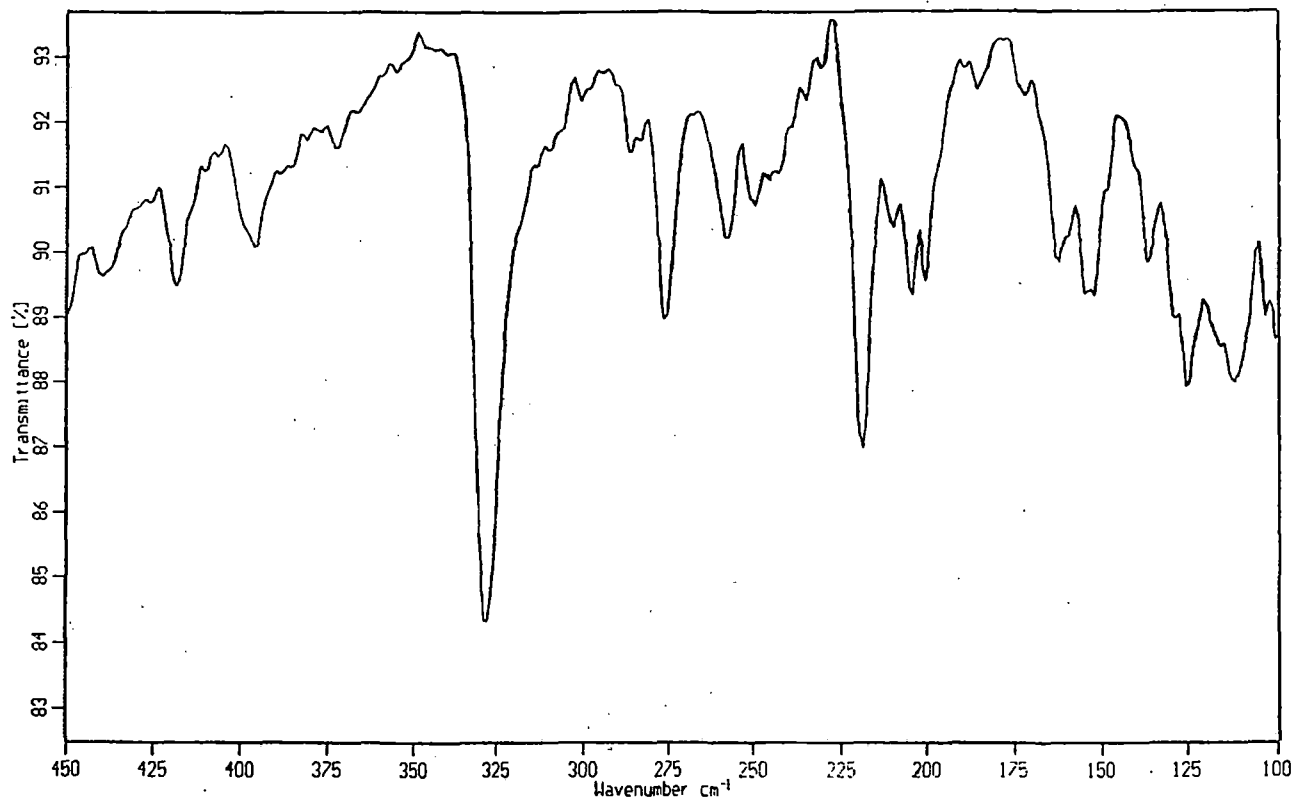


FIG. III. 4. FAR INFRARED SPECTRUM OF [Pd(L')Cl](3B) IN KBr DISC.

The far-IR spectra of cyclopalladates (2A) and (3B) are displayed in Fig. III.3 and III.4 respectively. The palladium-chlorine $\nu_{\text{Pd-Cl}}$ stretch of cyclopalladates (2A) & (3B) appear in the region of 326-328 cm^{-1} [18].

(b) Electronic Spectra:

The electronic spectral data for all the cyclopalladates are collected in the Table III.1. The electronic spectra of (2A) and (2B) are shown in the Figures III.5 and III.6 respectively as representative cases.

The divalent cyclopalladates A type (1A, 2A, 3A) & B type (1B, 2B, 3B) are soluble in common organic solvents like benzene, chloroform, dichloromethane. The compounds of type A show blue colour with intense absorptions in the region of 590-620 nm. All compounds of type B show pink colour due to strong absorptions in the visible range 500-525 nm.

Low energy absorption bands of the cyclopalladates originate from LMCT [ligand $\pi^* \rightarrow \pi$ d (Pd)] transitions [19]. The absorptions in the ultraviolet region originate from the intraligand electronic transitions.

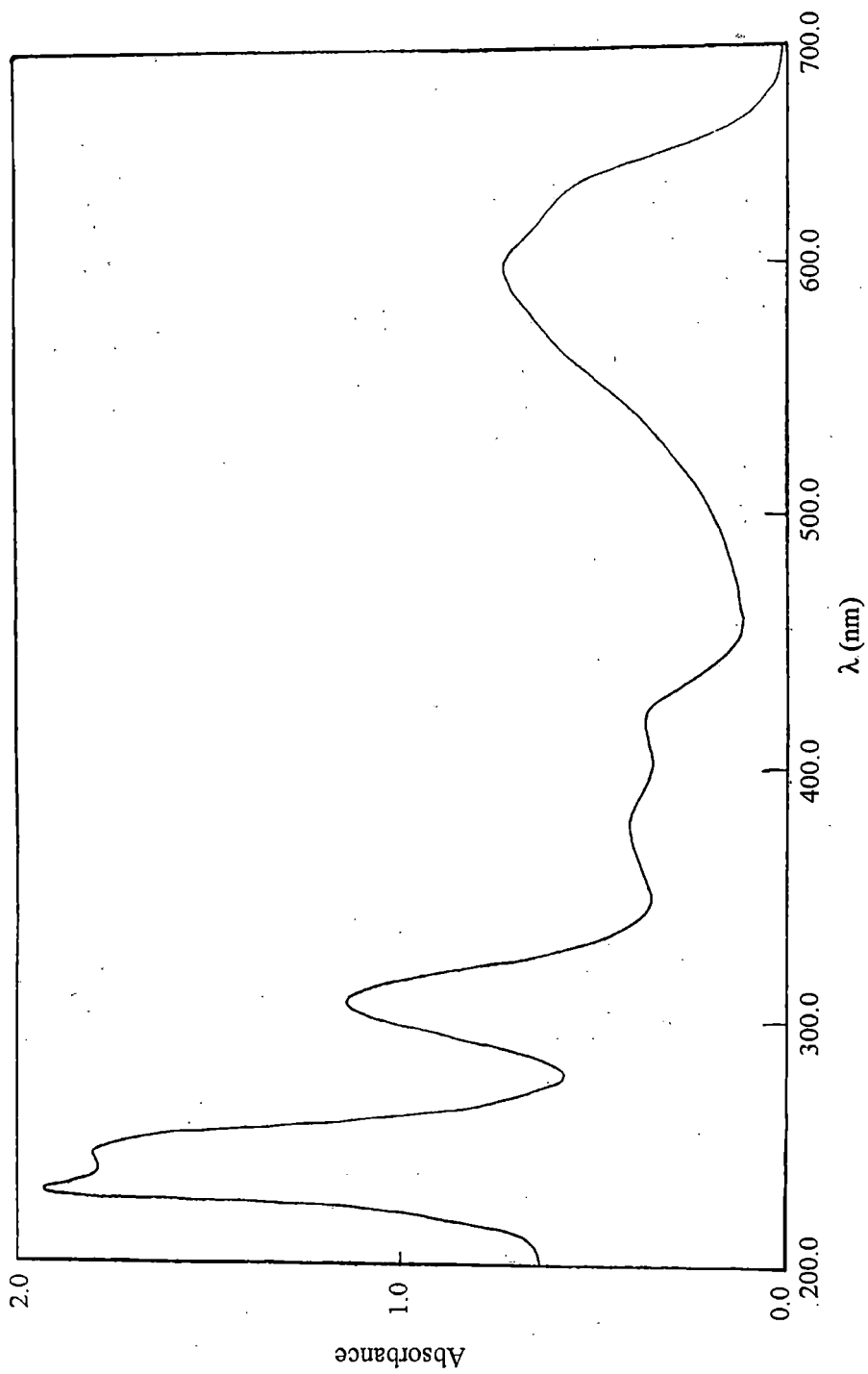


FIG. III. 5. ELECTRONIC SPECTRUM OF [Pd(L')Cl]2A IN CH₂Cl₂.

