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N,*N′*-Dialkylimidazolium Chloroplatinate(II), Chloroplatinate(IV), and Chloroiridate(IV) Salts and an *N*-Heterocyclic Carbene Complex of Platinum(II): Synthesis in Ionic Liquids and Crystal Structures

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The first imidazole-type carbene complex of platinum(II), *cis*-(C_2H_4)(1-ethyl-3-methylimidazol-2-ylidene)$PtCl_2$, has been obtained by reacting $PtCl_2$ and $PtCl_4$ with ethylene in the basic [EMIM]Cl/$AlCl_3$ (1.3:1) ionic liquid (where $[EMIM]^+$ = 1-ethyl-3-methylimidazolium) at 200 °C and structurally characterized (monoclinic $P2_1/c$ space group, $a = 10.416(2)$ Å, $b = 7.3421(9)$ Å, $c = 15.613(2)$ Å, $\beta = 101.53(2)^o$, $Z = 4$). This complex can be regarded as a stable analogue of the π-alkene−Pd(II)−carbene intermediate in the Heck reaction. In addition, a series of new *N*,*N′*-dialkylimidazolium salts of platinum group metals of the type $[RMIM]_2[MCl_n]$, where $[RMIM^+]$ = 1-alkyl-3-methylimidazolium and M = Pt(II), Pt(IV), or Ir(IV), have been prepared and characterized. The salts $[EMIM]_2[PtCl_6]$ (**1**) and $[EMIM]_2[PtCl_4]$ (**2**) were prepared in the ionic liquid [EMIM]Cl/$AlCl_3$ and the salts $[BMIM]_2[PtCl_4]$ (**3**) and $[BMIM]_2[PtCl_6]$ (**4**) (where $[BMIM]^+$ = 1-*n*-butyl-3-methylimidazolium) and $[EMIM]_2[IrCl_6]$ (**5**) in aqueous or acetonitrile media. From TGA measurements, salts **1**−**5** decompose in air in several steps eventually to form the corresponding metal, the onset of decomposition being observed at (°C) 260 (**1**), 220 (**2**), 200 (**3**), 215 (**4**), and 210 (**5**). The structures of **1**, **2**, and **5** were determined by single-crystal X-ray analysis. The three salts crystallize in the monoclinic $P2_1/n$ space group (**1**, $a = 7.6433(9)$ Å, $b = 16.353(2)$ Å, $c = 9.213(1)$ Å, $\beta = 113.56(1)^o$, $Z = 2$; **2**, $a = 8.601(1)$ Å, $b = 8.095(2)$ Å, $c = 13.977(2)$ Å, $\beta = 91.75(2)^o$, $Z = 2$; **5**, $a = 10.353(2)$ Å, $b = 9.759(2)$ Å, $c = 10.371(2)$ Å, $\beta = 92.98(3)^o$, $Z = 2$).

Introduction

Ambient temperature molten salts (ionic liquids) with very low vapor pressure, especially those comprising mixtures of *N*,*N′*-dialkylimidazolium (e.g., 1-ethyl-3-methylimidazolium, $[EMIM]^+$, and 1-*n*-butyl-3-methylimidazolium, $[BMIM]^+$) chloride and aluminum chloride, are increasingly finding a range of laboratory, developmental, and technical applications, for example, as media for organic and inorganic chemical synthesis, in materials production, in electrochemical and separation processes, and as prototype novel materials.[1−3] Much current research is focused upon the possible use of ionic liquids as media for cleaner organic synthesis and processing[4] and upon better understanding of liquid structure and solvation phenomena of ionic liquids and its relevance to reactivity.[2,5,6]

Ionic liquids containing transition-metal complexes, especially platinum group metal complexes, are of great interest regarding their potential catalytic applications.[4] However, relatively few studies have explored the use of ionic liquids for the purposeful synthesis and characterization of coordination complexes since Hussey reviewed the chemistry of transition-metal halide complexes in chloroaluminate ionic liquids over 10 years ago.[2c] Several reports have apppeared describing spectrochemical and electrochemical investigations of transition-metal complexes in solution in these media[5] and structural characterization in the solid state.[6,7] Recently ionic liquids have been used as media for the preparation of some halometalate complexes and clusters.[8] We ourselves have described the synthesis, thermostability, and single-crystal X-ray structure of two salts, [EMIM][$AuCl_4$] and [BMIM][$AuCl_4$].[8j] No attempt, however, has been made so far to study Pt(II) and Pt(IV) complexes in ionic liquids.

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In this paper we explore some preparative chemistry of the platinum group metals in ionic liquids. A series of new *N*,*N*′-dialkylimidazolium salts of platinum group metals of the type $[\mathrm{RMIM}]_2[\mathrm{MCl}_n]$, where $[\mathrm{RMIM}]^+ = $ 1-alkyl-3-methylimidazolium (R = ethyl or *n*-butyl) and M = Pt(II), Pt(IV), or Ir(IV), are reported. The $[\mathrm{EMIM}]^+$ salts of Pt(II) and Pt(IV) have been prepared in acidic, neutral, or basic ionic liquids, $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$, and the $[\mathrm{BMIM}]^+$ salts in aqueous or acetonitrile solutions. The salts have been characterized by thermogravimetric analysis (TGA), and X-ray structures have been collected for the $[\mathrm{EMIM}]^+$ salts. The reaction between ethylene and a mixture of PtCl_2 and PtCl_4 in the $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ ionic liquids has been studied. A new *N*-heterocyclic carbene−ethylene complex, *cis*-$(\mathrm{C}_2\mathrm{H}_4)$(1-ethyl-3-methylimidazol-2-ylidene)PtCl_2, has been isolated from the basic $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ and structurally characterized.

