

## Synthesis and Characterization of Palladium Acetylide Complexes with Heterocyclic N-Donor Ligands

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### Abstract

Mono- and bis-acetylide complexes of palladium with two different *N*-donor ligands of the type *cis*-[Pd (LL) (C≡CR)<sub>2</sub>] (LL = 1,10-phenanthroline, R = C<sub>6</sub>H<sub>5</sub> **3**, and LL = 2, 2'-bipyridine, R = C<sub>6</sub>H<sub>5</sub> **5**) and [Pd (LL) Cl (C≡CR)] (LL = 1,10-phenanthroline, R = C<sub>6</sub>H<sub>5</sub> **4**, and LL = 2, 2'-bipyridine, R = C<sub>6</sub>H<sub>5</sub> **6**) were prepared by the dehydrohalogenation reaction between *cis*-[Pd (LL) Cl<sub>2</sub>] and phenyl acetylene ligand. The complexes were characterized by IR, UV-vis spectroscopy. These palladium-carbon  $\sigma$ -bonded complexes were sensitive to air in contrast to the platinum analogues, that limits their characterization by NMR spectroscopy. The complexes were soluble in common organic solvent except methanol and hexane.

Keywords: Palladium; Dehydrohalogenation; Acetylide; Palladium-carbon  $\sigma$ -bond; 1,10-phenanthroline; 2, 2'-bipyridine.

### 1. Introduction

In recent years transition-metal  $\sigma$ -acetylide complexes and their polymers have attracted great interest from researchers because of their potential application in the field of electronic materials [1-3]. Among the transition metals, platinum containing  $\sigma$ -acetylide complexes and their polymers have been studied since the 1990s [4] due to their unique characteristics, such as catalytic activity [5, 6], conductivity [7, 8], photoconductivity [9-11], optical nonlinear susceptibility [12-17], chirality [18], liquid crystallinity [1, 19, 20], magnetic susceptibility [1, 21], photoluminescence [21-23], electroluminescence [22, 24], and for their versatile applications in different areas, for instance, solar energy conversion [25, 26] low-power up conversion [27-29], oxygen sensing [29, 30], vapochromism [31], photochromism [20, 32], and the active layer of light-emitting diodes [23, 24, 33-35].

Platinum acetylide complexes mainly use alkyl phosphines as auxiliary ligands [4]. However, diimine platinum(II) alkynyl complexes are also used to construct geometrically well-defined donor-sensitizer dyads and triads for photoluminescence [36]. The luminescence property is mainly exhibited by diimine

2, 2'-bipyridine or 1, 10-phenanthroline) and acetylide ligands, arising due to the transition from the metal triplet excited state to the ligand  $\pi^*$  [ $d\pi$  (Pt)  $\rightarrow \pi^*$  (diimine)] (MLCT), and there are also ligand-to-ligand charge transfer [ $\pi$  (aryalkynyl)  $\rightarrow \pi^*$  (diimine)] (LLCT) transitions arising from the triplet aryl alkynyl to the diimine [24, 26, 37-43]. These triplet emitters were investigated for practical use in molecular photochemical devices [35, 37]. For example, Jun Ni and coworkers synthesized 3, 8-bis (trimethylsilylethynyl)-Phen coordinated Pt(II)-acetylide complex and they observed that this complex in benzene solution shows a strong, selective, naked-eye perceivable, reversible, reproducible vapochromism and vapoluminescence properties [44]. The change in chromatic behavior was associated with the presence of a dual recognition site: the  $\pi$ - $\pi$  stacking site situated above the phen(1, 10-phenanthroline) rings, and the two phenylacetylene auxiliaries.

