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Highly efficient hydrosilylation catalysts based on chloroplatinate “ionic liquids”

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ABSTRACT

The reaction between ionic liquid $[Cat]^+Cl^-$ (where Cat stands for 1-butyl-3-methylimidazolium, 1-butyl-2,3-dimethylimidazolium or 1-butyl-4-methylpyridinium) and the metal precursor ($[PtCl_2(cod)]$, $PtCl_4$, $K_2[PtCl_4]$ or $K_2[PtCl_6]$) yielded two groups of derivatives: $[Cat]^+[PtCl_4]^-$ and $[Cat]^+[PtCl_6]^-$, which formally are counted among halometallate ionic liquids, however, due to their high melting points they should be classified into anionic platinum complexes rather than into ionic liquids. All the derivatives were isolated and characterized spectroscopically (NMR, ESI-MS) and crystallographic structures were determined for three derivatives: ($[BMPy]_2[PtCl_4]$, $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$. Moreover, their melting points were measured and thermal stability was assessed. The above derivatives were employed as catalysts for hydrosilylation of olefins with diverse properties. All the studied catalysts showed high activity and their insolubility in the reaction medium made easy their isolation and multiple use in subsequent catalytic runs. The most effective catalysts did not lose their activity even after ten runs, thereby they make a very good alternative to commonly used homogeneous catalysts. Their simple synthesis and stability make them interesting both for economic and ecological reasons.

1. Introduction

The reaction of hydrosilylation is unquestionably one of the most important methods for laboratory and industrial syntheses of various organosilicon compounds [1–4]. It is also extensively used in polymer chemistry and materials science [5,6].

The hydrosilylation reaction is usually performed in a single-phase homogeneous system. Because platinum and rhodium complexes are commonly employed as catalysts, therefore the recovery and recycling of the expensive catalysts make a challenging aspect of the process. Moreover, sometimes the presence of metals in the reaction products, even in trace amounts, is unacceptable. Unfortunately, the separation of the catalyst from the post-reaction mixture, particularly in the case of polymeric systems of high viscosity, is a serious problem. This is why efforts are made at applying heterogeneous catalysts or immobilized metal complexes to obtain both high catalytic activity in many recycled runs and easy product isolation, which is of crucial importance to “green chemistry”. One of examples of catalyst immobilizing agents are ionic liquids which have been employed with a considerable success for over 30 years in a wide range of laboratory scale reactions [7–9]. A number of excellent review papers as well as books were devoted to the role played by ionic liquids in catalysis [10–12]. Over 100 types of chemical reactions catalyzed by transition metal complexes were performed in the presence of ionic liquids [11–13]. Among them are also reactions of hydrosilylation, however, the number of literature reports on this aspect of their use is still small enough [14–19]. Our contribution to this field was the development of a number of effective catalytic systems based on diverse platinum and rhodium complexes immobilized in the most important kinds of ionic liquids, namely imidazolium [20,21], phosphonium [22,23], morpholinium [24], pyrylium [25] and ammonium [26] derivatives. All the systems developed by us are insoluble in the reaction medium, therefore they can be easily isolated from it and used many times without losing their catalytic activity. Our research has enabled to select suitable ionic liquids and complexes of rhodium or platinum that formed very active catalytic systems, however, they have not provided us with information on the kind of metal complex – ionic liquid interactions and on the structure of the actual catalyst. This is why we have recently

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made attempts to isolate and identify them. However, it has to be mentioned that this is a formidable task because of the complexity of the systems and large number of ions. There are, however, considerably simpler systems that have recently attracted our interest. These are halometallate ionic liquids which can be defined as ionic liquids formed by the reaction of metal halide with an organic halide salt. The first representatives of this group of compounds were chloroaluminate ionic liquids [27], however, at present, examples are known of the compounds that contain transition metals such as cobalt, nickel, iridium, gold, palladium as well as platinum [28–32]. Nevertheless, the number of theses complexes is still low. In the case of platinum compounds, there are only a few reports. One of the methods of the synthesis of latter compounds was based on the reaction of imidazolium chloroaluminate ionic liquids [EMIM]Cl/$AlCl_3$ with $PtCl_4$ and $PtCl_2$ at 150 °C as a result of which $[EMIM]_2[PtCl_6]$ and $[EMIM]_2[PtCl_4]$ were obtained with the yields of 80% and 71%, respectively [33]. Additionally, the single crystal structures of these compounds were determined by X-ray diffraction. Another compound, $[BMIM]_2[PtCl_4]$, was obtained with the yield of 55% using a standard method based on the reaction between [BMIM]Cl and $PtCl_2$ in acetonitrile medium under reflux [33]. The crystallographic structure of this compound has also been determined [34]. Also known is $[BMIM]_2[PtCl_6]$ which was synthesized from $K_2[PtCl_6]$ and [BMIM]Cl (in a large excess) and the product yield was 57% [33].

The aim of the present study was to synthesize and characterize chloroplatinate ionic liquids containing different cations and platinum at different oxidation states, as well as to evaluate their catalytic activity for the process of olefin hydrosilylation. Compounds of this type were never applied as catalysts for the above process, and since most of hydrosilylation catalysts are based on platinum compounds, it was advisable to determine their catalytic activity and possibility of multiple use in subsequent reaction runs. The present report describes our first efforts to explore this hypothesis.

2. Experimental

2.1. Materials

All reagents applied in catalytic measurements, i.e., 1-octene, allyl glycidyl ether, n-decane and 1,1,1,3,5,5,5-heptamethyltrisiloxane were purchased from Sigma Aldrich and used as received. Also metal precursors: $[PtCl_2(cod)]$, K_2PtCl_4 (for platinum(II)) and K_2PtCl_6 (for platinum(IV)) were supplied by Sigma Aldrich. The ionic liquids: 1-butyl-4-methylpyridinium chloride [BMPy]Cl, 1-butyl-3-methylimidazolium chloride [BMIM]Cl, and 1-butyl-2,3-dimethylimidazolium chloride [BMMIM]Cl were purchased from Iolitec GmbH, Germany.

2.2. Techniques

The yield of a product of a given reaction was determined using a Clarus 680 gas chromatograph (Perkin Elmer) equipped with a 30 m capillary column Agilent VF-5 ms and TCD detector, using the temperature program: 60 °C (3 min.), 10 °C min^{-1}, 290 °C (5 min.). For the products obtained, NMR spectra were made with Bruker BioSpin (400 MHz) spectrometer using acetonitrile-d_3 as a solvent; chemical shifts are given in ppm. ESI-MS spectra were recorded using a QTOF-type mass spectrometer (Impact HD, Bruker). Thermogravimetric analysis (TGA) was carried out using a TA Instruments TG Q50 analyzer at a linear heating rate of 10 °C/min under synthetic air (50 ml/min). The tested samples were placed in a platinum pan and the weight of the samples was kept within 9–10 mg. The experimental error was 0.5% for weight and 1 °C for temperature. Melting points were measured on Melting Point M-565 instrument (Buchi) equipped with a video camera. Temperature gradient: 10 °C/min. FT-IR *in situ* measurements were performed using a Mettler Toledo ReactIR 15 instrument. For selected samples, spectra were recorded with 256 scans for 1 or 2 h at 30 s intervals with the resolution of 1 cm^{-1}. Intensity change of the band at 903 cm^{-1}, characteristic of Si-H bond, was recorded using an ATR probe with diamond window. The ICP-MS analysis of post-reaction samples was carried out on a PerkinElmer Nexion 300D inductively coupled mass spectrometer. The powder XRD (pXRD) analysis was conducted by using a Brucker D8 Advance diffractometer equipped with a Johansson monochromator (λCu Kα1 = 1.5406 Å) and silicon strip detector LynxEye. Minimum measurement angle is 0.6 2Θ deg.