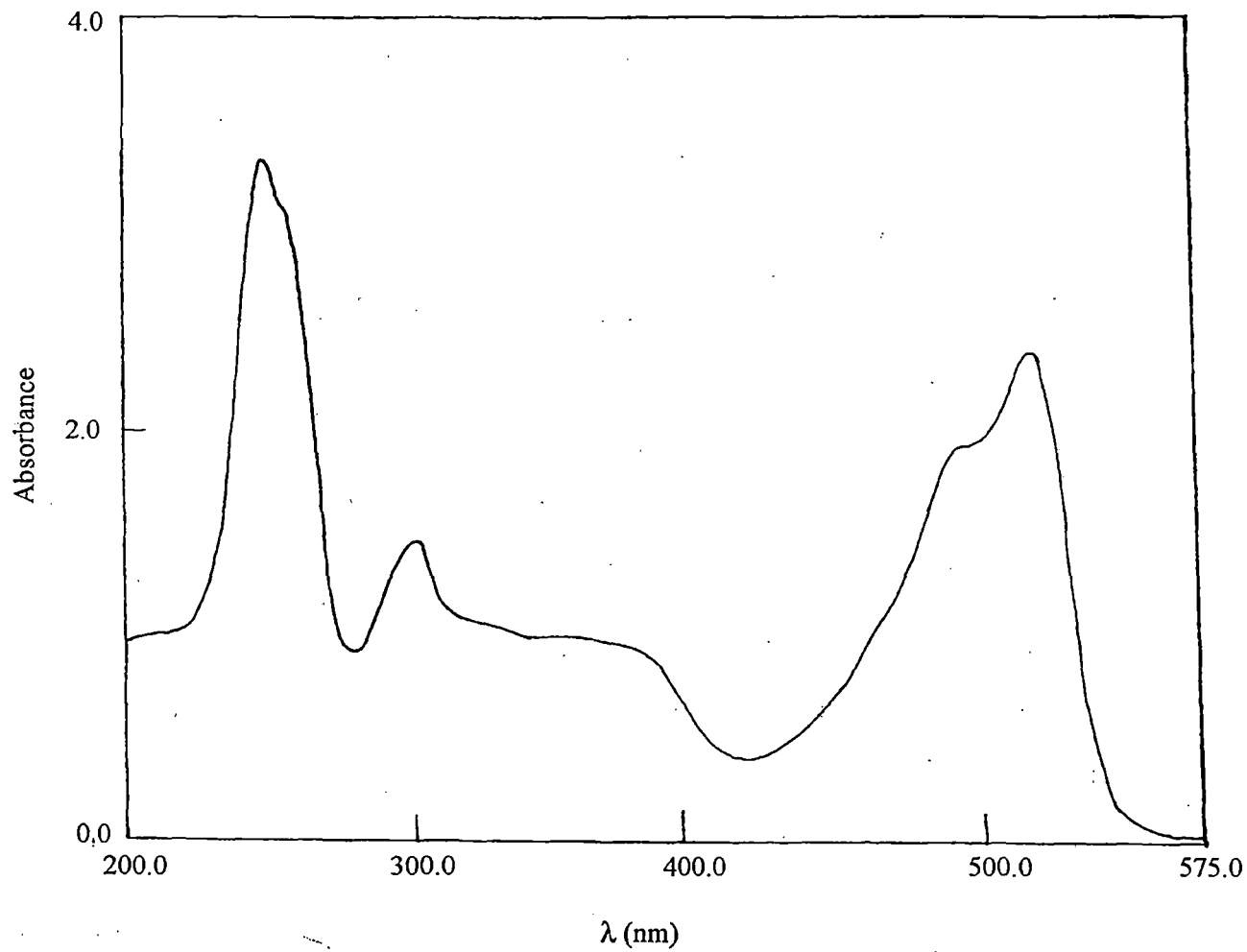


FIG. III. 6. ELECTRONIC SPECTRUM OF [Pd(L⁶)Cl](2B) IN CH₂Cl₂.

Table III. 1

IR and electronic spectral data of palladium compounds

| Compounds | $\nu_{N=N}$ (cm^{-1}) ^a | λ_{max} , nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) ^b |
|-----------------------------|---|--|
| [PdL ⁴ Cl], (1A) | 1462 | 592(8500), 422 ^{sh} (4200), 380 ^{sh} (550), 305(12300), 355(13500). |
| [PdL ⁴ Cl], (1B) | 1458 | 528(7700), 505 ^{sh} (6800), 297 ^{sh} (8200), 247(16250). |
| [PdL ⁶ Cl], (2A) | 1460 | 620 ^{sh} (9400), 595(11300), 420 ^{sh} (5600), 375(6300), 305(17600), 242(28100), 228(30300). |
| [PdL ⁶ Cl], (2B) | 1446 | 525(20600), 500(16600), 365 ^{sh} (8300), 298(12400), 235(28300). |
| [PdL ⁷ Cl], (3A) | 1458 | 622 ^{sh} (8700), 595(10500), 420 ^{sh} (5300), 378(5900), 305(16700), 245(26200), 230(28400). |
| [PdL ⁷ Cl], (3B) | 1456 | 525(15100), 500(11900), 365 ^{sh} (6500), 298(10300), 235(21800). |
| [PdL ⁶ OCl] | 1456 | 517(16400), 495(12600), 485(12200), 390(7500), 290(20600), 280(23900). |

^aIn KBr disc; ^bIn dichloromethane.

Table III. 2

¹H N.M.R. spectral data^a of some palladium(II) compounds

| Compounds | δ_{OCH_3} (ppm) | δ_{SCH_2} (ppm) | δ_{Ar} (ppm) |
|-----------------------------|-------------------------------|-------------------------------|----------------------------|
| [PdL ⁴ Cl], (1A) | - | 4.4 | 7.0—8.2 |
| [PdL ⁴ Cl], (1B) | - | 4.4 | 7.0—8.5 |
| [PdL ⁶ Cl], (2A) | 4.25 | 4.39 | 7.1—8.5 |
| [PdL ⁶ Cl], (2B) | 4.20 | 4.48 | 7.0—9.0 |

^aCDCl₃ and SiMe₄ were used as solvent and internal standard respectively.

(c) NMR Spectra:

In ^1H NMR spectra the signals for $-\text{SCH}_2-$ group of cyclopalladates (**1A**) & (**1B**) appear at 4.4 δ . The NMR spectrum of cyclopalladate (**2A**) (Fig.III.7) displays the signals for $-\text{OMe}$ and $-\text{SCH}_2-$ groups at 4.25 and 4.39 δ respectively. The signals for $-\text{OMe}$ and $-\text{SCH}_2-$ groups of cyclopalladate (**2B**) appear (Fig.III.8) at 4.19 and 4.47 δ respectively. The signals for aromatic protons of the cyclopalladates appear as complex pattern in the region 7.0-9.0 δ with correct integration ratio. The ^1H NMR data of the cyclopalladates are given in the Table III.2.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (**2A**) and (**2B**), the signals for palladated carbon appear at 224.21 and 209.46 δ respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**2B**) has been shown in the Fig.III.9 as representative case.

(d) FAB Mass:

The FAB mass spectra for cyclopalladates (**1A**) and (**1B**) are shown in the Fig.III.10 & Fig.III.11 respectively. Both the cyclometallates (**1A**) and (**1B**) show cluster of peaks centred at 510, 475, 460 and 384 amu, which correspond to $[\text{M-H}]^+$, $[\text{M-H-Cl}]^+$, $[\text{M-H-Cl-OH}]^+$ and $[\text{M-H-Cl-Bz}]^+$ peaks respectively [20]. FAB mass data show the cyclopalladates (**1A**) and (**1B**) are isomeric.

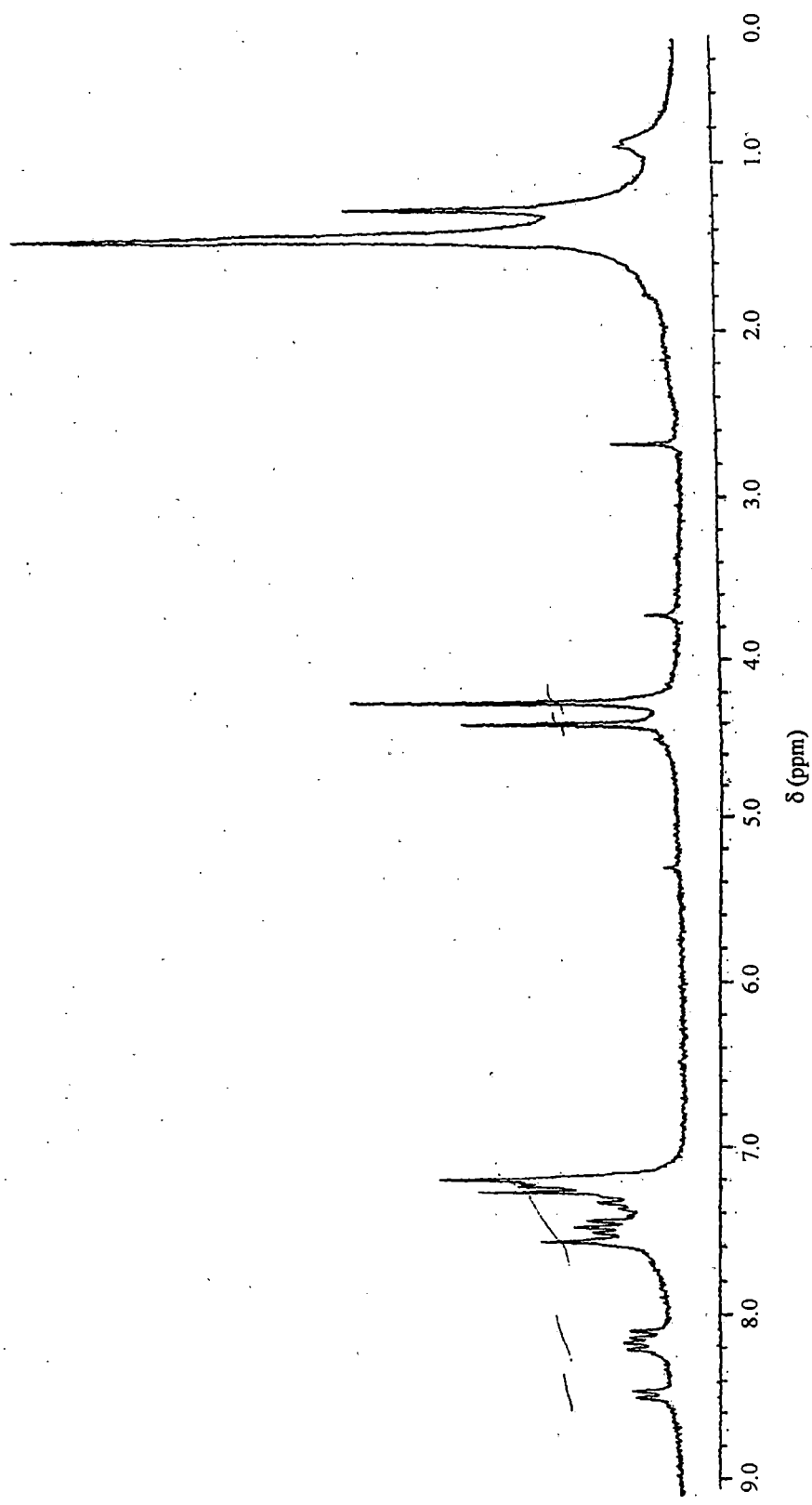


FIG. III. 7. ¹H NMR SPECTRUM OF [Pd(L⁹)Cl](2A) IN CDCl₃.