Hagihara et al. first synthesized transition metal acetylide complexes of Ni, Pd, and Pt by dehydrohalogenation or by ligand exchange reaction using CuI catalyst [45, 46]. Later, a large number of platinum acetylide complexes and poly-yne polymers

were prepared and their photophysics was well-studied [4]. Some palladium and nickel complexes were also reported, but their photophysical properties were not studied. Transition metal acetylides usually have alkyl phosphines as auxiliary ligands that impart solubility in common organic solvents and stability. Compared to the platinum, there have been a few reports on the preparation and study of the photophysical properties of palladium acetylide complexes. In this report, we studied the synthesis of palladium acetylide complexes. We used heterocyclic N-donor (diamine) chelated palladium as the starting material: *cis*-[Pd(1,10-phenanthroline)Cl<sub>2</sub>] and *cis*-[Pd(2,2'-bipyridine)Cl<sub>2</sub>].

## 2. Experimental

### 2.1. Materials and Measurements

Starting materials and solvents used in this study were obtained from Merck (Germany), Wako Pure Chemicals Industries Ltd. and JHD (China). These reagents and solvents were analytical grade, and were used for reactions and purification without further purification, unless otherwise mentioned. All the reactions were carried out under nitrogen atmosphere following vacuum line techniques [47]. Solvents were pre-dried, then refluxed for 24 h, and finally freshly distilled before use [47]. The formation of products was confirmed by TLC analysis, UV-Visible, and IR spectroscopy. The products were purified by column chromatography. UV-vis spectral measurements were carried out on a SHIMADZU (UV-1800) UV-vis spectrophotometer. Infrared spectral measurements were undertaken either as solutions in CH<sub>2</sub>Cl<sub>2</sub> or as KBr solid disks using SHIMADZU (Prestidge-21) FT-IR spectrometer.

### 2.2. Synthesis of Starting Materials

#### 2.2.1. Synthesis of *cis*-Pd(2,2'-bipyridine)Cl<sub>2</sub> 1

The complex *cis*-Pd(2,2'-bipyridine)Cl<sub>2</sub> was prepared following the procedure reported in the literature [37]. M.P.: 181 °C. IR (KBr, ν/cm<sup>-1</sup>): 1603 (C=N), 446 and 411 (Pd-Cl).

#### 2.2.2. Synthesis of *cis*-Pd(1,10-phenanthroline)Cl<sub>2</sub> 2

The complex *cis*-Pd(1,10-phenanthroline)Cl<sub>2</sub> was prepared following the procedure reported in the literature [37]. M.P.: 190 °C. IR (KBr, ν/cm<sup>-1</sup>): 1603 (C=N), 434 and 419 (Pd-Cl).

### 2.3. Synthesis of Palladium Acetylide Complexes

#### 2.3.1. Synthesis of *cis*-Pd(1,10-phenanthroline)(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> 3

To a degassed mixture of dichloromethane (30 ml) and diisopropylamine (15 ml) (2:1), *cis*-Pd(1,10-phenanthroline)Cl<sub>2</sub> (60 mg, 0.168 mmol), phenylacetylene (42.83 mg, 0.419 mmol) and copper(I) iodide (1 mg, 0.008 mmol, 5 mol % of precursor 1) were added and then stirred for 5.5 h under a strictly maintained atmosphere of nitrogen. As the reaction was proceeding, the color of the mixture turned into pale yellow within 10 minutes. After 5 h, the product was identified in the reaction by IR spectroscopy. Then the liquid solvent mixture was removed and the crude product was dissolved in a minimum amount of dried dichloromethane. Addition of hexane to the dichloromethane solution afforded compound 4 (mono-acetylide) which was further purified by neutral alumina column chromatography using dichloromethane as eluent (Yield: 34%). The remaining supernatant liquid, obtained from the precipitation of 4, was removed by rotary evaporator giving a solid product, which after subsequent purification by alumina column chromatography afforded compound 3 (bis-acetylide) in 57% yield. The pure product 3 was insoluble in methanol but highly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMSO and n-hexane. The reddish yellow product 4 was insoluble in n-hexane and methanol, but highly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and DMSO. Spectroscopic data of product 3: M.P.: 175 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>, ν/cm<sup>-1</sup>): 2119 (C≡C), 1605 (C=N), 1600 (Ar. C=C), 1477 (Ar. C=C), 3044 (Ar. H). Spectroscopic data for product 4: M.P.: 242 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>, ν/cm<sup>-1</sup>): 2150 (C≡C), 1604 (C=N), 1599 (Ar. C=C), 1499 (Ar. C=C), 3062 (Ar. H), 419 (Pd-Cl).

