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SYNTHESIS OF BIDENTATE PHOSPHORUS-CONTAINING LIGAND BASED ON IMIDAZOLIUM IONIC LIQUID

Annotation. The synthesis on a base of imidazolium ionic liquid of novel ligand (1-(3-diphenylphosphanyl-2-(diphenylphosphanyloxy)propyl)-3-methyl-1*H*-imidazol-3-ium chloride), containing both diphenylphosphine and diphenylphosphinite groups is reported. Phosphine group plays an important role for binding the transition metal in ionic liquid structure. Metal-containing ionic liquids are used both as catalysts and reaction media for the variety of organic synthesis reactions. Phosphinite, known as weakly coordinating group assists the transition metal in performing catalytic activity.

Keywords: ionic liquid, bidentate ligand, imidazolium, phosphinite.

Тірек сөздер: иондық сұйықтық, бидентантты лиганд, имидазолий, фосфинит.

Ключевые слова: ионная жидкость, бидентантный лиганд, имидазолий, фосфинит.

1. Introduction. Ionic liquids (ILs), which are organic salts with a melting point below 100 °C, have attracted much attention in recent years [1]. Because of their unique properties, such as negligible vapor pressure, non-flammability, good thermal stability, high ionic conductivity and excellent designable properties, ILs are favorable in a range of applications like organic synthesis, sample extractions, catalysis, spectroscopy, separations and electrochemistry [2]. Also ILs also have been used as plasticizers [3], lubricants [4], nucleating and antistatic agents [5] in various kinds of polymers and shown promising results.

ILs have received great attention as potential solvents and catalysts in a wide variety of chemical reactions, separation, and manufacturing processes to provide excellent protocols for ecological clean chemistry and green ideology [6].

ILs have profound effect on the reactivity and selectivity of chemical reactions, can be readily recycled and in some cases, facilitate the isolation of products [7]. The tunability of chemical and physical properties by selection of appropriate anion-cation combinations is a useful feature of ILs [8].

Over the last 60 years, the increasing knowledge of transition metal chemistry has resulted in an enormous advance of homogeneous catalysis as an essential tool in both academic and industrial fields. The positive effects of phosphine ligands in transition metal homogeneous catalysis have contributed largely to the organic synthesis and the industrial production of chemicals [9].

In comparison with monodentate phosphorus ligands, bidentate ones lead to increase stability of organometallic complexes due to the chelate effect, which has strong impact on the chemistry at the metal centre. Despite of their importance in transition – metal-catalyzed reactions there is still a lack of new bidentate phosphorus ligands.

Therefore, the synthesis of imidazolium ionic liquid for novel ligands with phosphine and phosphinite functionality, that can be used in transition metal homogeneous catalysis.

2. Experimental

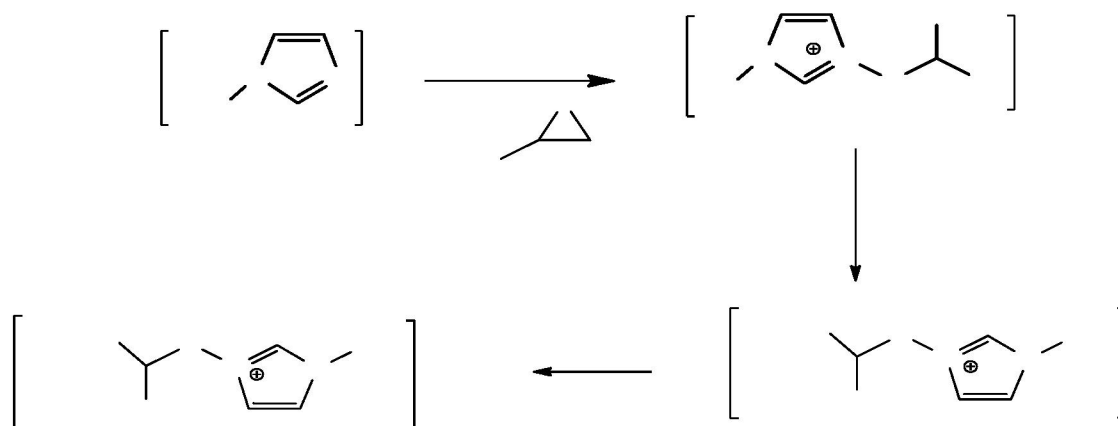
2.1. Materials and methods. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF) and benzene were purified by standard procedures [10]. Reactions were carried out under an atmosphere of argon using conventional Schlenk glass-ware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade, PPh_2Cl and KPh_2Cl , epichlorohydrin and 1-methylimidazole cation, deuterated solvents were purchased from Sigma Aldrich.