2.3. X-ray crystallography

Data were collected on a New Xcalibur EosS2 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 Å). For the data reduction, UB-matrix determination and absorption correction CrysAlisPro [35] software was used. Using Olex2 [36], the structures were solved by direct methods using ShelXT [37] and refined by full-matrix least-squares against F2 using the program SHELXL [37] refinement package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions by molecular geometry and refined as rigid groups. The positions of U_{iso} of hydrogen atoms were set as 1.2 (for C-carries) times U_{eq} of the corresponding carrier atom. Selected structural parameters are presented in Table S2 in the Supplementary Material.

The data have been deposited with the Cambridge Crystallographic Data Collection (CCDC), deposition numbers CCDC 1558450, 1,558,451 and 1860948. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2.

2.4. Synthesis of complexes bis(1-butyl-2,3-dimethylimidazolium) tetrachloroplatinate(II), $[BMMIM]_2[PtCl_4]$

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.45 g (2.4 mmol) of [BMMIM]Cl and 0.50 g (1.2 mmol) of $[K_2PtCl_4]$ in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux and then, after filtration by a cannula system, the solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 78% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.51 g (2.7 mmol) of [BMMIM]Cl and 0.51 g (1.35 mmol) of $[PtCl_2(cod)]$ in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. Then the solution was cooled to room temperature and the solvent was evaporated. The orange product was washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 92% anal. calcd.

2.5. Bis(1-butyl-2,3-dimethylimidazolium) hexachloroplatinate(IV), $[BMMIM]_2[PtCl_6]$

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.56 g (2.9 mmol) of [BMMIM]Cl and 0.5 g (1.5 mmol) of $PtCl_4$ in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. The solution was cooled to room temperature and the solvent was evaporated. The orange product was washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 96% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.4 g (2 mmol) of [BMMIM]Cl and 0.52 g (1.1 mmol) of K_2PtCl_6 in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux followed by filtration by a cannula system. The solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 91% anal. calcd.

2.6. Bis(1-butyl-3-methylimidazolium) tetrachloroplatinate(II), [BMIM]$_2$[PtCl$_4$]

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.42 g (2.4 mmol) of [BMIM]Cl and 0.50 g (1.2 mmol) of [K_2PtCl_4] in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux followed by filtration by a cannula system. The solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 74% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.54 g (3 mmol) of [BMIM]Cl and 0.58 g (1.5 mmol) of [$PtCl_2$(cod)] in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. The solution was cooled to room temperature and the solvent was evaporated. The obtained orange crystals were washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 87% anal. calcd.

2.7. Bis(1-butyl-2,3-methylimidazolium) hexachloroplatinate(IV), [BMIM]$_2$[PtCl$_6$]

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.5 g (2.9 mmol) of [BMIM]Cl and 0.5 g (1.5 mmol) of $PtCl_4$ in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. The solution was cooled to room temperature and the solvent was evaporated. The orange product was washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 95% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.36 g (2 mmol) of [BMIM]Cl and 0.5 g (1 mmol) of K_2PtCl_6 in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux followed by filtration by a cannula system. The solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 93% anal. calcd.

2.8. Bis(1-butyl-4-methylpyridinium) tetrachloroplatinate(II), [BMPy]$_2$[PtCl$_4$]

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.45 g (2.4 mmol) of [BMPy]Cl and 0.50 g (1.2 mmol) of [K_2PtCl_4] in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux followed by filtration by a cannula system. The solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 79% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.54 g (3 mmol) of [BMPy]Cl and 0.58 g (1.5 mmol) of [$PtCl_2$(cod)] in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. The solution was cooled to room temperature and the solvent was evaporated. The orange product was washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 97% anal. calcd.

2.9. Bis(1-butyl-4-methylpyridinium) hexachloroplatinate(IV), [BMPy]$_2$[PtCl$_6$]

Method 1. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.55 g (2.9 mmol) of [BMPy]Cl and 0.5 g (1.5 mmol) of $PtCl_4$ in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux. The solution was cooled to room temperature and the solvent was evaporated. The orange product was washed with diethyl ether (3 × 5 ml) and dried under vacuum. Product yield: 98% anal. calcd.

Method 2. To a 25 ml Schlenck tube equipped with a magnetic stirring bar 0.39 g (2 mmol) of [BMPy]Cl and 0.56 g (1.1 mmol) of K_2PtCl_6 in hot CH_3CN (2 ml) were added. The mixture was stirred for 3 h under reflux followed by filtration by a cannula system. The solvent was evaporated and the product was dried under vacuum to yield orange crystals. Product yield: 94% anal. calcd.

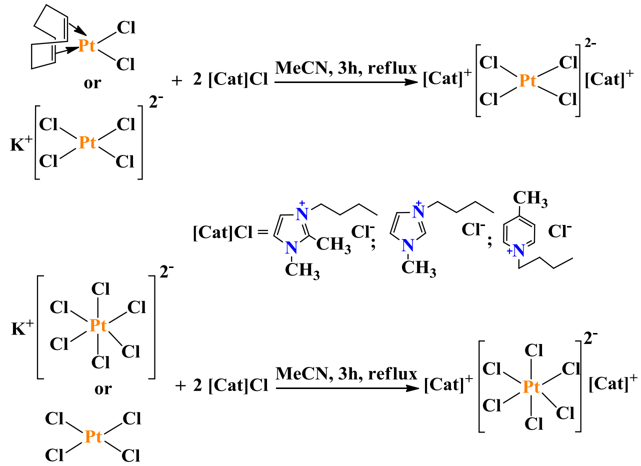
2.10. General procedure for catalytic tests

The catalytic activity of the obtained anionic platinum complexes was determined in the reaction of hydrosilylation of 1-octene or allyl glycidyl ether with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS). For this purpose, 10^{-4} mol of catalyst per 1 mol of Si-H, 3.68 mmol of 1-octene or 4.41 mmol of allyl glycidyl ether and 3.68 mmol of HMTS were used. Moreover, 1 mmol of n-decane as an internal standard was added. The reaction was carried out in a reaction vessel in the presence of air at 110 °C for 1 h without stirring. The reaction mixture was then cooled down and subjected to GC analysis to determine the reaction yield. The product was isolated and subjected to NMR analyses. Due to very small amount of catalyst and its total insolubility, the post-reaction mixture could be fully removed using a syringe with needle after the reaction completion. The catalyst remaining in the reaction vessel was not subjected to any washing and regeneration. After the complete removal of products, a new portion of the reaction substrates was added to the reaction vessel and the reaction was carried out in the same way as described above. The above operation was repeated 10 times and no further reaction runs were performed even if catalyst was still active. After each catalytic cycle, the post-reaction mixture was analyzed chromatographically. In each case, the catalysts were insoluble and formed a biphasic system with reagents. The color of products of the reaction with allyl glycidyl ether slightly changed from colorless to light orange as the reaction progressed and the most intense change was observed after the first run. In the case of the reaction with octene, no color change occurred and the mixture remained colorless.

