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Simple access to ionic liquids and organic salts containing the phosphoethynolate (PCO⁻) and Zintl (Sb₁₁³⁻) anions†

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Herein we report the synthesis of the first ionic liquids with the highly reactive and synthetically valuable phosphoethynolate (PCO⁻) anion. They are simply synthesised by the reaction of organic methylcarbonate salts with P(SiMe₃)₃. The products are obtained in near to quantitative yields and they are highly viscous liquids at room temperature or have low melting points for symmetric cations. Moreover, extending this synthetic strategy towards Sb(SiMe₃)₃ we discovered a simple synthesis for [P(*n*Bu)₃Me]⁺₃[Sb₁₁]³⁻, the first organic cation salt comprising the Zintl-anion [Sb₁₁]³⁻.

The first synthesis of the PCO⁻ anion goes back to the early 1990s when Becker *et al.* isolated the lithium salt bis(1,2-dimethoxyethan-*O,O'*)lithoxy-methylidiphosphan (Li(OCP)·2 DME) from the reaction of [LiP(SiMe₃)₂] with CO(OMe)₂.¹ Until lately this anion has attracted little attention, also due to limitations of its synthetic access. This situation changed upon introduction of new synthetic procedures by Grützmacher and coworkers that allow large scale access to sodium and lithium PCO salts.² Systematic investigations in recent years have brought up a fascinating diversity of PCO⁻ anion chemistry: like the homologous pseudo-halide NCO⁻, the PCO⁻ anion can act as a nucleophile by binding *via* the oxygen or phosphorous atom. For example, the *P*- or *O*-silylated compounds R₃Si-OCP and R₃Si-PCO are accessible from the reaction of NaPCO with triorganosilanechlorides or -triflates. In spite of the strong Si-O bond the phosphaketene structure is thermodynamically favoured and prevails as the main product.^{3,4} Besides its use as a ligand in transition metal^{5,6} and actinide complexes,⁷ the PCO⁻ anion can act as a precursor for [2+2] cycloadditions.^{4,8} The groups of Goicoechea and Grützmacher have developed a diversity of heterocycle forming reactions of the PCO⁻ anion with, *e.g.*, activated alkynes,⁹ carbodiimides¹⁰ and isocyanates.¹¹ Moreover, the PCO⁻ anion allows the synthesis of

unsubstituted or N-functionalised inorganic urea analogues,^{12,13} and acts as a phosphide transfer reagent.^{14,15}

The most common route to the PCO⁻ anion starts from NaPH₂, which is converted under CO pressure or with ethylene-carbonate in dimethoxyethane.¹² As the number of ionic synthons for PCO⁻ was limited to very few inorganic cations our interest was focused on developing a convenient preparation method for new organic salts containing this anion. It should be mentioned that simple ion exchange in water/methylene chloride or chloroform typically used in ionic liquid syntheses does not lead to this class of reactive organic PCO salts in the pure state. In view of the first synthesis of the PCO⁻ anion, which started from dimethyl carbonate, the class of methylcarbonate ionic liquids (ILs) attracted our attention. The easily accessible organic methylcarbonate salts [Cat]⁺[OCO₂Me]⁻ can be prepared *via* a water and halide free procedure and have proven as versatile starting materials for ILs.^{16,17} They were recently employed to synthesise organic salts with hydrochalcogenide and trimethylsilylchalcogenolate anions, starting from H₂E and E(SiMe₃)₂ (E = S, Se, Te), respectively.^{18,19} In the latter case the methylcarbonate anion acted not as a Brønsted base, which is its typical reactivity pattern, but as a nucleophile and a desilylating agent.²⁰ Our original motivation was to probe similar desilylation reactions at E(SiMe₃)₃ (E = P, As, Sb) in order to access reactive organic salts with E(SiMe₃)₂⁻ anions.

Subsequently we discovered a method to synthesise purely organic salts of the composition [Cat]⁺[PCO]⁻ with varying steric demands of the cation by reacting readily available methylcarbonate precursors with P(SiMe₃)₃. Many new PCO⁻ salts were obtained in almost quantitative yields from polar solvents like acetonitrile or THF without any need to use autoclaves (Scheme 1). Their formation can be explained by the nucleophilic attack of E(SiMe₃)₂⁻ anions formed *in situ* at CO₂ formed by the decay of unstable carbonate intermediate Me₃SiO-COOME followed by silyl migration and siloxane elimination.

