

Priority Programme

“Material Synthesis near Room Temperature”



Project Description – Project Proposal

Pseudohalogen Chemistry in Ionic Liquids with Non-innocent Cations and Anions

Applicant	Prof. Dr. Axel Schulz
Institution	Universität Rostock Institut für Chemie Lehrstuhl für Anorganische und Elementorganische Chemie Albert-Einstein-Straße 3a 18059 Rostock Tel.: 0381/498-6400 E-Mail: Axel.Schulz@uni-rostock.de

Summary of proposal

This project describes the utilization of Ionic Liquids (ILs) with non-innocent anions and cations to synthesize new pseudohalogen borates, silicates and phosphates. As non-innocent anions are used either decomposable ions such as carbonates ($[\text{CO}_2(\text{OMe})^-]$), borates ($[\text{B}(\text{OMe})_3\text{A}]^-$, $[\text{B}(\text{OMe})_4]^-$; with A = pseudohalogen, e.g. CN, SCN, N₃), silicates ($[\text{Si}(\text{OMe})_4\text{A}]^-$) and phosphates ($[\text{OP}(\text{OMe})_3\text{A}]^-$) or the highly nucleophilic (pseudo)halides, which also form ILs with corresponding organic cations. The goal of this project is the syntheses of new (often highly labile) pseudohalogen species such as $[\text{CO}_2\text{A}]^-$, $[\text{A}...\text{H}...\text{A}]^-$, $[\text{B}(\text{OMe})_3\text{A}]^-$, $[\text{B}(\text{OMe})_2\text{E}_1\text{A}]^-$ (E₁ = halogen), $[\text{B}(\text{OMe})\text{E}_2\text{A}]^-$ (E₂ = chalcogen), $[\text{A-B-E}_3]^-$ (E₃ = pnictogen) and salt bearing the $[\text{SiF}_6-n(\text{CN})_n]^{2-}$ and $[\text{PF}_6-n(\text{CN})_n]^-$ ions utilizing functionalized ILs for quenching or stabilizing, respectively. Non-innocent means that the used IL is both the reaction media as well as reactant.

The project splits into five interacting parts:

- Syntheses of pure pseudohalide containing ILs from ILs with decomposable anions. Preparation of pure pseudohalide containing ILs, $[\text{Cat}]^+\text{A}^-$ (A = e.g. CN, SCN, N₃), is well-established. Besides, the synthesis of pseudohalide containing ILs, special emphasis will be placed on the isolation of the intermediates such as $[\text{CO}_2\text{A}]^-$.
- Reactions of pseudohalide containing ILs with non-metal elements (e.g. P₄, S₈) and their oxides and sulfides. A special emphasis will be given to the solubility problem as well as the bond activation by the highly nucleophilic pseudohalides when they are part of an IL.
- Reactions of pseudohalide containing ILs with pure acids of pseudohalides (HA). As these ILs contain naked pseudohalides the formation of $[\text{A}...\text{H}...\text{A}]^-$ ions upon addition of the pure HA acid should be observed and the isolation attempted.
- Syntheses of pseudohalogen borate, silicate and phosphate species in pseudohalide containing ILs and their reaction with persilylated compounds of group 15-17.

(v) Syntheses of coordination polymers utilizing cyanido(fluorido)phosphates, -arsenates and -silicates containing ILs with decomposable cations such as $[nPr_3NH]^+$.