FTIR spectra were recorded using the KBr pellet on a Nicolet 5700 Fourier transform spectrophotometer ^{13}C NMR and ^{31}P - $\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument.

2.2. Synthesis of 1-(3-Diphenylphosphanyl-2-(diphenylphosphanyloxy) propyl)-3-methyl-1H-imidazol-3-ium chloride (3). To a stirred solution of 5.2 g of (2) and 55 ml of THF, 10 ml of KPPH_2 were added dropwise. The process was carried out under stirring with periodic formation of yellow-orange solution. After completion of the addition, the resulting reaction mixture was placed in the refrigerator for 2-3 days. At the end of this time, THF was evaporated to a volume of 15 ml. Then 25 ml of hot benzene was added to this solution and the resulting solution was filtered through Celite and then evaporated to a viscous mass (3). Yield, 11 g (89%). IR (KBr) cm^{-1} : 1437,1 (PPh); 1166,5 (CH_2Cl); 1128,5(C-O). ^{31}P NMR, δ , ppm: 33.32, 22.23; ^{13}C NMR, δ , ppm: 137.71 (imidazolium N-C-N), 132.69 & 132.72 (P-C1 phenyl) 131.22, 131.12, 130.86, 130.75, 130.42, 129.09, 128.96, 128.44 (other phenyl C's), 122.11 & 123.84 (imidazolium N-C-C-N), 68.61 (PO-CH), 61.47 (P- CH_2), 60.18 (N- CH_2), 34.28 (N- CH_3). Anal. Calc. for $\text{C}_{31}\text{H}_{34}\text{ON}_2\text{Cl}_2\text{P}_2$, %: C, 67.9; H, 6.21. Found., %: C, 67.99; H 6.24.

3. Results and discussion

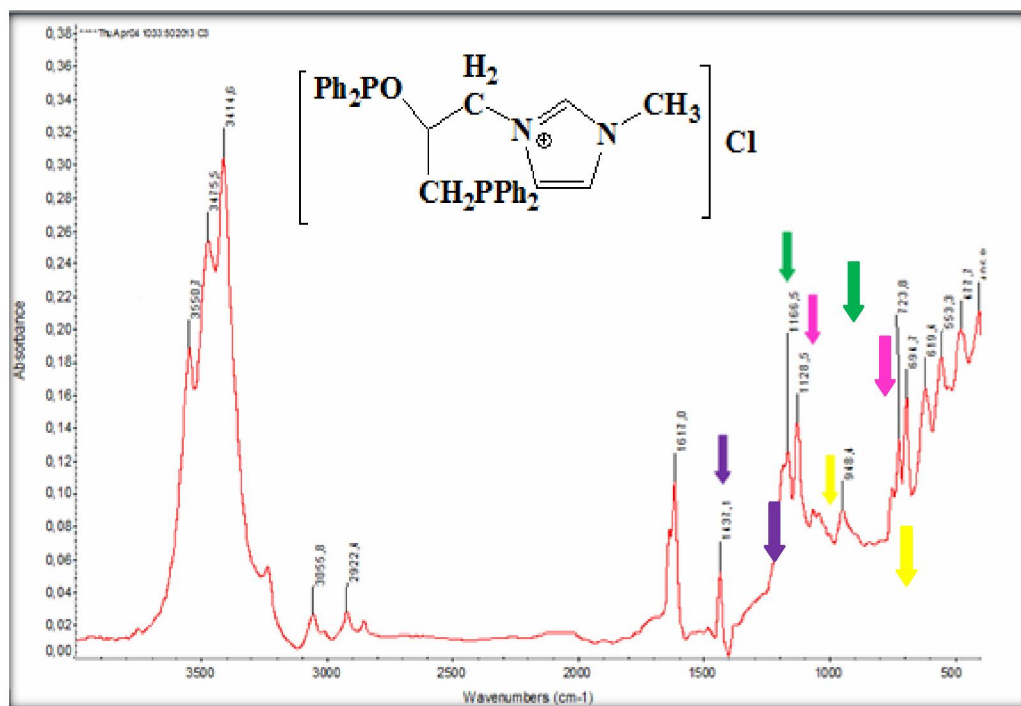
At first we have synthesized novel ionic liquid - 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (1) [11], m.p. $^{\circ}\text{C}$:



Then by adding 1 equiv. Ph_2PCl , 1 equiv. $n\text{-BuLi}$ in CH_2Cl_2 at -78°C to (1), 1-(3-chloro-2-(diphenylphosphanyloxy)propyl)-3-methyl-1H-imidazol-3-ium chloride (2) [11] had been obtained.

