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Simple access to ionic liquids and organic salts containing the phosphoethynolate (PCO[−]) and Zintl (Sb₁₁^{3−}) 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.

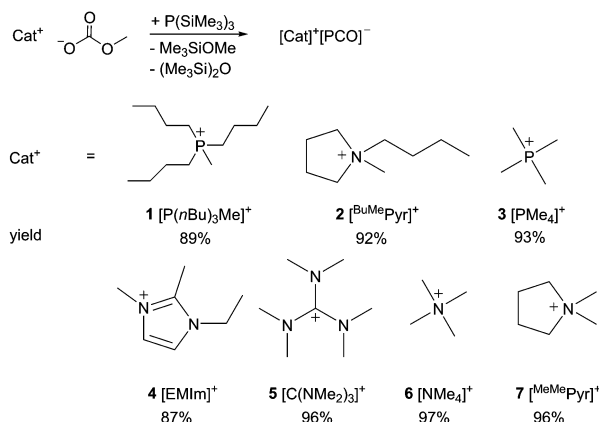
Subsequently we discovered a method to synthesise purely organic salts of the composition [Cat]⁺[PCO][−] with varying steric demands of the cation by reacting readily available methylcarbonate precursors with P(SiMe₃)₃. Many new PCO[−] salts were obtained in almost quantitative yields from polar solvents 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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Scheme 1 Synthesis of organic phosphoethynolate salts, yields in parentheses (^{Bu}MePyr: 1-butyl-1-methylpyrrolidinium, ^{Me}MePyr: 1,1-dimethylpyrrolidinium, EMIm: 1-ethyl-2,3-dimethylimidazolium).

therefore be regarded as room temperature ILs; all other PCO[−] salts presented in this work were received as yellow to orange powders. While the salts [^{Bu}MePyr]⁺[PCO][−] (**2**) and [PMe₄]⁺[PCO][−] (**3**) melt reversibly below 100 °C, the compound [NMe₄]⁺[PCO][−] (**6**) decomposes at 215 °C. Symmetric [C(NMe₂)₃]⁺[PCO][−] (**5**) decomposes at 230 °C while asymmetric [^{Me}MePyr]⁺[PCO][−] (**7**) melts reversibly at 125 °C.

The prepared phosphoethynolate salts were investigated by ¹H, ¹³C and ³¹P NMR spectroscopy. In good agreement with literature reports, the phosphorus atom of the anion displays a resonance between −382.6 ppm and −390.3 ppm²¹ and ¹³C{¹H} NMR resonance signals are consistent with other published values in the range of 167.7 to 170.0 ppm, which show ¹J_{CP} coupling constants consistent with literature known compounds such as [K(18c6)]⁺[PCO][−] with ¹J_{CP} = 62 Hz.²¹

The IR spectra of compounds **1–7** show two characteristic bands in the range from 1757 to 1772 cm^{−1} and from 1791 to 1799 cm^{−1} of the PCO[−] anion, which are in agreement with the spectra of [K(18c6)]⁺[PCO][−] (1730 cm^{−1}) and NaOCP-DME (1760 cm^{−1}, 1780 cm^{−1}).^{12,21}

The salts [PMe₄]⁺[PCO][−] (**3**), [C(NMe₂)₃]⁺[PCO][−] (**5**) and [NMe₄]⁺[PCO][−] (**6**) could be obtained as single crystals and were investigated by X-ray diffraction. [PMe₄]⁺[PCO][−] (**3**) crystallises in the orthorhombic crystal system in the space group *Pnma* and includes one ion pair in the asymmetric unit (Fig. 1). The phosphorus–carbon bond length in the anion is 1.579(1) Å and is thus in good agreement with the bond length in [K(18c6)]⁺[PCO][−] (1.579(3) Å). Also the carbon–oxygen bond length in the anion ((C5–O1): 1.213(1) Å) is similar to the value described by Goicoechea (*d*(C–O): 1.212(4) Å).²¹

[C(NMe₂)₃]⁺[PCO][−] (**5**, Fig. 2) crystallises in the monoclinic crystal system in the space group *P2₁/c* with two independent ion pairs and one equivalent of acetonitrile in the asymmetric unit. In comparison with **3**, the P–C bond of the PCO[−] anion is elongated, while the C–O bond is shortened. A P–C–O angle of 179.9° suggests an almost linear geometry around the central carbon atom in the anion and is in good agreement with the P–C–O angle in [K(18c6)]⁺[PCO][−] (178.9°).

