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Synthesis and characterization tris N-2,4-dinitrophenyl N/-3-nitrobenzylidenehydrazine palladium chloride and tris N-2,4-dinitrophenyl N/-3-phenyl alilidine hydrazine

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ABSTRACT

The reaction between two acetohydrazide ligands that are, N-2,4dinitrophenyl $N^{/}$-3-nitrobenzylidenehydrazine and Tris N-2,4dinitrophenyl $N^{/}$-3-phenyl alilidinehydrazine with $PdCl_2$ produced two new ionic palladium complexes. One of them is TNBH which is easily synthesized in a nearly quantitative yield using a direct reaction between $PdCl_2$ and N-2,4dinitrophenyl $N^{/}$-3-nitrobenzylidenehydrazine. Another is TDPH which has been synthesized by the reaction of Tris N-2,4dinitrophenyl $N^{/}$-3-phenyl alilidinehydrazine with $PdCl_2$. These compounds are characterized by spectroscopic techniques. The electronic and vibrational spectra of TDPH and TNBH have been measured and studied.

Keywords: synthesis, characterization, TNBH, TDPH

INTRODUCTION

Particularly palladium has been the subject of an intense scientific discussion since the first synthesis of such a compound.[1,2] This is because of the important prerequisites for a palladiuminating agents that makes it useful which are its mildness, versatility, selectivity and operational simplicity. The subject of this investigation is to prepare inorganic palladiumes and its complexes[3]. As the biological activity of a complex strongly depends on the nature of the ligands and on the metal coordination pattern, the recent research has been directed to synthesis and evaluation of complexes with biologically interesting ligands with the aim of widening the spectrum of complex activity. The combination of metallic and organic activity may reveal new modes of action.

Another reason that encourages researchers for synthesizing this range of palladiuminated compounds is the fewer and rare amounts of the spectroscopic data about this group of compounds. For the above reasons and in the course of our investigations in palladium compounds of transition metals[4-8] and in the continuation of our studies on the synthesis of nitrophenyl palladium complexes[9] we were prompted to react $PdCl_2$ with $C_{13}H_{10}N_5O_6$ and $C_{13}H_{10}N_4O_5$. We had prepared and reported the syntheses of a number of $[PdCl_2]^-$ anion with TDPH and TNBH counter ions previously.[10,11] We have managed to prepare two new palladium compounds of nitrophenyl that are the analogs of the above transition metal compounds. Palladium chloride has not been synthesized and reported so far. In this paper, a direct, simple and one-stage method has been used to synthesize these compounds. There were two primary incentives for the selection of $C_{13}H_{10}N_5O_6^+$ and $C_{13}H_{10}N_4O_5^+$ as the counterions. Firstly, quaternary ions such as

TDPH and TNBH are often used as phase transfer catalysts. Secondly, quaternary ions such as TDPH and TNBH are used as crystal growing agents.

MATERIALS AND METHODS

Materials and Instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before using, thereby reducing its water content to <4 ppm. Nitrophenyl was purchased from Merck company. $PdCl_2$ (Merck, p.a.) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Bruker Tensor model 27 spectrophotometer. The UV-Visible measurements were made on an Cam spec model 350 spectrophotometer. TDPH and TNBH were estimated iodometrically. The percentage of elements in compositions were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tris N-2,4dinitrophenyl $N^/$-3-nitrobenzylidenehydrazine palladiumchloride, $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$

TNBH, $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$ was prepared by dissolving $PdCl_2$ (0.01g, 0.05 mmol) in DMS and adding this solution to a solution of Tris N-2,4dinitrophenyl $N^/$-3-nitrobenzylidenehydrazine (0.1 g, 0.33 mmol) in DMSO under stirring at 90 °C temperature until a brown precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with hexane and dried at room temperature. The TNBH is some what hygroscopic, and it was better to be stored under a layer of hexane, whereas all of the salts aren't photosensitive and moisture sensitive, both in solution and solids. UV-Visible(Fig1) and IR(Fig2) spectra were all consistent with the TNBH structure. m.p. 239 °C. IR (KBr): υ 3279, 3099, 1615, 1512-1330, 523cm^{-1}.