The compounds [P(*n*Bu)₃Me]⁺[PCO]⁻ (**1**) and [EMIm]⁺[PCO]⁻ (**4**) were obtained as yellow to orange, very viscous oils and can

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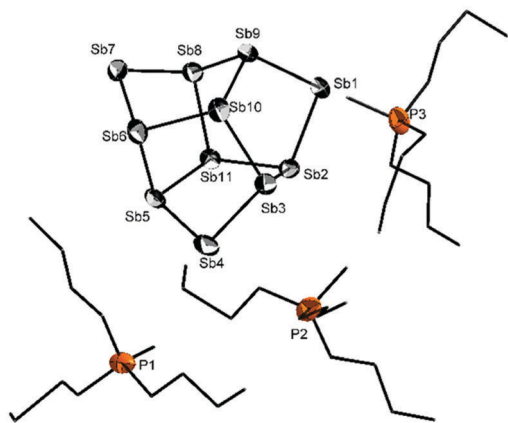


Fig. 3 Molecular structure of $[P(nBu)_3Me]^+_3[Sb_{11}]^{3-}$ (**8**). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent a 50% probability level. The organic substituents of the phosphonium cations are shown in the Wire/Sticks model for clarity. Selected distances [Å] and angles [°]: Sb1–Sb9 2.759(1), Sb1–Sb2 2.762(3), Sb2–Sb11 2.830(1), Sb2–Sb3 2.811(1), Sb3–Sb4 2.754(3), Sb3–Sb10 2.841(1), Sb4–Sb5 2.752(2), Sb5–Sb6 2.814(2), Sb5–Sb11 2.820(2), Sb6–Sb7 2.766(1), Sb6–Sb10 2.840(2), Sb7–Sb8 2.764(1), Sb8–Sb9 2.816(2), Sb8–Sb11 2.840(2), Sb9–Sb10 2.833(2); Sb9–Sb1–Sb2 95.5(3) to Sb1–Sb9–Sb10 106.11(3).

quaternary phosphonium counterions, the most base/nucleophile-robust among the organic cations, have been used to stabilize only the $[P_{11}]^{3-}$ anion, so far.^{26,27}

The anion consists of three Sb^- (pseudo-tellurium) atoms, which are twofold bonded. The bond length between the twofold and threefold bonded antimony atoms varies from 2.752(2) to 2.766(1) Å (respectively from 2.811(1) to 2.841(1) Å for the threefold bonded antimony atoms) and matches with known $[Sb_{11}]^{3-}$ clusters ($[Na(2,2,2-crypt)]^+_3[Sb_{11}]^{3-}$; 2.757 Å and 2.827 Å).²³

The crystals are stable for several months at room temperature in the mother liquid but decompose very quickly if they are removed from the solvent. The investigation of **8** by NMR spectroscopy showed partial decomposition of the cation and as a consequence decomposition of the cluster anion by deprotonation of the methyl group, resulting in the formation of a phosphorous ylide, which shows a singlet resonance at 20.48 ppm in the $^{31}P\{^1H\}$ NMR spectra.

We have shown that the reaction between organic methyl-carbonate salts and $P(SiMe_3)_3$ leads to new ionic liquids and reactive synthons of the type $[Cat]^+[PCO]^-$. Our method is comparably benign with respect to hazards. In contrast to already known procedures, no autoclaves or high reaction temperatures nor the handling of carbon monoxide and PH_3 gases is needed to form these valuable PCO^- synthons. The latter stand out due to excellent yields, good solubility and a simple preparative procedure. The new salts comprising an uncoordinated, highly nucleophilic PCO^- anion will serve as transfer agents of this ligand to transition metal complexes or main group compounds, for the formation of crystalline metallate complexes or as stable and nicely soluble synthons in heterocyclic

chemistry. Furthermore, we obtained the first organic cation salt of the Zintl ion $[Sb_{11}]^{3-}$. In future we will focus on similar reactions with $As(SiMe_3)_3$ and $Bi(SiMe_3)_3$ to establish the scope and limits of ECO^- ($E = As, P, As, Sb, Bi$) versus Zintl anion reaction paths.

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