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Original article

Synthesis and identification of copper (II) complexes using phosphonium salt resulting from the combination of trinylphosphine and ethyl bromoacetate, using stereoscopic methods

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ABSTRACT

Phosphonium salts have the general formula $R_4P^+X^-$ and are derived from the sub-ion phosphonium tetrahedral (pH_4^+), such as phosphonium iodide $[p(CH_3)_4^+]^-$. Generally, phosphonium is attributed to an organic derivative, such as tetra-phenyl phosphonium chloride and tetra tetra-methylphosphonium iodide. In this project, the phosphonium compounds [C_2H_5COO (CH_2PPh_3Br)] and its copper (II) complex [C_2H_5COO (CH_2PP_3Br)] [Cu_2Cl_6] were prepared and identified. Phosphonium species were prepared from the reaction of ethyl bromoacetate with terphenylphosphine. Then the final compounds were prepared using the reaction between the phosphonium compound with Na_2 [Cu_2Cl_6]. Then, using spectroscopic methods, preparation of these compounds was investigated.

1. Introduction

Alkyl Tri- phenyl Phosphonium salts are used to prepare Wittig reagents in Wittig reaction, widely. Such salts are made easily by using tri-phenyl phosphine reaction with an Alkyl halide. If the alkyl, methyl or primary group alkyl have not space prevention, the reaction well done. But usually react with secondary alkyl halides is a weak reaction. Tertiary alkyl groups can't form Aylyd. Phosphonium salt is a stable compound which often is achieved from ethanol, by recrystallization (Hertly, 1994). In recent years, Phosphonium salts are of great interest due to their structure, properties and reactivity. Aylyd reaction with aldehydes or ketones, which is one of the most common methods for the formation of region specific alkenes, was first reported in 1953 by George Wittig. This reaction is a key step to produce a large number of natural and biological products. The Main reagent in the Wittig process is prepared through the deprotonated Phosphonium salt, which has been achieved through four coordination of phosphine with a combination of Hollow. The main advantage of Wittig reaction is it's stereo selectivity. Stereochemistry depends on several factors. Phosphonium salt structure is the presence of metal cationsand laboratory conditions (Moussaousi and Said, 2006).

Wittig reaction in addition to done applied research, has broad applications to produce pharmaceutical and industrial materials. Wittig, to start the reaction, react an alkyl halide with a phosphine to obtain four coordinate kation phosphine. To produce a neutral compound, which is called P aylyd, this cation is then deprotonated by a strong base such as butyl lithium. Aylyd negatively charged carbon, acts as nucleophile and attacks to carbonyl Aldehyde group or ketone. Protective and corrosion inhibitor metals play an important role in industry. Most of protectors and inhibitors are organic compounds which have hetero atoms such as phosphorus, nitrogen, sulfur and oxygen. These compounds and their derivatives are corrosion inhibitors for iron and steel. Many of these corrosion inhibitors and protective have hazardous effects on the environment. So achieving effective and non-toxic organic inhibitors for iron and steel is a crucial point. Suitable inhibitors for the environment should have biodegradability properties and should not be destructive for environment. Phosphonium compounds in Acidic solutions are used as protective for most metals (Bhrara et al., 2008).

Four coordinated Phosphonium compounds have been identified in many systems as factors inhibiting the growth of bacteria, which are highly adapted to the environment (Incomopoulou et al., 2005). The benefits of these compounds including very low toxicity, rapid degradation in the environment (Via hydrolysis, oxidation, light degradation and biodegradation), and destructive or non-destructive effects on the environment (Aldridge et al., 2007s). For example, Tri phenyl phosphonium bromide in 0.5 M sulfuric acid solution is known as a corrosion inhibitor for iron and steel, and has been proven by Galvanostatic and Potentiostatic measurements and using FT-IR spectroscopy and images from electron microscopy and quantum computing (Kenawy et al., 2006). Also, some reports provided about the preparation of biologically active polymers using ammonium groups and four coordinated Phosphonium, which have medical use (Cieniecka-Roslonkiewicz et al., 2005). Production of ionic liquids is another application of phosphonium salts, which the liquids are organic salts which are in liquid state at low temperatures (less than 100 °C) (Tseng et al., 2007) and has advantages such as wide temperature range of liquid output, high thermal and chemical stability, strong solvents and very low vapor pressure in the synthesis of organic compounds, chemical catalysts, different separation methods and the role of new electrolytes in the manufacture of solar and fuel cells (Sons and Gong, 2002). In recent years, many studies have been done on four coordinated Phosphonium systems and the new composition of the phosphonium known as ionic liquids and the use of phosphonium salts is more than ever (Wang and Tian, 2007).

