



Université Blaise Pascal

UNIVERSITÉ BLAISE PASCAL  
U.F.R de Recherche Scientifique et Technique



## CYCLE DE CONFÉRENCES DE CHIMIE

Avec le concours de : *Manufacture Française des Pneumatiques MICHELIN*  
*Centre de Développement Préclinique, Schering-Plough*  
*Fédération de Chimie (FR 2404)*  
*Section Auvergne de la Société Française de Chimie*  
*U.F.R.S.T. / Master de Chimie / Département de Chimie*

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**Mercredi 27 Octobre 2010 à 16 h**

**Salle C du Bâtiment de Chimie - (Site des Cézeaux)**

**Pr. Chris Hardacre**

*School of Chemistry and Chemical Engineering/QUILL, Queen's University,  
Belfast UK*

### **Structural properties of ionic liquids and their ability to controlled chemistry of moisture sensitive reagents**

The structure of liquids has been studied for many years. Investigations have, in general, been focused on the arrangements in molecular solvents such as water, *t*-butanol, and simple chlorinated solvents. The field of molten salts and the structures thereof is much less studied and within this field the study of the structure of room temperature ionic liquids is in its infancy. This is despite the fact that the area has been the subject of an increasing number of publications concentrating mainly on their use for electrochemical processes or as reaction media. An understanding of the microscopic structure of liquids is paramount in understanding the macroscopic properties of the system. Given the number of potential ionic liquids, quantifying the interactions in the liquid state is of enormous benefit when selecting candidate ionic liquids, or at least narrowing any potential search. However, for even simple molecular solvents the complex interplay between species in the liquid state presents challenge enough – the introduction of charged species provides even more variety and directionality to the interactions and deepens the problem. What are the local environments of the individual species? Which are the important interactions between them? How, in the case of ionic liquids, can the individual ions be tailored to adjust the properties of choice? Experimentally, several techniques have begun to answer these questions but remain restricted to relatively simple systems. Combined with theoretical insights, however, a detailed and useful picture of the microscopic structure in these systems may be built. In this talk the importance of the elucidation of liquid structures will be demonstrated and example where a detailed understanding of the interactions is important and where they dominate the chemical and physical properties of the liquid, for example solvation, density, viscosity, and polarity, will be discussed.

In addition, the effect that the ionic liquid can have on controlling the reactivity and selectivity of moisture sensitive reagents will be demonstrated. Specifically the reactivity of  $\text{PCl}_3$  will be examined. Whether neat or in organic solvents,  $\text{PCl}_3$  and its derivatives are highly air and water sensitive and must be used under strictly anhydrous conditions, often in excess at low temperatures to allow for

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some level of control in order to achieve chemoselectivity and avoid side-product formation. For instance, excess of phosphitylating reagent must be used in aprotic organic solvents at low temperature under anhydrous and dissolution conditions in order to obtain mono-derivatised chlorophosphines and overcome the high chemical reactivity of the trivalent chlorophosphine's P-Cl bonds. As such, by virtue of their chemical instability in organic media, the use of chlorophosphines in the direct phosphitylation of alcohols and amines has been limited and very difficult to control. We have established that ionic liquids can alleviate many of the issues surrounding the use and preparation of P-X containing compounds as synthetic reagents. The ionic liquid provides a medium to stabilise  $\text{PCl}_3$  and control the reactivity. Ionic liquids have been shown to permit the selective conversion of individual P-Cl bonds (Figure 1) to be performed with control not observed in molecular solvent systems. This has been particularly valuable in the formation of nucleotide phosphoramidites.

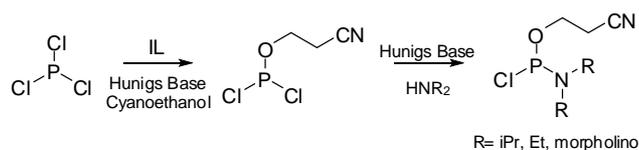


Figure 1: Efficient synthesis of chlorophosphoramidites in ILs at room temperature in air.