Synthesis of Tris N-2,4dinitrophenyl $N^/$-3-phenyl alilidinehydrazine $[Pd(C_{15}H_{13}N_4O_4)]Cl_2$

Tris N-2,4dinitrophenyl $N^/$-3-phenyl alilidinehydrazine palladiumchloride $[Pd(C_{15}H_{13}N_4O_4)]Cl_2$ was prepared as follow:

To a solution of $PdCl_2$ (0.01 g, 0.05 mmol) in DMSO, the solid powder Tris N-2,4dinitrophenyl $N^/$-3-phenyl alilidinehydrazine (0.1 g, 0.33 mmol) was added under stirring at 90 °C temperature until a red solid precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with hexane, and dried at room temperature. UV-Visible(Fig3) and IR(Fig4) data were all consistent with the TDPH structure. m.p.: 256-258 °C. IR (KBr): υ 3279, 2925, 1620, 1504,1336, 516cm^{-1}.

RESULTS AND DISCUSSION

We had reported the synthesis of transition metal, with the belief that those reagents could be used for the palladiumination of organic substrates. It has been shown that transition metals are useful as new palladiumation agents for organic chemists. Those compounds showed palladiumination properties like other previously reported transition metals. We now report the synthesis of the two new nitrophenyl complexes, TDPH and TNBH.

The advantages of the new method are: a) there is no side product, b) the reaction is quite fast, c) mild conditions and d) the accompanied color change provides visual means for ascertaining the progress of the reaction.

Tris N-2,4dinitrophenyl $N^/$-3-phenyl alilidinehydrazine $[Pd(C_{13}H_{10}N_4O_4)]Cl_2$, TDPH

$[Pd(C_{13}H_{10}N_4O_4)]Cl_2$ was prepared by the reaction of $C_{13}H_{10}N_4O_5$ and $PdCl_2$ in DMSO solvent as follows:

$$3C_{13}H_{10}N_4O_5 + PdCl_2 \rightarrow [Pd(C_{13}H_{10}N_4O_4)]Cl_2$$

In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as $\nu_{C=N}$ which was found at 1620 cm^{-1} and confirmed with literature data (TABLE1). There is one absorption in the compound electronic spectrum. Electronic spectrum of TDPH shows five transitions for acetonitrile at 223 nm (ε = 110 mol.$^{-1}$lit.cm^{-1}), 237 nm (ε = 98 mol.$^{-1}$lit.cm^{-1}), 266 nm (ε = 76 mol.$^{-1}$lit.cm^{-1}), 305 nm (ε = 82 mol.$^{-1}$lit.cm^{-1}), 395 nm (ε = 234 mol.$^{-1}$lit.cm^{-1}) (TABLE 3). These transitions are expected in monosubstituted palladium ions, because of the position of palladium in the second series of transition metal elements and thus making strong crystalline field complexes.

Tris N-2,4dinitrophenyl $N^{/}$-3-nitrobenzylidenehydrazine palladiumchloride, $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$, TNBH

$[Pd(C_{13}H_{10}N_5O_4)]Cl_2$ was prepared by the reaction of $PdCl_2$ with $C_{13}H_{10}N_5O_6$ in DMSO solvent as follows:

$3C_{13}H_{10}N_5O_6 + PdCl_2 \rightarrow [Pd(C_{13}H_{10}N_5O_4)]Cl_2$

In the vibrational spectrum of TNBH the cationic and anionic bands were seen such as $\nu_{C=N}$ which was found at $1615cm^{-1}$ along the literature data (TABLE 2). There are three absorption bands in the electronic spectrum of this compound (TABLE 4).

