

Determination and Characterization of New Palladium Complexes and Study of Their Properties

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Abstract: In the current study, two complexes prepared using ligands derived from acetohydrazide, tris [(naphthylene 1-yl methylen) acetohydrazide $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and tris [(3-phenyl alylidene) acetohydrazide] $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ using spectrometry techniques of UV-VIS, IR, ¹HNMR and ¹³CNMR methods. In the current compounds, the way these ligands bonding with central metal investigated using IR and ¹HNMR methods. Substitutions of C=N and C=O indicate that palladium being coordinated with ligands.

Key words: Heterocyclic Compounds • Coordination Chemistry • FT-IR And UV-Visible Spectroscopy • Acetohydrazide

INTRODUCTION

In the last decade Schiff base ligands have received more attention mainly because of their wide application in the field of catalysis and due to their antimicrobial, anti-tuberculosis and antitumor activity [1]. They easily form stable complexes with most transition metal ions.

Schiff base complexes (derived from heterocyclic compounds) have increased the interest in the development of the field of bioinorganic chemistry [2]. Heterocyclic compounds are good ligands due to the presence of at least one ring nitrogen atom with a localized pair of electrons. The successful application has led to the formation of series of novel compounds with a wide range of physical, chemical and biological properties [3-6], spanning a broad spectrum of reactivity and stability. Keeping in view of the pronounced biological activity of the metal complexes of Schiff bases derived from heterocyclic compounds. Palladium (Pd), named after the asteroid Pallas, is arguably the most versatile and ubiquitous metal in modern organic synthesis [7, 8]. Palladium-mediated processes have become essential tools, spanning countless applications in the syntheses of natural products, polymers, agrochemicals and pharmaceuticals. Palladium can be used to conduct myriad transformations with organic molecules. In fact, there are a number of well-known name reactions that feature this metal, including the Heck, Suzuki, Stille and Buchwald-

Hartwig cross-couplings; the Wacker process; [9] and the Tsuji-Trost allylation. In addition, Pd also enables hydrogenation; hydrogenolysis; carbonylation; the formation of C-C, C-O and C-N and C-S bonds, cycloisomerization and even per cyclic reactions. Palladium-based methods often proceed under mild conditions affording high yields, with excellent levels of stereo-, regio- and chemo selectivity. Domino catalysis, where multiple Pd-catalyzed transformations are carried out in a single operation, is also a powerful extension of this chemistry. Acidhydrazides have frequently been investigated for testing their potentiality as tuberculostats [10]. Hydrazides and their condensation products have displayed diverse range of biological properties such as bactericidal, anti-fungal, anti-convulsant, anti-helminthic, anti-tumor, anti-leprotic, anti-malarial, anti-cancer, anti-depressant, anti-HIV, analgesic-anti-inflammatory, leishmanicidal, vasodilator activities [11]. We are reporting the synthesis and characterization of [(naphthylene 1-yl methylen) acetohydrazide $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and tris [(3-phenyl alylidene) acetohydrazide] $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$.

MATERIALS AND METHODS

All reagents were supplied by Merck and were used without further purification. Melting point was determined in an Electro thermal 9200. The FT-IR spectra

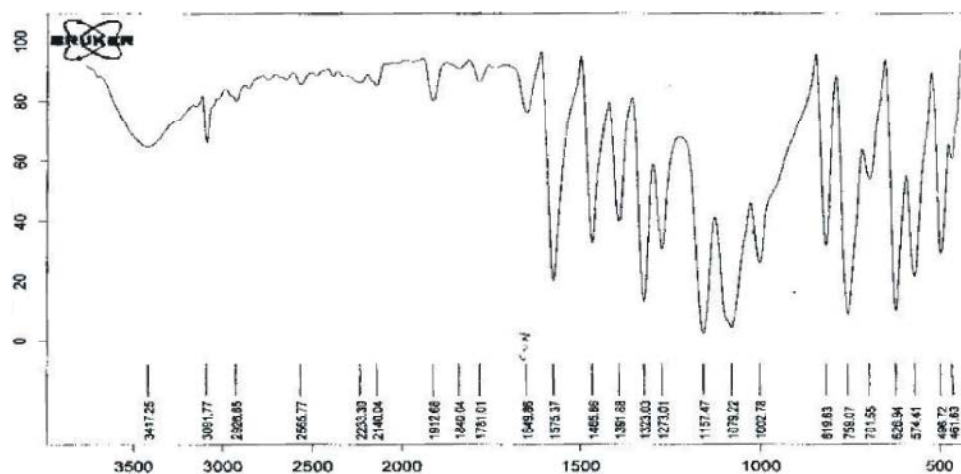


Fig. 1: FT-IR spectra of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ in KBr disk