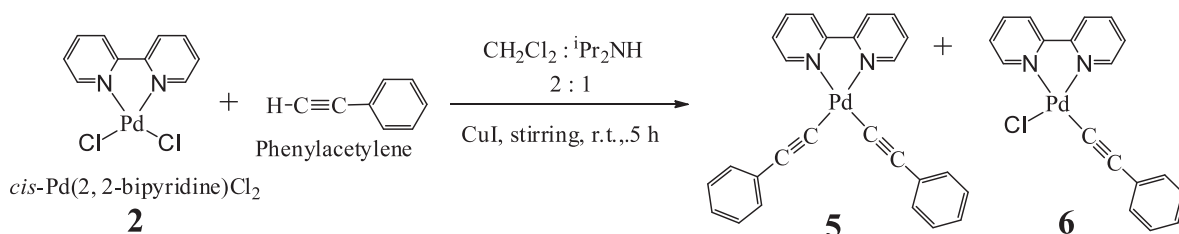
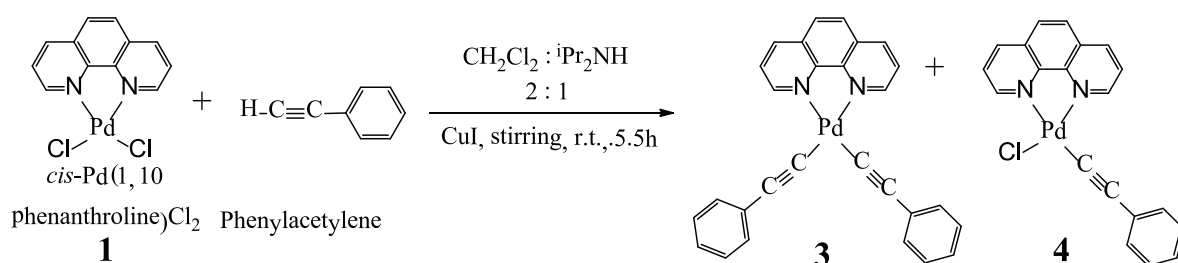
#### 2.3.2. Synthesis of *cis*-Pd(2,2'-bipyridine)(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> 5

To a degassed 2:1 mixture of dichloromethane (30 ml) and diisopropylamine (15 ml), *cis*-Pd(2,2'-bipyridine)Cl<sub>2</sub> (60 mg, 0.177 mmol), phenylacetylene (46 mg, 0.449 mmol) and copper(I) iodide (1.7 mg, 0.009 mmol, 5 mol %) were added and then stirred for 5 h under a strictly maintained atmosphere of nitrogen. As the reaction was proceeding, the color of the mixture turned into pale yellow within 10 minutes. The product was identified in the reaction by IR spectroscopy. Compound 5 (bis-acetylide) and 6 (mono-acetylide) were obtained similarly in 54% and 30% respectively, as for compound 3 and 4 (section 2.3.1). Compound 5 was highly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMSO and n-hexane except methanol, whereas compound 6 was soluble in most organic solvent except methanol and hexane. Spectroscopic data of product 5: M.P.: 189 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, ν/cm<sup>-1</sup>): 2120 (C≡C), 1606 (C=N), 1599 (Ar. C=C), 1488 (Ar. C=C), 3069 (Ar. H). Spectroscopic data for product 6: M.P.: 209 °C IR (CH<sub>2</sub>Cl<sub>2</sub>, ν/cm<sup>-1</sup>): 2149 (C≡C), 1606 (C=N), 1598 (Ar. C=C), 1471 (Ar. C=C), 3052 (Ar. H), 453 (Pd-Cl).