3. Results and discussion

In our research we have employed dialkylimidazolium (or trialkylimidazolium) and N-alkylpyridinium-based salts as they are among the most frequently studied ionic liquids due to their easy synthesis. As metal precursors we have applied compounds of platinum at different oxidation states. In this way we have obtained two series of tetrachloroplatinate and hexachloroplatinate compounds differing in cations as shown in Scheme 1. Each of the compounds was obtained by two methods.

The first series (tetrachloroplatinates(II)) has been prepared by two methods based on the use of potassium tetrachloroplatinate or dichloro(cyclooctadiene)platinum(II). In both cases the reactions yields were high, however, those obtained in the latter reaction appeared to be higher because cyclooctadiene released in the reaction can be easily removed by evaporation, contrary to potassium chloride produced in the former reaction. The second series of compounds (hexachloroplatinates(IV)) was obtained using potassium tetrachloroplatinate or platinum(IV) chloride. Also in this case, yields were very high, but those obtained in the reactions with $K_2[PtCl_6]$ were slightly lower. However, the differences were small compared to those observed in the case of the first series of compounds. It is important that all the methods make it possible to obtain, in a very simple way and with high yields, the compounds that are easy to isolate and stable in air. Moreover, it is worth mentioning that the synthesis of [BMIM]$_2$[PtCl$_4$] with the use of $K_2[PtCl_4]$ resulted in the yield of 74%, despite the opinion expressed in the literature [33] that the above product is not



Scheme 1. Methods of the synthesis of chloroplatinate ionic liquids applied in the study.

formed in such a reaction. All the obtained compounds are orange solids that are soluble in chloroform, acetonitrile and water and insoluble in benzene and ether.

Due to ionic character of the complexes, their identification was based on the comparison of ^{1}H and ^{13}C NMR spectra of synthesized complexes and relevant ionic liquids used for their preparation, as well as ESI-MS spectra. A clear difference was observed in chemical shifts of the signal originating from hydrogen atom in position C2, i.e. that linked to carbon atom located between two nitrogen atoms in imidazolium salts or between nitrogen atom and carbon atom C3 in pyridinium salt. We attribute this shift to the formation of weak hydrogen bonds C—H···Cl between proton and chlorine atom originating from either $[PtCl_4]^{2-}$ or $[PtCl_6]^{2-}$ anion. The difference in chemical shifts in the newly formed anionic platinum complexes and ionic liquids depends on the kind of cation and ranges from 0.4 to 0.6 ppm. The presence of hydrogen bond has no significant effect on chemical shift values in ^{13}C NMR spectra. The chemical shifts in ^{1}H NMR of NC*H*N on imidazolium rings in $[BMIM]_2[PtCl_6]$ appeared at 9.13–9.11 ppm. In the case of $[BMIM]_2[PtCl_4]$, the chemical shifts moved to 9.13 ppm. In NMR spectra reported in the literature for $[BMIM]_2[PtCl_4]$, the chemical shifts of NC*H*N on imidazolium rings appeared at 9.42 ppm [34] – 8.71 ppm [33], whereas for $[BMIM]_2[PtCl_6]$ – at 8.74 ppm [2]. The results obtained by us are convergent with literature data [33,34].

In ESI-MS spectra, visible are MS(+) signals originating from cations and MS(−) ones coming from anions of the new platinum complexes. These signals have characteristic shape of a multiplet due to the presence of three isotopes of platinum. Each signal can be ascribed to a given isotope on the basis of the intensity corresponding to its percentage in the sample. For all the tested compounds, the most intensive peak in the positive mode corresponded to the molecular peak of the cations: m/z 139.12 $[BMIM]^+$, m/z 153 $[BMMIM]^+$ and m/z 150.13 $[BMPy]^+$. In the case of tetrachloroplatinate complexes, the MS(−) spectra showed the presence of ions with two negative charges, $[PtCl_2]^{2-}$ and $[PtCl_4]^{2-}$, as well as with one negative charge $[PtCl_3]^-$. The most pronounced signal in the negative spectra of Pt(II) was m/z 335.84 corresponding to $[PtCl_4]^{2-}$, but the anions $[PtCl_2]^{2-}$ (m/z 265.15) and $[PtCl_3]^-$ (m/z 300.89) were also detected, however, they were always far less intense than those corresponding to $[PtCl_4]^{2-}$. Di Marco et al. [38,39] and Kebarle [40] postulated that the ions observed in the gas phase can be different from those present in the solution owing to processes which occur at the threshold between solution and gas phase and ion-molecule reactions in the gas phase.

The best evidence that the obtained compounds have the assumed structure comes from X-ray structural analysis. In the case of four of the above compounds we were able to grow crystals and determine their structures. However, because the structure of $[BMIM]_2[PtCl_4]$ has been previously reported in the literature [34], we will discuss below the three remaining structures.

3.1. Crystal structures of salts $[BMPy]_2[PtCl_4]$, $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$

Selected bond lengths and angles are given in Table S1 in the Supplementary Material.

3.1.1. Crystal structures of salts $[BMPy]_2[PtCl_4]$

X-ray quality crystal of $[BMPy]_2[PtCl_4]$ was grown by slow evaporation from acetonitrile. The complex crystallizes as trapezoid orange crystals in a monoclinic system with the space group C2.

The asymmetric unit contains one molecule of 4-butyl-1-methyl-pyridinium and one-half molecule of $PtCl_4^{2-}$ with the other half generated by an inversion center, which lies at the midpoint of the Pt(II) atom. As expected, $PtCl_4^{2-}$ ions show square planar geometry with an average Pt-Cl bond length of 2.296 Å. Eight molecules of cationic 4-butyl-1-methyl-pyridinium surround the anionic $PtCl_4^{2-}$ in a distorted cubic fashion (Fig. 1a). In turn, each of the cationic units is surrounded by four $PtCl_4^{2-}$ anions (Fig. 1b). Several close interionic C—H···Cl type interactions involving both aromatic and aliphatic protons of the pyridinium moieties (the average length 2.841 Å) and chlorine atoms from $PtCl_4^{2-}$ were found. Comparable C—H···Cl distances are observed for aromatic and aliphatic protons (from 2.725 to 2.942 Å and from 2.805 to 2.870 Å, respectively).

In addition, close contacts between cations are observed in the complex $[BMPy]_2[PtCl_4]$. The C—H···π type interactions between methyl hydrogen of the butyl moiety and the pyridinium ring system of another cation (C—H···C_5N ring centroid of 2.644 Å) lead to 1D arrays of cations in $[BMPy]_2[PtCl_4]$ (Fig. 2).

