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Molecularly Nonstoichiometric Crystals in Phosphorus Compounds

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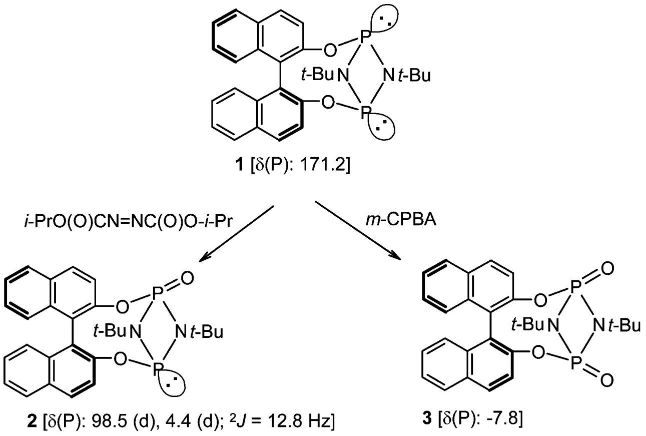
Molecularly nonstoichiometric crystals obtained as a result of differential occupation of sites with oxygen atom/phosphorus lone pair of electrons or with sulfur/selenium in three sets of phosphorus compounds are described. These are formed by a combination of (a) $[CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2]PNMe_2$ (**11**) and $[CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2]P(O)NMe_2$ (**13**), (b) $[CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2]P(S)NMe_2$ (**14**) and $[CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2]P(Se)NMe_2$ (**15**), and (c) $[(2,6\text{-Me}_2C_6H_3O)(O)P\text{-}\mu\text{-N-}t\text{-Bu}]_2$ (**16**) and $(2,6\text{-Me}_2C_6H_3O)(O)P(\mu\text{-N-}t\text{-Bu})_2P(O\text{-}2,6\text{-Me}_2C_6H_3)$ (**17**). In the case of c, three different types of crystals with varying stoichiometry of **16** and **17** (1:9, 1:1.5, and 1:0.43) are obtained. The results are substantiated by the combined use of ^{31}P NMR spectroscopy and X-ray crystallography. These observations suggest that we should be cautious with regards to the purity of samples when syntheses involving the oxidation of P(III) systems are reported. It is also emphasized that the apparent P–X distances in some of these crystals cannot actually be taken as true bond lengths.

Introduction

In our investigations on phosphorus chemistry, we had a need for amino-substituted phosphoryl/thiophosphoryl compounds for structural studies as well as organic transformations such as asymmetric reduction of ketones, aldol reactions, and the Baylis−Hillman reaction.[1,2] One of the very common ways to synthesize such compounds is by oxidation of the corresponding P(III) compounds.[3] In this connection, we had recently communicated a fairly straightforward synthesis of compounds **1** and **3** (Scheme 1).[4] What was perhaps more interesting, however, was that mixed molecularly nonstoichiometric crystals of **[1+2]** and **[2+3]** could be readily synthesized by making use of the similar volumes occupied by the oxygen and lone pair of electrons on phosphorus. The results on the crystal structures were duly corroborated by solution-state ^{31}P NMR spectra on as-obtained crystals. It may be noted that nonstoichiometry is a familiar topic in solid-state chemistry[5] because of various defects that are thermodynamic in origin, while this phenomenon is extremely rare in molecular chemistry. Although it appears simple, to our knowledge, there was no previous report of such molecularly nonstoichiometric[6] phosphorus compounds. In fact, this feature made the isolation of *pure*

Scheme 1



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(1) (a) Kommana, P.; Kumara Swamy, K. C. *Inorg. Chem.* **2000**, *39*, 4384. (b) Praveen Kumar, K.; Chakravarty, M.; Kumara Swamy, K. C. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2063.

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(3) (a) Corbridge, D. E. C. *Phosphorus 2000: Chemistry, Biochemistry and Technology*, 4th ed.; Elsevier: Amsterdam, The Netherlands, 2000; Chapter 3, p 64. (b) Osman, F. H.; El-Samahy, F. A. *Chem. Rev.* **2002**, *102*, 629.