### 3. Results and Discussion

*N*-donor ligands **1** and **2** were prepared following the procedure reported in the literature [36] and the formation of the products was confirmed by M.P. and IR (Experimental section 2.2). Palladium ethynyl complexes **3** and **4** were formed by the Hagihara coupling reaction between *cis*-Pd (1, 10 phenanthroline) Cl<sub>2</sub> and 2.5 equivalent of phenylacetylene in the mixture of dichloromethane and diisopropylamine (2:1), at room temperature, in the presence of catalyst CuI, and the reaction was completed within 5.5 h (Scheme 1). Pure pale yellow solid product **3** was obtained as 57% yield. The pure reddish yellow solid product **4** was obtained as 34% yield.

The complexes **5** and **6** were prepared similarly using *cis*-Pd (2, 2'-bipyridine) Cl<sub>2</sub> as starting material instead of *cis*-Pd (1,10 phenanthroline) Cl<sub>2</sub> (Scheme 2). Pure yellow solid product **5** was obtained as 54% yield. The pure pale black solid product **6** was obtained as 30% yield. The complexes **3**, **4**, **5**, and **6** were identified by FT-IR and UV-vis spectroscopy. Due to the slow decomposition of the complexes in solution, it was not possible to characterize the compound by NMR spectroscopy.



#### 3.1. UV-vis Spectroscopy

The UV-vis spectral measurements of **1**, 10-phenanthroline and **2**, 2'-bipyridine were carried out in methanol, spectral data is shown in Table 1. The spectrum of **1**, 10-phenanthroline showed two absorption peaks at 268 and 224 nm, and that of **2**, 2'-bipyridine also showed two peaks at 270 and 230 nm that were assigned to  $n-\pi^*$  and  $\pi-\pi^*$  transition, respectively. The spectral measurements of palladium precursor **1** and **2** were performed in DMSO and the data are also given in Table 1. Complex **1** displayed three peaks at 279, 357 and 341 nm, and **2** gave peaks at 274, 360 and 345 nm which are tentatively assigned to the  $n-\pi^*$ ,  $\pi-\pi^*$  and  $d-d$  ( ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (*P*) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (*F*)) transitions, respectively. The spectra of complex **3**, **4**, **5** and **6** in CH<sub>2</sub>Cl<sub>2</sub> showed two absorption bands (Table 1), the first bands at around 270 nm are designated to ligand-to-ligand charge transfer (LLCT) [ $\pi$ (arylalkynyl)  $\rightarrow \pi^*$  (diimine)] transitions and the broad second bands at around 320-360 nm are identified as the MLCT transitions. The M  $\rightarrow$  L charge-transfer transitions originate from the filled orbitals of metal-ion to the low-lying empty  $\pi^*$  orbitals of ligands [48-51]. Representative spectra of compounds **3** and **4** are shown in Fig.1. The broad charge transfer transitions (MLCT) obscured the  $d-d$  ( ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (*P*) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (*F*)) and one intra ligand transition bands [24, 52]

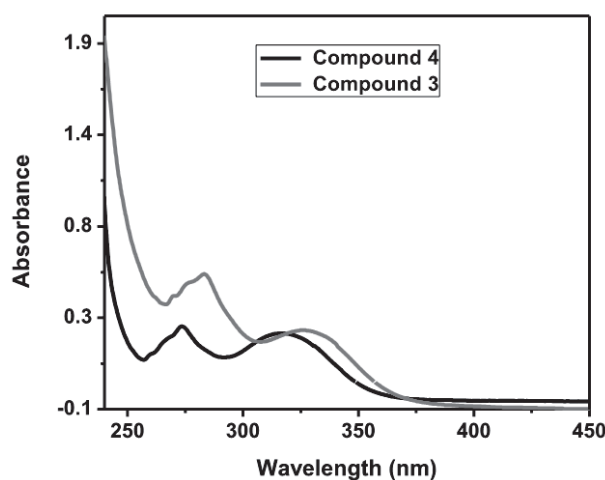


Fig. 1 : UV-vis spectra for the compound 3 and 4

Table 1. UV-Visible spectral data of Pd acetylide complexes and their precursors.