3.1.2. Crystal structures of salts $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$

X-ray quality crystals of $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$, suitable for X-ray crystallographic measurements, were obtained by slow evaporation of their acetonitrile solutions. Both complexes crystallize in the monoclinic system with the space group $P2_1/c$ as a shiny orange rectangular block. The Pt nucleus lies on a center of symmetry. The coordination sphere of the Pt atom can be described as a typical octahedral geometry. The structure of both complexes consists of octahedral hexachloroplatinate(IV) anions and either 1-butyl-3-methylimidazolium in $[BMIM]_2[PtCl_6]$ (Fig. 3a and b) or 1-butyl-2,3-dimethylimidazolium in $[BMMIM]_2[PtCl_6]$ (Fig. 3c and d) cations, respectively. In both complexes ionic pairs are joined in chains by C—H···Cl type interactions (Fig. 3b and d) (relevant bond distances and angles are marked and given in Fig. 3). The Pt-Cl bond lengths range from 2.318 to 2.322 Å and are comparable to those found in other hexachloroplatinate(IV) structures [41,42] (relevant bond distances and angles are given in Table S1 in the Supplementary material). The imidazolium rings are essentially planar, the C—C and C—N bond distances are consistent with the values of the known imidazolium salts [43]. The ionic packing for the $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$ crystal structures can be described approximately as that of an anti-fluorite lattice. Eight cations surround the anionic unit in a distorted cubic fashion and the cation unit is surrounded tetrahedrally by four $PtCl_6^{2-}$ anions in both ionic liquids. The crystal packing in $[BMIM]_2[PtCl_6]$ and $[BMMIM]_2[PtCl_6]$ complexes, besides coulombic attractions between positive and negative charges, is significantly determined by C—H···Cl interactions involving C—H atoms

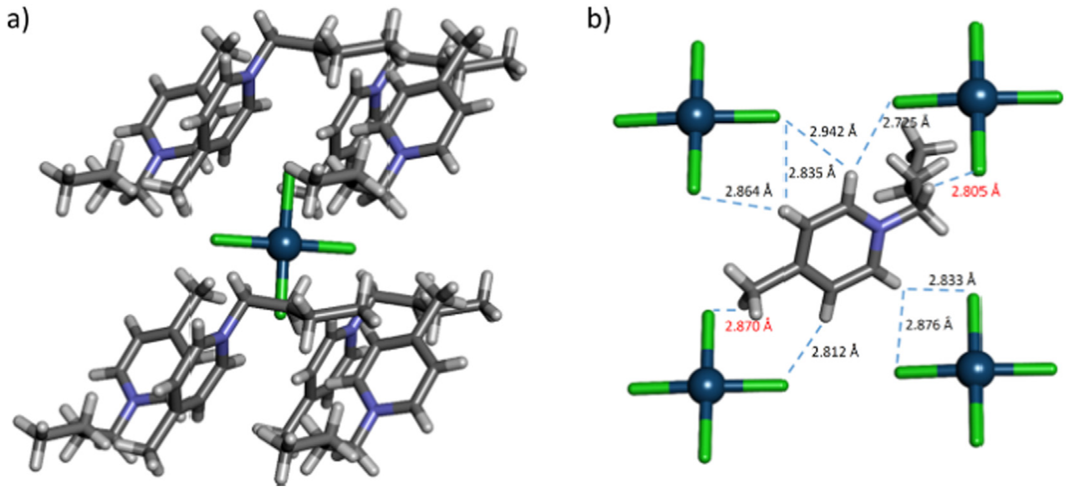


Fig. 1. X-ray structures of $[BMPy]_2[PtCl_4]$ complex: (a) side view of $PtCl_4^{2-}$ anion surrounded by cationic 4-butyl-1-methyl-pyridinium moieties in a distorted cubic fashion, (b) top view of the cationic unit surrounded by four $PtCl_4^{2-}$ anions.

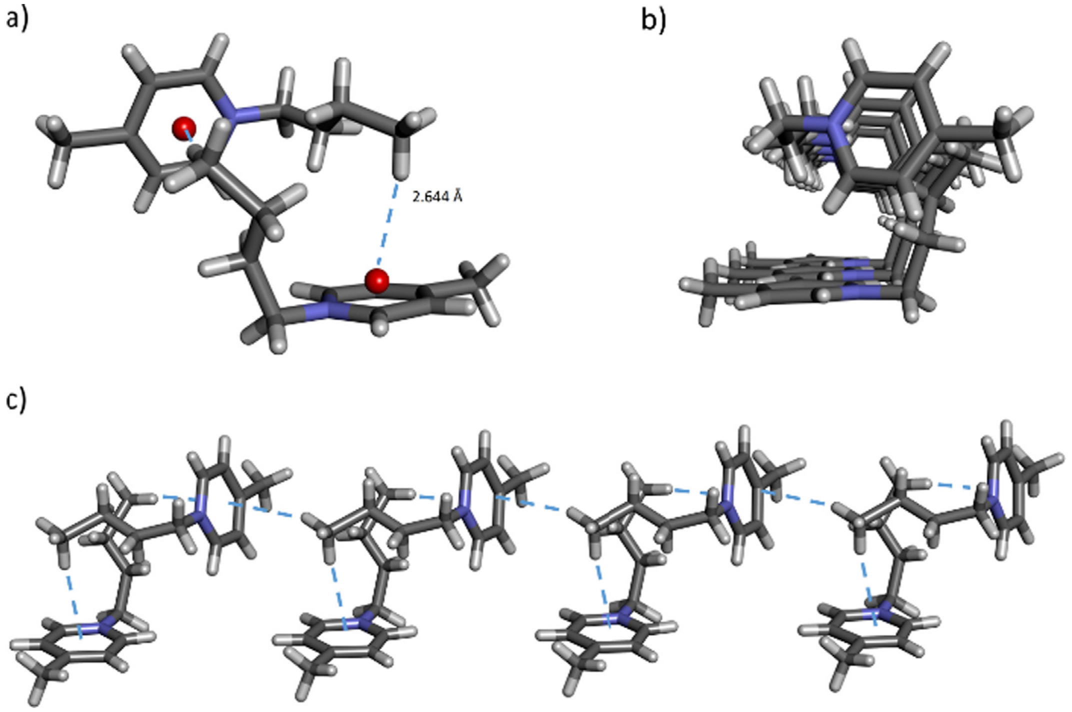


Fig. 2. X-ray structures of $[BMPy]_2[PtCl_4]$ complex: (a) C—H···π type interactions between methyl hydrogen of the butyl moiety and the pyridinium ring of adjacent cation; (b) top view of C—H···π type interactions which lead to 1D arrays, (c) side view of 1D arrays; anions omitted for clarity.

of methyl, butyl and imidazolium moieties of the cation and a chlorine atom of $PtCl_6^{2-}$ anion, which results in the formation of a supramolecular assembly. Close interionic C—H···Cl distances are observed in $[BMIM]_2[PtCl_6]$ for aromatic protons (from 2.699 to 2.815 Å) compared to their aliphatic counterparts (from 2.880 to 2.910 Å). In $[BMIM]_2[PtCl_6]$ ionic liquid, both H^2 (—N—**C**H═N—) and $H^{4/5}$ (—**CH**═**CH**—) protons are involved in hydrogen bonding interactions. The bond lengths observed between the atoms involved in these H-bonds can suggest stronger interactions with H^2 than $H^{4/5}$ (2.699 Å and 2.769 to 2.815 Å for H^2 and $H^{4/5}$, respectively). The hydrogen bonds between H and Cl ions are shorter than expected from the sum of the van der Waals radii of H and Cl atoms, which is 2.95 Å, while weaker interactions C—H···Cl occur in $[BMMIM]_2[PtCl_6]$, where lengths are from 2.741 and 2.835 Å for $H^{4/5}$ (—**C**H═**C**H—) aromatic protons. The lengths of bonds for their aliphatic counterparts are ranging from 2.880 to 3.414 Å, respectively.