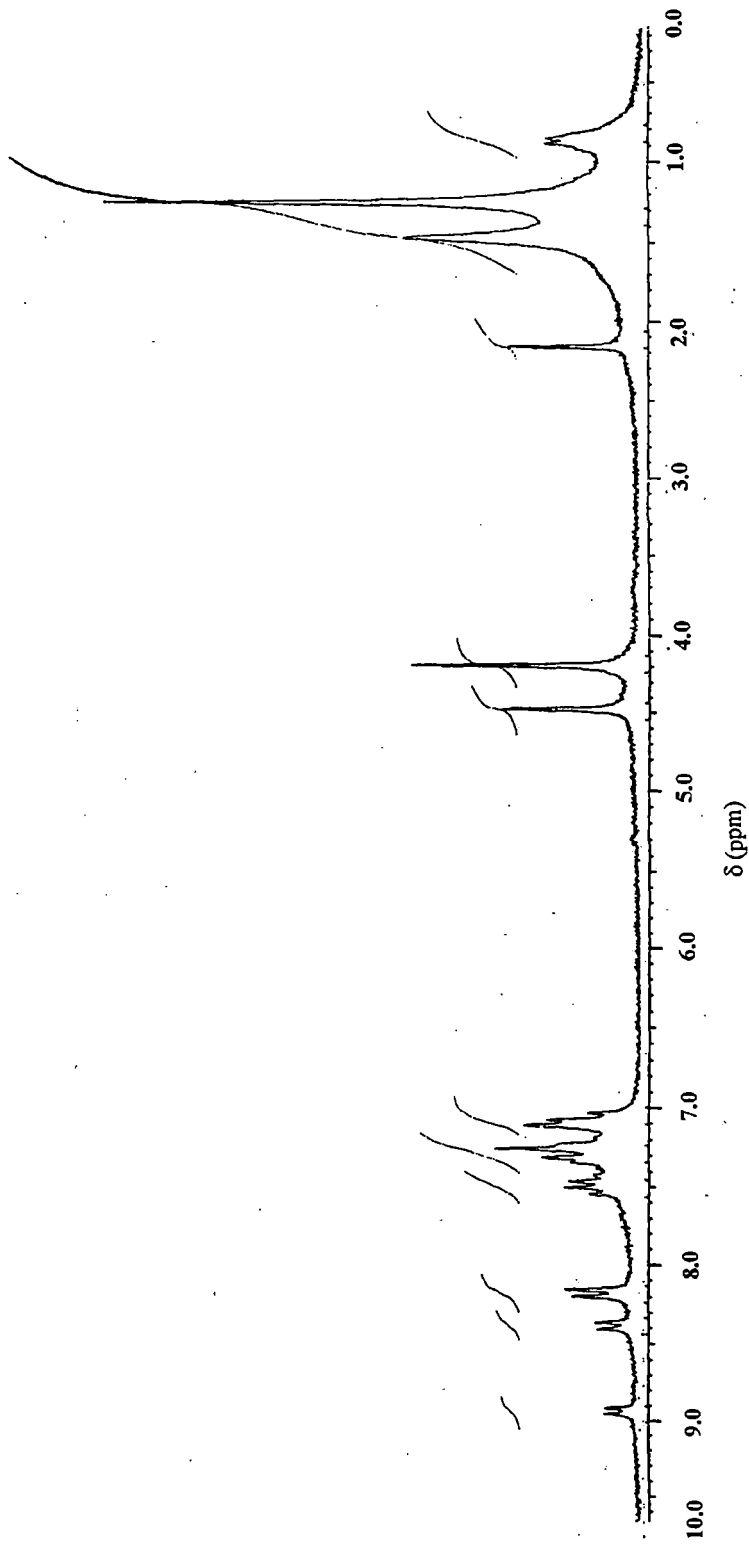


FIG. III. 8. ^1H NMR SPECTRUM OF $[\text{Pd}(\text{L}^*)\text{Cl}](2\text{B})$ IN CDCl_3 .

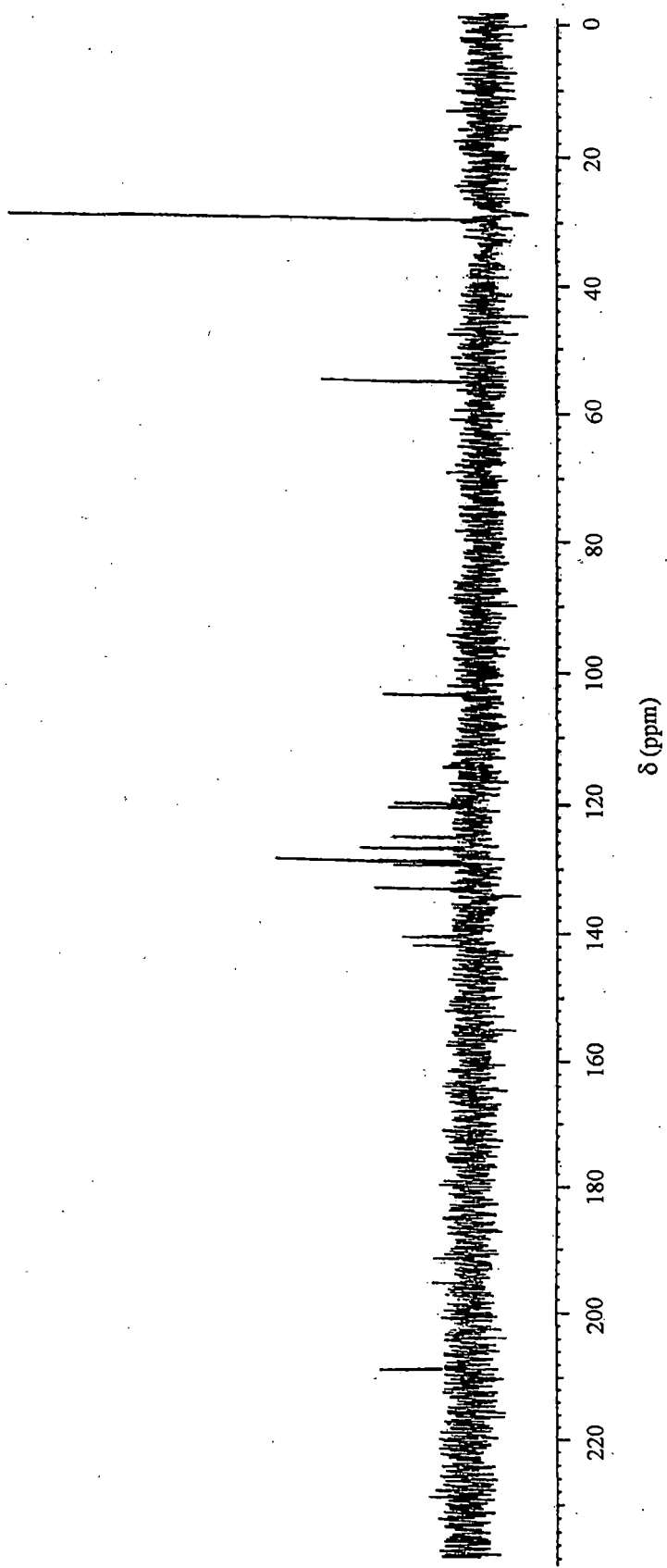


FIG. III. 9. $^{13}\text{C}\{^1\text{H}\}$ NMR SPECTRUM OF $[\text{Pd}(\text{L}^{\circ})\text{Cl}](2\text{B})$ IN CDCl_3 .