In recent years, important polymer humidity sensors are built. Different types of monomers sensitive to moisture have been used to build the humidity sensors, including cationic or anionic salt. Phosphonium salts due to the simplicity and easy preparation and high stability under different conditions are used, in a very large extent, for the manufacture of polymer humidity sensors. Most recently, tri-phenyl phosphonium chloride salts have been prepared and used for the production waterproof humidity sensors. You can also use Tri-butyl phosphonium chloride, as monomer, to prepare the sensors (Terada and Kouchi, 2006). Phosphonium salts successfully have been usedas a catalyst for many types of organic reactions such that it can be notedissimple phosphonium salt catalytic activity as benzyl chloride phosphonium Alkoxysilylcyano reaction of the ketones (Nandurkar and Bhanage, 2008) and the use of phosphonium salt as the catalyst Lewis acid without metal, which has been rapid growth in the field of organic catalysts (Terada and Kouchi, 2006). Recent studies have been carried out on quasironephosphonic systems and new compounds of phosphonium are known as ionic liquids. And has resulted in the use of more phosphonium salts (Tseng et al., 2007). Phosphonium salts are used as phase transfer catalysts in organic synthesis (Cerichelli et al., 2000). Phosphonium salts are also used to synthesize Macrocycle peptides in solution (Jou et al., 1997).

2. Materials and methods

2.1. The process of preparing the compound [C_2H_5COO (CH_2PPh_3Br)]

In this study, 10 m mol Bromine ethyl acetate (1.1 ml) and 10 m mol Tri phenyl phosphine (2.62 gr) was solved separately in 50 ml of benzene and then was added to a 100 ml balloon, which starts to precipitate after 2 to 3 minutes, and was stirred at room temperature for 24 hours. Then the solution was refined after washing with ethyl ether and then was dried in the desiccator. The resulting sediment weight was 2.98 gr and efficiency of reaction was 69%. The precipitate was melted at 165 °C (Fig. 1).

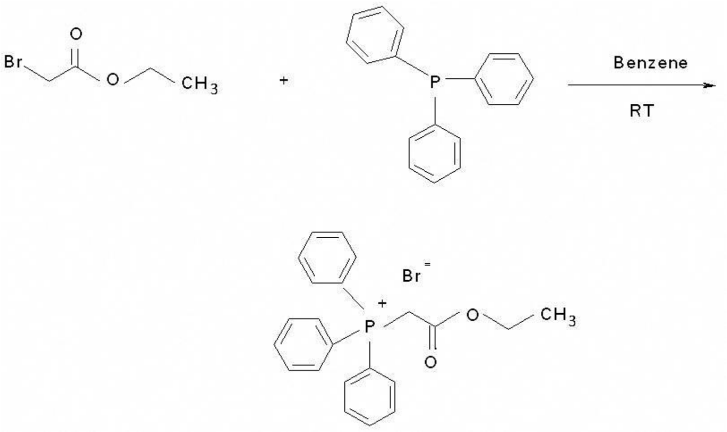


Fig. 1. Preparation process of [C_2H_5COO (CH_2PPh_3Br)].

2.2. Preparation of copper complex (II)

2.2.1. The process of preparing the complex [C_2H_5COO (CH_2PPh_3Br)] [Cu_2Cl_6]

At this stage, 0.1 g $CuCl_2$ (0.74 m mol) and 0.15 g NaCl (2.9 m mol) were poured into a tube hose. Then 10 ml of methanol was added to it. And the solution was stirred at 50 °C for 5 hours until a clear greenish yellow solution was obtained according to the following scheme (Fig. 2). Then, 0.32 g of phosphonium (76.8 mmol) was added to it, which quickly began to form turquoise blue sediment. Its weight was 15.0 g and the reaction efficiency was 25.86% and melted at 218 °C.

