**SHORT PAPER**

*J. Chem. Research (S),*
2000, 392–393

# A novel N-heterocyclic carbene of platinum(II): synthesis in ionic liquids and crystal structure†

**Masihul Hasan[a], Ivan V. Kozhevnikov[a*], M. Rafiq H. Siddiqui[a], Alexander Steiner[b] and Neil Winterton[a]**

[a]*Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

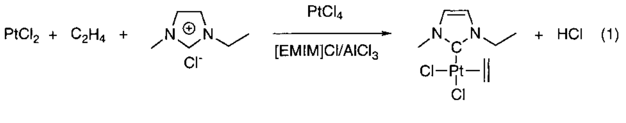
[b]*Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UK*

A novel imidazole-type carbene of platinum(II), cis-($C_2H_4$)(1-ethyl-3-methylimidazol-2-ylidene)PtCl$_2$ (**1**), has been obtained by reacting a mixture of PtCl$_2$ and PtCl$_4$ with ethylene (50 atm) in the basic [EMIM]Cl/AlCl$_3$ (1.3:1) ionic liquid at 200°C (where [EMIM]$^+$ = 1-ethyl-3-methyl-imidazolium) and characterised by X-ray analysis.

Transition metal N-heterocyclic carbenes derived from imidazoles (imidazol-2-ylidenes) with the five-centre $\pi$-delocalisation have attracted significant interest in catalysis,[1,2] especially since Arduengo *et al.*[3] 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.*[1,2] The corresponding carbenes of Pt(II), however, have not yet been prepared.

Ambient temperature molten organic salts (ionic liquids) comprising mixtures of N,N'-dialkylimidazolium (*e.g.* 1-ethyl-3-methylimidazolium, [EMIM]$^+$) chloride and aluminium chloride[4] find various applications, especially as versatile solvents for chemical and electrochemical processes.[5] Much current research is focused upon the use of ionic liquids as solvents for catalytic organic synthesis.[6] Ionic liquids containing transition metal complexes, especially platinum group metal complexes, are of great interest regarding their potential catalytic applications.[6] No attempt, however, has been made so far to study Pt(II) and Pt(IV) complexes in ionic liquids.

In this work, we have isolated and characterised 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$_2$ (**1**). 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 (eqn 1):



(1)

PtCl$_4$ assists the reaction by enhancing the formation of PtCl$_4^{2-}$ which is likely to be the intermediate in reaction (1). PtCl$_2$ was found to be insoluble in [EMIM]Cl/AlCl$_3$ but the addition of a tiny amount of PtCl$_4$ promotes the formation of PtCl$_4^{2-}$. The basicity of the ionic liquid [EMIM]Cl/AlCl$_3$ is essential for reaction (1) to occur. No carbene was formed when using acidic (1:2) or neutral (1:1) medium, only mixtures of [EMIM]$_2$[PtCl$_4$] and [EMIM]$_2$[PtCl$_6$] were isolated. This is well in line with Arduengo's work,[3] *i.e.* the basic medium is required for the deprotonation of 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 the ethylene pressure below 30 atm. This indicates that the carbene – Pt(II) bond is stabilized by the alkene, apparently *d$\pi$–p$\pi$* bonding between the ethylene double bond and Pt(II) playing a role.

Complex **1** crystallizes from the ionic liquid as shiny brown rectangular plates. It has a *cis* arrangement of the chloride ligands and a distorted square planar core geometry (Fig. 1). 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.[1,2] The bond lengths and angles in the ring are similar to those reported for other imidazol-2-ylidenes.[1,2] The Pt–C(carbene) bond length in **1** [1.93(1) Å] seems quite short; it is shorter than in bis(imidazol-2-ylidene) of Pt(0) [1.959(8) Å][3d] and significantly shorter than in imidazolidin-2-ylidenes of Pt(II) such as *cis*-(1,3-diethylimidazolidin-2-ylidene)Pt(CO)Cl$_2$ [2.01(1) Å],[7a] *cis*-(1,3-dibenzylimidazolidin-2-ylidene)Pt(CO)Cl$_2$ [1.97(1) Å] and *cis*-(1,3-dibenzylimidazolidin-2-ylidene)Pt(PPh$_3$)Cl$_2$ [1.970(6) Å].[7b] 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-ylidenes of Pt(II) (1.50–1.51 Å).[7b] The $\pi$-$C_2H_4$ group has its normal geometry, being, however, shifted upwards by *ca* 5° relative to the PtCl$_2$ plane, which is