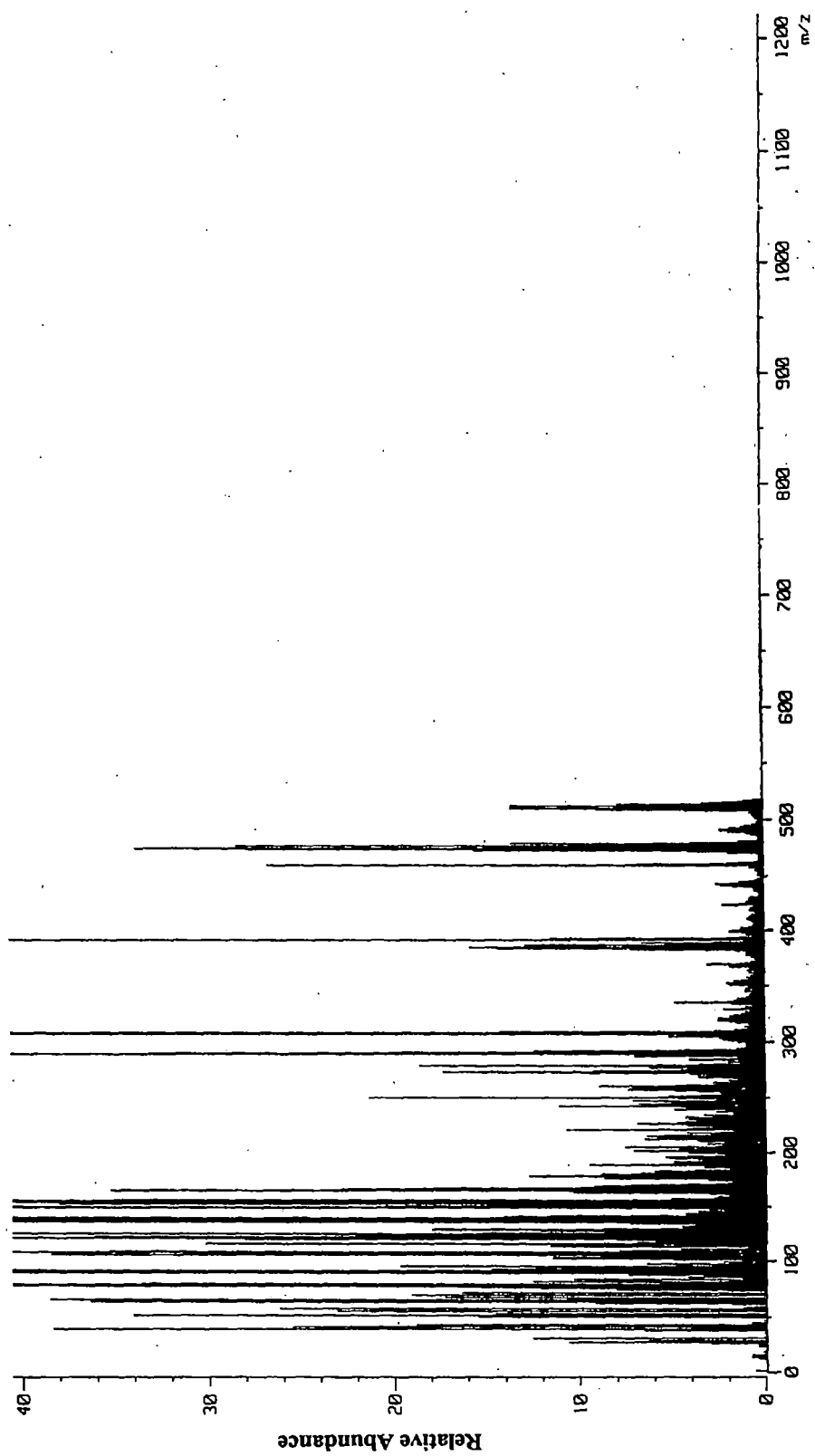


FIG. III.10. FAB MASS SPECTRUM OF [Pd (L⁴) Cl](1A) IN *m*-NBA AS MATRIX.

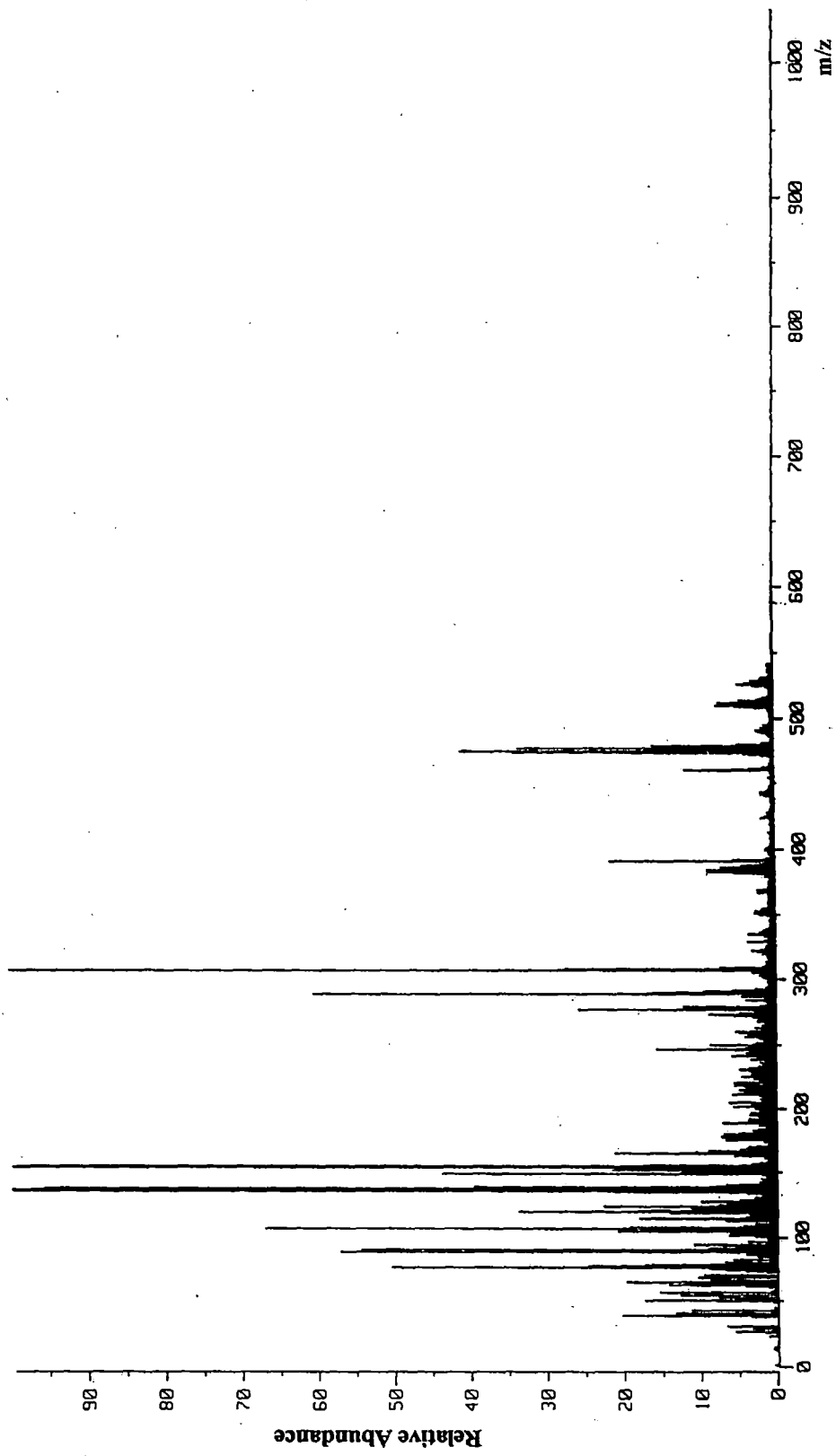


FIG. III. 11. FAB MASS SPECTRUM OF $[Pd(L')Cl](1B)$ IN *m*-NBA AS MATRIX.

III.2.3 STRUCTURE

The structures of cyclopalladates (2A) & (2B) have been determined by X-ray diffraction study. The molecular structure of (2A) is shown in Fig.III.12 along with the adopted atomic numbering schemes. The label for C(2) in chemical structure in our discussion is made C(14) in crystallographic atomic numbering scheme. Significant crystal data and data collection parameters for (2A) are listed in Table III.3. The selected bond lengths and bond angles with estimated standard deviation for (2A) are given in Table III.4.

Compound (2A) contains a palladium metal centre which is four coordinated to C(14) of naphthyl group, N(1) of primary donor azo group, S(1) of thioether as auxiliary donor and Cl in essentially planar but in a distorted square-planar geometry (Fig.III.12). The angles between adjacent atoms in the coordination sphere lie in the range of $98.8(2)^\circ$ [C(14)-Pd-Cl] to $78.2(2)^\circ$ [N(1)-Pd-C(14)]. The maximum deviation is represented by the bite angle N(1)-Pd-C(14) of $78.2(2)^\circ$. This type of distortion is characteristics of *ortho*-cyclopalladates [6,21].

The Pd-C(14) bond length of $1.994(5)$ Å is very close to the reported [9] bond length of Pd-C(2)[naphthyl] of $2.014(8)$ Å. The Pd-N bond distance of $1.960(4)$ Å is within the value expected based on the sum of the covalent radii [22] for palladium (1.31 Å) and sp^2 nitrogen (0.7 Å) and similar to other distances reported previously [23]. The C(15)-N(2) bond of *five-membered* diazapalladacycle is shorter than C(1)-N(1) bond of other *five-membered* azapalladacycle (1.367 vs 1.428 Å). This suggests