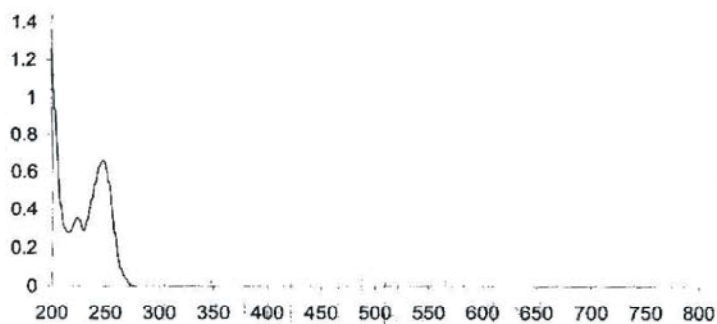


Fig. 2: UV/Vis spectrum of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ (in acetonitrile, $C = 5 \times 10^{-3}\text{M}$)

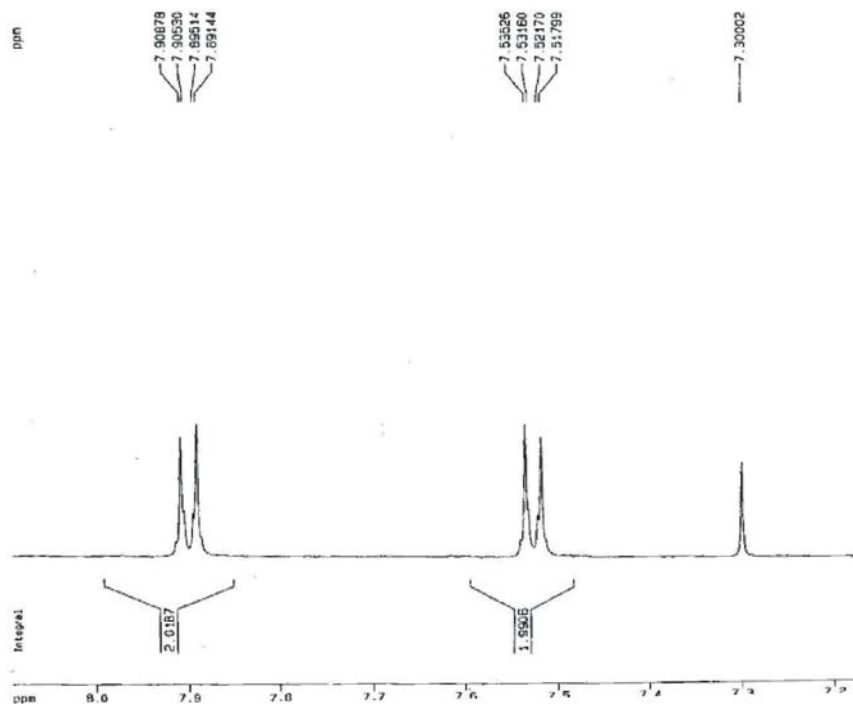


Fig. 3: $^1\text{H-NMR}$ spectrum of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$

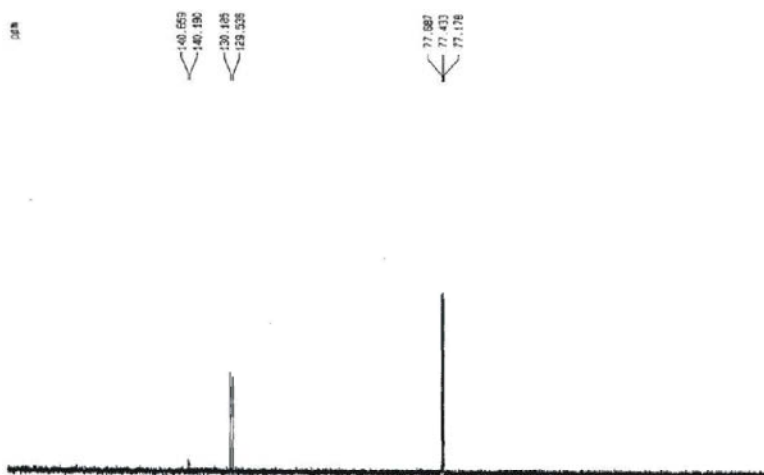


Fig. 4: ^{13}C -NMR spectrum of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$