TABLE 1. The frequencies (cm^{-1}) and assignment of cation and anion of TDPH

$\nu(cm^{-1})$	Assignment	Intensity
	$C_{13}H_{10}N_4O_4$	
1620	$\nu_{(C=N)}$	(s)
3279	$\nu_{(N-H)}$	(W)
2925	$\nu_{(C-H)}$	(W)
1504,1336	$\nu_{(NO2)}$	(S)
1504	$\nu_{(C=C)}$	(s)
516	$\nu_{(Pd-N)}$	(W)

TABLE 2. The frequencies (cm^{-1}) and assignment of cation and anion of TNBH

$\nu(cm^{-1})$	Assignment	Intensity
	$C_{13}H_{10}N_5O_4$	
1615	$\nu_{(C=N)}$	(S)
3279	$\nu_{(N-H)}$	(w)
3099	$\nu_{(C-H)}$	(w)
523	$\nu_{(Pd-N)}$	(m)
1330, 1512	$\nu_{(NO2)}$	(s)

TABLE 3. Transitions specifications of TDPH

λ_1 (nm) (ε, $M^{-1}cm^{-1}$)	λ_2 (nm) (ε, $M^{-1}cm^{-1}$)	λ_3 (nm) (ε, $M^{-1}cm^{-1}$)	λ_4 (nm) (ε, $M^{-1}cm^{-1}$)	λ_5 (nm) (ε, $M^{-1}cm^{-1}$)
223 (110)	237 (98)	266 (76)	305 (82)	395 (234)

TABLE 4. Transitions specifications of TNBH

λ (nm) (ε, $M^{-1}cm^{-1}$)	λ (nm) (ε, $M^{-1}cm^{-1}$)	λ (nm) (ε, $M^{-1}cm^{-1}$)
255 (176)	379 (128)	381 (298)

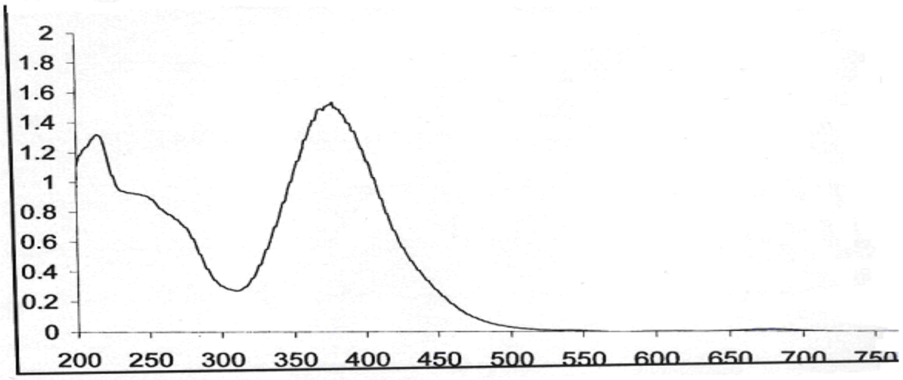

Figure 1. UV/Vis spectra of $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$

