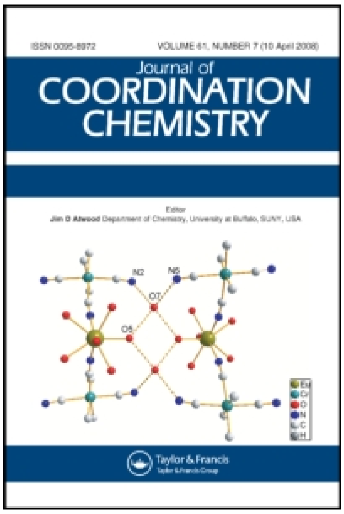

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The formation of [PtCl(diphosphine-I)(β^1-diphosphine-II)]$^+$ species in the *N*-butyl-*N'*-methylimidazolium hexafluorophosphate ionic liquid: An NMR study

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The formation of [PtCl(diphosphine-I)(η^1-diphosphine-II)]$^+$ species in the *N*-butyl-*N'*-methylimidazolium hexafluorophosphate ionic liquid: An NMR study

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(Trichlorostannato)diphosphineplatinum(II) complexes of catalytic importance were investigated in the [BMIM][PF_6] (BMIM = *N*-butyl-*N'*-methylimidazolium ion) ionic liquid by NMR. Formation of mononuclear [PtCl(diphosphine-I)(η^1-diphosphine-II)]$^+$ species involving monodentate coordination of one of the two diphosphines as well as dinuclear complexes [Pt_2Cl_2(diphosphine-I)$_2$(η^1,η^1-diphosphine-II)]$^{2+}$ with a bridging bidentate phosphine was observed. Assignment of the structures is based on diagnostic $^2J(P,P)$ and $^1J(Pt,P)$ coupling constants obtained from typical second-order AMX ^{31}P NMR spectra.

Keywords: Platinum; Phosphine; Ionic liquid; Nuclear magnetic resonance; Ligand exchange

1. Introduction

Ionic liquids, especially those that are liquids at room temperature, provide a useful extension to the range of solvents used in chemical research. Currently a major drive in industry and research concerns the substitution of environmentally friendly processes for traditional ones in which volatile and toxic solvents are used. Ionic liquids are considered as being environmentally friendly ('green') substitutes, since they possess a number of desirable chemical and physical properties (low volatility, non-corrosiveness, high chemical and thermal stability, non-flammability, etc.). Surprisingly, it is only in the past few years that significant reviews have appeared in this field [1–3]. The potential of ionic liquids both in classical organic reactions

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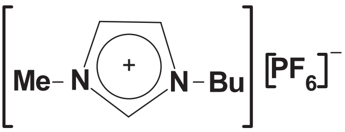


Figure 1. The *N*-butyl-*N*′-methylimidazolium hexfluorphosphate salt.

and homogeneous catalysis has been already shown [4–6]; application of ionic liquids as 'alternative solvents' in homogeneous catalytic reactions was reported in the 1990s and has recently been reviewed [2,3,7].

Due to the high practical importance of various aldehydes easily accessible in hydroformylation, the fused salt $[NEt_4][SnCl_3]$, as solvent, has been used for the platinum-catalysed hydroformylation of ethane [8]. Room temperature ionic liquids (RTIL) possessing dialkylimidazolium cations, especially $[BMIM][PF_6]$ (BMIM = *N*-butyl-*N*′-methylimidazolium cation; figure 1), have been used in homogeneous catalytic oxidation [9] and coupling reactions [10,11], as well as in rhodium-catalysed hydroformylation of 1-pentene (the catalyst is $[Rh(CO)_2(acac)]/PPh_3$ [12]) and long-chain α-olefins [13]. In addition, the application of trichlorostannate-type ionic liquids ($[BMIM][SnCl_3]$) in platinum-catalysed hydroformylations has been reported [14].

Although the number of catalytic reactions in ionic liquid is steadily increasing, only sporadic reports have been published concerning elementary reactions of complexes (including even the simplest ligand exchange) aimed at mechanistic investigations in ionic liquids. In this article NMR results concerning ligand exchange reactions of platinum-phosphine-halide (tin(II)-halide) systems of potential catalytic importance in the $[BMIM][PF_6]$ ionic liquid are presented.

2. Experimental

2.1. *Materials*

$Pt(diphosphine)Cl_2$ catalytic precursors were prepared according to a known procedure [15]. The ligands dppb (1,4-bis(diphenylphosphino)butane), dppe (1,2-bis(diphenylphosphino)ethane) and bdpp (2,4-bis(diphenylphosphino)pentane), and $[BMIM][PF_6]$, were purchased from Aldrich and Strem. Anhydrous tin(II) chloride was prepared from $SnCl_2 \cdot 2H_2O$ (Aldrich) by treating it with two mol equivalents of acetic anhydride and washing with ether.

