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Interaction between triphenylphosphine or 1,2-bis(diphenylphosphino)ethane with some complexes K[$PtCl_3$(olefin)] (olefin: methyleugenol, safrole, isopropyl eugenoxyacetate)

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Abstract

Novel study on the interaction between K[$PtCl_3$(olefin)] (olefin: methyleugenol, safrole and isopropyl eugenoxyacetate) with TPP and DPPE shows that TPP and DPPE readily replace the olefins to form complexes [$PtCl_2(TPP)_2$] (P4), [$PtCl_2$(DPPE)] (P5) and [$Pt(DPPE)_2]Cl_2$ (P6). P4 possesses *trans* configuration when the molar ratio of the mono olefin and TPP of 1:1. When the ratio is 1:2, P4 is a mixture of *trans* and *cis* isomers of which *trans* one is prevailing. The *cis* isomer trends to convert to *trans* one in chloroform solvent. P5 and P6 were formed when the molar ratio of mono isopropyl eugenoxyacetate and DPPE of 1:1 and 1:2, respectively. The structures of P4÷P6 were elucidated by Pt analysis, ESI-MS, IR and ^{1}H NMR spectra studies.

Keywords. Pt(II) complexes, olefins, phosphine derivatives.

1. INTRODUCTION

Organometallic compounds are ones with direct metal-carbon bonds (M-C), compounds containing M-P or M-H bonds are now also included. In chemical industry, with the presence of Pt and Pd, many of the most important catalysts for numerous vital manufacturing processes have been prepared. In these processes, organometallic complexes of Pt or Pd are well known key intermediates [1, 2]. The high impact of these processes is confirmed by the Nobel prizes, such as Nobel prize (2010) for Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for the cross-coupling reactions using complex [$Pd(P(Ph)_3)_4$] as catalyst [3].

Recently, several organoplatinum complexes with type of K[$PtCl_3$(olefin)] (mono olefin) have been synthesized [4, 5]. Interaction between these key mono olefins and amines has prepared many promising anticancer complexes [6]. However, research on interaction between these critical complexes with derivatives of phosphine to form complexes for orientation of using in organic synthesis has not been published. Herein, we describe the results of study on reaction of mono methyleugenol, mono safrole and mono isopropyl eugenoxyacetate with $P(Ph)_3$ / $P(Ph)_2CH_2CH_2P(Ph)_2$.

2. EXPERIMENTAL AND RESULTS

2.1- Interaction between K[$PtCl_3$(olefin)] and $P(Ph)_3$ / $P(Ph)_2CH_2CH_2P(Ph)_2$

2.1.1. Synthesis of starting complexes

K[$PtCl_3$(methyleugenol)] (P1), K[$PtCl_3$(safrole)] (P2), K[$PtCl_3$(isopropyl eugenoxyacetate)] (P3) were synthesized according to the procedure described in [4, 5].

2.1.2. Interaction between P1, P2, P3 with triphenylphosphine (TPP)

The reactions of mono olefin P1, P2, P3 with TPP were conducted by changing reaction conditions such as concentration, molar ratio of reactants and experimental manipulation. The solvent, time and temperature were fixed on acetone, 2 hours and 25÷30 ^oC. The results are listed in table 1, the experiments N^o of 1÷5, 6÷10, 11÷15 respond to the interactions between TPP and P1, P2, P3, respectively.