We have also performed pXRD on two selected compounds, i.e. $[BMMIM]_2[PtCl_6]$ and $[BMIM]_2[PtCl_6]$, and compared the obtained data with those simulated from the single crystal structure (results are given in the Supplementary material). The experimental pXRD pattern for $[BMMIM]_2[PtCl_6]$ complex exactly corresponds with that simulated from the single-crystal data which undoubtedly identifies the species in the bulk. The second studied complex, i.e. $[BMIM]_2[PtCl_6]$, showed phase compatibility in around 80%. The difference between the patterns obtained from the powder XRD and those generated from a single crystal is quite common and can result from the presence of e.g. more than one phase (poly-

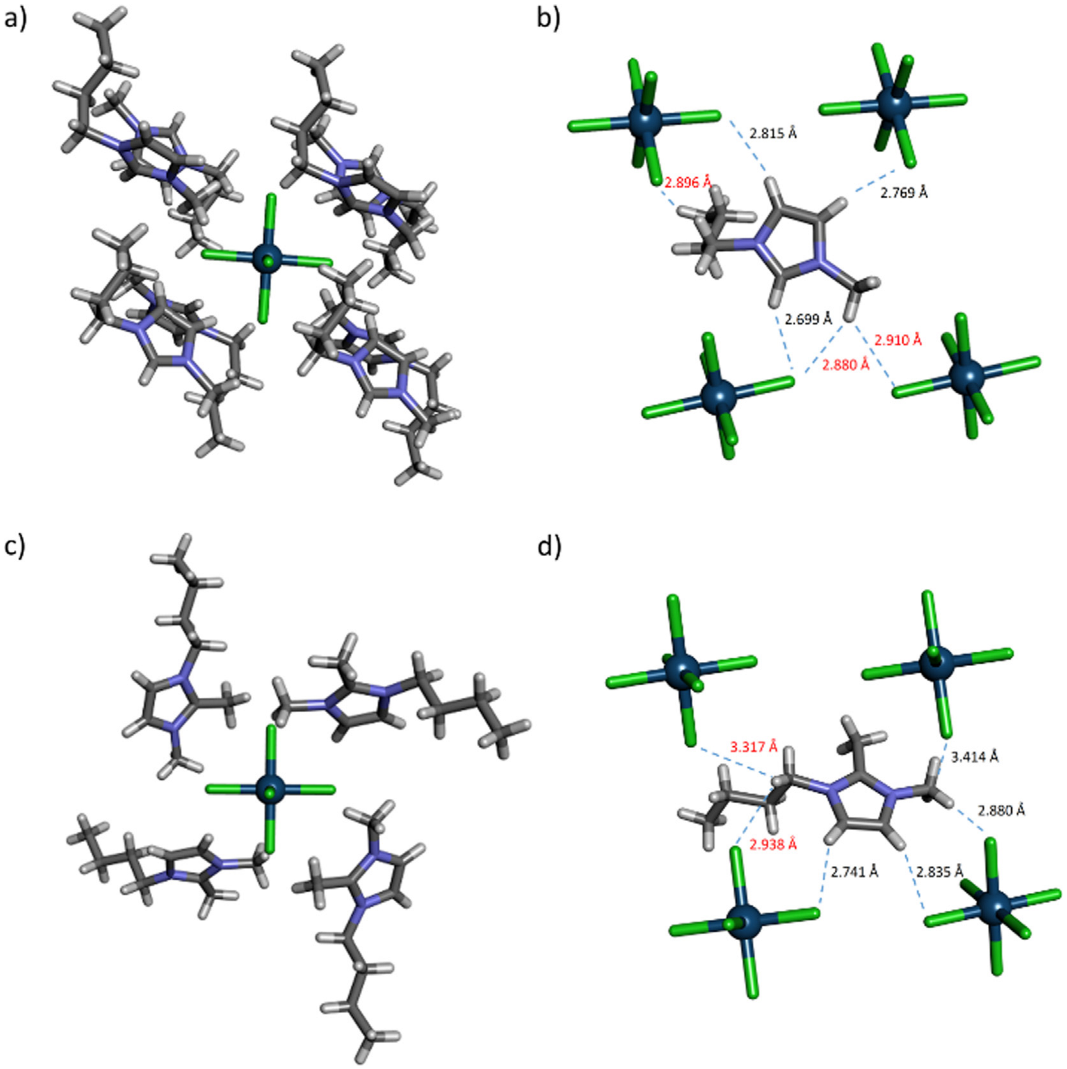


Fig. 3. X-ray structures of [BMIM]$_2$[PtCl$_6$] and [BMMIM]$_2$[PtCl$_6$] complexes: (a) side view of PtCl$_6^{2-}$ anion surrounded by eight 1-butyl-3-methylimidazolium cations; (b) top view of the cationic unit surrounded by four [PtCl$_6$]$^{2-}$ anions; (c) side view of [PtCl$_6$]$^{2-}$ anion surrounded by four 1-butyl-2,3-dimethylimidazolium cations; (d) top view of the cationic unit surrounded by four PtCl$_6^{2-}$ anions with marked lengths of C—H···Cl type interactions.

morph) of this complex in the bulk material. In such cases each polymorph has its own characteristic arrangement of atoms within the material examined that strongly influences the resulting pattern. On the other hand, the difference in reflection intensities between the simulated and experimental patterns comes from variation in preferred orientation of the powder samples during collection of the experimental pXRD data.

3.2. Melting points and thermal stability of the obtained compounds

Melting points of all the synthesized compounds were determined and the results of the measurements were presented in Table 1.

According to literature data, melting points of such compounds depend on many factors, among others on the symmetry of cations [44] and anions [34]. The higher symmetry, the higher melting point. A comparison of melting points (Table 1) of compounds containing the same cation show that melting points of hexachloroplatinates are higher than those of tetrachloroplatinates because the symmetry of [PtCl$_6$]$^{2-}$ anion is higher (O$_h$) than that of [PtCl$_4$]$^{2-}$ anion (with D$_{4h}$ symmetry). On the other hand, when taking into consideration compounds with the same anion, one can notice that melting points increase in the series corresponding to the cations: [BMIM] < [BMPy] < [BMMIM]. All the above compounds are formally classified into the group of halometallate ionic liquids, however, their melting points which exceed 128 °C make it difficult to classify them among ionic liquids, whose melting points should be below 100 °C. This is why it would be better to call them anionic platinum complexes.

The thermal stability of the above compounds was evaluated by thermogravimetric analysis (TGA) and the results are shown in Fig. 4. Decomposition temperatures were estimated by taking temperature at 10% of weight loss (Table 2). Such a value of weight loss was chosen to discriminate between decomposition temperature

Table 1
Melting points of the synthesized chloroplatinate ionic liquids.