Experimental Section

Materials. Platinum dichloride, platinum tetrachloride, potassium tetrachloroplatinate, potassium hexachloroplatinate, potassium hexachloroiridate, aluminum trichloride (99%), and 1-ethyl-3-methylimidazolium chloride (97%) were purchased from Aldrich and used without purification. 1-*n*-Butyl-3-methylimidazolium chloride was prepared as described elsewhere.[8j] Ethylene was purchased from BOC Speciality Gases, Surrey, U.K., and used as supplied. Schlenck techniques were applied where necessary to protect the reaction system from air and moisture. Solvents were dried and distilled under an atmosphere of dry nitrogen using standard procedures.

Techniques. A Carlo Erba Instruments Co. elemental analyzer (model 1106) was used for carbon, hydrogen, and nitrogen analysis. ^{1}H NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer; chemical shifts were measured relative to TMS. The TGA of solids was performed using a Perkin-Elmer TGA 7 or Setaram TG-DSC 111 analyzer. The carrier gas was air, and the sample (5−8 mg) was heated from 40 to 700 °C at a heating rate of 20 °C/min. The thermogravimetric analyzer was calibrated using iron, nickel, and perkalloy Curie temperatures. The TGA of solutions was recorded on a Netzsh STA 429 instrument at ICI, Chemical & Polymers, Runcorn, U.K. The sample (15−20 mg) was heated from 30 to 500 °C at 10 °C/min. The positive ion fast atom bombardment (FAB) mass spectra were obtained on a VG Analytical 7070 E double-focusing magnetic sector mass spectrometer using xenon gas at 1 mA (70 eV). Solid samples were placed in a 3-nitrobenzyl alcohol matrix.

X-ray Crystallography. Data were collected on a STOE-IPDS image plate diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K unless otherwise stated. The face-indexing routine FACEIT has been applied for absorption corrections.[9] Structure solution and refinement were carried out using the program SHELX97.[10] Structure refinement by full-matrix least-squares was based on all data using F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated with C−H distances of 0.99 Å (methylene C−H), 0.98 Å (methyl C−H), and 0.95 Å (aryl C−H), and assigned isotropic thermal parameters of $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for methylene and aryl H positions and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H positions.[11]

Preparation of Ionic Liquids. The acidity of *N*,*N*′-dialkylimidazolium chloroaluminate ionic liquids depends on the molar ratio of $[\mathrm{EMIM}]\mathrm{Cl}$ and AlCl_3.[2c] The neutral ionic liquid $[\mathrm{EMIM}][\mathrm{AlCl}_4]$ was prepared in a glovebox by slowly adding AlCl_3 (9.1 g) to an equimolar amount of $[\mathrm{EMIM}]\mathrm{Cl}$ (10.3 g) with mechanical stirring according to a literature method.[1a] The acidic ionic liquid $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ (1:2) was prepared similarly by reacting AlCl_3 (18.2 g) with $[\mathrm{EMIM}]\mathrm{Cl}$ (10.6 g). The basic ionic liquid $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ (1.3:1) was made by adding $[\mathrm{EMIM}]\mathrm{Cl}$ (1.47 g) with stirring to a 10 mL aliquot of the neutral $[\mathrm{EMIM}][\mathrm{AlCl}_4]$ to give a colorless basic melt containing 1M $[\mathrm{Cl}^-]$.

Synthesis of Bis(1-ethyl-3-methylimidazolium) Hexachloroplatinate(IV) (1). A three-necked round-bottom flask (50 mL) fitted with a N_2 inlet and outlet and a thermometer was charged with PtCl_4 (0.1 g, 0.297 mmol) and neutral or acidic $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ (4 mL) in the glovebox. The reaction vessel was transferred to a fume hood and heated on an oil bath at 150 °C for 1 h to give a dark yellow (in neutral medium) or orange (in acidic medium) solution. On cooling to room temperature, orange crystals formed on the walls of the vessel, which were collected manually and identified by elemental analysis and single-crystal X-ray study as $[\mathrm{EMIM}]_2[\mathrm{PtCl}_6]$. The excess ionic liquid was washed off with dry benzene (25 mL) to give **1,** which was recrystallized from an acetonitrile/benzene (1:2) mixture (mp 242 °C, 80% yield). Anal. Calcd for $\mathrm{C}_{12}\mathrm{H}_{22}\mathrm{PtCl}_6\mathrm{N}_4$: C, 22.87; H, 3.52; N, 8.89. Found: C, 22.8; H, 3.5; N, 8.8. ^{1}H NMR (300 MHz, $\mathrm{D}_2\mathrm{O}$, δ/ppm): 8.69 (s, 1H), 7.47 (s, 1H), 7.40 (s, 1H), 4.21 (q, $\mathrm{N}^2\mathit{CH_2}\mathrm{CH}_3$), 3.88 (s, $\mathrm{N}^1\mathrm{CH}_3$), 1.48 (t, $\mathrm{N}^2\mathrm{CH}_2\mathit{CH_3}$). Positive ion FAB-MS [*m/z* (rel intens)]: 670 (0.1), 741 (0.2) assigned to $[\mathrm{EMIM}]_3[\mathrm{PtCl}_4]^+$ and $[\mathrm{EMIM}]_3[\mathrm{PtCl}_6]^+$, respectively.