Table 1 shows that the yield of reaction between P1/ P2/ P3 with TPP is the highest at the experiment N^o 4, 9, 14, respectively. The general chemical

equation and detailed implementation as below:

$K[PtCl_3(olefin)] + 2TPP \rightarrow [PtCl_2(TPP)_2] + KCl + olefin$

Mono olefin P1/ P2/ P3 (1.0 mmol) was dissolved in 5 mL acetone to afford a clear solution. To this solution, triphenylphosphine with different amounts (table 1) in acetone was added in small portion while stirring at room temperature. After 5÷10 minutes, the product (denoted as P4) in powder form appeared. The reaction mixture was then stirred further for 2 hours. The product was filtered and purified by washing with water (3 x 3 mL), acetone (3 x 2 mL) and diethyl ether (1 x 3 mL). Yielded 85÷95 %. Recrystallization of P4 in chloroform afforded light-yellow block crystals. P4 is very soluble in chloroform, insoluble in water, ethanol and acetone. Anal. Calc. For $[PtCl_2C_{36}H_{30}P_2]$: Pt 24.68 %, H_2O 0%; Found: Pt 25.12 %, H_2O 0 %.

Table 1: Experiments for the interaction between P1, P2, P3 and TPP

N°.	Concentration	Manipulation	Molar ratio of P1/P2/P3:TPP	Feature of products	Yield (%)
1	Saturated	Drop TPP into P1	1:1	Light-yellow powder	86
2	Diluted	Drop TPP into P1	1:1	Light-yellow powder	85
3	Saturated	Drop P1 into TPP	1:1	Light-yellow powder	88
4	Saturated	Drop TPP into P1	1:2	Pale-yellow powder	90
5	Diluted	Drop TPP into P1	1:2	Pale-yellow powder	80
6	Saturated	Drop TPP into P2	1:1	Light-yellow powder	87
7	Diluted	Drop TPP into P2	1:1	Light-yellow powder	90
8	Saturated	Drop P2 into TPP	1:1	Light-yellow powder	90
9	Saturated	Drop TPP into P2	1:2	Pale-yellow powder	92
10	Diluted	Drop TPP into P2	1:2	Pale-yellow powder	91
11	Saturated	Drop TPP into P3	1:1	Light-yellow powder	90
12	Diluted	Drop TPP into P3	1:1	Light-yellow powder	90
13	Saturated	Drop P3 into TPP	1:1	Light-yellow powder	90
14	Saturated	Drop TPP into P3	1:2	Pale-yellow powder	95
15	Diluted	Drop TPP into P3	1:2	Pale-yellow powder	92

In terms of solvent, temperature and reaction time: We employed acetone as reaction solvent for all experiments since the reactants (P1, P2, P3 and TPP) are very soluble in acetone. At the first experiments (N° 1, 6, 11 in Table 1), the light-yellow powder appeared very fast after dropping slowly the TPP solution into the solution of P1, P2, P3 at room temperature (25÷30 °C). The yields were high 86÷ 90 % after 2 hours. Therefore, we maintained the room temperature condition and reaction time of 2 h for all the surveyed experiments.

In terms of concentration, manipulation and molar ratio: To enhance interaction between the reactants, they were used with saturated concentration with the molar ratio of 1:1 at the first tests (N° 1, 6, 11 in table 1), the experiments with diluted concentration of them were also conducted (N° 2, 5, 7, 10, 12, 15, 16 in table 1). In addition, we changed experimental manipulation by adding the solution of TPP in small portion into the mono olefin solution and vice versa (table 1). The obtained products of all experiments are light-yellow powder. Based on characteristic of the products, analysis of Pt proportion, the IR and ^1H NMR spectra it can be determined that the products have the same formula of $[PtCl_2(TPP)_2]$ (symbolized as P4), but not $[PtCl_2(olefin)(TPP)]$ as expected. This means that TPP replaces not only Cl^- but also the olefin in P1, P2, P3. Thus, in the following experiments (N° 4, 5, 9, 10, 14÷16) we implemented the reaction with the molar ratio of mono olefin and TTP of 1:2 to optimize reactive amount of the mono olefin. Surprisingly, all the resulting products are pale-yellow powder but still have formula of $[PtCl_2(TPP)_2]$ (P4). According to [7], complex $[PtCl_2(TPP)_2]$ is white in *cis* configuration and light-yellow in *trans* isomer. Therefore, we assume that the products of experiments with the molar ratio of 1:1 and 1:2 are *trans* -$[PtCl_2(TPP)_2]$ and mix of *trans/cis*-$[PtCl_2(TPP)_2]$, respectively. This is further demonstrated by the ^1H NMR spectrum (Section 2.2).