Compound	Melting point [°C]
[BMIM]$_2$[PtCl$_4$]	128
[BMIM]$_2$[PtCl$_6$]	170
[BMMIM]$_2$[PtCl$_4$]	165
[BMMIM]$_2$[PtCl$_6$]	185
[BMPy]$_2$[PtCl$_4$]	130
[BMPy]$_2$[PtCl$_6$]	180

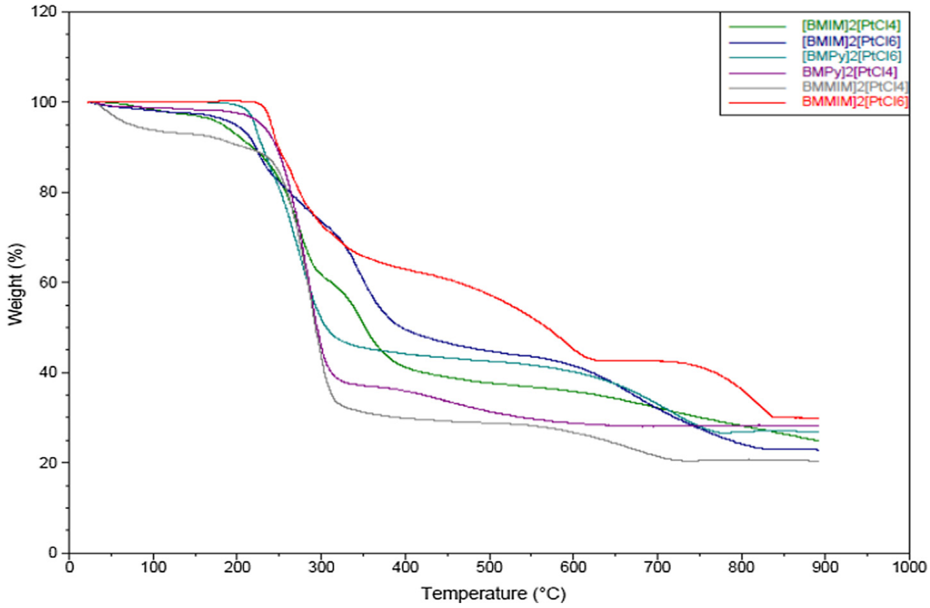


Fig. 4. Thermogravimetric curves of anionic platinum complexes.

Table 2
Decomposition temperatures of compounds at 10% of weight loss.

Compound	Decomposition temperature [°C]
[BMMIM]Cl	277
$[BMMIM]_2[PtCl_4]$	208
$[BMMIM]_2[PtCl_6]$	249
[BMIM]Cl	244
$[BMIM]_2[PtCl_4]$	218
$[BMIM]_2[PtCl_6]$	222
[BMPy]Cl	234
$[BMPy]_2[PtCl_4]$	247
$[BMPy]_2[PtCl_6]$	230

and water desorption temperature. An example illustrating the problem of water desorption can be the TGA curve of $[BMMIM]_2[PtCl_4]$ (Fig. 4), where weight loss is observed already at a relatively low temperature (above 70 °C), however, when the criterion of 10% weight loss is applied, then the temperature is 208 °C and this is in agreement with literature data [34].

The obtained results show that in the case of imidazolium derivatives the decomposition temperatures of chloroplatinates (both tetra- and hexachloroplatinates) are lower than those of starting chlorides, albeit decomposition temperatures of chloroplatinates are higher compared to tetrachloroplatinates. On the other hand, in the case of pyridinium derivatives, the decomposition temperatures of both chloroplatinates and starting chlorides are close to each other and range between 230 and 247 °C. Nevertheless, one can state that all the obtained platinum complexes are stable up to 200 °C.

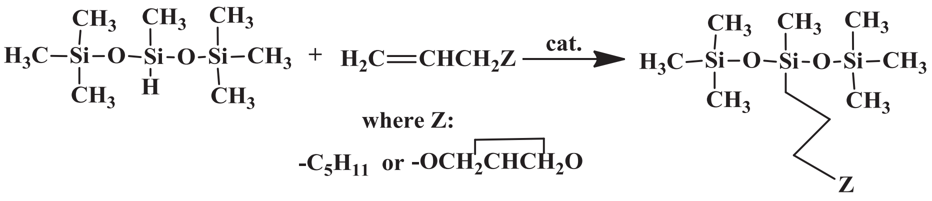
3.3. Catalysis

All the synthesized anionic platinum complexes were employed as catalysts for olefin hydrosilylation. The reactants were 1-octene, which is nonpolar and hydrophobic, and allyl glycidyl ether, which is polar and hydrophilic. Both olefins were subjected to hydrosilylation with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) (Scheme 2).

Chromatographic analysis of post-reaction mixtures showed that in each case only the product of β-addition was formed. No other side products, e.g. α-adducts or products of olefin isomerization were observed.

To determine catalytic activity and optimize reaction conditions, the FT-IR *in situ* analysis was performed for the reaction of octene hydrosilylation. Real-time monitoring of the reaction catalyzed by the platinum complexes using an *in situ* FT-IR probe enabled to determine respective reaction profiles and show differences in their activity. Fig. 5 presents the change in the hydrosilylation product yield as a function of time as observed for respective reactions catalyzed by anionic platinum complexes (at the concentration 10^{-5} mol Pt/mol Si—H), conducted at 110 °C.

The conducted research unequivocally shows that the activity of respective catalysts differs, but mainly due to the induction period, whereas most of the catalysts at the moment of the activation enable a very fast reaction course (vertical courses of the curves). Differences in the induction periods can be associated with diffusion processes (characteristic of heterogeneous processes), particularly in the absence of the reagent stirring. Taking into account that the reaction times for respective systems differed so much, we took one hour as the time interval enabling a proper comparison of catalytic activity.



Scheme 2. Hydrosilylation of olefins with 1,1,1,3,5,5,5-heptamethyltrisiloxane.

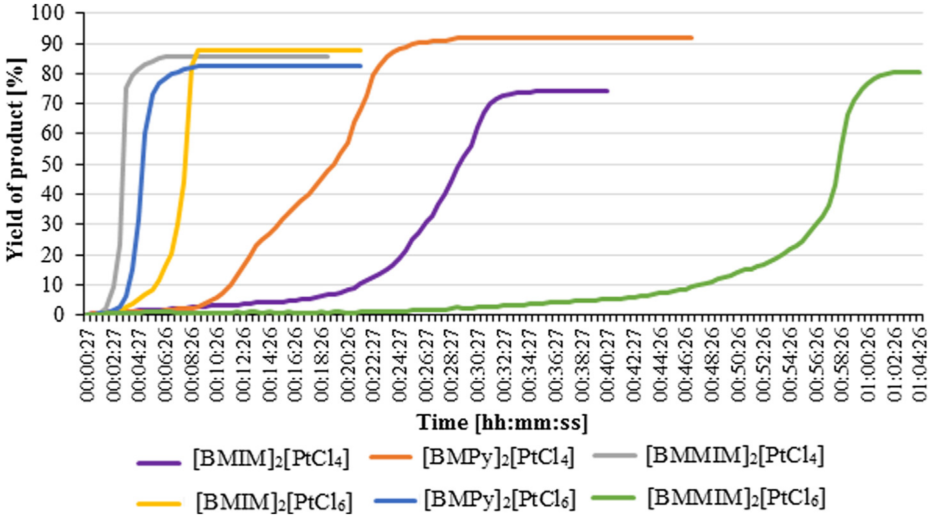


Fig. 5. The change in the hydrosilylation product yield as a function of time for the reaction catalyzed by anionic platinum complexes.