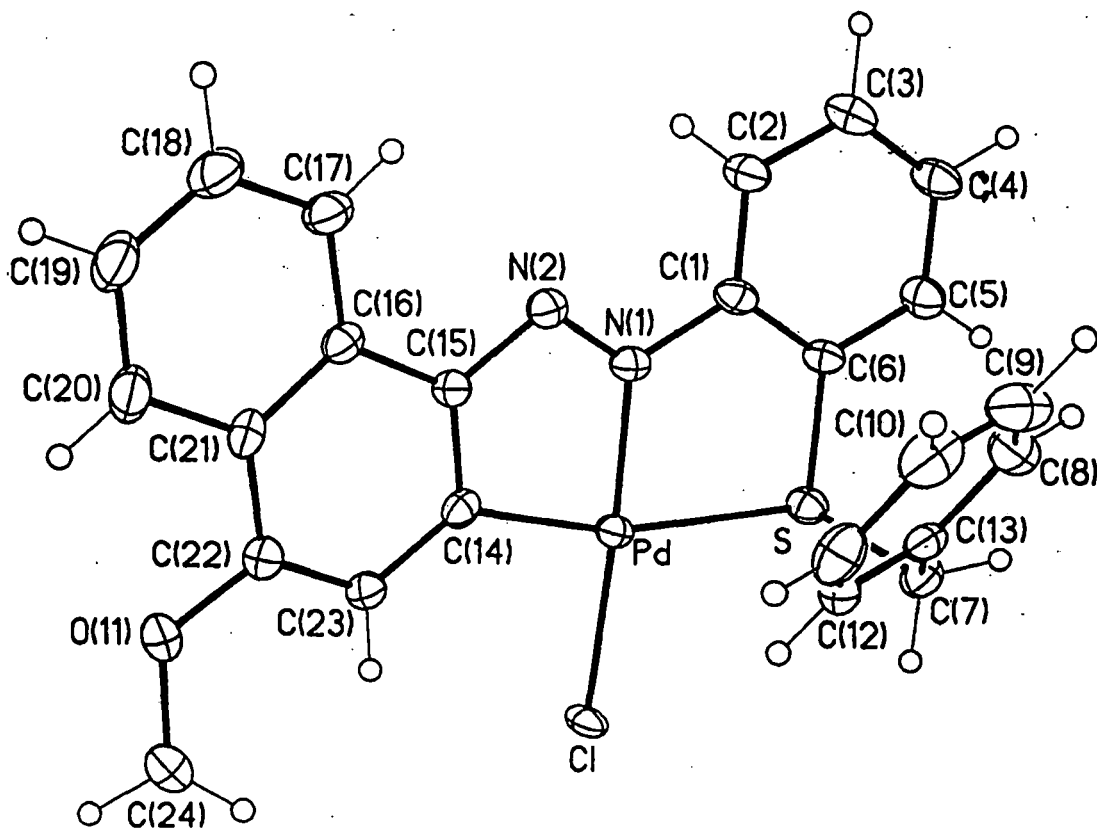


FIG. III. 12. ORTEP DIAGRAM OF MOLECULAR STRUCTURE OF [Pd(L⁶)Cl](2A).

Table III. 3

Crystal data and structure refinement for [PdL⁶Cl] (2A)

| | |
|-----------------------------------|--|
| Identification code | [PdL ⁶ Cl] (2A) |
| Empirical formula | C ₂₄ H ₁₉ ClN ₂ OPdS |
| Formula weight | 525.32 |
| Temperature | 249(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n |
| Unit cell dimensions | a = 10.700(9) Å, α = 90° b = 10.963(2) Å, β = 95.93(4)° c = 18.083(5) Å, γ = 90° |
| Volume, Z | 2109.9(19) Å ³ , 4 |
| Density (calculated) | 1.654 g/cm ³ |
| Absorption coefficient | 1.124 mm ⁻¹ |
| F(000) | 1056 |
| Crystal size | 0.45 X 0.30 X 0.25 mm |
| Crystal color | Black block |
| θ range for data collection | 2.18 to 25.00° |
| Limiting indices | -1 ≤ h ≤ 12, -13 ≤ k ≤ 1, -21 ≤ l ≤ 21 |
| Reflections collected | 4818 |
| Independent reflections | 3696 (R _{int} = 0.0382) |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3696 / 0 / 271 |
| Goodness-of-fit on F ² | 1.352 |
| Final R indices [I > 2σ (I)] | R1 = 0.0426, wR2 = 0.0948 |
| R indices (all data) | R1 = 0.0630, wR2 = 0.1013 |
| Largest diff. peak and hole | 0.914 and -0.696 eÅ ⁻³ |

Table III. 4

Selected Bond lengths [\AA] and angles [$^{\circ}$] for $[\text{PdL}^6\text{Cl}]$, (2A)

| <i>Bond lengths</i> | \AA | <i>Bond lengths</i> | \AA |
|---------------------|--------------|---------------------|--------------|
| Pd-N(1) | 1.960(4) | Pd-C(14) | 1.994(5) |
| Pd-Cl | 2.3271(12) | Pd-S | 2.392(2) |
| S-C(6) | 1.775(5) | S-C(7) | 1.838(5) |
| O(1)-C(22) | 1.359(6) | O(1)-C(24) | 1.436(6) |
| N(1)-N(2) | 1.280(5) | N(1)-C(1) | 1.428(6) |
| N(2)-C(15) | 1.367(6) | C(1)-C(2) | 1.386(7) |
| C(7)-C(13) | 1.492(7) | C(14)-C(15) | 1.394(6) |
| C(15)-C(16) | 1.450(6) | C(14)-C(23) | 1.391(7) |
| <i>Bond angles</i> | $(^{\circ})$ | <i>Bond angles</i> | $(^{\circ})$ |
| N(1)-Pd-C(14) | 78.8(2) | N(1)-Pd-Cl | 177.28(11) |
| C(14)-Pd-Cl | 98.8(2) | N(1)-Pd-S | 85.17(12) |
| C(14)-Pd-S | 163.71(14) | Cl-Pd-S | 97.27(5) |
| C(6)-S-C(7) | 101.4(2) | C(6)-S-Pd | 95.7(2) |
| C(7)-S-Pd | 106.8(2) | C(22)-O(1)-C(24) | 119.2(4) |
| N(2)-N(1)-C(1) | 117.7(4) | N(2)-N(1)-Pd | 120.9(3) |
| C(1)-N(1)-Pd | 121.4(3) | N(1)-N(2)-C(15) | 110.6(4) |
| C(2)-C(1)-C(6) | 120.9(4) | C(2)-C(1)-N(1) | 121.9(4) |
| C(6)-C(1)-N(1) | 117.2(4) | C(5)-C(6)-C(1) | 118.9(4) |
| C(5)-C(6)-S | 120.5(4) | C(1)-C(6)-S | 120.6(4) |
| C(13)-C(7)-S | 114.7(3) | C(23)-C(14)-C(15) | 119.7(4) |
| C(23)-C(14)-Pd | 130.2(4) | C(15)-C(14)-Pd | 110.0(3) |
| N(2)-C(15)-C(14) | 119.7(4) | N(2)-C(15)-C(16) | 118.4(4) |
| C(14)-C(15)-C(16) | 121.8(4) | | |

Symmetry transformations used to generate equivalent atoms.

^a Estimated standard deviations in the least significant digits are given in parentheses.

the presence of more π -electron density in the diaza palladacycle. Here the Pd(II)-S bond length is 2.392(2) Å which is relatively longer other reported Pd-S bond lengths of 2.25-2.31 Å [24-25]. This arises due to the strong *trans* influence of the metallated carbon [26-28]. The sp^2 C(6)-S bond length (1.775 Å) is shorter than sp^3 C(7)-S bond length (1.838 Å) as expected.

The molecular structure of (2B) is shown in Fig.III.13 along with the adopted atomic numbering schemes. The label for C(8) in chemical structure (2B) in our discussion is made C(14) in crystallographic atomic numbering scheme. Significant crystal data and data collection parameters for (2B) are listed in Table III.5. The selected bond lengths and bond angles with estimated standard deviation for (2B) are given in Table III.6.

In cyclopalladate (2B) divalent palladium is bonded to *peri*-C(14) of naphthyl ring, N(1) of primary donor azo group, S(1) of auxiliary donor thioether along with Cl(1). The coordination sphere around palladium centre is essentially planar and also coplanar with naphthyl ring. The square planar coordination sphere around the palladium-centre of the *peri*-palladated compound (2B) shows coordination angles that are closer to the ideal value of 90° than *ortho*-palladated isomer (2A) (Table III.4). It is important to observe that the 'bite' angle at palladium centre of C-Pd-N in (2B) is 91.5(2)° is remarkably higher than 78.2(2)° present in the *ortho*-palladated isomer (2A). The six membered diaza palladacycle has a rather distorted hexagonal

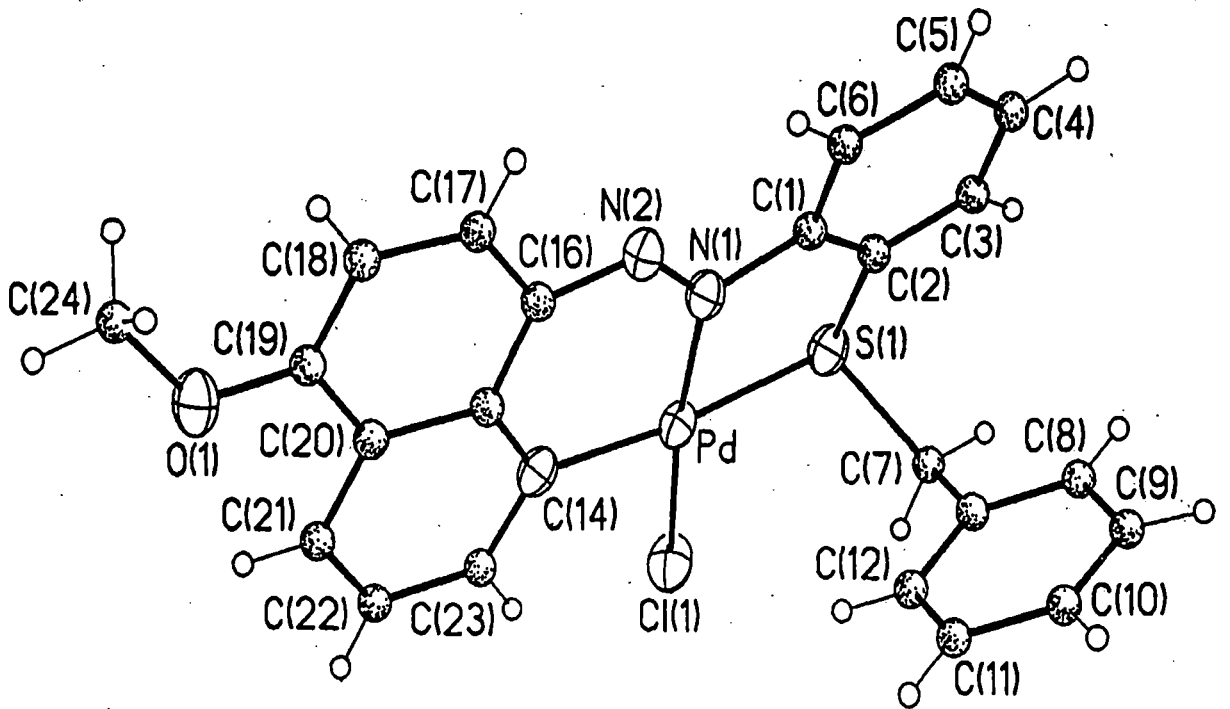


FIG. III. 13. ORTEP DIAGRAM OF MOLECULAR STRUCTURE OF $[Pd(L)Cl](2B)$.

geometry with all angles wider than 120° except for the 'bite' angle at the palladium centre which indicates clearly the geometrical constraints exerted by the palladium(II) ion.