The mentioned results above have indicated that the interaction between P1, P2, P3 with TPP in many

different reaction conditions all form P4. In other words, TPP can coordinate with Pt(II) very favorably and it is so easy for TPP to replace olefin in complex with type of $K[PtCl_3(olefin)]$. Meanwhile, numerous of aliphatic/aromatic/ heterocyclic amines react with P1, P2, P3 producing *trans*-$[PtCl_2(olefin)(amine)]$ but not $[PtCl_2(amine)_2]$ [6]. This implies that these amines cannot replace the olefin in P1, P2 and P3.

2.1.3. Interaction between P3 with 1,2-bis(diphenylphosphino)ethane (DPPE)

To study of reaction of P3 and DPPE, we implemented experiments as described in (*) and (**). The results of some selected experiments are shown in table 2.

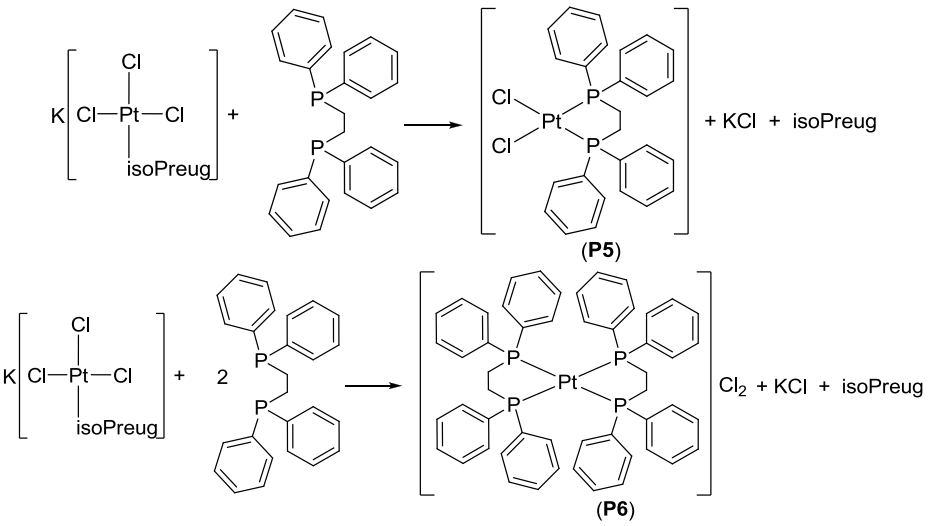
(*): P3 (1.0 mmol) was dissolved in acetone with different concentrations to afford a clear solution. To this solution, DPPE (1.0 mmol) in 5 mL acetone was added in small portion while stirring at room temperature. After about 5 minutes, white powder appeared. The reaction mixture was then stirred further for 2 hours. The product (labeled as P5) was filtered and purified by washing with water (3 x 2 mL), acetone (2x3 mL) and diethyl ether (1 x 3 mL). Yielded 90÷95 %. P5 is very soluble in chloroform, insoluble in water, ethanol and acetone. Recrystallization of P5 in chloroform afforded white block crystals. Anal. Calc. For $[PtCl_2C_{26}H_{24}P_2]$ 29.37 %, H_2O 0 %. Found: Pt 30.06 %, H_2O 0 %.

(**): The experiments were proceeded from 2.0 mmol P3 according to the procedure in the (*) part. The white product (named as P6) insoluble in acetone and chloroform, very soluble in water and ethanol. Recrystallization of P6 in ethanol afforded white block crystals. Yielded 90÷92 %. Anal. Calc. For $[PtC_{52}H_{48}P_4]Cl_2$: Pt 20.68 %, H_2O 0 %. Found: Pt 19.92 %, H_2O 0 %.