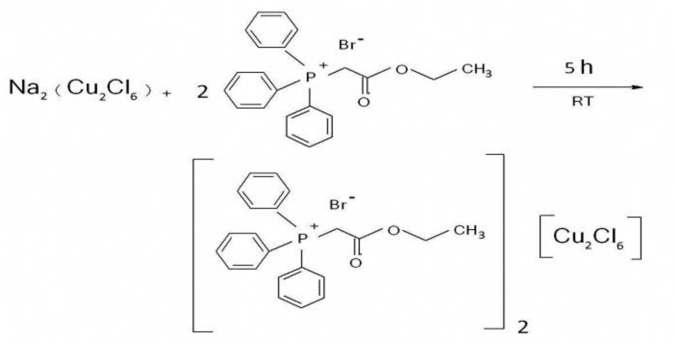
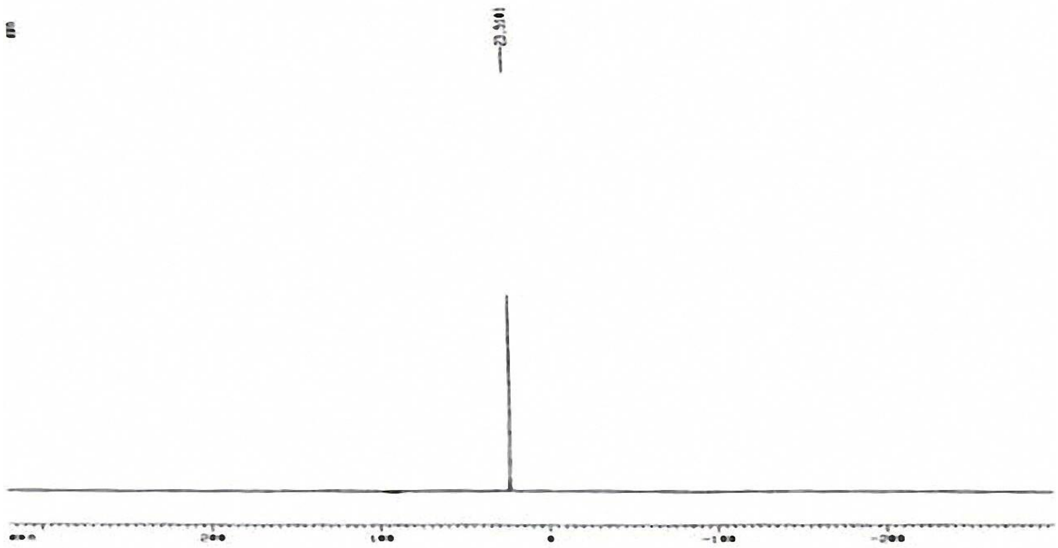


Fig. 2. The process of preparing the complex [C_2H_5COO (CH_2PPh_3Br)] [Cu_2Cl_6].

3. Results and discussion

In order to determine the obtained combinations the NMR spectrum, including PNMR-CNMR-HNMR was measured using FT-NMR400. The infrared spectrum was evaluated using the FT-IR. Bommen model and Nojoloil and KBr tablet, the following results was obtained: The spectrum 1 shows the 31PNMR spectrum of [C_2H_5COO (CH_2PPh_3Br)] [Cu_2Cl_6] composition. In this spectrum, the phosphor resonance in $\delta = 23.66$ PPm appears in the form of a unique peak. $\delta = 4.8$ PPm indicating that the atom of phosphorus has created a new bond with a carbon atom that, by decreasing the density of electrons in the phosphorus atom, the peak of phosphorus moves to the lower fields. For same compounds the peak appears in δ = 24.22 PPm. This peak represents the formation of the desired composition, and the unique P-peak in this spectrum represents the high purity of the composition.



Spectrum 1. 31PNMR [C_2H_5COO (CH_2PPh_3Br)] [Cu_2Cl_6] compound.