The length of the Pd-C bonds of *peri*-palladated compound (**2B**) is 2.026(4) Å is very close to that of 1.994(5) Å length of the Pd-C bonds of *ortho*-palladated compound (**2A**). In contrast the length of the Pd-N bond of (**2B**) differ significantly from that of (**2A**) (2.014 vs. 1.960 Å), obviously for geometrical constraints. The Pd-S(1) bond length in compound (**2B**) is 2.399 Å, which is longer than reported Pd-S bond length of 2.25-2.31 Å [24-25]. The strong *trans* influence of the metallated carbon is responsible for lengthening of Pd-S bond like in compound (**2A**). The C(16)-N(2) bond (1.38 Å) of six membered diazapalladacycle is significantly shorter than C(1)-N(1) bond (1.459 Å) of five membered azapalladacycle. Here this difference (0.08 Å) in bond lengths is more pronounced for the *peri*-compound (**2B**) compared to the *ortho*-compound (**2A**) (0.06 Å) indicating the presence of more π electron density in the six membered diazapalladacycle.

In general cyclopalladation reactions involving N-donors as cyclometallands lead to five membered palladacycles as observed in compound (**2A**). It is quite unusual that palladium(II) activates the *peri* C-H bond forming a six membered palladacycles with coordination of the palladium centre to the more distant azo N atom, N(1). This is the *second example* [6] of a *peri*-palladated naphthalene derivative with six membered palladacycle.

Table III. 5

Crystal data and structure refinement for [PdL⁶Cl], (2B)

| | |
|-----------------------------------|--|
| Identification code | [PdL ⁶ Cl] (2B) |
| Empirical formula | C ₂₄ H ₁₉ ClN ₂ OPdS |
| Formula weight | 525.32 |
| Temperature | 222(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | a = 8.96700(10) Å, α = 90 ⁰ b = 21.3809(3) Å, β = 90 ⁰ c = 22.5022(2) Å, γ = 90 ⁰ |
| Volume, Z | 4314.18(9) Å ³ , 8 |
| Density (calculated) | 1.618 Mg/m ³ |
| Absorption coefficient | 1.100 mm ⁻¹ |
| F(000) | 2112 |
| Crystal size | 0.30 X 0.20 X 0.20 mm |
| Crystal color | Deep red block |
| θ range for data collection | 1.81 to 28.11 ⁰ |
| Limiting indices | -11 ≤ h ≤ 11, -28 ≤ k ≤ 11, -28 ≤ l ≤ 27. |
| Reflections collected | 14188 |
| Independent reflections | 4866 (R _{int} = 0.0304) |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4866 / 0 / 271 |
| Goodness-of-fit on F ² | 1.250 |
| Final R indices [I > 2σ (I)] | R1 = 0.0462, wR2 = 0.1248 |
| R indices (all data) | R1 = 0.0724, wR2 = 0.1415 |
| Largest diff. peak and hole | 0.622 and -0.736 eÅ ⁻³ |

Table III. 6

Selected Bond lengths [Å] and angles [°] for [PdL⁶Cl], (2B)

| <i>Bond lengths</i> | Å | <i>Bond lengths</i> | Å |
|---------------------|------------|---------------------|------------|
| Pd-N(1) | 2.014(3) | Pd-C(14) | 2.026(4) |
| Pd-Cl(1) | 2.3685(12) | Pd-S(1) | 2.3988(12) |
| S(1)-C(2) | 1.778(5) | S(1)-C(7) | 1.855(5) |
| O(1)-C(19) | 1.354(6) | O(1)-C(24) | 1.444(6) |
| N(1)-N(2) | 1.284(5) | N(1)-C(1) | 1.459(5) |
| N(2)-C(16) | 1.380(5) | C(1)-C(6) | 1.382(7) |
| C(7)-C(13) | 1.496(7) | C(14)-C(23) | 1.411(7) |
| C(15)-C(16) | 1.447(6) | C(16)-C(17) | 1.425(7) |
| <i>Bond angles</i> | (°) | <i>Bond angles</i> | (°) |
| N(1)-Pd-C(14) | 91.5(2) | C(14)-Pd-Cl(1) | 95.97(12) |
| C(14)-Pd-S(1) | 173.78(12) | N(1)-Pd-Cl(1) | 172.24(10) |
| N(1)-Pd-S(1) | 85.14(10) | Cl(1)-Pd-S(1) | 87.63(4) |
| C(2)-S(1)-C(7) | 103.1(2) | C(2)-S(1)-Pd | 96.9(2) |
| C(7)-S(1)-Pd | 110.6(2) | C(19)-O(1)-C(24) | 118.2(4) |
| N(2)-N(1)-C(1) | 111.9(3) | N(2)-N(1)-Pd | 129.5(3) |
| C(1)-N(1)-Pd | 118.6(3) | N(1)-N(2)-C(16) | 124.3(4) |
| C(6)-C(1)-N(1) | 121.8(4) | C(6)-C(1)-C(2) | 119.7(4) |
| N(1)-C(1)-C(2) | 118.5(4) | C(3)-C(2)-C(1) | 119.1(4) |
| C(3)-C(2)-S(1) | 121.6(4) | C(1)-C(2)-S(1) | 119.3(4) |
| C(13)-C(7)-S(1) | 114.6(3) | C(23)-C(14)-Pd | 120.1(3) |
| C(15)-C(14)-C(23) | 116.4(4) | C(15)-C(14)-Pd | 123.5(3) |
| C(14)-C(15)-C(16) | 123.6(4) | C(14)-C(15)-C(20) | 120.6(4) |
| C(16)-C(15)-C(20) | 115.7(4) | N(2)-C(16)-C(17) | 112.6(4) |
| N(2)-C(16)-C(15) | 127.2(4) | C(17)-C(16)-C(15) | 120.2(4) |

Symmetry transformations used to generate equivalent atoms.

^a Estimated standard deviations in the least significant digits are given in parentheses.

III.2.4 PHOTOCHEMICAL BEHAVIOUR

The pink solution of cyclopalladate (**2B**) in dichloromethane, which absorbs at 525 and 500 nm gradually turns into blue solution in presence of sunlight or tungsten lamp (Fig.III.14). The resulting solution shows strong absorption at 622 and 595nm, characteristic of cyclopalladate (**2A**). The photochemical conversion of cyclopalladate (**2B**) to (**2A**) is monitored by spectrophotometer and the maximum spectroscopic yield is ~70%. No conversion is observed in acetonitrile or benzene medium. The conversion of cyclopalladate (**2B**) to cyclopalladate (**2A**) in solution is solvent dependent. No colour change of (**2B**) in dichloromethane is observed in absence of light. The photochemical behaviour of cyclopalladate (**3B**) follows the same pattern. Studies related to the photochemical isomerisation of these species and related compounds are in progress.

III.2.5 OXYGENATION OF Pd-C(NAPHTHYL) BOND

The oxygen insertion into Pd-C bond of organopalladates [29-32] is an important area of organic synthesis, which may lead to selective catalytic processes. We have examined the reactivity cyclopalladates with oxygen transfer agent. At room temperature, a new band at 515 nm develops with the gradual addition of *m*-CPBA to the blue solution of cyclopalladate (**2A**) in dichloromethane and the absorbance

