## Supporting Information

Title: Molecularly Non-stoichiometric Crystals in Phosphorus Compounds

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Figure S1. An ORTEP drawing of $\mathbf{1 1}$ (Hydrogen atoms are omitted for clarity).


Figure S2. An ORTEP drawing of [11+13]. The methyl groups of $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}$ are disordered. (Hydrogen atoms are omitted for clarity).


Figure S3. An ORTEP drawing of $\mathbf{1 4}$ (Hydrogen atoms are omitted for clarity).


Figure S4. An ORTEP drawing of $\mathbf{1 5}$ (Hydrogen atoms are omitted for clarity).


Figure S5. An ORTEP drawing of 12 (Hydrogen atoms are omitted for clarity)


Figure S6. An ORTEP drawing of $\mathbf{1 6}$ (Hydrogen atoms are omitted for clarity) in the asymmetric unit.


Figure S7. An ORTEP drawing of [16+17]a (Hydrogen atoms are omitted for clarity)


Figure S8. An ORTEP drawing of [16+17]b (Hydrogen atoms are omitted for clarity).



Figure S9. An ORTEP drawing of [16+17]c (Hydrogen atoms are omitted for clarity)


Fig.S10. Packing in 12. No short contacts.


Fig. S11. Packing in 16. Short contacts: $\mathrm{C}(21)-\mathrm{H}(21) \quad \mathrm{O}(7)^{\prime}[0.93,2.68,3.338(4) \AA$, $128.0^{\circ}$ symmetry code: $\left.-1+\mathrm{x}, \mathrm{y}, \mathrm{z}\right]$; C(13)-H(13) $\mathrm{O}(8)^{\prime}\left[0.93,2.69,3.452(4) \AA, 139.6^{\circ}\right.$ symmetry code: $1-\mathrm{x}, 2-\mathrm{y},-1 / 2+\mathrm{z}] ; \mathrm{C}(36)-\mathrm{H}(36) \quad \mathrm{O}(4)^{\prime}\left[0.93,2.62,3.511(4) \AA\right.$, $159.5^{0}$ symmetry code: $1 / 2+x, 1-y, z]$


Fig. S12. Packing in [16+17]a. Short contacts. C(4)-H(4A)...O(1)' 0.962 .68 3.487(5) $\AA$ $141.7^{0}$ symmetry code: $\mathrm{x}, 1+\mathrm{y}$, z ]; C(11)-H(11)...O(3)' [0.93 $2.703 .479(5) \AA 141.9^{\circ}$ symmetry code: -x, $-1 / 2+y, 1 / 2-z] ; \mathrm{C}(20)-\mathrm{H} 20 \ldots \mathrm{O}(4)^{\prime}\left[\begin{array}{llll}0.93 & 2.46 & 3.199(8) \AA 136.8^{\circ}\end{array}\right.$ symmetry code: $1-\mathrm{x},-1 / 2+\mathrm{y}, 1 / 2-\mathrm{z}]$


Fig. S13. Packing in [16+17]b. Short contacts: C(7)-H(7A)...O(1)' [0.96 2.69 $3.447(11) \AA 135.7^{\circ}$ symmetry code: x, $1+y$, z ]; C(36)-H(36)...O(4)' [0.93 2.62 $3.515(10) \AA 160.7^{0}$ symmetry code: $x,-1+y, z$ ]


Fig. S14. Packing in [16+17]c. Short contact: C(12)-H(12) ...O(3)' 0.932 .47 3.217(5) Å, $137.6^{\circ}$ symmetry code: -x, $\left.0.5+y, 0.5-z\right]$.


Fig. S15. PLATON drawing of packing in 13 (left) and $\mathbf{1 4}$ (right). Short contact in $\mathbf{1 4}$ : [C(24)-H(24C)...Se’ [0.96, 2.93, 3.783(3) $\AA, 148.3^{\circ}$; symmetry code: $\left.-0.5+\mathrm{x}, 1.5-\mathrm{y}, 2-\mathrm{z}\right]$.