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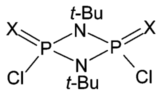
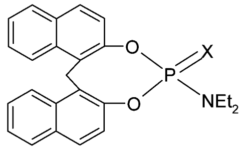
monooxidized compound **2** difficult. Because of this, the P═O “distances” in these crystals vary in the rather abnormal range 1.30−1.45 Å, which has similarities to the so-called (nonexistent) “bond stretch isomerism”.[7]

Oxidation of P(III) to P(V) is fairly common in phosphorus chemistry, and pure compounds are required for meaningful applications. In the five pairs of compounds **4**−**8** for which the X-ray structures (unsolvated molecules) of both P(III) and its oxidized product are determined [Cambridge Structural Database (CSD) search],[8] the above phenomenon of nonstoichiometry was not reported. In the first three pairs, the two compounds did not crystallize in the same space group, although the difference in volume between the oxygen and the lone pair (on phosphorus) in each set is ≤5 Å^3. However, on the basis of our results above, it appears that mixed crystals must form readily in the case of **7a,b** and **8a,b**. The cell dimensions in these cases are fairly similar.[9]

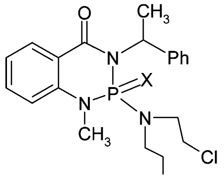
Although replacement among groups having similar volumes/shapes (Kitaigorodskii’s theory; e.g., chloro vs methyl that differ by 5.0 Å^3 in volume) is well-known,[10] to our knowledge, similar features involving a lone pair of electrons and oxygen have not been documented prior to our work. Because there are no reports concerning the difference in volume up to which two groups can interchange their positions, we looked for possible interchangeability of sulfur and selenium also in analogous phosphorus compounds with P═S and P═Se bonds. A CSD survey on P═S and P═Se compounds revealed two pairs of compounds, **9a,b** and **10a,b**. Interestingly, each of **10a** and **10b** crystallized in different space groups.[11] In each set, the unit cell dimensions for compounds are nearly the same and the difference in volume occupied by sulfur and selenium is ≤5.85 Å^3. Hence, we can expect the interchangeability between sulfur and selenium also for a pair of compounds with P═X (X = S, Se) bonds, leading to single crystals containing both sulfur and selenium.



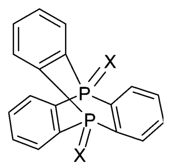
X = lone pair (**4a**: *Pbca*)
O (**4b**: *P42/n*)



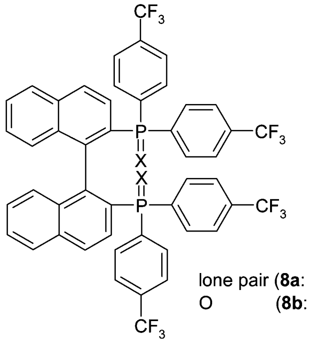
lone pair (**5a**: *Pbca*)
O (**5b**: $P2_12_12_1$)



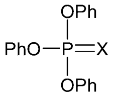
lone pair (**6a**: $P\bar{1}$)
O (**6b**: $P2_12_12_1$)



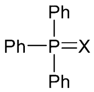
X = lone pair (**7a**: *C2/c*)
O (**7b**: *C2/c*)



lone pair (**8a**: *C2/c*)
O (**8b**: *C2/c*)



X = S (**9a**: $P2_12_12_1$)
= Se (**9b**: $P2_12_12_1$)



X = S (**10a**: $P2_1/c$ or $P\bar{1}$)
= Se (**10b**: $P2_1/c$ or $P\bar{1}$)

In this paper, we primarily focus on the nonstoichiometry involving three sets of phosphorus compounds. The first two sets are based on $[CH_2(6\text{-}t\text{-}Bu\text{-}4\text{-}MeC_6H_2O)_2]PNMe_2$ (**11**),[12] while the third one is based on $[(2,6\text{-}Me_2C_6H_3O)P\text{-}\mu\text{-}N\text{-}t\text{-}Bu]_2$ (**12**).[13,14] The formation of mixed crystals, confirmed by detailed single-crystal X-ray structural studies and ^{31}P NMR spectroscopy as observed here, should act as a caveat when syntheses involving the oxidation of P(III) systems are reported in the literature. We also emphasize that the “P═O

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(6) One of the reviewers did not like the use of the term “nonstoichiometric crystals” on the grounds that this term applies to solid-state (ionic) compounds but not molecular compounds. The term “mixed crystals” was suggested. Another reviewer preferred a more explicit term. While we do agree that these are “mixed crystals”, in our opinion, the true nature of the system presented here is not conveyed by this term. Also, to distinguish these from the ionic compounds, we have used the term “molecularly nonstoichiometric”.