2.2. *Analytical methods*

^{31}P NMR spectra were measured at 323 K on a Varian Inova 400 spectrometer operating at 161.9 MHz. Chemical shifts (ppm) are reported downfield relative to 85% H_3PO_4. All operations (including the preparation of the complexes) were carried out under argon. The appropriate complex was measured into an NMR tube, flooded with argon and appropriate amounts of $[BMIM][PF_6]$ as well as further reagents (tin(II) chloride, phosphine) were added. Locking and referencing was performed using an insert tube (2 mm od) filled with D_2O.

3. Results and discussion

Although the role of phosphine ligands added to a $PtCl_2$(diphosphine) precursor has been discussed and found to be of catalytic importance in conventional hydroformylation [16], to the best of our knowledge, there is no precedent for the investigation of ligand exchange reactions with diphosphines in ionic liquids. According to previous investigations [17], reaction of $PtCl_2$(bdpp) with an equimolar amount of bdpp results in the quantitative formation of $[Pt(bdpp)_2]^{2+}$ in [BMIM][PF_6].

However, a different reaction pattern has been found for systems containing two different α,ω-bis(diphenylphosphino)alkanes. The reactions can be run either in the absence or in the presence of tin(II) chloride, this being essential for the facile substitution of the chloro ligands. Accordingly, trichlorostannato complexes are formed upon addition of tin(II) chloride via insertion into the Pt–Cl bond, resulting in the formation of $PtCl(SnCl_3)$(diphosphine) and $Pt(SnCl_3)_2$(diphosphine) complexes. The trichlorostannato ligand serves as good leaving group and its facile substitution with a second phosphine ligand may take place (equilibria between $PtCl_2$(PP)- and $PtCl(SnCl_3)$(PP)-type complexes are solvent-dependent and have been investigated in detail both in chlorinated hydrocarbons [18] and ionic liquids [17]).

$PtCl_2$(dppe), **1**, reacts with dppb in the presence of anhydrous tin(II) chloride in [BMIM][PF_6]. Two species, **1a** and **1b**, of very similar NMR characteristics (table 1) are obtained (figure 2, scheme 1). Due to the diagnostic $^1J(\mathrm{Pt,P})$ coupling constants, the geometric arrangement of the ligands in the square planar platinum(II) complexes can be identified. The P^A phosphorus (*trans* to the chloro ligand) shows a doublet of doublets due to coupling to two *cis* phosphorus atoms ($^2J(P^A,P^B) = 17.1$ Hz; $^2J(P^A,P^C) = 15.6$ Hz) both in **1a** and **1b**. Similarly, overlapping doublets of doublets have been obtained for P^B. However, the two coupling constants refer to one phosphorus *cis* and another one *trans* to P^B ($^2J(P^A,P^B) = 17.1$ Hz; $^2J(P^B,P^C) = 384$ Hz).

Table 1. ^{31}P NMR data (ppm, Hz) for $[Pt(P\text{-}P)(\eta^1\text{-}P\text{-}P)Cl]^+$ and $[Pt_2(P\text{-}P)_2(\mu_2\text{-}P\text{-}P)]^{2+}$ in [BMIM][PF_6]^a.

Complex phosphorus		$\delta(P)^b$	$^1J(^{195}Pt,^{31}P)$	$^2J(^{31}P,^{31}P)$
1a	P^A	45.0	3537	17.1; 15.6
	P^B	54.7	2390	17.1; 384
	P^C	18.0	2400	15.6; 384
	P^D	11.1		
1b	P^A	44.9	3537	17.1; 15.6
	P^B	54.6	2400	17.1; 384
	P^C	18.7	2400	15.6; 384
2a	P^A	13.1	3480	17.1; 25.3
	P^B	20.2	2330	17.1; 384
	P^C	18.2	2270	25.3; 384
	P^D	11.1		
2b	P^A	12.5	3500	18.2; 25.3
	P^B	19.0	2400	18.2; 384
	P^C	17.6	2010	25.3; 384
3a	P^A	15.8	3584	17.5; 23.4
	P^B	19.5	2440	394; 17.5
	P^C	17.0	2334	394; 23.4

[a] Spectra were measured at 323 K. [b] All phosphorus nuclii show doublet of doublet patterns except for P^D (a singlet assigned to non-coordinated phosphorus).