Salt **1** was also prepared by a standard method,[6] using acetonitrile as solvent in 60% yield.

Synthesis of Bis(1-ethyl-3-methylimidazolium) Tetrachloroplatinate(II) (2). This salt was prepared in neutral $[\mathrm{EMIM}]\mathrm{Cl}/\mathrm{AlCl}_3$ in 71% yield in the manner described for **1**. However, to achieve better yields, it was necessary to add a tiny amount of PtCl_4 (8 mg) prior to the addition of PtCl_2 (0.10 g, 0.376 mmol) to the ionic liquid and to heat the reaction mixture for a longer period (24 h).

Salt **2** was also prepared by a standard method,[6] using acetonitrile as solvent. PtCl_2 (0.10 g, 0.376 mmol) and excess $[\mathrm{EMIM}]\mathrm{Cl}$ (0.25 g, 1.71 mmol) were refluxed in acetonitrile (30 mL) for 3 h, after which half the solvent was boiled off. After cooling to room temperature, benzene (25 mL) was added, and on storing overnight in a refrigerator (5 °C), rust-colored crystals of **2** were obtained (mp 228 °C, 65% yield). Anal. Calcd for $\mathrm{C}_{12}\mathrm{H}_{22}\mathrm{PtCl}_4\mathrm{N}_4$: C, 25.77; H, 3.96; N, 10.02. Found: C, 25.8; H, 3.9; N, 9.9. ^{1}H NMR (300 MHz, $\mathrm{D}_2\mathrm{O}$, δ/ppm): 8.73 (s, 1H), 7.43 (s, 1H), 7.50 (s, 1H), 4.24 (q, $\mathrm{N}^2\mathit{CH_2}\mathrm{CH}_3$), 3.91 (s, $\mathrm{N}^1\mathrm{CH}_3$), 1.51 (t, $\mathrm{N}^2\mathrm{CH}_2\mathit{CH_3}$). Positive ion FAB-MS [*m/z* (rel intens)]: 670 (0.5) assigned to $[\mathrm{EMIM}]_3[\mathrm{PtCl}_4]^+$.

Synthesis of Bis(1-*n*-butyl-3-methylimidazolium) Tetrachloroplatinate(II) (3). This salt was prepared in the manner described for **2** by a standard method,[6] using acetonitrile as solvent. PtCl_2 (0.10 g, 0.376 mmol) and excess $[\mathrm{BMIM}]\mathrm{Cl}$ (0.40 g, 2.264 mmol) were refluxed in acetonitrile (30 mL) for 30 min, after which half the solvent was boiled off. After cooling to room temperature, diethyl ether (25 mL) was added, and on storing overnight in a refrigerator (5 °C), red crystals of **3** were obtained (mp 68 °C, 55% yield). Anal. Calcd for $\mathrm{C}_{16}\mathrm{H}_{30}\mathrm{PtCl}_4\mathrm{N}_4$: C, 31.23; H, 4.91; N, 9.11. Found: C, 32.0; H, 4.9; N, 9.2. ^{1}H NMR (300 MHz, $\mathrm{D}_2\mathrm{O}$, δ/ppm): 8.71 (s, 1H), 7.48 (s, 1H), 7.43 (s, 1H), 4.20 (t, $\mathrm{N}^2\mathit{CH_2}(\mathrm{CH}_2)_2\mathrm{CH}_3$), 3.88 (s, $\mathrm{N}^1\mathrm{CH}_3$), 1.85 (m, $\mathrm{N}^2\mathrm{CH}_2\mathit{CH_2}\mathrm{CH}_2\mathrm{CH}_3$), 1.32 (m, $\mathrm{N}^2(\mathrm{CH}_2)_2\mathit{CH_2}\mathrm{CH}_3$), 0.92 (t, $\mathrm{N}^2(\mathrm{CH}_2)_3\mathit{CH_3}$). Positive ion FAB-MS [*m/z* (rel intens)]: 753 (1.0) assigned to $[\mathrm{BMIM}]_3[\mathrm{PtCl}_4]^+$.

Synthesis of Bis(1-*n*-butyl-3-methylimidazolium) Hexachloroplatinate(IV) (4). An aqueous solution (20 mL) containing $\mathrm{K}_2[\mathrm{PtCl}_6]$ (0.05 g, 0.103 mmol) and $[\mathrm{BMIM}]\mathrm{Cl}$ (0.26 g, 1.489 mmol) was reduced to half its volume by boiling to give yellow crystals of **4** on cooling to room temperature (mp 168 °C, 58% yield). Anal. Calcd for $\mathrm{C}_{16}\mathrm{H}_{30}\mathrm{PtCl}_6\mathrm{N}_4$: C, 28.00; H, 4.41; N, 8.16. Found: C, 28.0; H, 4.3; N, 8.1. ^{1}H NMR (300 MHz, $\mathrm{D}_2\mathrm{O}$, δ/ppm): 8.74 (s, 1H), 7.51 (s, 1H), 7.46 (s, 1H), 4.23 (t, $\mathrm{N}^2\mathit{CH_2}(\mathrm{CH}_2)_2\mathrm{CH}_3$), 3.92 (s, $\mathrm{N}^1\mathrm{CH}_3$), 1.88 (m, $\mathrm{N}^2\mathrm{CH}_2\mathit{CH_2}$-

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CH_2CH_3), 1.34 (m, $N^2(CH_2)_2CH_2CH_3$), 0.94 (t, $N^2(CH_2)_3CH_3$). Positive ion FAB-MS [*m/z* (rel intens)]: 824 (0.2) assigned to $[BMIM]_3[PtCl_6]^+$.