Spectrum 2

The 1HNMR spectrum shows [C_2H_5COO (CH_2PP_3Br)] [Cu_2Cl_6] composition. In this spectrum, the unique peak in 21281 corresponds to the methyl group attached to phosphorus. Quintuple peak is related to the hydrogen of the ethyl group, which appears in the field 24397 due to an increase in the electron density resulting from the connection to the oxygen atom. And multiple peaks in 14496 to 14771 are related to aromatic hydrocarbons. The summary of the results of this spectrum is presented in the table below (Table 1).

Table 1
The results of spectrum 2.

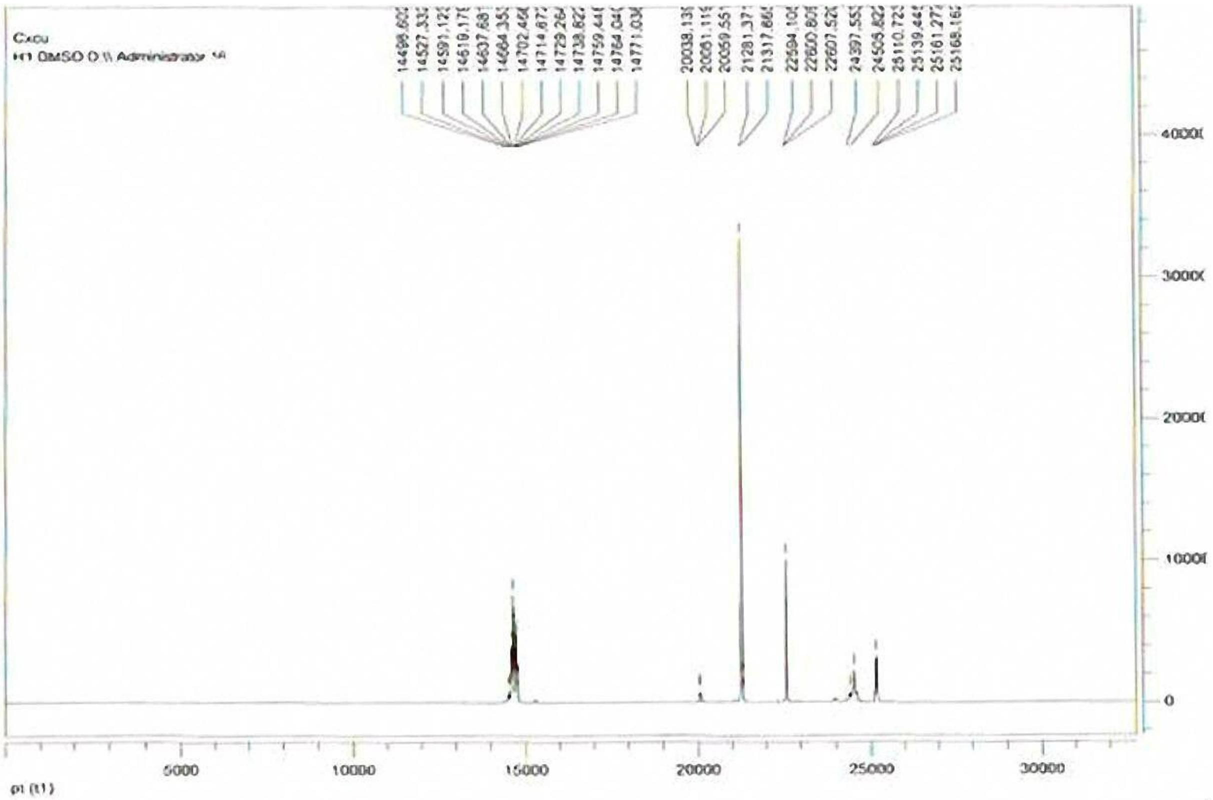
The peak shape	The number of protons	δ (PPm)	Proton type
A unique peak	2	21281	CH_2P
A quintuple peak	5	24397	C_2H_5O
Multiple peaks	15	14702	$3C_6H_5$