The catalysts studied by us are characterized by a high activity. For the sake of comparison, we conducted the reactions of hydrosilylation of octene and allyl glycidyl ether in the presence of the metal precursor alone (i.e. K_2PtCl_4) and in the presence of ionic liquids (in the amount of 10% relative to the amount of all substrates of hydrosilylation reaction). The reactions catalyzed by K_2PtCl_4 proceeded with very low yields, 13% with octene and 17% with allyl glycidyl ether, respectively. On the other hand, the platinum complex dissolved in respective ionic liquids showed relatively high activity only in the liquid [BMPy]Cl, whereas in the remaining liquids the yields were considerably lower compared to the complexes studied. The results are given in the Supplementary material.

The catalysts do not dissolve in the reagents. For this reason easy separation from the reaction mixture and reuse in a subsequent reaction run were possible. In this way 10 reaction runs (using the same catalyst portion in the successive runs) were carried out. Albeit it should be mentioned that the FT-IR *in situ* measurements were carried out for the catalyst concentration of 10^{-5} mol per 1 mol Si—H, whereas further measurements with the use of the same portion of catalyst were performed for 10 times greater concentration because of an easier separation of the catalyst (however, even in the latter case, the amount of catalyst was still very small compared to the reagents).

The product yields in subsequent runs of 1-octene hydrosilylation are presented in Fig. 6.

In the first run, all catalysts, except $[BMPy]_2[PtCl_4]$, enabled to obtain the product with the yield above 90%. In the subsequent runs, the yields changed but to a different extent. For the catalysts $[BMIM]_2[PtCl_6]$ and $[BMPy]_2[PtCl_6]$ the yield was almost constant and after 10 runs exceeded 90%. It is worth mentioning that the catalytic measurements were finished after 10 runs, although most of the catalysts were still highly active. Turnover numbers (TON) for each catalyst after 10 reaction runs are shown in Table 3 to easy compare the catalytic activity.

When comparing complexes containing the same cation, one can notice that in each case the complexes with hexachloroplatinate anion are more active. Moreover, all complexes containing the hexachloroplatinate anion show similar high activity, whereas tetrachloroplatinate-containing complexes are more diverse in this respect. On the other hand, when comparing complexes that contain the same anion (particularly in the case of imidazolium deriva-

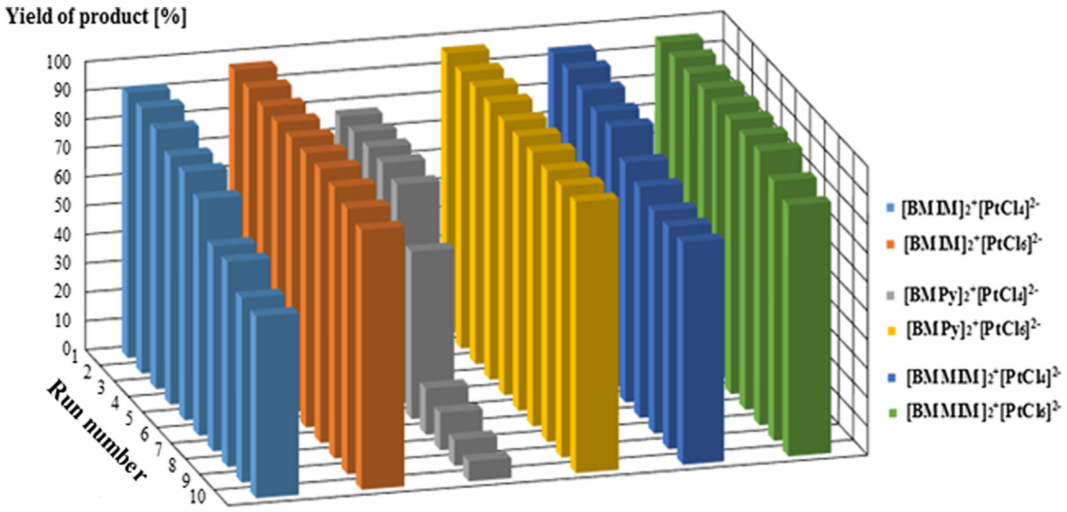


Fig. 6. Yields of the product of hydrosilylation of 1-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane as determined for 10 subsequent reaction runs catalyzed by the same catalyst portion.

Table 3
Yields of the product and TON values for hydrosilylation 1-octene with HMTS, catalyzed by anionic platinum complexes.

Catalyst	Yield [%]	Total TON
$[BMIM]_2^+[PtCl_4]^{2-}$	92 (92, 90, 86, 86, 82, 71, 71, 64, 63)	79 700
$[BMIM]_2^+[PtCl_6]^{2-}$	97 (96, 95, 95, 95, 95, 95, 94, 92, 90)	94 400
$[BMPy]_2^+[PtCl_4]^{2-}$	78 (78, 78, 78, 76, 58, 16, 13, 9, 7)	49 100
$[BMPy]_2^+[PtCl_6]^{2-}$	97 (96, 96, 96, 95, 95, 95, 94, 94, 94)	95 200
$[BMMIM]_2^+[PtCl_4]^{2-}$	94 (94, 92, 90, 83, 80, 77, 77, 77)	85 400
$[BMMIM]_2^+[PtCl_6]^{2-}$	95 (95, 95, 95, 95, 95, 95, 95, 90, 87)	93 700

Reaction conditions: [H—Si]:[CH═CH]:[Pt] = 1:1:10^{-4}; T = 110 °C, t = 1 h.

Table 4
Yields of the product of hydrosilylation of allyl glycidyl ether with HMTS catalyzed by anionic platinum complexes.

Catalyst	Yield [%]	Total TON
$[BMIM]_2^+[PtCl_4]^{2-}$	73 (73, 73, 73, 73, 73, 73, 73, 73, 73)	73 000
$[BMIM]_2^+[PtCl_6]^{2-}$	97 (87, 87, 87, 82, 71, 8, 2, 0)	52 100
$[BMPy]_2^+[PtCl_4]^{2-}$	62 (45, 45, 43, 43, 43, 43, 43, 39, 37)	44 300
$[BMPy]_2^+[PtCl_6]^{2-}$	97 (93, 88, 88, 81, 66, 57, 33, 0)	60 300
$[BMMIM]_2^+[PtCl_4]^{2-}$	98 (91, 91, 91, 90, 21, 6, 0, 0, 0)	48 800
$[BMMIM]_2^+[PtCl_6]^{2-}$	98 (98, 97, 80, 59, 12, 4, 0, 0, 0)	44 800

Reaction conditions: [H—Si]:[CH═CH]:[Pt] = 1:1.2:10^{-4}, T = 110 °C, t = 1 h.

tives), one can state that such significant differences in the catalytic activity do not occur. In particular, $[PtCl_6]$ anion-containing complexes have shown a very similar activity. A potential possibility of the formation of NHC carbene complex in the reaction with [BMIM] does not occur in this case (due to conditions at which hydrosilylation reaction was carried out), therefore one can say that blocking of the C2 position in [BMMIM] does not affect the activity of the produced catalysts.