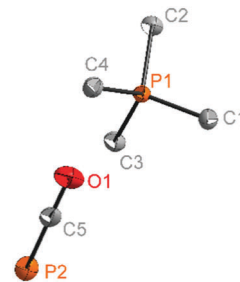


Fig. 1 Molecular structure of [PMe₄]⁺[PCO][−] (**3**). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent a 50% probability level. Selected distances [Å] and angles [°]: P2–C5 1.579(1), C5–O1 1.213(1), P1–C3 1.782(1); P2–C5–O1 179.9(15).

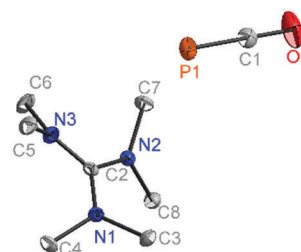


Fig. 2 Molecular structure of [C(NMe₂)₃]⁺[PCO][−] (**5**). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent a 50% probability level. Only one of two independent ion pairs in the asymmetric unit is displayed. **5** crystallises with one molecule of acetonitrile per asymmetric unit. Selected distances [Å] and angles [°]: P1–C1 1.594(1), C1–O1 1.188(1), C2–N1 1.344(1); P1–C1–O1 179.3(4).

[NMe₄]⁺[PCO][−] (**6**) crystallises in the monoclinic crystal system in the space group *P2₁/m*. The P–C and C–O bond lengths are 1.601(1) Å and 1.203(2) Å, respectively, and within the typical range of the PCO[−] anion. The P–C–O angle is 179.2° and shows the expected nearly linear geometry.

Besides the reaction of methylcarbonate ILs with P(SiMe₃)₃ we investigated their behaviour towards the heavier homologue Sb(SiMe₃)₃ in order to synthesise a compound of an unknown SbCO[−] anion. Its existence and stability at ambient temperature was postulated by Schaefer and co-workers on the basis of DFT calculations.²²

Similar to the previously mentioned procedure, [P(*n*Bu)₃Me]⁺[OCO₂Me][−] was dissolved in DME and Sb(SiMe₃)₃ was slowly added at 0 °C. The reaction mixture turned dark brown. Obviously a different competitive reaction path of desilylated anionic antimony species is involved. After filtration of some solid material, black plates crystallized from solution at room temperature. The XRD analysis revealed an antimony cluster of the composition [P(*n*Bu)₃Me]⁺₃[Sb₁₁]^{3−} (**8**). We did not find any indication of the formation of analogues of a salt with the SbCO[−] anion. **8** crystallises in the monoclinic crystal system in the space group *Cc*. Fig. 3 displays the [Sb₁₁]^{3−} Zintl anion crystallised with three tri-*n*-butylmethyl-phosphonium cations. The [Sb₁₁]^{3−} anion and all lighter congeners have been well known in the literature for years; the [Bi₁₁]^{3−} anion was obtained by Dehnen and co-workers only recently.^{23–25} While the counterions are usually alkali metal cations, which are coordinated by crown ethers or cryptands,



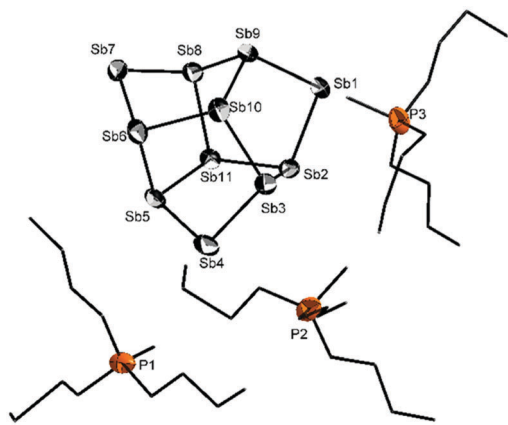


Fig. 3 Molecular structure of $[P(nBu)_3Me]^+_3[Sb_{11}]^{3-}$ (**8**). Hydrogen atoms are omitted for clarity; thermal ellipsoids represent a 50% probability level. The organic substituents of the phosphonium cations are shown in the Wire/Sticks model for clarity. Selected distances [Å] and angles [°]: 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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