1-(3-Diphenylphosphanyl-2-(diphenylphosphanyloxy)propyl)-3-methyl-1H-imidazol-3-ium chloride (3) was easily synthesized by the reaction of 1-(3-chloro-2-(diphenylphosphanyloxy)-propyl)-3-methyl-1H-imidazol-3-ium chloride (2) with KPPH_2 in THF.

Infrared spectrums of 1-(3-diphenylphosphanyl-2-(diphenylphosphanyloxy)propyl)-3-methyl-1H-imidazol-3-ium chloride (3) can be seen below:



Absorption bands of the following groups remain in the spectrum of **3**: PPh, CH₂Cl, CO, (1437,1 cm⁻¹, 1166.5 cm⁻¹, 1128.5 cm⁻¹), respectively. Group P-O-alkyl appears as absorption bands at about the same range as was the spectrum of **2** (995,7 cm⁻¹).

Conclusions. Thus, new compound capable to play the role of bidentate ligand - 1-(3-diphenylphosphanyl-2-(diphenylphosphanyloxy)propyl)-3-methyl-1*H*-imidazol-3-ium chloride-containing both diphenylphosphine and diphenylphosphinite groups, were synthesized by means of consecutive functionalization of ionic liquid 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (**1**).

The reported ionic liquid is a starting for phosphorus-containing ligand of catalysts have proved promising in both Kharasch addition reaction and Williamson synthesis.

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Резюме

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СИНТЕЗ БИДЕНТАНТНОГО ФОСФОРНОГО ЛИГАНДА НА ОСНОВЕ ИМИДАЗОЛЬНОЙ ИОННОЙ ЖИДКОСТИ

В работе представлен синтез новой ионной жидкости-хлорида 1 - (3-дифенилфосфанил-2-(дифенилфосфанилокси)пропил)-3-метил-1*H*-имидазол-3-ия, содержащую как дифенилфосфиновую, так и дифенилфос-

финитную группы. Фосфиновая группа играет важную роль для связывания переходных металлов в структуре ионной жидкости. Металлсодержащие ионные жидкости используются в качестве катализаторов и реакционных сред для различных реакций органического синтеза. Фосфинит, представляет собой слабо координирующую группу, способствующую каталитически активировать переходной метал. Синтезированная ионная жидкость является перспективным катализатором в реакциях присоединения Хараши и синтеза Вильямсона.

Ключевые слова: ионная жидкость, бидентантный лиганд, имидазолий, фосфинит.

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ИМИДАЗОЛИЙ НЕГІЗІНДЕГІ ИОНДЫҚ СҰЙЫҚТЫҚТЫҢ БИДЕНТАНТЫҚ ФОСФОР ЛИГАНДЫНЫҢ СИНТЕЗІ

Жұмыста жаңа дифенилфосфин және дифенилфосфинит қамтитын иондық сұйықтық: 1-(3-дифенилфосфанил-2-(дифенилфосфанилокси)пропил)-3-метил-1*H*-имидазол-3-ий хлориды синтезделген. Фосфин тобы ауыспалы металдың иондық сұйықтықтың құрылымында байланыстырушы ретінде маңызды рөл атқарады. Металл қамтитын иондық сұйықтықтар органикалық синтездің түрлі реакцияларында катализатор және реакциялық орта негізінде пайдаланылады. Фосфинит, ауыспалы металдың каталитикалық белсенділігін жоғарылататын байланыстырушы топ болып табылады. Синтезделген иондық сұйықтық, Хараштың қосылу және Вильямсонның синтез реакцияларында перспективалы катализатор ретінде ұсынылады.

Тірек сөздер: иондық сұйықтық, бидентантты лиганд, имидазолий, фосфинит.