The most stable and reproducible catalyst of the studied reaction is $[BMPy]_2[PtCl_6]$, however, tetrachloroplatinate complex containing the same cation $[BMPy]_2[PtCl_4]$ has the lowest activity. One of the reasons for decreasing yield is catalyst leaching by reagents which results in a decrease in the catalyst concentration after the isolation of reaction products. Among factors influencing catalyst leaching are its hydrophobic/hydrophilic properties. In the case of octyltrisiloxane, which is hydrophobic, the leaching of ionic catalyst is small. The higher platinum oxidation state (and thereby stronger ionic effect), the lower catalyst solubility which is reflected by better reproducibility of the catalytic activity of hexachloroplatinate anion-containing complexes. Some confirmation of the above comes from results obtained in the reaction of hydrosilylation of allyl glycidyl ether which has polar character (Fig. 7 and Table 4). In the first runs of the latter reaction, higher activity was shown by hexachloroplatinate complexes, however, after the fifth run their activity decreased considerably as a result of easier leaching caused by a greater compatibility of polar product with ionic complex having a higher partial charge. To verify this observation, platinum content in the post-reaction mixture was determined by ICP-MS both for the reaction of hydrosilylation of octene and allyl glycidyl ether catalyzed by $[BMIM][PtCl_6]$ after the 1-st and 5-th run of the reactions. In both reactions studied, the latter catalyst was characterized by the highest yield in the first run. The ICP-MS analysis has shown (for results see Supplementary material) that after the first run of the reaction with octene 0.32% of the initial platinum content was leached to the post-reaction mixture, whereas after the fifth run the amount of leached platinum was non-measurable. In the case of the reaction with allyl glycidyl ether as much as 2.5% of the initial platinum was leached after the first run, whereas after the fifth run it was a bit smaller, namely 1.9%. Assuming that each run of the reaction with allyl glycidyl ether resulted in leaching the same amount of platinum, one can conclude that platinum content after the fifth run was too low to effectively catalyze the reaction.

Tetrachloroplatinate complexes are characterized by higher stability and reproducibility (despite a lower activity in subsequent runs). This is why the highest activity, when comparing TON values, was shown by the complex $[BMIM]_2[PtCl_4]$.

The conducted studies made it possible to select catalysts which are characterized by very high activity. The aforementioned catalysts, due to the possibility of their isolation and multiple use, make a very good alternative to homogeneous catalysts applied hitherto.

4. Conclusion

Reactions of imidazolium and pyridinium ionic liquids with simple salts or complexes of platinum yielded six compounds, which formally could be classified into halometallate ionic liquids. However, their melting points that exceed 100 °C do not meet the definition of ionic liquids and therefore they should be regarded rather as anionic complexes of platinum. Nevertheless, taking into consideration their similarity to halometallate ionic liquids (as concerns synthesis) we put the term "ionic liquids" (although in

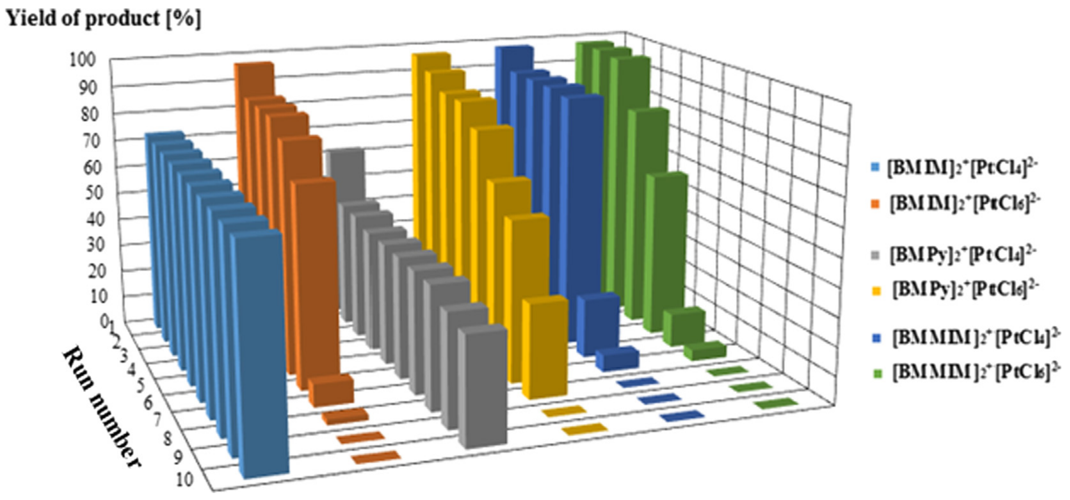


Fig. 7. Yields of the product of hydrosilylation of allyl glycidyl ether with 1,1,1,3,5,5,5-heptamethyltrisiloxane during 10 subsequent reaction runs catalyzed by the same catalyst portion.

inverted commas) in the title of the paper. Each of the above compounds was obtained by two distinct methods and it was shown that the best metal precursor for the synthesis of tetrachloroplatinates is [$PtCl_2$(cod)], whereas the best precursor for obtaining hexachloroplatinates is $PtCl_4$. All the methods employed led to very high yields and enabled us to synthesize, in a very simple way, complexes that were air-stable at temperatures of at least 200 °C. All the complexes obtained were isolated and fully characterized spectroscopically and crystallographically (for three of them crystallographic structures were determined for the first time). The most important achievement of this work was to demonstrate the extraordinary high activity of the generated complexes in the hydrosilylation reaction. It is worth mentioning that complexes of this type have never been employed in the process of hydrosilylation, despite the fact that this process is catalyzed mainly by platinum compounds. In addition to very high catalytic activity for hydrosilylation of olefins with different polarity (octene, allyl glycidyl ether), another asset of the aforementioned complexes is their easy isolation from post-reaction mixtures (due to their insolubility in the reaction medium) and possibility of reusing in subsequent catalytic runs. The most active complexes did not lose their activity even after 10 catalytic runs. However, the activity of complexes (and strictly speaking their stability in successive runs) appeared to depend on the kind of olefin and product formed (its polarity). In the case of nonpolar (hydrophobic) products, the most active are hexachloroplatinate derivatives, whereas in that of polar products tetrachloroplatinate derivatives show a better stability, which can be explained by their lower susceptibility to leaching by polar reagents (compared to hexachloroplatinate derivatives whose ionic character is stronger). The obtained results made it possible to select the most effective catalysts for olefins of different polarities. To the best of our knowledge this is the first example of the application of chloroplatinate complexes as hydrosilylation catalysts which can be reused many times without losing their high activity. Taking into consideration the simple way of their synthesis and thermal stability, one can recommend them as a very good alternative to commonly used homogeneous catalysts.

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Declaration of interest

None

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.05.005.

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