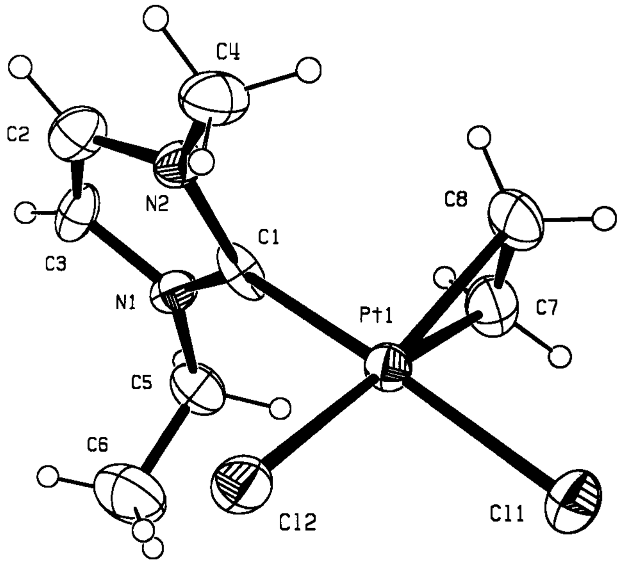


**Fig. 1** The structure of **1**. Selected bond lengths (Å) and angles (deg) are: Pt(1)–C(1) 1.93(1), Pt(1)–C(8) 2.14(1), Pt(1)–C(7) 2.12(2), Pt(1)–Cl(2) 2.300(3), Pt(1)–Cl(1) 2.353(4), C(2)–C(3) 1.33(2), C(7)–C(8) 1.40(2), C(1)–Pt(1)–C(8) 92.1(6), C(1)–Pt(1)–C(7) 91.7(5), C(8)–Pt(1)–C(7) 38.3(5), C(8)–Pt(1)–Cl(2) 155.9(5), C(7)–Pt(1)–Cl(2) 165.7(5).

---

[*] To receive any correspondence.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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(7) Å] between the two Pt-Cl bond lengths in **1**, 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 carbene ligand.

In summary, we have isolated a novel N-heterocyclic carbene complex of Pt(II) in the reaction of $PtCl_2$ and $PtCl_4$ with ethylene in the [EMIM]Cl/$AlCl_3$ ionic liquid. To our knowledge, this is the first imidazol-2-ylidene of Pt(II) reported. Imidazole-type carbenes of Pd(II) have been reported as very efficient catalysts for the Heck arylation of alkenes.[1,2,8] Complex **1** can be regarded as a stable analogue of the π-alkene-Pd(II)-carbene intermediate in the Heck reaction.

## Experimental

*Preparation of* **1**: Under an atmosphere of dry nitrogen in a glove box, $PtCl_2$ (0.1 g, 0.376 mmol) and $PtCl_4$ (0.1 g, 0.297 mmol) were dissolved at 150$^{o}$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 $^{o}$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 glove box. Brown crystals of pure **1** were obtained (26% yield based on total Pt) from which a single crystal was selected for X-ray analysis. 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%. M.p. 193$^{o}$C (uncorrected). **1** is insoluble in water, boiling acetonitrile and in the [EMIM]Cl/$AlCl_3$ ionic liquid.

*Preparation of ionic liquids*: The acidity of [EMIM]Cl/$AlCl_3$ ionic liquids depends on the molar ratio of $AlCl_3$ and [EMIM]Cl.[5c] The neutral ionic liquid [EMIM]$AlCl_4$ was prepared in a glove box by slowly adding $AlCl_3$ (9.1 g) to equimolar amount of [EMIM]Cl (10.3 g) with mechanical stirring according to a literature method.[4a] The acidic ionic liquid [EMIM]Cl/$AlCl_3$ (1 : 2) was prepared similarly by reacting $AlCl_3$ (18.2 g) with [EMIM]Cl (10.6 g). The basic ionic liquid [EMIM]Cl/$AlCl_3$ (1.3 : 1) was made by adding [EMIM]Cl (1.47 g) with stirring to a 10 ml aliquot of the neutral [EMIM]$AlCl_4$ to give a colourless basic melt.