Table 2: Some experiments for the interaction between P3 and DPPE

N°.	Concentration	Manipulation	Molar ratio of P3:DPPE	Feature of products	Yield (%)
1	Saturated	Drop DPPE into P3	1:1	White powder	95
2	Diluted	Drop DPPE into P3	1:1	White powder	92
3	Saturated	Drop DPPE into P3	1:2	White powder	92
4	Diluted	Drop DPPE into P3	1:2	White powder	90

It is surprising that product of the reaction between P3 and DPPE is much different when the molar ratio of P3 and DPPE is changed. The ratio of 1:1 or 1:2 responds to the resulting compound $[PtCl_2(DPPE)]$ (P5) or $[Pt(DPPE)_2]Cl_2$ (P6). Since P5 is a neutral complex but P6 is a cation one, solubility of them in some usual solvents is absolutely different. For example, P5 is very soluble in chloroform and insoluble in water, while P6 is insoluble in chloroform and very soluble in water. The structures of P5 and P6 were determined by analysis of Pt proportion, the IR and ^1H NMR spectra. The reaction equations are quoted as below:



(isoPreug: isopropyl eugenoxyacetate)

2.2. Determination of component and structure of P4÷P6

Pt and water of hydration proportion were determined using weight method [8] at Department of Chemistry, Hanoi National University of Education. The results from analyzing Pt, water of hydration proportion (section 2.1) showed a good agreement between the theoretical and actual values.

In addition, molecular mass of P6 was determined by using ESI-MS measurements on Finnigan LCQ at the National University of Singapore. In the positive mode ESI-MS, there is a peak at m/z 1027.2 au with relative intensity consistenting with pseudomolecular ion [P6-Cl$^-$] i.e. $[PtCl(DPPE)_2]^+$ (Fig. 1a). Besides, the isotopic envelopes match with the calculated pattern as illustrated in Fig. 1b.

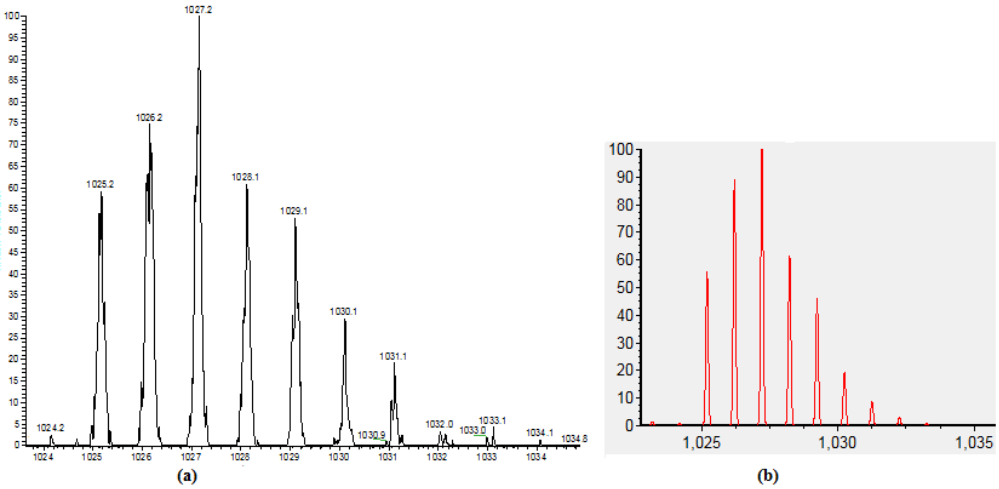


Figure 1: Experimental (a) and simulated (b) isotopic patterns for fragment $[P6\text{-}Cl]^+$

The IR spectra were recorded on IMPACK-410 NICOLET spectrometer in KBr discs in the range 400÷4000 cm^{-1} at Institute of Chemistry, Vietnam Academy of Science and Technology. Main bands in the IR spectra are listed in table 3.