A similar reaction using $K_2[PtCl_4]$ to obtain **3** resulted in a black paste that was not characterized.

Synthesis of Bis(1-ethyl-3-methylimidazolium) Hexachloroiridate(IV) (5). This salt was prepared by a modification of published procedures.[6] To a stirred solution of $K_2[IrCl_6]$ (0.10 g, 0.207 mmol) in water (10 mL) was added a solution of [EMIM]Cl (0.40 g, 2.728 mmol) in acetonitrile (30 mL). The reaction mixture was heated with mechanical stirring at 70 °C for 30 min to give a tiny amount of white precipitate that was removed by filtration. The resulting brown filtrate was reduced to half its volume by boiling, and on cooling, a red sticky solid was formed. Recrystallization from a benzene/acetonitrile mixture (2:1) gave lustrous black crystals of $[EMIM]_2[IrCl_6]$ (mp 220 °C dec, 80% yield), from which a single crystal was selected for an X-ray study. Anal. Calcd for $C_{12}H_{22}Cl_6IrN_4$: C, 22.98; H, 3.54; N, 8.93. Found: C, 22.9; H, 3.5; N, 8.8.

Synthesis of *cis*-(Ethylene)(1-ethyl-3-methylimidazol-2-ylidene)-platinum(II) Chloride (6). Under an atmosphere of dry nitrogen in a glovebox, $PtCl_2$ (0.1 g, 0.376 mmol) and $PtCl_4$ (0.1 g, 0.297 mmol) were dissolved at 150 °C in basic $[EMIM]Cl/AlCl_3$ ionic liquid (5 mL) in a glass-lined Parr autoclave. The reactor was charged with ethylene (50 atm) and heated at 200 °C on an oil bath with mechanical stirring for 48 h. On cooling to room temperature, the gas pressure was released, and the reaction mixture was filtered overnight inside the glovebox. Brown crystals of pure **6** were obtained (mp 193 °C, 26% yield), from which a single crystal was selected for X-ray analysis. **6** is insoluble in water, boiling acetonitrile, and the $[EMIM]Cl/AlCl_3$ ionic liquid. Anal. Calcd for $C_8H_{14}PtCl_2N_2$: C, 23.77; H, 3.49; N, 6.93. Found: C, 23.8; H, 3.5; N, 6.7.

Results and Discussion

Ionic liquids have remarkable solvency for organic and inorganic substrates whose exploitation is limited by poor understanding of microsolvation phenomena (and associated effects on solute reactivity) and their relationship to composition and to cation and anion structure. Nevertheless, the non-hydroxylic aprotic polar character of ionic liquids, particularly quaternary ammonium haloaluminates, such as $[RR'IM]X/AlX_3$ (R, R′ = alkyl; X = Cl, Br), has been used to obtain solutions of halometalate complexes, $[M_xX_y]^{z-}$,[5−8] which would suffer solvolysis in conventional polar solvents, such as water, methanol, acetonitrile, pyridine, etc.

Preparation of $[RMIM]^+$ Salts 1−5. $PtCl_4$ reacts with neat basic, neutral, or acidic $[EMIM]Cl/AlCl_3$ ionic liquid on heating (150° C) to give **1** with 80% isolated yield (eq 1). $PtCl_2$ was

$$2[EMIM]Cl + PtCl_4 \rightarrow [EMIM]_2[PtCl_6] \qquad (1)$$

found to be poorly soluble in $[EMIM]Cl/AlCl_3$, but the addition of a tiny amount of $PtCl_4$ promotes the formation of $[EMIM]_2[PtCl_4]$ (**2**). Consistently higher yields of the Pt salts were obtained in ionic liquids as the reaction medium compared to acetonitrile. Similar results were obtained for $[EMIM][AuCl_4]$.[8j] Interestingly, $[BMIM]_2[PtCl_6]$ (**4**) can be crystallized from aqueous solutions of [BMIM]Cl and $K_2[PtCl_6]$ (58% yield), whereas no product was obtained with $K_2[PtCl_4]$. Salt **5** of Ir(IV) with $[EMIM]^+$ readily forms in aqueous acetonitrile in 80% yield.

Salts **1**−**5** are brightly colored lustrous crystals, are stable to the atmosphere, and have high melting points except $[BMIM]_2[PtCl_4]$ (**3**) (mp 68 °C). Salts **1**−**5** are soluble in water, chloroform, and acetonitrile and insoluble in ether and benzene. These salts are readily soluble in imidazolium chloroaluminate ionic liquids and may be useful as catalysts or catalyst precursors for reactions carried out in such media.[4]

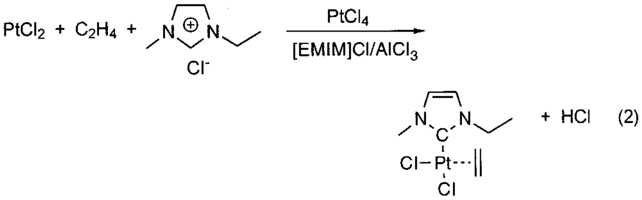
Thermogravimetric Analysis. Many pure ionic liquids are intrinsically thermally very stable. TGA has shown decomposition temperatures to be as high as 400 °C for ionic liquids containing weakly nucleophilic anions, such as $[N(SO_2CF_3)_2]^-$.[12] The chloroaluminates decompose at ca. 200 °C.[13] However, as far as we are aware, there are no reports of the effect on the thermal stability of an ionic liquid of the presence of a dissolved solute, such as a catalytically active metal salt.