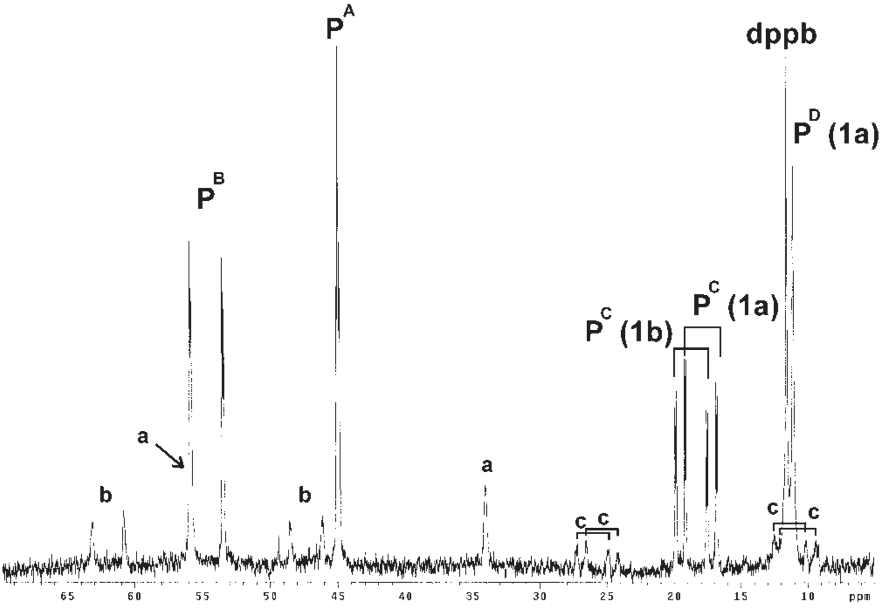
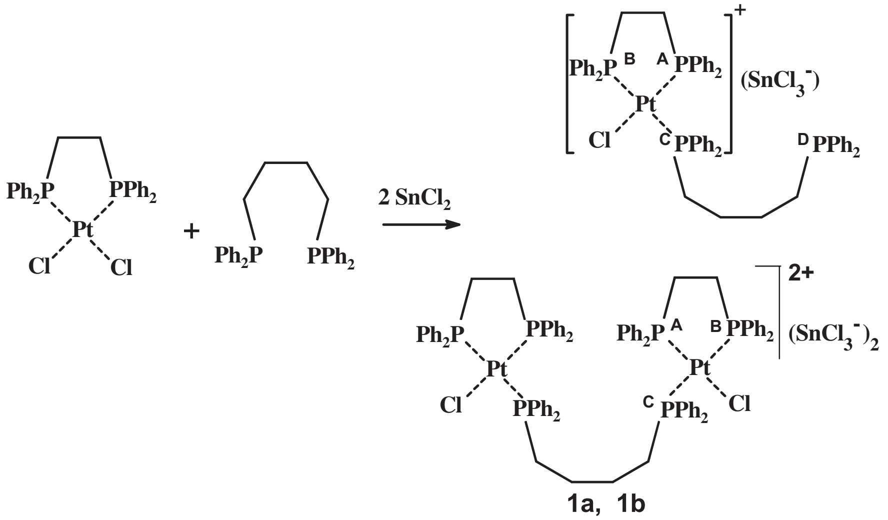
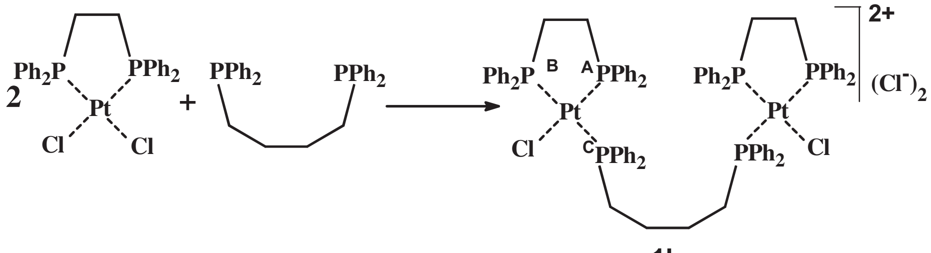


Figure 2. ^{31}P NMR of **1a** and **1b** in [BMIM][PF$_6$] at 323 K (lower case letters refer to platinum satellites).



Scheme 1. Formation of ‘PtP$_3$’ cations in mixed diphosphine (dppe–dppb) systems.

The doublet of doublets pattern of P^C is very similar to that of P^B, but is clearly separated in **1a** and **1b**. The *trans* arrangement of P^B and P^C can also be envisaged from the corresponding ^1J(Pt, P) coupling constants of about 2400 Hz. A singlet for P^D (non-coordinated phosphorus of dppb) is also observed (a signal for non-reacted dppb is seen at 11.6 ppm in figure 2). The two sets of patterns can be interpreted as follows. The entering ‘second’ diphosphine coordinates as a monodentate ligand, resulting in [PtCl(*dppe*)(η^1-*dppb*)]$^+$, **1a**. The second three sets of doublet of doublets can be



1b

Scheme 2. Formation of the dinuclear cation in mixed diphosphine (dppe–dppb) systems.

