

From Chemical Curiosities to Versatile Reagents: Heavy Group 15 Pseudohalides

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The 2-phosphaethynolate anion (PCO^- ; the phosphorus-containing analogue of cyanate) was first isolated by Becker and co-workers as a lithium salt in 1992.^[1] Due to difficulties associated with its manipulation, the chemistry of this remarkable species laid dormant for decades. The report of a high yielding, multi-gram synthesis of $[\text{Na}(\text{dioxane})_x][\text{PCO}]$ in 2014 rekindled the interest in this fundamental ion.^[2] Since then, the reactivity of PCO^- and its use in decarbonylative and deoxygenative processes has been extensively explored.^[3]

Following Becker's original report on the isolation of PCO^- , heavier analogues have also become synthetically accessible (PnCCh^- where $\text{Pn} = \text{P}, \text{As}$; $\text{Ch} = \text{O}, \text{S}, \text{Se}$).^[4, 5] These ions are rare inasmuch as they contain highly reactive pnictogen-carbon multiple bonds, yet can be manipulated with ease due to their negative charges, which preclude common decomposition pathways (e.g. oligomerization), associated with neutral valence-isoelectronic species. This talk will survey recent studies on this family of anions paying particular attention to the use of PCO^- as a precursor to the elusive cyaphide ion (CP^-).

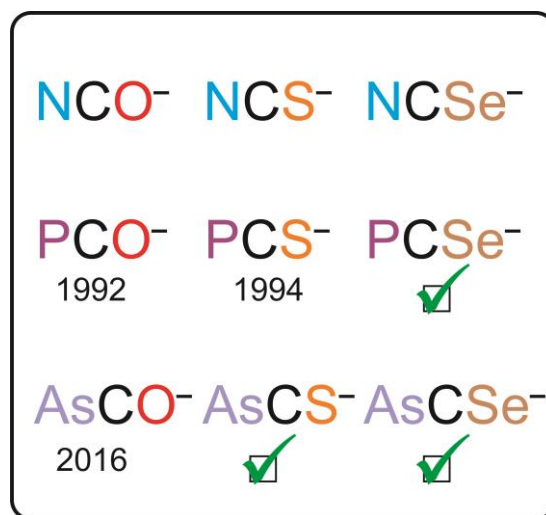


Figure 1. The cyanate ion and its heavier analogues.

References

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