Compound	UV-Vis (nm) peaks/		
1,10-phenanthroline <sup>a</sup>	268 ( $\lambda_{\max}$ )	224	-
2, 2'-bipyridine <sup>a</sup>	270 ( $\lambda_{\max}$ )	230	-
[ <i>cis</i> -Pd(1, 10-phenanthroline)Cl <sub>2</sub> ] <sup>b</sup> <b>1</b>	279 ( $\lambda_{\max}$ )	357	341
[ <i>cis</i> -Pd(2, 2'-bipyridine)Cl <sub>2</sub> ] <sup>b</sup> <b>2</b>	274 ( $\lambda_{\max}$ )	360	345
Phenylacetylene (ligand) <sup>c</sup>	279 ( $\lambda_{\max}$ )	326	-
[ <i>cis</i> -Pd(1, 10 phenanthroline)(C≡CC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>c</sup> <b>3</b>	283 ( $\lambda_{\max}$ )	326-360	-
[ <i>cis</i> -Pd(1, 10 phenanthroline)Cl(C≡CC <sub>6</sub> H <sub>5</sub> )] <sup>c</sup> <b>4</b>	273 ( $\lambda_{\max}$ )	320-350	-
[ <i>cis</i> -Pd(2, 2'-bipyridine)(C≡CC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>c</sup> <b>5</b>	280 ( $\lambda_{\max}$ )	328-354	-
[ <i>cis</i> -Pd(2, 2'-bipyridine)Cl(C≡CC <sub>6</sub> H <sub>5</sub> )] <sup>c</sup> <b>6</b>	271 ( $\lambda_{\max}$ )	322-352	-

<sup>a</sup> In DMSO solution. <sup>b</sup> In CH<sub>3</sub>OH solution. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution.