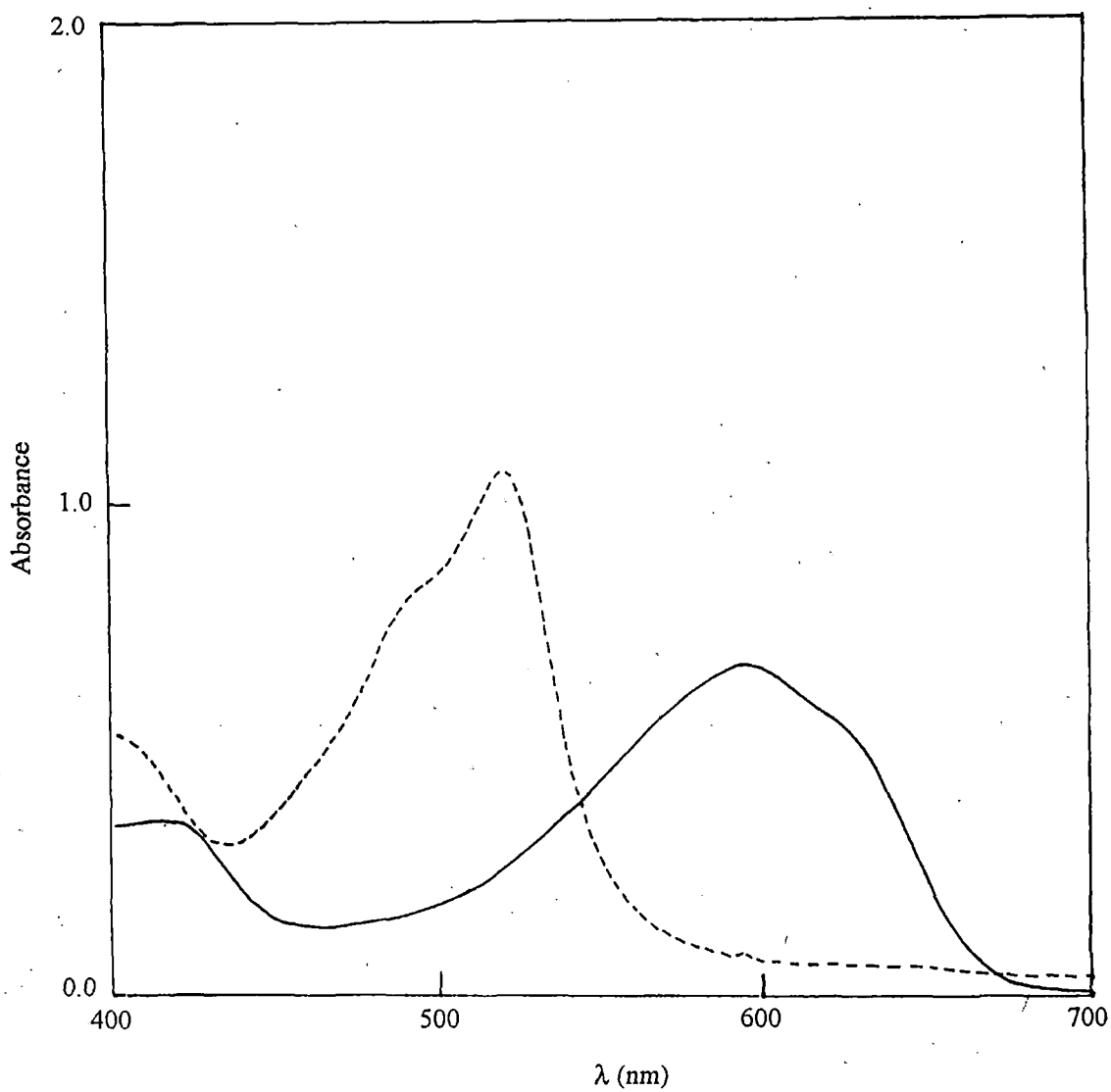


FIG.III. 14. CONVERSION OF [2B] (- - - -) IN DICHLOROMETHANE INTO [2A] (—) IN PRESENCE OF SUN LIGHT.

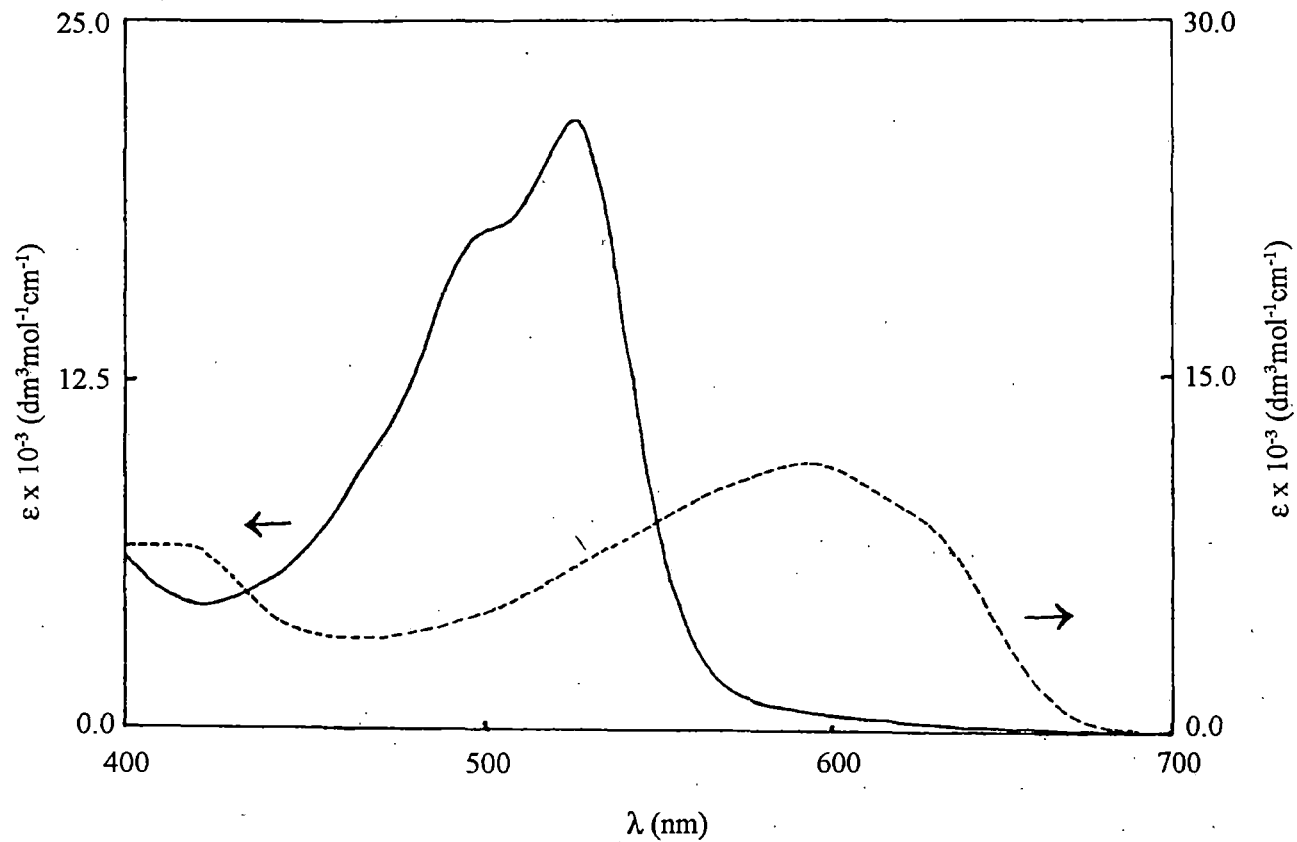


FIG. III. 15. ELECTRONIC SPECTRA OF PURE [2A] (-----) AND AFTER METALOXYLATION (——) IN DICHLOROMETHANE AT 298 K.

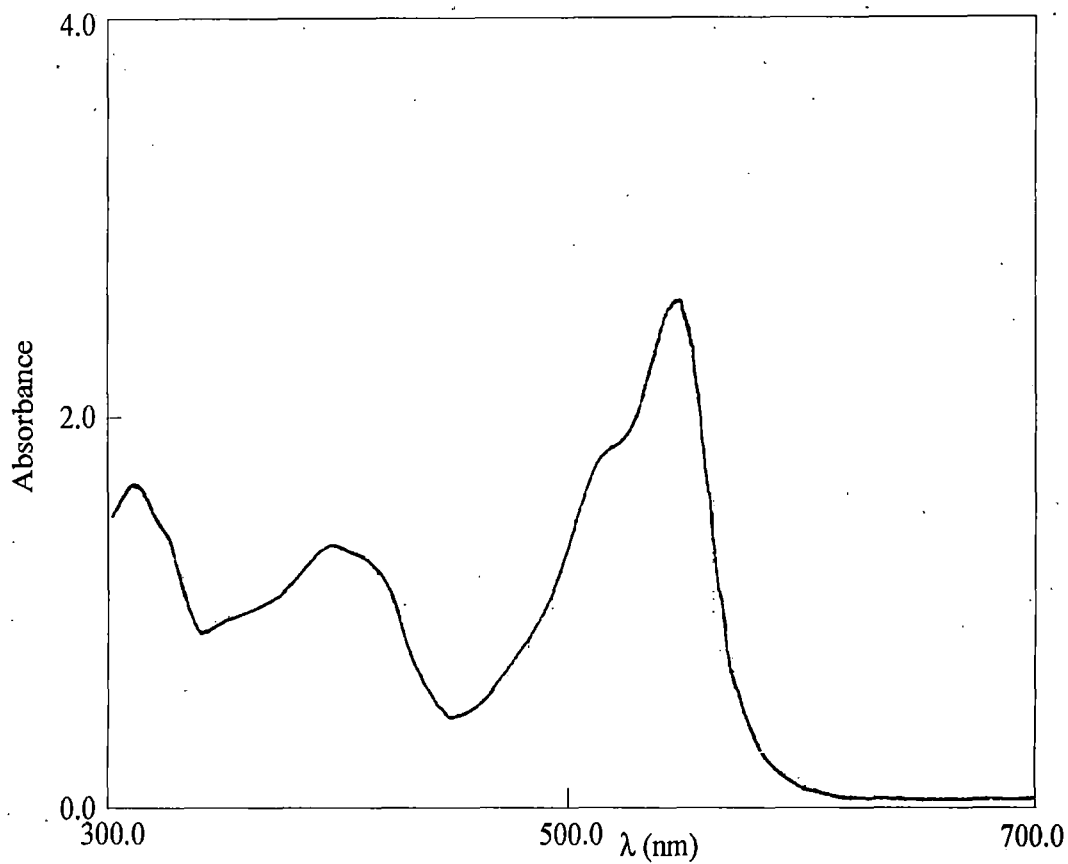


FIG. III. 16. ELECTRONIC SPECTRUM OF [Pd(L⁹)Cl] IN CH₂Cl₂

reaches maximum value when the molar ratio reaches 3:1 at the expense of the absorption bands at 622 and 595 nm of (2A) and remains unchanged in solution (Fig.III.15). The spectrum profile of the reaction mixture is similar to that of the complex $[Pd(L^9)Cl]$, where HL^9 is 1-(2'-benzylthiophenylazo)-2-naphthol (Fig.III.16). The strong absorption at 515 nm [$\epsilon = 16400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, on the basis of the initial concentration of (2A) and limiting absorbance] strongly suggests the presence of one tridentate naphtholato-O,N,S chelate ring per palladium(II), which implies that the Pd(II)-C(naphthyl) σ -bond of (2A) has been selectively oxygenated [10].