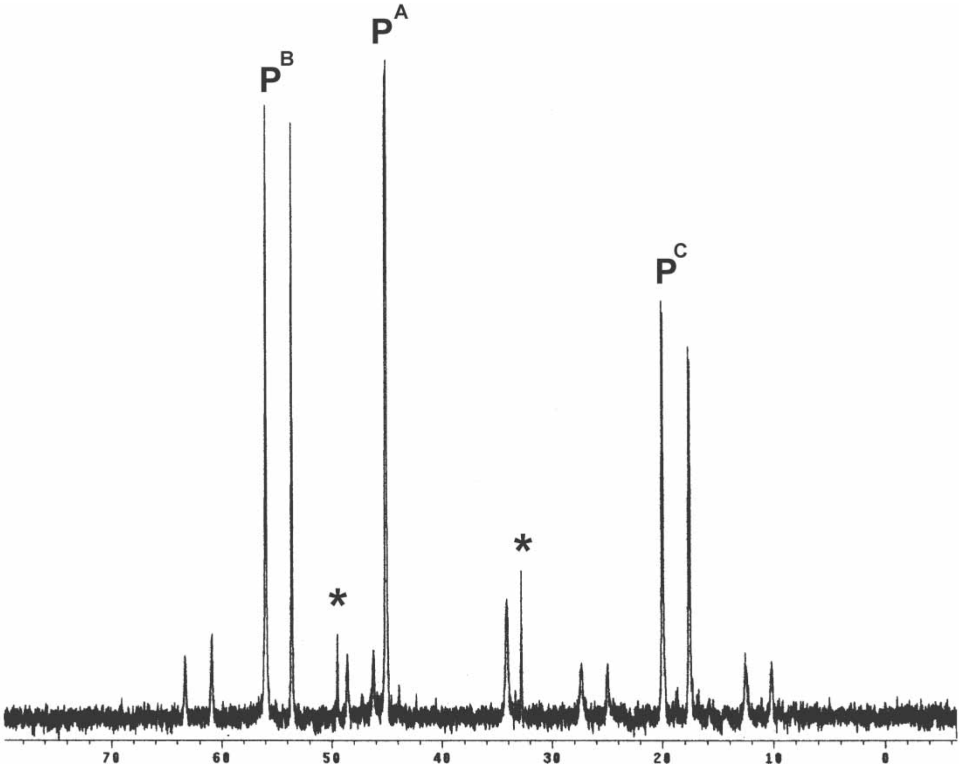


Figure 3. ^{31}P NMR of **1b** in [BMIM][PF$_6$] at 323 K (the asterisks refer to impurities; central lines of PtCl$_2$(dppe) and PtCl$_2$(dppb)).

assigned to the dinuclear species **1b** with bridging dppb (scheme 1). Similar results are obtained when PtCl$_2$(bdpp), **2**, and dppb are reacted. The 'PtP$_3$'-type complex **2a** and the dinuclear complex **2b** with bridging dppb form at a mol ratio of 70/30 at 323 K.

Under appropriate conditions, keeping the **1**/dppb ratio at 2/1, dinuclear species **1b** with bridging dppb is obtained quantitatively (scheme 2). In the light of previous findings for similar systems in chlorinated hydrocarbons, it is worth noting that the reaction is complete even in the absence of tin(II) chloride. NMR characteristics of the AMX pattern (chemical shifts and ^1J(Pt, P) coupling constants for P^A, P^B [the two phosphorus atoms of dppe] and P^C [phosphorus of bridging dppb]) are practically identical with those of **1a** (figure 3).

Surprisingly, the reaction of the $PtCl_2$(dppb), **3**, precursor with dppe results in a more complex mixture in the presence of tin(II) chloride and led to the formation of the dinuclear species $[\{PtCl(dppb)\}_2(\eta\text{-}dppe)]^{2+}$, **3a**, as the major product. A typical AMX pattern with diagnostic coupling constants is obtained (table 1). The further sets of signals (responsible for *ca* 30% of the total) are assigned to minor species such as $[PtCl(dppb)(\eta^1\text{-}dppe)]^+$, $PtCl(SnCl_3)$(dppb) and $Pt(SnCl_3)_2$(dppb). Complete assignment of these latter species can not be achieved because of the inherently broad and low intensity platinum satellites, as well as their overlap with some of the central lines.

In conclusion it is clear that both tin(II) chloride insertion and ligand exchange reactions take place in [BMIM][PF_6]. In the presence of two different diphosphines Pt(diphosphine-I)(η^1-diphosphine-II)Cl]$^+$ cationic species of unprecedented structure are dominant in the ionic liquid. This is in contrast to the fact that under similar conditions various $[Pt(PP)_2]^{2+}$ cations are found as major products in chloroform. Furthermore, even in the absence of tin(II) chloride, facile substitution of the chloro ligands by phosphines is observed; not only the trichlorostannato but also the chloro ligands behave as good leaving groups in the ionic liquid.

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