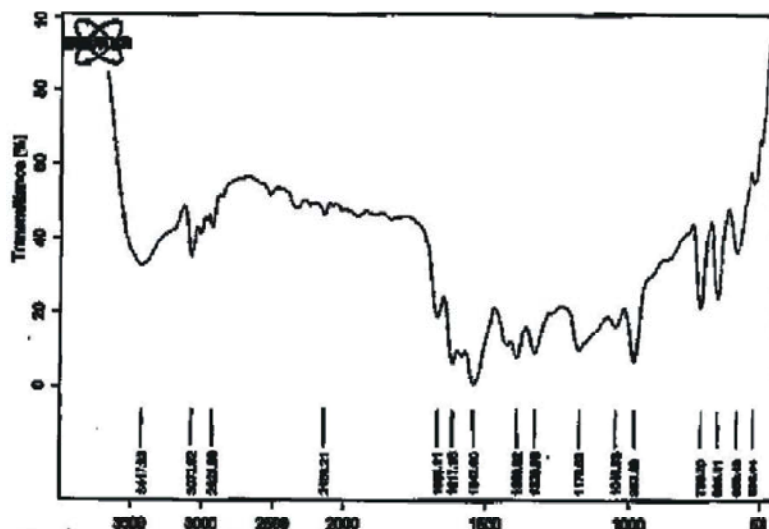


Fig. 5: FT-IR spectra of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ in KBr disk

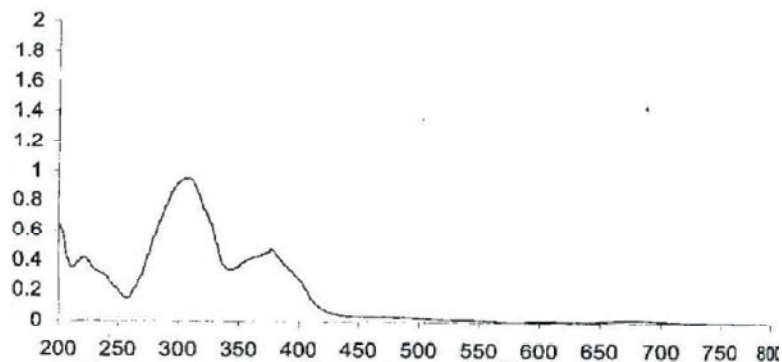


Fig. 6: UV/Vis spectrum of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ (in acetonitrile, $C = 5 \times 10^{-3}\text{M}$)

were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ by KBr disk using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV-Vis spectra in CH_3CN were recorded with a Camspec M 350 spectrophotometer. Elemental CHN

analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. ^1H -NMR and ^{13}C NMR spectra were measured on a BRUKER AVANCE DRX-500 spectrometer at 500 MHz.

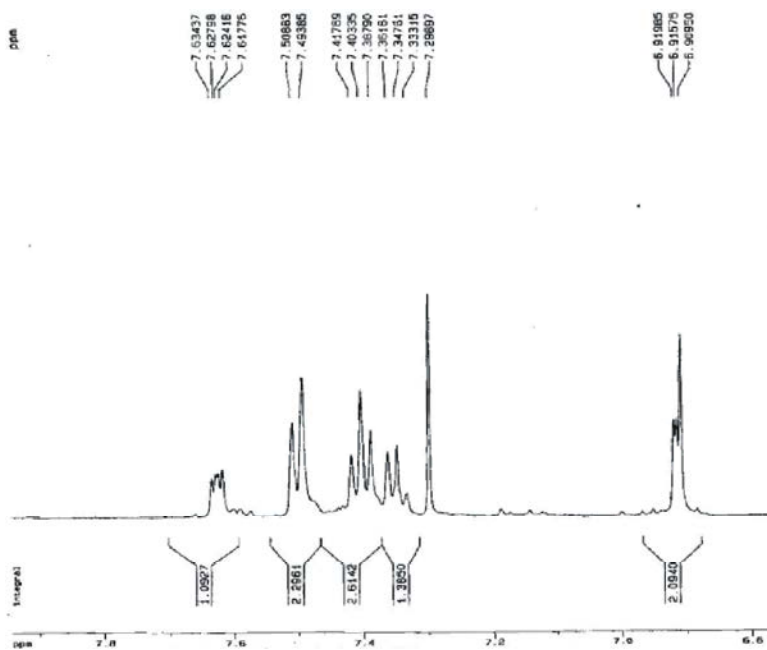


Fig. 7: $^1\text{H-NMR}$ spectrum of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$