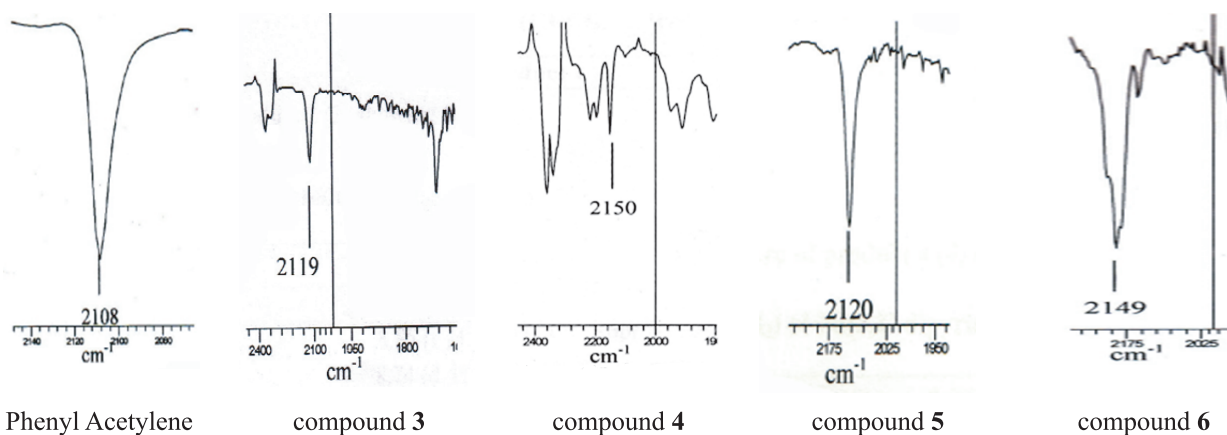
### 3.2. IR Spectroscopy

The carbon-carbon triple bond (C≡C) stretching frequency is diagnostic of the characterization of the stretching metal ethynyl complexes. The IR spectra (C≡C str.) of the ligand and metal acetylide complexes are shown in Fig. 2. The IR spectrum of phenylacetylene has characteristic absorption bands at 3298 cm<sup>-1</sup> and 2108 cm<sup>-1</sup> which indicate the presence of the acetylenic (C-H) and (C≡C) bonds, respectively. The bis acetylide complexes **3** and **5** depicted one (C≡C) bond stretching peak at 2119 cm<sup>-1</sup> and 2120 cm<sup>-1</sup>, respectively, which are similar to the literature values of platinum bis-acetylide complexes [26]: [Pt(phen)(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>;  $\nu$ /cm<sup>-1</sup> 2106, 2116 (C≡C)] and [Pt(phen)(C≡CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>;  $\nu$ /cm<sup>-1</sup> 2110, 2120 (C≡C)].

The (C≡C) bond stretching frequency of mono acetylide complexes **4** and **6** depicted at 2150 cm<sup>-1</sup> and 2149 cm<sup>-1</sup> respectively. In general, the (C≡C) bond stretching frequency of Pt/Pd mono acetylide complexes is found at higher frequency than bis acetylide complexes e.g. [*trans*-PtCl(PBu<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>5</sub>);  $\nu$ /cm<sup>-1</sup> 2119 (C≡C)] and [*trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>;  $\nu$ /cm<sup>-1</sup> 2101 (C≡C)][51]. For complexes **4** and **6**, the (Pd-Cl) stretching frequency was observed at 419 cm<sup>-1</sup> and 453 cm<sup>-1</sup>, respectively [49]. Thus, the presence of  $\nu$ (C≡C) and  $\nu$ (Pd-Cl) confirmed the formation of mono-acetylide complexes **4** and **6**. However, for complex **3** and **5**, no  $\nu$ (Pd-Cl) around 400-450 cm<sup>-1</sup> indicated that both chlorides of *cis*-Pd(1,10 phenanthroline)Cl<sub>2</sub> and *cis*-Pd(2,2'-bipyridine)Cl<sub>2</sub> were substituted by the C≡C-Ph.

Table 2. IR spectral data of Pd acetylide complexes and their precursors

Compound	IR Stretching frequency $\nu/\text{cm}^{-1}$					
	$\nu(\text{C}=\text{N})$	$\nu(\text{Pd}-\text{Cl})$	$\nu(\text{C}\equiv\text{C})$	$\nu(\equiv\text{C}-\text{H})$	$\nu(\text{Ar.C}=\text{C})$	$\nu(\text{Ar.C}-\text{H})$
Phenylacetylene	-	-	2108	3298	1606 1489	3078
[ <i>cis</i> -Pd (1, 10-phenanthroline) $\text{Cl}_2$ ] <b>1</b>	1603	438 419	-	-	-	-
[ <i>cis</i> -Pd (1, 10-phenanthroline) ( $\text{C}\equiv\text{CC}_6\text{H}_5$ ) $_2$ ] <b>3</b>	--	419	2120	-	1600 1500	3076 3062
[ <i>cis</i> -Pd (1, 10-phenanthroline) Cl ( $\text{C}\equiv\text{CC}_6\text{H}_5$ )] <b>4</b>	1604	419	2150	-	1599 1499	3062
[ <i>cis</i> -Pd (2, 2'-bipyridine) $\text{Cl}_2$ ] <b>2</b>	1603	446 411	-	-	-	-
[ <i>cis</i> -Pd (2, 2'-bipyridine) ( $\text{C}\equiv\text{CC}_6\text{H}_5$ ) $_2$ ] <b>5</b>	1606	-	2120	-	1599 1488	3069
[ <i>cis</i> -Pd (2, 2'-bipyridine)Cl ( $\text{C}\equiv\text{CC}_6\text{H}_5$ )] <b>6</b>	1607	453	2149	-	1598 1471	3052

Fig 2: Selected portions IR ( $\text{CH}_2\text{Cl}_2$ ) spectra of the phenyl acetylene and palladium acetylide complexes **3**, **4**, **5**, **6**, showing