TGA measurements show that the solid salts **1**−**5** decompose in air in several steps eventually to form the corresponding metal. The onset of decomposition is observed at (°C) 260 (**1**), 220 (**2**), 200 (**3**), 215 (**4**), and 210 (**5**). **1** and **2** are thus more stable than 1,3-dimethylbenzimidazolium chloroplatinate(II) and -(IV), which liberate 2 mol of HCl between 195 and 210 °C.[14] The salts $[EMIM][AuCl_4]$ and $[BMIM][AuCl_4]$ are stable up to 220 and 250 °C, respectively.[8j]

To examine the effect of the presence of **1** and **2** on the thermal stability of an ionic liquid, the TGA for a mixture of **1** and **2** in basic $[EMIM]Cl/AlCl_3$ was recorded. It was found that the presence of the solutes had no effect on the thermal behavior of the ionic liquid up to 200 °C. Salts **1** and **2** may be recovered unchanged after heating to 150 °C in neutral $[EMIM]Cl/AlCl_3$.

An *N*-Heterocyclic Carbene Complex of Pt(II). Transition-metal *N*-heterocyclic carbenes derived from imidazoles (imidazol-2-ylidenes) with the five-center π-delocalization have attracted significant interest in catalysis,[15,16] especially since Arduengo et al.[17] opened access to the free carbenes by deprotonating an imidazolium precursor with the use of a strong base. The imidazol-2-ylidenes of platinum group metals [e.g., Rh(I), Ru(II), Pd(II)] have been reported as efficient catalysts for hydrosilylation, hydrogenation, hydroformylation, the Heck reaction, etc.[15,16] The corresponding carbenes of Pt(II), however, have not yet been prepared, although a few related imidazolidin-2-ylidenes of Pt(II) with the three-center π-delocalization have been prepared and characterized recently.[18,19]

In this work, we have isolated and characterized by single-crystal X-ray analysis a novel imidazole-type 16-electron carbene complex of platinum(II)−*cis*-(C_2H_4)(1-ethyl-3-methylimidazol-2-ylidene)$PtCl_2$ (**6**). The complex was obtained by reacting a mixture of $PtCl_2$ and $PtCl_4$ with ethylene (50 atm) in the basic ionic liquid $[EMIM]Cl/AlCl_3$ (1.3:1) at 200 °C (eq 2).



$PtCl_4$ probably assists the reaction by enhancing the formation of **2** (see above), which is likely to be the intermediate in reaction 2. The basicity of the ionic liquid $[EMIM]Cl/AlCl_3$ is

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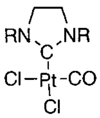
Table 1. Crystal Structure Data for **1**, **2**, **5**, and **6**

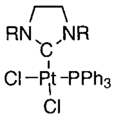
	1	**2**	**5**	**6**
empirical formula	$C_{12}H_{22}PtCl_6N_4$	$C_{12}H_{22}PtCl_4N_4$	$C_{12}H_{22}Cl_6IrN_4$	$C_8H_{14}PtCl_2N_2$
fw	630.13	559.23	627.24	404.23
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	7.6433(9)	8.601(1)	10.353(2)	10.416(2)
b/Å	16.353(2)	8.095(2)	9.759(2)	7.3421(9)
c/Å	9.213(1)	13.977(2)	10.371(2)	15.613(2)
β/deg	113.56(1)	91.75(2)	92.98(3)	101.53(2)
V/Å^3	1055.6(2)	972.7(3)	1046.4(4)	1169.9(3)
Z	2	2	2	4
ρ_{calcd}/g cm^{-3}	1.982	1.909	1.991	2.295
T/K	293	293	200	293
λ(Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα)/mm^{-1}	7.408	7.761	7.148	11.924
no. of data/params	1975/108	1872/100	1932/108	1835/119
max/min transm	0.912/0.443	0.982/0.757	0.668/0.956	0.891/0.505
R1 ($I > 2\sigma(I)$)[a]	0.029	0.043	0.020	0.035
WR2 (all data)[b]	0.068	0.113	0.040	0.074

[a] $R1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

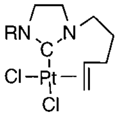
essential for reaction 2 to occur. No carbene was formed when using an acidic (1:2) or neutral (1:1) medium; only mixtures of **1** and **2** were isolated. This is well in line with Arduengo's work;[17] i.e., the basic medium is required for the deprotonation of the imidazolium cation to proceed. Another important feature is the participation of ethylene in the reaction. No carbene complex is formed in the absence of ethylene or at an ethylene pressure below 30 atm. This indicates that the carbene−Pt(II) bond is stabilized by the alkene, apparently dπ-pπ bonding between the ethylene double bond and Pt(II) playing a role. To our knowledge, this is the first imidazol-2-ylidene of Pt(II) reported. Recently related imidazolidin-2-ylidenes of Pt(II), with the three-center π-delocalization, stabilized by CO (**7**) or PPh_3 (**8**) have been prepared and structurally characterized.[18,19] A similar diaminocarbene of Pt(II) stabilized intramolecularly by alkene (**9**) has been reported,[19] but its structure was not determined.