In the IR spectra of P4÷P6, there is no characteristic band for functional groups of the olefins such as intensive bands at around 1720 cm^{-1} for $\nu_{C=O}$ of isopropyl eugenoxiacetate in P5, P6 and bands at around 2900 cm^{-1} for $\nu_{CH\ aliphatic}$ of safrole, methyleugenol and isopropyl eugenoxyacetate in P4. This demonstrates absence of the olefins in P4 ÷ P6, in other word TPP has replaced the olefins in P1, P2, P3. Meanwhile, characteristic bands for the functional groups of TPP and DPPE in the compounds can be observed clearly (table 3). Especially, the Pt-P stretching vibrations in P4, P5, P6 are observed in the region 536÷522 cm^{-1} showing that TPP and DPPE have coordinated with Pt(II) in these complexes.

Table 3: Main bands in IR spectra of P4 ÷ P6 (cm^{-1})

Compound	$\nu_{CH\ aromatic}$	$\nu_{CH\ aliphatic}$	$\nu_{C=C}$	$\delta_{CH\ aliphatic}$	ν_{C-C}	ν_{Pt-P}
$[PtCl_2(P(Ph)_3)]$ (P4)	3053	-	1572	-	-	522
$[PtCl_2(P(Ph)_2CH_2CH_2P(Ph)_2)]$ (P5)	3057	2986; 2922	1587; 1513	1439	1273; 1147	536
$[Pt(P(Ph)_2CH_2CH_2P(Ph)_2)_2]Cl_2$ (P6)	3080	3009; 2928	1620; 1581	1435	1103	535

The ^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz, all at 298-300 K, with TMS as the internal standard at Institute of Chemistry, Vietnam Academy of Science and Technology. In order to analyze ^{1}H NMR spectra, we name the hydrogen atoms of TPP and DPPE as in Fig. 2. The assigned results are listed in table 4 and Fig. 3 shows the assigned ^{1}H NMR spectra of P4 (the product of N^o 14 in table 1-representing for experiments with the molar ratio of 1:1) measured after dissolving it in $CDCl_3$ (Fig. 3a) and 8 hours later (Fig. 3b) as an example.

In the ^{1}H NMR spectra of P5 and P6 display only one particular set of signals for DPPE. Nevertheless, the ^{1}H NMR spectrum of P4 (Fig. 3a) immediately after being dissolved in $CDCl_3$ shows two sets of signals for TPP (P4A and P4B) with the ratio of P4A:P4B of 7:1. After 8 hours, only the

signal set of P4A remains in the ^{1}H NMR spectrum (Fig.3b). Additionally, we also recorded ^{1}H NMR of P4 from the experiment N^o 14 after recrystallization in chloroform and from the experiment N^{o}3 - representing for the experiments with the molar ratio of 1:2 in Table 1. Interestingly, their spectra are the same one in Fig.3b. Consequently, the product of the experiments with the ratio of 1:2 is mixture of *cis*/*trans*-[$PtCl_2(TPP)_2$], of which the *trans* isomer is dominant while the *trans* isomer is unique product of the experiments with the ratio of 1:1. In chloroform solvent, complex *cis*-[$PtCl_2(TPP)_2$] tends to convert to *trans*-[$PtCl_2(TPP)_2$] more stable. This conclusion is in good agreement with the assumption mentioned in the 2.1.2 section