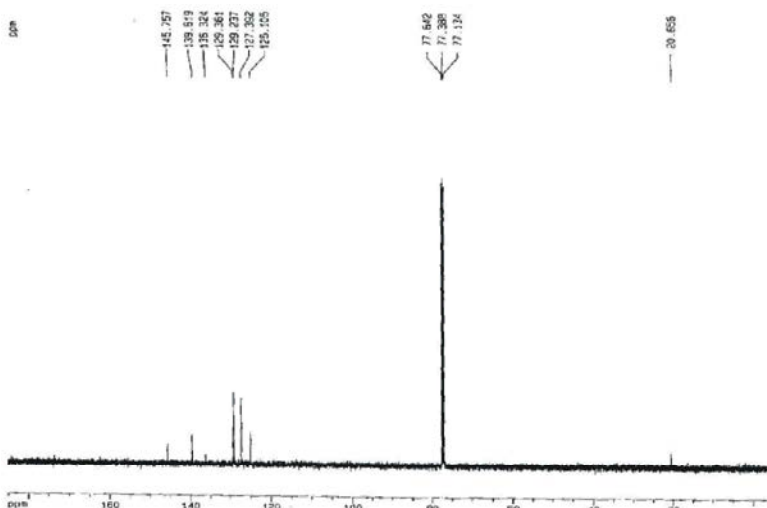
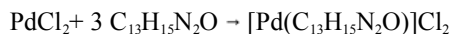


Fig. 8: $^{13}\text{C-NMR}$ spectrum of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$

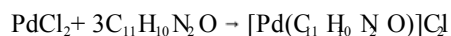
Synthesis of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$: $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$ (0.1g) was stirred in THF (10cc) at 50°C for 15 min and then PdCl_2 (0.027g) were dissolved in solution. The mixture was stirred and for 2 hrs to give a clear solution. After cooling to room temperature, the resulting gray precipitate was filtered, washed with n-hexane (20 ml) and dried. Mp: $142-144^\circ\text{C}$ Yield: 83%. *Anal.* Calc. for $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$: C, 39.76; H, 3.82; N, 7.13 %. Found: C, 39.95; H, 3.98; N, 7.28%. FTIR (Kbr pellet, cm^{-1}): 1575 (s, $\text{C}=\text{N}$), 1649 (m, $\text{C}=\text{O}$); 3091 (w, CH), 496(s, Pd-N). UV-Vis, λ_{max} (nm)/ ϵ ($\text{M}^{-1}\text{cm}^{-1}$); 227 (71), 250(131). $^1\text{H-NMR}$ (CDCl_3 , δ

(ppm)):7.3-7.9 (protons of naphthylene), 2.2 (protons of CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)):129-140 (carbons of naphthylene ring) (Figure 1, 2, 3, 4).



Synthesis of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$: $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ (0.09g) was stirred in THF (10cc) at 50°C for 15 min and then PdCl_2 (0.028g) were dissolved in solution. The mixture was stirred and for 2 h to give a clear solution. After cooling to room temperature, the resulting yellow precipitate was

filtered, washed with n-hexane (20 ml) and dried. Decomposition point: 238°C Yield: 75%. *Anal. Calc.* for $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$: C, 36.33; H, 2.75; N, 7.70%. Found: C, 36.45; H, 2.83; N, 7.92%. FTIR (KBr pellet, cm^{-1}): 1617 (w, C=N), 1669 (w, C=O); 3073 (w, CH), 536 (w, Pd-N). UV-Vis, λ_{max} (nm)/ ϵ ($\text{M}^{-1}\text{cm}^{-1}$): 226 (84), 314 (194), 377 (96). $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 7.2-7.6 (protons of benzene ring), 2.1 (protons of CH_3). $^{13}\text{CNMR}$ (CDCl_3 , δ (ppm)): 20 (carbons of aliphatic), 139 (carbon of ethylene group) (Figure 5-8).