7 (R = Et, Bz)



8 (R = Et, Bz)



9 (R = pentenyl)

Detailed mechanistic speculation would be premature in the absence of further spectroscopic and kinetic investigations of the reaction pathway. However, two possibilities may be suggested. Reaction might proceed via a deprotonation at C-2 of the imidazolium cation, possibly by a chloride ion or another basic component of the medium, such as an *N*-alkylimidazole resulting from the thermal decomposition of the ionic liquid which may occur at these temperatures. It thus may be significant that **1** is obtained only from a basic ionic liquid, which would be consistent with Arduengo's work on deprotonated imidazolium precursors.[17] Alternatively, an oxidative addition of the imidazolium cation to the platinum(II) center might occur, followed by reductive elimininination of HCl from the resulting platinum(IV) intermediate. Imidazole-type carbenes of Pd(II) have been reported as very efficient catalysts for the Heck arylation of alkenes.[15,16] Complex **6** may be regarded as a stable analogue of the π-alkene−Pd(II)−carbene intermediate in the Heck reaction.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Salts **1**, **2**, and **5** (M = Pt or Ir)

	1	**2**	**5**
M(1)−Cl(1)	2.309(2)	2.306(2)	2.332(1)
M(1)−Cl(2)	2.315(2)	2.309(2)	2.323(1)
M(1)−Cl(3)	2.311(2)		2.324(2)
Cl(1)−M(1)−Cl(1a)	180.0	180.0	180.0
Cl(1)−M(1)−Cl(3)	90.29(9)		90.3(1)
Cl(1)−M(1)−Cl(2)	89.55(8)	89.27(9)	90.20(9)
Cl(3)−M(1)−Cl(2)	89.08(7)		89.86(5)
Cl(1a)−M(1)−Cl(2)	90.45(8)	90.73(9)	89.80(9)

Crystal Structures of Salts 1, 2, and 5. The crystal structure data for **1**, **2**, and **5** are given in Table 1, and selected bond lengths and angles are given in Table 2. The crystal structures and crystal packings are shown in Figures 1−5. The three salts crystallize in the monoclinic space group $P2_1/n$. With regard to A_2B-type salts, the ionic packing for the three crystal structures can be described approximately as that of an *anti*-fluorite lattice. Eight $[EMIM]^+$ cations surround the anionic unit in a distorted cubic fashion and, in turn, are surrounded tetrahedrally by four anions. As expected $[PtCl_4]^{2-}$ ions show a square planar geometry (Figure 2), whereas $[PtCl_6]^{2-}$ (Figure 1) and $[IrCl_6]^{2-}$ (Figure 3) are octahedral. In all cases the metal atoms are located on crystallographic inversion centers.

Close interionic C−H···Cl contacts involving both the ring and alkyl H atoms of the $[EMIM]^+$ cations are present in all three salts (Figures 1−3), suggesting the presence of hydrogen bonds (Table 3).[6b] The closest C−H···Cl distances toward octahedral dianionic complexes were found to be 2.815(3) Å in **1** and 2.915(2) Å in **5**. Significantly shorter C−H···Cl distances are observed in **2**, ranging from 2.752(2) Å. This can be attributed to the higher effective negative charge of chlorine atoms in $[PtCl_4]^{2-}$, compared with the $[MCl_6]^{2-}$ (M = Pt, Ir) ions where the charge is distributed over six chlorine atoms.[6b] Consequently, the interionic interactions in salt **2** are comparable

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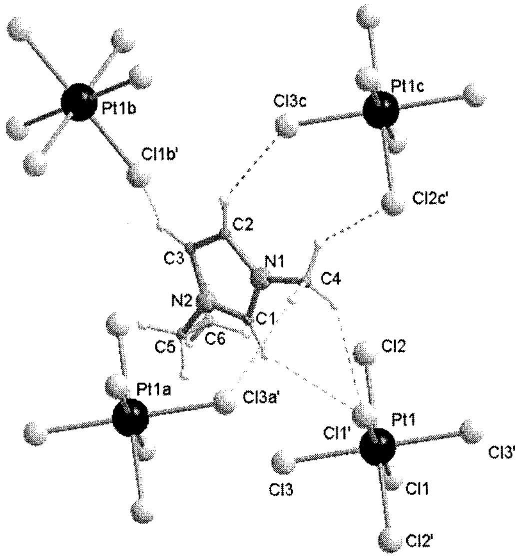

Figure 1. Crystal structure of $[EMIM]_2[PtCl_6]$ (**1**) emphasizing C−H···Cl bond interactions around the $[EMIM]^+$ cations.

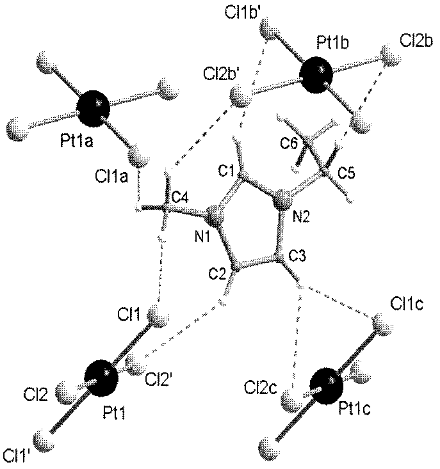

Figure 2. Crystal structure of $[EMIM]_2[PtCl_4]$ (**2**) emphasizing C−H···Cl bond interactions around the $[EMIM]^+$ cations.