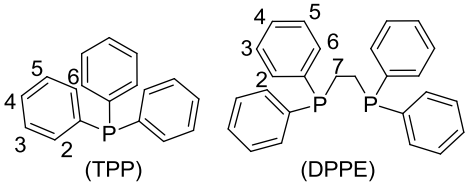


Figure 2: The numeration specially for analysis of ^{1}H NMR spectra

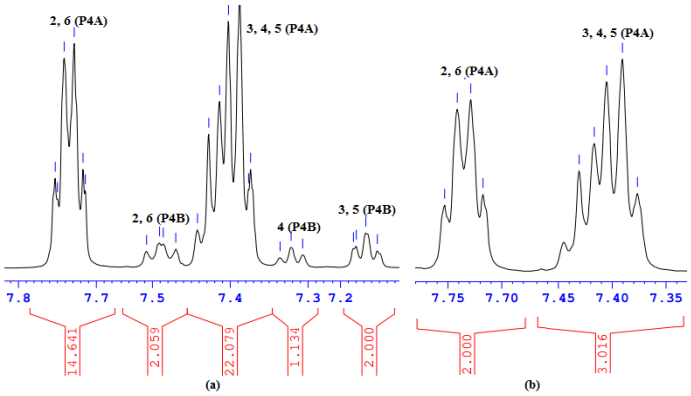
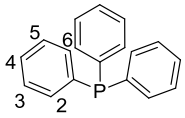
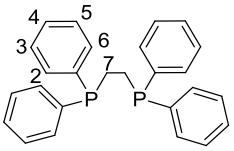


Figure 3: The assigned ^{1}H NMR spectra of P4 measured after dissolving it in $CDCl_3$ (a) and 8 hours later (b)

Table 4: ^{1}H NMR signals of non-coordinated TPP, DPPE and in P4 ÷ P6, δ (ppm), *J* (Hz)

Phosphine*		**H2**	**H3**	**H4**	**H5**	**H6**	**H7**
	Free	7.28-7.35					-
	P4A[(a)]	7.74 dd; $^3J_{PH}$ 12 ^3J 6	7.43-7.38 ov				-
	Free	7.30-7.40					2.10
	P5[(a)]	7.86 dd $^3J_{PH}$ 12 ^3J 7.5	7.48 m	7.53 m	7.48 m	7.86 dd $^3J_{PH}$ 12 ^3J 7.5	2.34 d $^2J_{PH}$ 18 $^3J_{PtH}$ 40
	P6[(b)]	7.93 dd; $^3J_{PH}$ 12 ^3J 7.5	8.04 t; ^3J 7.5	8.16 t; ^3J 7.5	8.04 t; ^3J 7.5	7.93 dd; $^3J_{PH}$ 12 ^3J 7.5	3.31 m

*: solvent, (a): $CDCl_3$; (b): CD_3OD

Table 4 shows no signal for the olefin protons in the ^{1}H NMR spectrum of P4÷P6. This means that the olefins in P1, P2, P3 have been replaced by TPP and DPPE to produce complexes P4÷P6. Besides, the chemical shift of the protons in TPP and DPPE increases compared to the free ligands. As a result, TPP and DPPE have coordinated with Pt(II) through the P atom.

4. CONCLUSION

The interaction between K[$PtCl_3$(olefin)] (olefin: methyleugenol, safrole and isopropyl eugenoxyacetate) with triphenylphosphine (TPP) and 1,2-bis(diphenylphosphino)ethane (DPPE) have been studied for the first time. The results show that TPP and DPPE can coordinate with Pt(II) very favorably and they are able to replace the olefin in complex with structural analog of K[$PtCl_3$(olefin)] easily. In the case of TPP, the product of the experiments with the ratio of 1:2 is mixture of *cis*/*trans*-[$PtCl_2(TPP)_2$], of which the *trans* isomer is dominant while the *trans* isomer is unique product of the experiments with the ratio of 1:1. The *cis* isomer tends to convert to the *trans* isomer in chloroform solvent. For DPPE, two different products, [$PtCl_2$(DPPE)] (P5) and [Pt(DPPE)$_2$]Cl_2 (P6), were obtained responding to the two reaction conditions of molar ratio of mono olefin:DPPE, which are 1:1 and 1:2, respectively. The structures of P4÷P6 were determined by Pt analysis, ESI-MS, IR and ^{1}H NMR spectra studies.

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