RESULT

Synthesis and Stability: Pd (II) salt reacts with Schiff base ligands in solvent to afford complex. These complexes are stable at room temperature. These $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ were obtained in relatively high yield, 83 and 75% respectively. In this study we have reported the synthesis of new complexes of hydrazine derivative. The structural characterizations of synthesized compounds were made by using the elemental analysis, IR and UV spectral techniques. In summary, the synthesis and characterization of complexes have been described.

FT-IR, $^1\text{HNMR}$, $^{13}\text{CNMR}$ and UV-Vis Spectroscopic Studies: The IR spectra of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ show characteristic bands due to $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C-H})$ and $\nu(\text{Pd-N})$ in the region 1575cm^{-1} , 1649cm^{-1} , 3091cm^{-1} and 496cm^{-1} respectively. The strong band in the region 1575 and 496cm^{-1} in the IR spectra of the $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ are assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{Pd-N})$ respectively. In the case of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ we observed the following changes. The bands appeared around 1617cm^{-1} due to $\nu(\text{C}=\text{N})$, 1669cm^{-1} due to $\nu(\text{C}=\text{O})$, 3073cm^{-1} due to $\nu(\text{C-H})$. IR spectra of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ show a broad weak intensity band in the region 536cm^{-1} due to Pd-N. The $^1\text{H-NMR}$ spectra of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ compound displays a signal at 7.3-7.9 ppm which is assigned to protons of naphthylene ring and other signal at 2.2 ppm which is assigned to protons of methyl. The $^{13}\text{C-NMR}$ spectra of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ compound displays a signal at 129-140 ppm which is assigned to carbons of naphthylene ring. The $^1\text{H-NMR}$ spectra of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ compound displays a signal at 7.2-7.6 ppm which is assigned to protons of benzene ring and other signal at 2.1 ppm which is assigned to protons of

methyl. The $^{13}\text{C-NMR}$ spectra of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ compound displays a signal at 20 ppm which is assigned to carbons of aliphatic. The formation of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ were also confirmed by UV-vis spectra. The absorption spectra of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ were recorded as 5×10^{-3} M CH_3CN solutions in the range 200-800 nm using a quartz cuvette of 1 cm path length. The spectrum of $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ in CH_3CN solutions is shown that absorption band observed at 227 and 250 nm and the spectrum of $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ in CH_3CN solutions is shown that absorption bands observed at 226, 314 and 377 nm.

DISCUSSION

Heterocyclic compounds constitute about sixty-five percent of organic chemistry literature. From straight chain aliphatic to branched to cyclic to aromatic, attention is currently paid to heterocyclic moieties, which are essential to life. Hydrazides are compounds derived from oxoacids by replacing -OH groups by -NR-NR' groups (R groups are commonly H). Schiff's bases possess important activities such as antimicrobial, analgesic, anti-inflammatory, anti-convulsant, antifungal and anticancer activity [12]. These complexes are stable at room temperature. In this paper, a direct, simple and one-step method has been used to synthesize these compounds. The advantages of the method are; that there is no side product, the reaction is quite fast, there are mild conditions and the accompanied color change that provides visual means for ascertaining the progress of the reaction. This compound soluble in dimethyl sulfoxide (DMSO) and in dichloromethane insoluble. In summary, Pd (II) has had and continues to have, far-reaching impacts on organic synthesis. The versatile nature of palladium, in conjunction with the mechanistic understanding and predictive models that have been elucidated, has permitted a wealth of exploration into the seemingly endless potential of this metal. The synthesis and characterization of complexes have been described. Two complexes of Pd (II) were synthesized simply. $[\text{Pd}(\text{C}_{13}\text{H}_{15}\text{N}_2\text{O})]\text{Cl}_2$ and $[\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{Cl}_2$ were prepared by the reaction of $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$ and $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ with $\text{Pd}(\text{Cl})_2$. Electronic and vibrational spectra of these new complexes were studied. These compounds were characterized by FTIR, UV/Visible and $^1\text{H-NMR}$, $^{13}\text{CNMR}$ spectroscopy techniques.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the Research Council of Takestan Islamic Azad University and many technical supports that provided by TarbiatModarresUniversity.

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