The cyclopalladate (3A) follows the same reactivity pattern with *m*-CPBA in dichloromethane. *Peri*-palladates (2B) and (3B) fail to react with *m*-CPBA.

III.2.6 CONCLUSIONS:

1. Palladium(II) successfully activates C(2)-H & C(8)-H bonds of 1-azonaphthyl fragment with neutral thioether as auxiliary donor. Both the isomeric cyclometallates have been isolated and their structures have been determined.
2. The cyclopalladate having C(2)-Pd bond has five membered Pd-C(2)-C(1)-N(1)-N(2) chelate ring whereas the cyclopalladate having C(8)-Pd bond has six membered Pd-C(8)-C(9)-C(1)-N(1)-N(2) chelate ring.
3. In presence of sun light the cyclometallate containing C(8)-Pd bond is converted into its isomer having C(2)-Pd bond in dichloromethane solution. In absence of light conversion of C(8)-Pd \rightarrow C(2)-Pd is not observed.

4. The C(2)-Pd bond undergoes transformation to C(2)-O-Pd with *m*-chloroperbenzoic acid in dichloromethane but the C(8)-Pd bond fails to undergo any transformation.

III.3 EXPERIMENTAL SECTION

III.3.1 PREPARATION OF COMPOUNDS

a. Chemicals:

Commercial palladium dichloride was purchased from Arora Matthey, Calcutta, India. Disodium tetrachloropalladate was prepared following reported method [33].

m-Chloroperbenzoic acid (Fluka AG, Switzerland) and dimethyl sulphate (Riedel-de-Haen, Germany, AG), purified by standard procedure[34-35]. 2-Aminothiophenol (Merck, Germany), 1-naphthol (E. Merck, India), silica Gel (60-120 mesh size) and benzyl chloride (SD Fine Chemicals, India) were used without further purification. All solvents were purified according to standard procedures.

b. Syntheses of substituted 2'-arylazonaphthalene:

(i) Preparation of 2'-benzylthiophenylazo-4-hydroxy-1-naphthalene, (HL⁴)

Preparative procedures for the above mentioned compound have already been described in the chapter II [Sec. II.3.1b. (iv). (a)].

(ii) Preparation of 2'-benzylthiophenylazo-4-methoxy-1-naphthalene, (HL⁶)

Preparative procedures for the above mentioned arylazo compound have already been described in the chapter II [Sec. II.3.1b. (iv)].

(iii) Preparation of 2'-methylthiophenylazo-4-methoxy-1-naphthalene, (HL⁷)

Preparative procedures for the above mentioned compounds have already been described in the chapter II [Sec. II.3.1b. (v)].

(iv) Preparation of 2'-benzylthiophenylazo-4-hydroxy-1-naphthalene, (HL⁹)

The compound HL⁹ was synthesised by following the method similar to the preparation of 2'-benzylthiophenylazo-4-hydroxy-1-naphthalene (HL⁴) using 2-naphthol instead of 1-naphthol according to reported procedure in literature [36].

c. Syntheses of cyclopalladates:

(i) Preparation of isomers of [PdL⁴Cl], (1A) & (1B)

An ethanolic solution (10 cm³) of HL⁴, (0.04 g, 0.11 mmol) was slowly added to sodium tetrachloropalladate (0.035 g, 0.12 mmol) in ethanol (10 cm³). Immediately the colour of the mixture changed to pink violet and the mixture was stirred for 2 h at 300 K. The mixture was kept for 24 h at room temperature. The solvent was removed by evaporation and the residue was thoroughly washed with water followed by a mixture of ethanol and water (1:1 v/v). The residue was dried and dissolved in dichloromethane. The mixture was chromatographed on thin layer of silica gel in preparative scale, a blue band containing (1A) followed by a pink band of (1B) were separated by 10% methanol in benzene (v/v). The separation step was repeated twice

to obtain pure compounds (1A) and (1B). The removal of solvents affords shining blue and pink crystals from the respective solution.

(Yield: 1A, 0.011 g, 0.0215 mmol, *ca.* 20 % & 1B, 0.008 g, 0.0156mmol, *ca.* 15%).

(ii) Preparation of isomers of [Pd L⁶Cl], (2A) & (2B)

The preparation & isolation of isomers of [Pd L⁶Cl], (2A) & (2B) have been made following the above procedure [III.3.1c(i)] except using 5% methanol in benzene(v/v) instead of 10% solution. The following yields are based on sodium tetrachloropalladate (0.035 g, 0.12 mmol) and HL⁶, (0.04 g, 0.1 mmol).

(Yield: 2A, 0.015 g, 0.0285 mmol, *ca.* 25% & 2B, 0.025 g, 0.0476 mmol, *ca.* 40%).

(iii) Preparation of isomers of [Pd L⁷Cl], (3A) & (3B)

The preparation & isolation of isomers of [Pd L⁷Cl], (3A) & (3B) have been made following the above procedure [III.3.1c(i)] except using 4% methanol in benzene(v/v) instead of 10% solution. The following yields are based on sodium tetrachloropalladate (0.03 g, 0.1 mmol) and HL⁷ (0.03 g, 0.1 mmol).

(Yield: 3A, 0.008 g, 0.0178 mmol, *ca.* 18 % & 3B, 0.020g, 0.0445 mmol, *ca.* 45 %).

d. Preparation of complex [PdL⁹Cl]

The synthesis of [PdL⁹Cl] has been made following the above procedure [III.3.1c(i)] except using pure benzene as eluant. Removal of the solvent affords pink micro-crystals of complex and dried in vacuo. The yield is based on disodium tetrachloropalladate (0.035 g, 0.12 mmol) and HL⁹ (0.04 g, 0.11 mmol).

(Yield: 0.020g, 0.039 mmol, 35%).

III.3.2 CHARACTERISATION OF COMPOUNDS

All compounds were characterized by C, H and N microanalysis, which was done from I.A.C.S., Calcutta and C.D.R.I., Lucknow, India. The microanalytical data are given in the Table III.7.

III.3.3 Physical Measurements

(i) *Infrared Spectra:*

IR spectra were recorded on JASCO 5300 FT-IR spectrometer with samples prepared as KBr pellets. Far-IR spectra were obtained from Bruker IFS-65 spectrophotometer.

(ii) *Electronic spectra:*

Electronic spectra were obtained on Shimadzu UV 240 and Hitachi U-3400 spectrophotometer.

Table III. 7

Elemental analysis data of palladium compounds

| Compounds | % C | % C | % H | % H | % N | % N |
|-----------------------------|--------|-------|--------|-------|--------|-------|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| [PdL ⁴ Cl], (1A) | 54.00 | 53.46 | 3.32 | 3.55 | 5.48 | 5.12 |
| [PdL ⁴ Cl], (1B) | 54.00 | 53.35 | 3.32 | 3.77 | 5.48 | 5.09 |
| [PdL ⁶ Cl], (2A) | 54.85 | 54.59 | 3.62 | 3.89 | 5.33 | 5.37 |
| [PdL ⁶ Cl], (2B) | 54.85 | 55.12 | 3.62 | 3.83 | 5.33 | 5.39 |
| [PdL ⁷ Cl], (3A) | 48.1 | 46.93 | 3.34 | 3.12 | 6.23 | 5.86 |
| [PdL ⁷ Cl], (3B) | 48.1 | 47.68 | 3.34 | 3.23 | 6.23 | 6.07 |

(iii) NMR spectra:

^1H and $\{^1\text{H}\}^{13}\text{C}$ NMR spectra were recorded on Bruker DPX 300 spectrometer.

(iv) FAB mass spectra:

The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass Spectrometer/ Data System using Argon/Xenon (6 kV, 10 mA) at C.D.R.I., Lucknow, India. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix. The matrix peaks may appear at m/z 136, 137, 154, 289, 307 in the absence of any metal ions.

(v) X-ray crystallography:

Single crystals of $[\text{PdL}^6\text{Cl}]$ (**2A**) were grown by slow diffusion of hexane into a dichloromethane solution of the compound (5:2 v/v). The single crystals of $[\text{PdL}^6\text{Cl}]$ (**2B**) were also collected following the above method (7:3 v/v).

Data collection and structure refinement has been done by Professor A. L. Rheingold and his group, Department of Chemistry & Biochemistry, University of Delaware, Newark, U.S.A.

Detailed bond lengths and bond angles data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters and also hydrogen coordinates and isotropic displacement parameters of compound (**2A**) are

given in Appendix II (Table 1., Table 2., Table 3. and Table 4. respectively) and those of (2B) are given in Appendix II (Table 5., Table 6., Table 7. and Table 8. respectively).

(vi) *Elemental Analysis:*

Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyser.

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