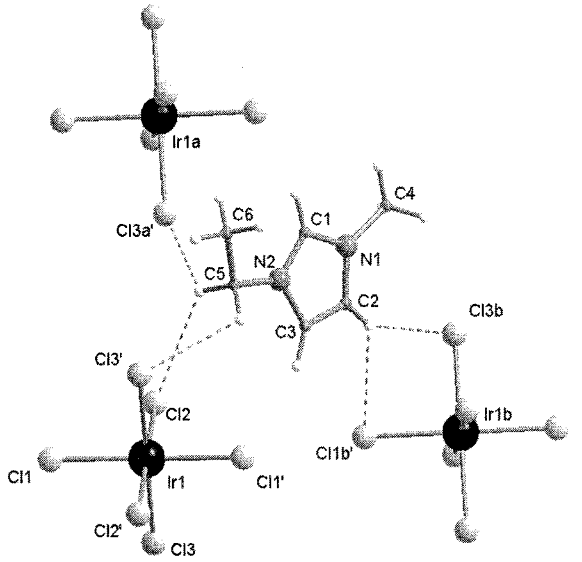

Figure 3. Crystal structure of $[EMIM]_2[IrCl_6]$ (**5**) emphasizing C−H···Cl bond interactions around the $[EMIM]^+$ cations.

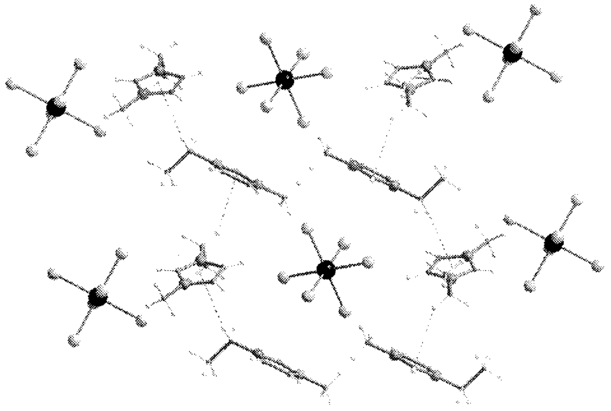

Figure 4. Crystal packing of $[EMIM]_2[PtCl_4]$ (**2**). View along [001] emphasizing C−H···π interactions between the $[EMIM]^+$ cations.

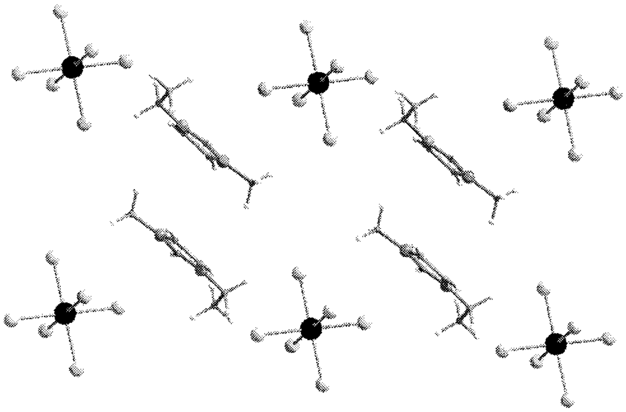

Figure 5. Crystal packing of $[EMIM]_2[IrCl_6]$ (**5**). View along [001] emphasizing π-stack clusters of the $[EMIM]^+$ cations.

with those observed for the corresponding tetrachloropalladate(II)[6d] and slightly shorter than those seen in the tetrachloroaurate(III) derivative.[8j]

In addition, close contacts between cations are observed in salts **1** and **5**. C−H···π interactions between one methylene hydrogen position on C5 and the imidazolium ring system of another cation [C−H···C_3N_2 ring (centroid) 2.86 Å] lead to 1-D arrays of cations in **1** (Figure 4). The C−H···π interactions are in agreement with those reported in the literature.[20] However, those that we observe seem to be rather short for interactions between two cation units. Two imdiazolium rings in **5** are arranged in a parallel fashion (Figure 5). The short distance between the two ring systems of ca. 3.6 Å suggests the presence of π-π interactions.

Crystal Structure of Carbene Complex 6. The crystal structure data and selected bond lengths and angles for **6** are provided in Tables 1 and 4, respectively. Complex **6** crystallizes in the monoclinic group $P2_1/c$ as shiny brown rectangular plates. Figure 6 shows the molecular structure of **6** with atom labeling. Complex **6** has a cis arrangement of the chloride ligands and a distorted square planar core geometry. The imidazol-2-ylidene ring is planar and twisted by 81.9(4)° relative to the $PtCl_2$ plane, which is typical of *N*-heterocyclic carbene complexes to relieve steric congestion.[15,16a] The bond lengths and angles in the ring are similar to those reported for other imidazole-type carbene complexes.[15] The Pt−C(carbene) bond length in **6** [1.93(1) Å] seems quite short; it is shorter than in the bis(imidazol-2-ylidene) complex of Pt(0) [1.959(8) Å][17d] and significantly shorter than

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[20] (a) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669. (b) Dupont, J.; Suarez, P. A. Z.; De Souza, R. F.; Burrow, R. A.; Kintzinger, J. P. *Chem. Eur. J.* **2000**, *6*, 2377.