Spectrum 3

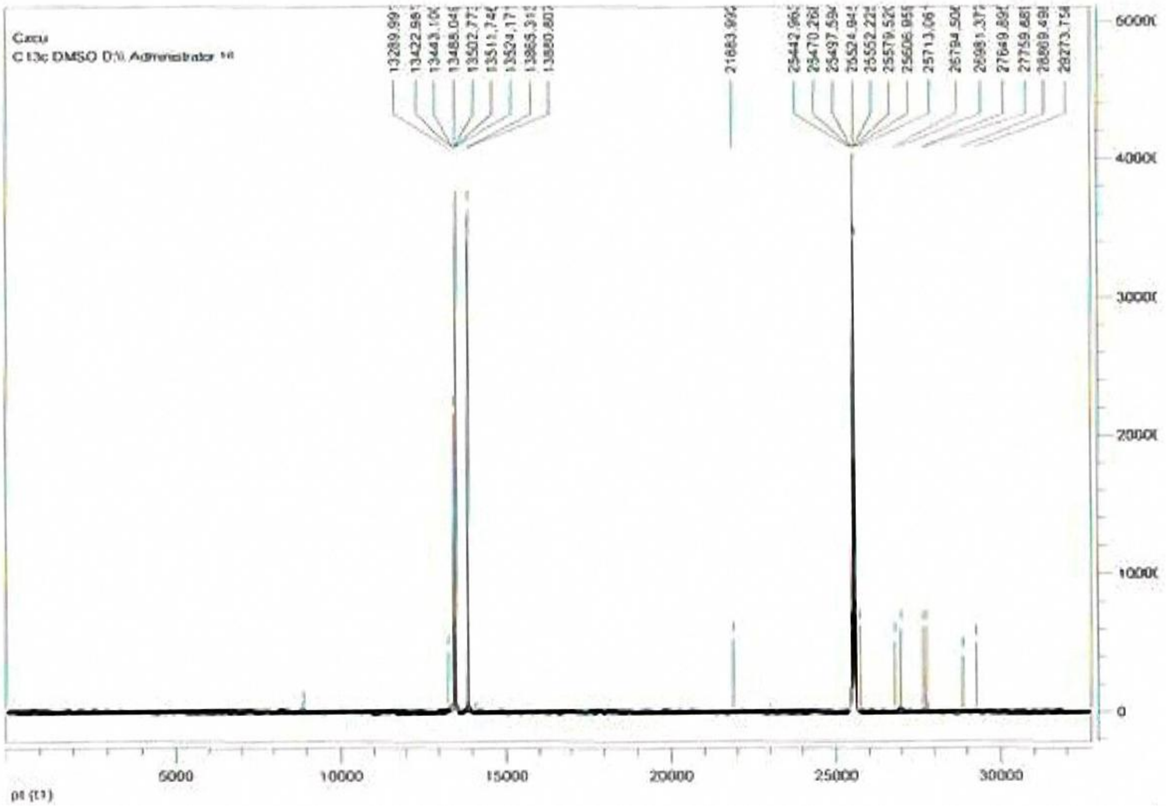
The CNMR spectrum shows the composition of [C_2H_5COO (CH_2PPh_3)] [Cu_2Cl_6]. In this spectrum, the double peak at 26981-2694 corresponds to the carbon atoms of the ethyl group attached to the oxygen atom, and the peaks in the 25713-25442 correspond to the DMSO solvent. The double peaks in 29863-28869 are related to the carbon in methyl coupled to the phosphorus atom and double peaks in 27759- 27649 are correspond to carbon in phenyl attached to phosphorus atom, and unique peak in 21883 is correspond to the carbon of the carbonyl group and the existing multiple peaks in 13880-13289 are correspond to the aromatic carbons of benzene rings. A summary of the results is presented in the table below (Table 2).

Table 2
The results of spectrum 3.