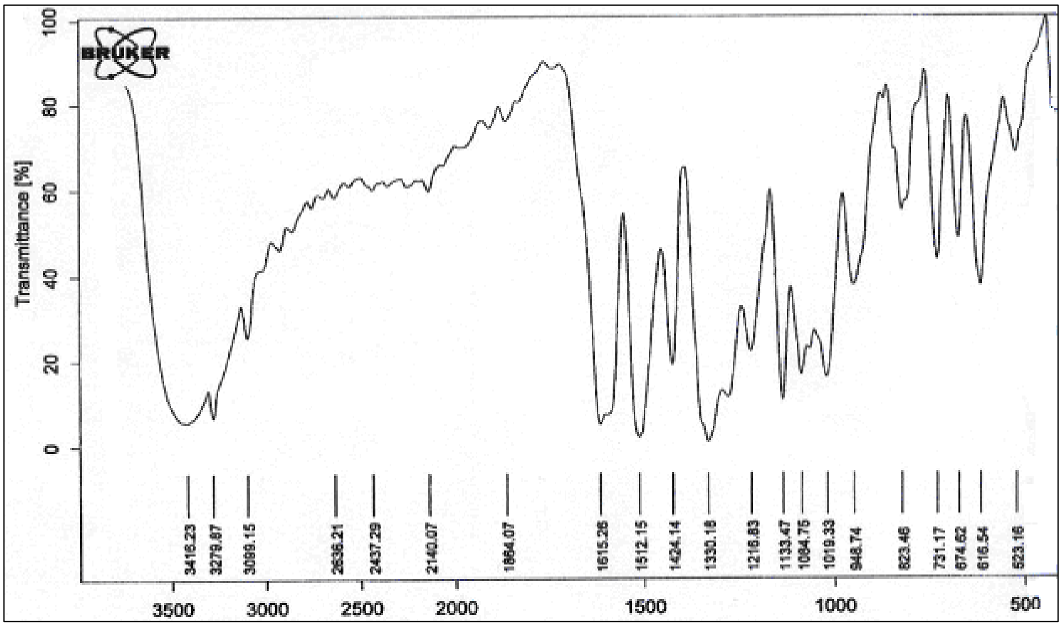

Figure 2. IR spectra of $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$

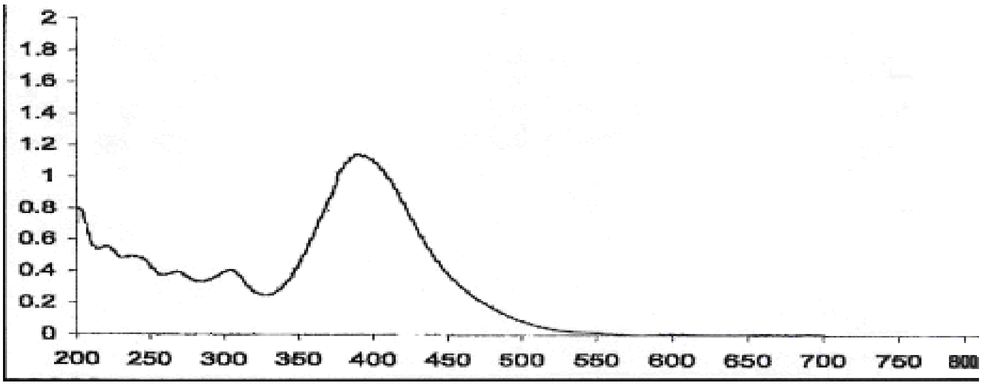

Figure 3. UV/Vis spectra of $[Pd(C_{13}H_{10}N_4O_4)]Cl_2$

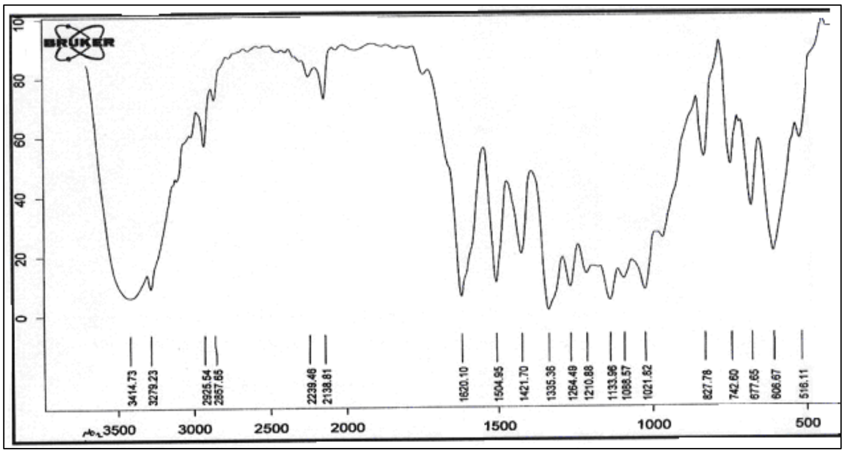

Figure 4. IR spectra of $[Pd(C_{13}H_{10}N_4O_4)]Cl_2$

CONCLUSION

Two TDPH and TNBH of $PdCl_2$ were synthesized simply. $[Pd(C_{13}H_{10}N_4O_4)]Cl_2$was prepared by the reaction of $C_{13}H_{10}N_4O_5$ and $PdCl_2$ in DMSO solvent and $[Pd(C_{13}H_{10}N_5O_4)]Cl_2$ was prepared by the reaction of $C_{13}H_{10}N_5O_4$ and $PdCl_2$ in DMSO solvent. Electronic and vibrational spectra of these two new palladium-complexes were studied. These compounds were characterized by IR and UV-Visible, techniques. Production of these compounds shows the ability of palladium chloride in chloride addition to transition metal and main group elements compounds.

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