Table 3. C−H···Cl Distances (Å) for Salts **1**, **2**, and **5**

1		**2**		**5**	
C1−H1···Cl1′	2.849(1)	C1−H1···Cl1b′	2.768(5)	C2−H2···Cl1b′	2.916(4)
C2−H2···Cl3c	2.992(1)	C2−H2···Cl2′	2.771(2)	C2−H2···Cl3b	2.932(2)
C3−H3···Cl1b′	2.949(0)	C3−H3···Cl1c	2.842(2)	C5−H5A···Cl2	2.985(4)
C4−H4A···Cl3a′	2.976(3)	C3−H3···Cl2c	2.840(5)	C5−H5A···Cl3a′	2.931(6)
C4−H4B···Cl2c′	2.900(8)	C4−H4A···Cl2b′	2.901(3)	C5−H5B···Cl3′	2.915(2)
C4−H4C···Cl1′	2.815(3)	C4−H4B···Cl1	2.752(2)		
		C4−H4C···Cl1a	2.963(2)		
		C5−H5A···Cl2b	2.930(3)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6**

Compound	**6**		
Pt(1)−C(1)	1.93(1)	N(1)−C(1)	1.34(1)
Pt(1)−C(8)	2.14(1)	N(2)−C(1)	1.42(2)
Pt(1)−C(7)	2.12(2)	C(7)−C(8)	1.40(2)
Pt(1)−Cl(2)	2.301(3)	C(2)−C(3)	1.33(2)
Pt(1)−Cl(1)	2.353(3)		
C(1)−Pt(1)−C(8)	92.0(5)	C(8)−Pt(1)−Cl(1)	90.1(4)
C(1)−Pt(1)−C(7)	91.7(5)	C(7)−Pt(1)−Cl(1)	89.0(4)
C(8)−Pt(1)−C(7)	38.3(5)	Cl(2)−Pt(1)−Cl(1)	91.5(1)
C(1)−Pt(1)−Cl(2)	87.2(3)	N(1)−C(1)−N(2)	102.3(1)
C(8)−Pt(1)−Cl(2)	155.9(5)	N(1)−C(1)−Pt(1)	130.6(1)
C(7)−Pt(1)−Cl(2)	165.8(5)	N(2)−C(1)−Pt(1)	126.9(8)
C(1)−Pt(1)−Cl(1)	177.4(4)		

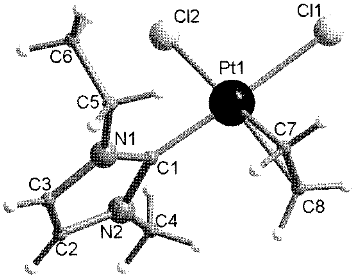

Figure 6. Molecular view and atom-labeling scheme of *cis*-(C_2H_4)-(1-ethyl-3-methylimidazol-2-ylidene)PtCl$_2$ (**6**).

in imidazolidin-2-ylidene complexes of Pt(II) such as *cis*-(1,3-diethylimidazolidin-2-ylidene)Pt(CO)Cl$_2$ [2.01(1) Å],[18] *cis*-(1,3-dibenzylimidazolidin-2-ylidene)Pt(CO)Cl$_2$ [1.97(1) Å][19] (**7**), and *cis*-(1,3-dibenzylimidazolidin-2-ylidene)Pt(PPh$_3$)Cl$_2$ [1.970(6) Å][19] (**8**). The C(2)−C(3) bond in the ring has its typical length of 1.33(2) Å, which is much shorter than in the imidazolidin-2-ylidene complexes of Pt(II) (1.50−1.51 Å).[19] The π-C_2H_4 group has its normal geometry, being, however, shifted upward by ca. 5° relative to the PtCl$_2$ plane, which is indicative of steric interactions between the Pt−C_2H_4 group and the ethyl group of the carbene ligand. There is a significant difference [0.053(6) Å] between the two Pt−Cl bond lengths in **6**, the bond Pt−Cl(2), trans to the C_2H_4, being shorter. This may be attributed to the differing trans influences of the C_2H_4 and carbene ligands and/or to steric interactions between the Pt−Cl(2) bond and the ethyl group of the carbene ligand.

Conclusions

In a demonstration of the novel use of ionic liquids as preparative media, PtCl$_2$ and PtCl$_4$ have been found to react in a basic [EMIM]Cl/AlCl$_3$ ionic liquid in the presence of ethylene (50 atm, 48 h, 200 °C) to give the new *N*-heterocyclic carbene complex *cis*-(C_2H_4)(1-ethyl-3-methylimidazol-2-ylidene)PtCl$_2$ (**6**). Complex **6**, which has a short Pt−C(carbene) bond [1.93(1) Å], may be regarded as a stable analogue of the π-alkene−Pd(II)−carbene intermediate in the Heck reaction.[15,16] The new *N*,*N*′-dialkylimidazolium salts [EMIM]$_2$PtCl$_6$ (**1**) and [EMIM]$_2$PtCl$_4$ (**2**) isolated from chloroaluminate ionic liquid media (basic, neutral, and acidic) as well as the separately prepared [BMIM]$_2$PtCl$_4$ (**3**), [BMIM]$_2$PtCl$_6$ (**4**), and [EMIM]$_2$IrCl$_6$ (**5**) may be useful as catalysts or catalyst precursors for reactions carried out in ionic liquids.[4] X-ray crystallography of complexes **1**, **2**, and **5** reveals C−H···Cl contacts in the range 2.752(2) Å in **2** and 2.915(2) Å in **5**, indicative of hydrogen bonding. In addition, C−H···π and π-π cation−cation interactions are seen in **1** and **5**, respectively.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This information is available free of charge via the Internet at http://pubs.acs.org.

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