

Ionic Liquids – Media for Unique Phosphorus Chemistry

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EXPERIMENTAL

With the exception of [C₅mim][FAP] supplied by Merck KGaA, all the ILs were prepared in house using standard literature methods.¹⁻³

Spectroscopic details

All the ³¹P, ³¹P-¹H and ¹⁹F nuclear magnetic spectra have been recorded on a Bruker advance DPX 300 at 25 °C. The ³¹P chemical shifts are in parts per million (p.p.m.) relative to an internal probe (capillary tube) of triethylphosphate (PO(OEt)₃) or hexamethylphosphotriamidite (HMPA) in CD₃CN. The PO(OEt)₃ probe was referenced at 0.2 ppm while the HMPA was referenced at 24 ppm.

Preparation of dry ILs

All ILs were dried under high vacuum (10 mmHg) 60°C for 18 h. A sample was evaluated for water content *via* Karl Fischer titration.

Stability of PCl₃ and POCl₃ in dry ILs

All experiments in dry ILs were carried out using oven dried glassware and the solutions stirred under argon under Schlenk line conditions. To 2 ml of dry IL were added 88 µl of PCl₃ to obtain a 500 mM solution. For POCl₃, 93 µl of POCl₃ was added to 2 ml of dry ILs to give a 500 mM solution of POCl₃. After 15 min of stirring, a 0.4 ml sample was taken, added to an NMR tube kept under argon and examined by NMR. Similar aliquots were examined every hour for 3 h, unless stated otherwise.

Preparation of “wet” ILs

For the study of the stability of phosphorus trichloride and phosphorus oxychloride in “wet” ionic liquids, all the IL samples were left open to the air for two days prior to use to achieve air equilibration. A sample of each ionic liquid was removed for water content analysis *via* Karl Fischer Titration.

Stability of PCl₃ and POCl₃ in “wet” ILs

All experiments in “wet” ILs were carried out using oven dried glassware while the solutions were stirred in air. To 2 ml of dry IL were added 88 µl of PCl₃ to obtain a 500 mM solution. For POCl₃, 93 µl of POCl₃ was added to 2 ml of dry IL to give a 500 mM solution of POCl₃. After 15 min of stirring, a 0.4 ml sample was taken, added to an NMR tube kept under argon and examined by NMR. Similar aliquots were examined every hour for 3 h, unless stated otherwise.

Synthesis of triimidazoliumphosphine

To a 2 ml sample of dry [C₈mim][NTf₂], stirred under argon, was added 0.2 g (0.003 mol) of imidazole. Hünigs' base (EtNPrⁱ₂, 0.003 mol, 530 µl) was then added followed by PCl₃ (0.001 mol, 88 µl). Triimidazoliumphosphine was identified by NMR. No attempts were made to further characterize this compound as it hydrolysed rapidly in air. However, it matched NMR data obtained from reacting PCl₃ and imidazole in the presence of EtNPrⁱ₂ in CDCl₃.

³¹P NMR (IL): (300 MHz, PO(OEt)₃ internal probe, ppm) δ 63.6

¹H-³¹P-NMR (IL): (300 MHz, PO(OEt)₃ internal probe, ppm) δ 63.6 (Sept, 24.4 Hz)

¹H NMR: (300MHz, CDCl₃) δ 6.85 (s, 1H), 6.26 (bs, 2H)

¹³C NMR: (300MHz, CDCl₃) 139.4; 132.0; 119.1

Bromide exchange on PCl₃ in the [C₈mim][NTf₂]

To 2 ml of the “wet” [C₈mim][NTf₂] ionic liquid stirred in air, 88 µl PCl₃ was added to give a 500 mM solution and a sample was extracted for NMR analysis. The mixture was then doped with 0.5 g of [C₈mim][Br] and another aliquot was taken for NMR analysis.

Fluoride exchange on PCl₃ and POCl₃ in [C₄mim][NTf₂]

To 2 ml of the “wet” [C₄mim][NTf₂] ionic liquid stirred in air, PCl₃ (0.001 mole, 88 µl) or POCl₃ (0.001 mol, 93 µl) was added. A portion of CsF was then added (0.003 mo, 0.25g) and the ³¹P- and ¹⁹F-NMR spectra of aliquots taken over a 2 h period were recorded.

References

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- 2 Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *32*, 1168-1178.
- 3 Cammarata, L.; Kazarian, S.G.; Salter, P.A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192-5200.

Selected NMRs