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(9) These values are as follows: **7a**, a = 15.068(5) Å, b = 8.276(3) Å, c = 13.315(3) Å, β = 120.26(2)°; **7b**, a = 15.411(17) Å, b = 8.301(7) Å, c = 13.827(9) Å, β = 122.24(5)°; **8a**, a = 28.422(1) Å, b = 8.058(1) Å, c = 18.787(1) Å, β = 110.05(1)°; **8b**, a = 28.723(1) Å, b = 8.494(1) Å, c = 17.998(1) Å, β = 109.82(1)°.

(10) (a) Jones, W.; Nakanishi, H.; Theocharis, C. R.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 610. (b) Theocharis, C. R.; Desiraju, G. R.; Jones, W. *J. Am. Chem. Soc.* **1984**, *106*, 3606. (c) Desiraju, G. R.; Sarma, J. A. R. P. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1986**, *96*, 599. (d) Muthiah, C.; Kumar, K. P.; Kumaraswamy, S.; Kumara Swamy, K. C. *Tetrahedron* **1998**, *54*, 14315.

(11) (a) Codding, P. W.; Kerr, K. A. *Acta Crystallogr.* **1978**, *34B*, 3785. (b) Codding, P. W.; Kerr, K. A. *Acta Crystallogr.* **1979**, *35B*, 1261. (c) Foces-Foces, C.; Liamas-Saiz, A. L. *Acta Crystallogr.* **1998**, *54C*, 9800013. (d) Ziemer, B.; Rabis, A.; Steinberger, H.-U. *Acta Crystallogr.* **2000**, *56C*, e58. (e) Clade, J.; Jansen, M. *Z. Kristallogr.* **2005**, *220*, 234. (f) Jones, P. G.; Klenitz, C.; Thones, C. *Z. Kristallogr.* **1994**, *209*, 80. (g) Hernández, J.; Goycoolea, F. M.; Zepeda-Rivera, D.; Juárez-Onofre, J.; Martínez, K.; Lizardi, J.; Salas-Reyes, M.; Gordillo, B.; Velázquez-Contreras, C.; García-Barradas, O.; Cruz-Sánchezd, S.; Domínguez, Z. *Tetrahedron* **2006**, *62*, 2520.

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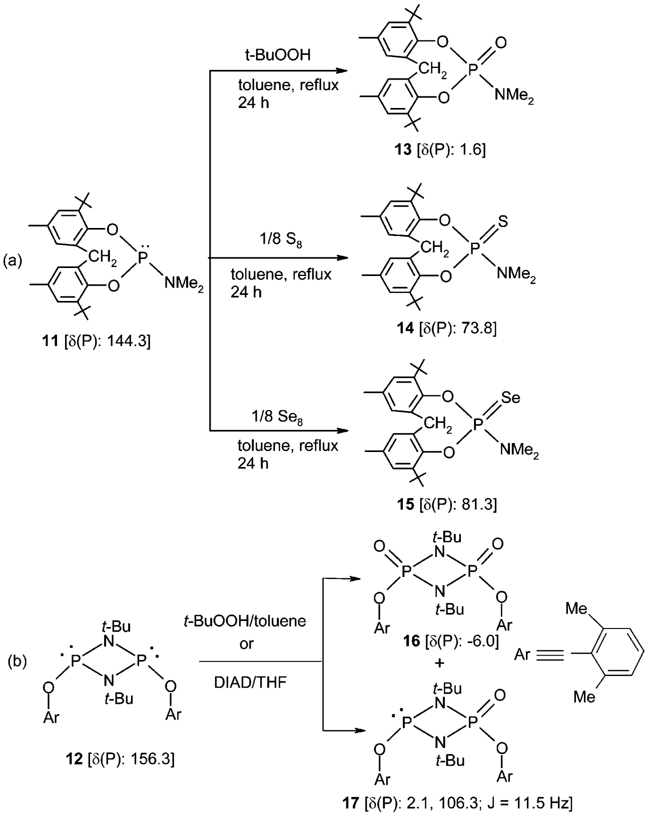
(13) This compound had been reported by us before: Vijjulatha, M.; Kumara Swamy, K. C.; Vittal, J. J.; Koh, L. L. *Polyhedron* **1999**, *18*, 2249.