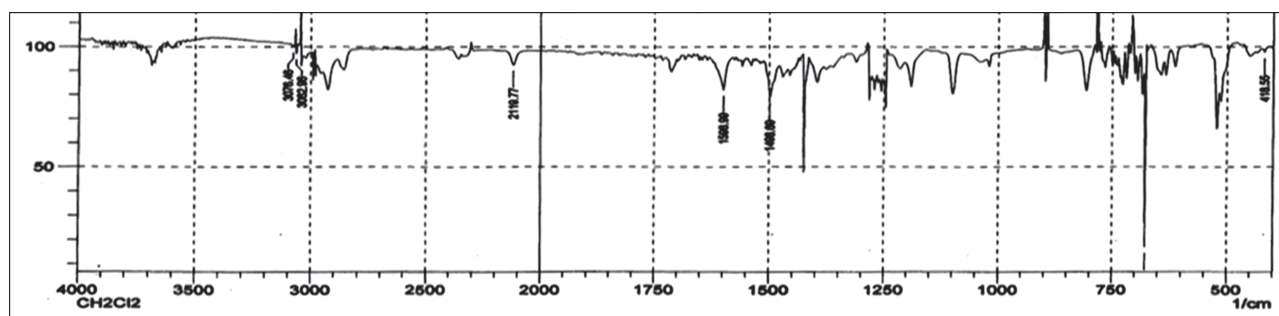


Fig. 3 IR ( $\text{CH}_2\text{Cl}_2$ ) spectrum of palladium acetylide complex 3

### 3.3. General Discussion

A large number of  $\sigma$ -acetylide complexes and polymers of platinum has been reported for the last four decades because of their application in materials chemistry [4]. Though palladium [53] is equally important as platinum, both induce spin-orbit coupling – an important characteristic for triplet emitters, reports on the synthesis of palladium acetylide are rare. This is due to the fact that the stability of palladium acetylides is lower than platinum acetylide [51, 54]. However, there are some reports of palladium acetylide with tri-alkyl phosphine as auxiliary ligands [54]. Environmentally friendly *N*-donor ligands were first made by our group for the synthesis of a series of platinum acetylide that are stable in solid state and in solution [55], after that, a good number platinum (diamine) $\text{Pt}(\text{C}\equiv\text{C-R})_2$  complexes was prepared, and their photophysical properties were studied for their applications in optoelectronics [36, 37, 40-42, 44]. In this study, the synthesis of palladium acetylides using 2, 2'-bipyridine and 1,10 phenanthroline as auxiliary ligand was explored. The structures of newly formed mono- and bis-acetylides were established by UV-Vis and IR spectroscopy. However, further characterizations by NMR spectroscopy were not possible due to the slow decomposition of the complexes in solvents.

### 4. Conclusions

A series of palladium acetylide complexes of the type *cis*- $[\text{Pd}(\text{LL})(\text{C}\equiv\text{CR})_2]$  (LL= 1,10-phenanthroline, R =  $\text{C}_6\text{H}_5$  3, and LL = 2, 2-bipyridine, R =  $\text{C}_6\text{H}_5$  5) and  $[\text{Pd}(\text{LL})\text{Cl}(\text{C}\equiv\text{CR})]$  (LL = 1, 10-phenanthroline, R =  $\text{C}_6\text{H}_5$  4, and LL = 2, 2'-bipyridine, R =  $\text{C}_6\text{H}_5$  6) were synthesized by the dehydrohalogenation reaction of *cis*- $[\text{Pd}(\text{LL})\text{Cl}_2]$  with phenylacetylene ligand in presence of CuI catalyst. All of the synthesized products were purified by recrystallization and alumina column chromatography, and identified by FT-IR and UV-visible spectroscopy. Since the Pd-acetylide complexes are unstable in solid state and in solution at room temperature, and are also sensitive to air and moisture, it was not possible to further characterize them by the NMR spectroscopy.

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