*Crystal data:* $C_8H_{14}PtCl_2N_2$, M = 404.23, monoclinic space group $P2_1/c$, $a$ = 10.4156(15), $b$ = 7.3421(9), $c$ = 15.613(2) Å, $\beta$ = 101.525(17)$^{o}$, $U$ = 1169.(3) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 2.295 g/cm$^{-3}$, $\mu$(Mo$K_\alpha$) = 11.924 mm$^{-1}$, $T$ = 293 K. Data were collected on a STOE-IPDS image plate diffractometer using graphite monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Face-indexing routine FACEIT has been applied for absorption corrections.[9] Structure solution and refinement were carried out using the programme SHELX97.[10] Structure refinement by full-matrix least-squares was based on all 1519 unique data using $F^2$, $R_1$ ($F$) > 2σ($F$) = 0.034, $wR_2$ (all data) = 0.072, max. diff. peak/hole: 1.175/–0.851 e/Å$^3$.

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–H), and assigned isotropic thermal parameters of $U$(H) = 1.2 $U_{eq}$(C) for methylene and aryl-H positions and $U$(H) = 1.5 $U_{eq}$(C) for methyl-H positions.[11] Full crystallographyc details will be deposited at the Cambridge Crystallographic Data Centre (CCDC).

We gratefully acknowledge ICI Chemicals & Polymers Ltd, Runcorn, Cheshire, UK and the EPSRC for financial support.

*Received 5 July 2000; accepted 26 July 2000*
*Paper 00/415*

## References

1 W.A. Herrmann and C. Kocher, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2162.
2 D. Bourissou, O. Guerret, F.P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
3 (a) A.J. Arduengo, R.L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361. (b) A.J. Arduengo, H.V.R. Dias, R.L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530; (c) A.J. Arduengo, R.L. Harlow, W.J. Marshall and T. Prakasha, *Heteroatom Chem.*, 1996, **7**, 421; (d) A.J. Arduengo, S.F. Gamper, J.C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1994, **116**, 4391.
4 (a) J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263; (b) A.A. Fannin, D.A. Floreani, L.A. King, J.S .Landers, B.J. Piersma, D.J. Stech, R.L. Vaughn, J.S. Wilkes, J.L. Williams, *J. Phys. Chem.*, 1984, **88**, 2614.
5 (a) T.M. Laher and C.L. Hussey, *Inorg. Chem.*, 1983, **22**, 3247; (b) D. Appleby, C.L. Hussey, K.R. Seddon and J. Turp, *Nature*, 1986, **323**, 614; (c) C.L. Hussey, *Pure Appl. Chem.*, 1988, **60**, 1763.
6 (a) Y. Chauvin, H. Olivier, C.N. Wyrwalski, L.C. Simon and R.F. De Souza, *J. Catal.*, 1997, **16**, 275; (b) J.A. Boon, J.A. Levinsky, J.L. Pflug and J.S. Wilkes, *J. Org. Chem.*, 1986, **51**, 480; (c) Y. Chauvin, S. Einloft and H. Olivier, *Ind. Eng. Chem. Res.* 1995, **34**, 1149; (d) S. Einloft, F.K. Dietrich, R.F. De Souza and J. Dupont, *Polyhedron*, 1996, **15**, 3257; (e) J.E.L. Dullius, P.A.Z. Suarez, S. Einloft, R.F. De Souza and J. Dupont, *Organometallics*, 1998, **17**, 815; (f) M.J. Earle, P.B. McCormac and K.R. Seddon, *J. Chem. Soc.,Chem. Commun.*, 1998, 2245; (g) T. Welton, *Chem. Rev.*, 1999**, 99**, 2071; (h) M. Hasan, I.V. Kozhevnikov, M.R.H. Siddiqui, A. Steiner and N. Winterton, *Inorg. Chem.*, 1999, **38,** 5637.
7 (a) S.T. Liu, T.Y. Hsieh, G.H. Lee and S.M. Peng, *Organometallics*, 1998, **17**, 993; (b) R.Z. Ku, J.C. Huang, J.Y. Cho, F.M. Kiang, K.R. Reddy, Y.C. Chen, K.J. Lee, J.H. Lee, G.H. Lee, S.M. Peng and S.T. Liu, *Organometallics*, 1999, **18**, 2145.
8 (a) D.S. McGuinness, M.J. Green, K.J. Cavell, B.W. Skelton, A.H. White, *J. Organometal. Chem.*, 1998, **565**, 165; (b) L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19,** 1123.
9 FACEIT, Stoe & Cie GmbH, Darmstadt, 1996.
10 G.M. Sheldrick, SHELX-97, Program for Crystal Structure Determination, Göttingen, 1997.
11 Applied C–H distances and $U$(H) values are default settings in SHELX97.[10]