Peak shape	δ (PPm)	Carbon type
A double peak	26794 - 26981	C_2H_5O
A double peak	28869 - 29273	CH_2P
A unique peak	21883	C - O
Multiple peaks	13289 - 13880	Aromatic
A double peak	27649 - 27759	P - C



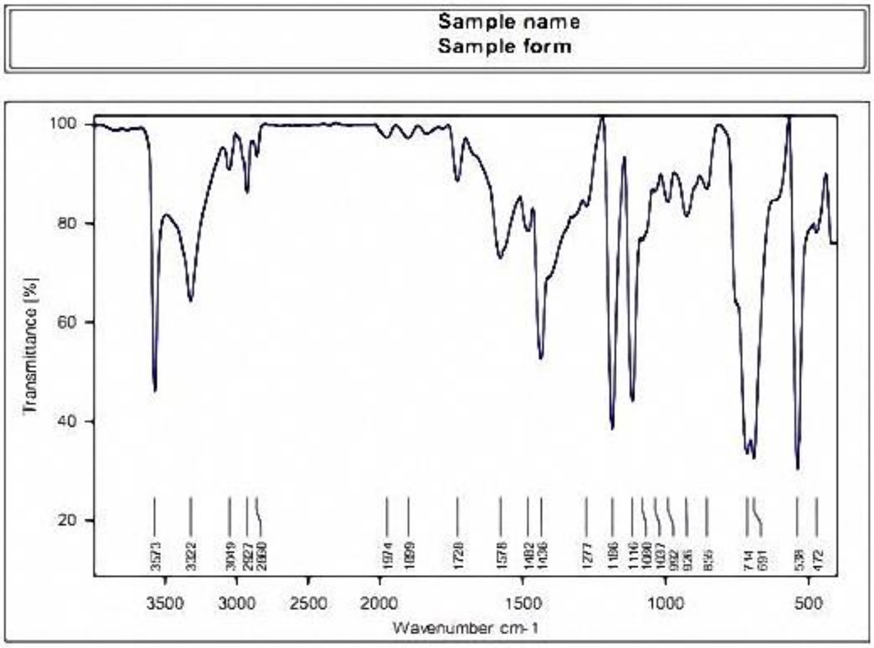
Spectrum 2. The 1HNMR spectrum of the composition $[C_2H_5COO\ (CH_2PPh_3Br)]\ [Cu_2Cl_6]$.



Spectrum 3. The CNMR spectrum of $[C_2H_5COO\ (CH_2PPh_3)]\ [Cu_2Cl_6]$.

Spectrum 4

The IR spectrum shows the composition of [C_2H_5COO (CH_2PPh_3)] [Cu_2Cl_6Br]. In this spectrum, the strong absorption in region 538 is related to the tensile vibrations of the C-Br bond. Also, strong absorption due to non-steric C-O stretching vibrations appears in area 734. The adsorption observed in 1116 and 1186 are respectively correspond to the tensile vibrations of C-C and C-O-ester bonds. The optical absorption in region 1436 correspond to the tensile vibrations of P-CH_3 and the vibration of the P-carbon bond in the phenyl, and absorption in the region 1728 is correspond to the tensile vibrations of the C = O bond. Finally, spectral adsorption in 2860, an average absorption in 3322 and strong absorption in 3573 are correspond to symmetric tensile vibrations CH_3, tensile symmetrical and asymmetric vibrations of CH_2, as well as the tensile vibrations of the C-H of the methyl ring in the composition, respectively.



Spectrum 4. The IR spectrum of the compound [C_2H_5COO (CH_2PPh_3)] [Cu_2Cl_6Br].

The results of the elemental analysis of this composition with the experimental formula $C_{44}H_{44}Cl_6Cu_2BrO_4$ are given in the following table.

Table 3
The results of spectrum 4.

$C_{44}H_{44}Cl_6Cu_2BrO_4$	%C	%H	%N
Experimental	45.15	3.92	-
Theoretical	46.49	3.87	-

4. Conclusion

In this research, the synthesis of copper (II) complexes was investigated by using phosphonium salt produced by PPh3 with ethyl bromoacetate. And the composition [C_2H_5COO (CH_2PPh_3)] [Cu_2Cl_6Br] was obtained by spectroscopic methods. Copper phosphonium complexes (II) can be excellent catalysts for different chemical reactions. It has a variety of applications in the chemical industry, including catalysts in the Heck reaction, Suzuki reaction and carbon hydrogenation reaction, terminal isomyramination of terminal olefins, and variation of the group in vinyl ethers. Therefore, more attention can be paid to the use of these compounds in different branches. The ability of phosphonium compounds to catalyze a wide variety of chemical reactions makes it very convenient to choose these compounds to work with.

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