Scheme 2



distances" in some of the crystals cannot actually be taken as true "P═O bond lengths".

Results and Discussion

Straightforward routes shown in Scheme 2 afforded compounds **13**−**16** and **17**. In addition to the hydroperoxide route, compound **17** along with a small quantity (ca. 10%) of **16** is also obtained by the reaction of **12** with diisopropyl azodicarboxylate [DIAD, Pr-*i*-O(O)CN═NC(O)O-*i*-Pr] taken in a 1:1 molar ratio. The two phosphoryl oxygen atoms in **16** are cis to each other, showing that there is no change in the configuration upon oxidation. The spectroscopic data are consistent with those available in the literature for similar compounds.[12,13,15] The selenium compound **15** shows a ^1J(P−Se) of 942.8 Hz.[16] All of these compounds are highly crystalline in nature.

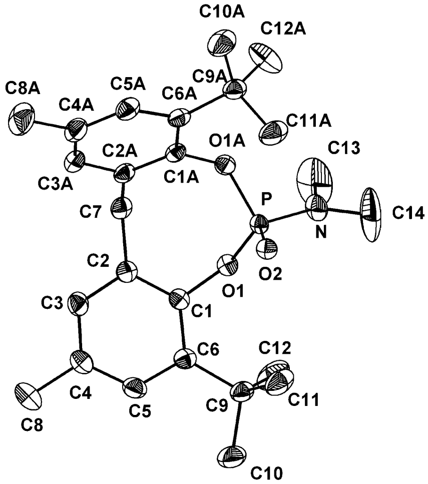


Figure 1. ORTEP diagram of compound **13**. The methyl groups of $N(CH_3)_2$ are disordered; the second positions of the corresponding carbons are not shown. The numbering is identical with those in **11** and the mixed crystal **[11+13]**.

Selected crystallographic data for the crystals for which structures have been determined herein are shown in Table 1. X-ray structures of compounds **11** and **13** show that both compounds crystallize in orthorhombic space group *Pnma* with fairly similar crystal cell dimensions (Table 1), i.e., isostructural.[17] The ORTEP diagram for compound **13** is shown in Figure 1; the structural details and numbering in the tricoordinate compound **11** are essentially identical with those in **13**, except that the phosphoryl oxygen O2 is missing. In both cases, the methyl groups of the $N(CH_3)_2$ group show some disorder and the conformation of the eight-membered 1,3,2-dioxaphosphocin ring is that of anti (or boat-chair). These features show that here the powerful hydrogen-bond-acceptor property of the phosphoryl (P═O) group[18] does not have a role in changing cell dimensions and the space group in **13** compared to **11**. The apparent difference in volume/molecule between **11** and **13** is only 4.6 Å^3, and, hence, we reasoned that mixed crystals of **11** and **13** should readily form from a suitable solvent.[19] This was indeed the case, and from a 1:1 (mole ratio) mixture of these compounds, the crystals of **[11+13]** (*Pnma* space group) with essentially identical cell dimensions were obtained. Here the lone pair of electrons on P(III) of crystal **11** interchanges with oxygen on P(V) of crystal **13**, and as a result, refinement of the occupancy factor proceeded satisfactorily. This fact is further demonstrated using a solution-state ^{31}P NMR spectrum

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(14) For some recent literature on the chemistry of cyclodiphosphazanes, see: (a) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203. (b) Moser, D. F.; Carrow, C. J.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1246. (c) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev*. **2002**, *237*, 233. (c) Moser, D.; Grocholl, L.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **2003**, 1402. (d) Dodds, F.; García, F.; Kowenicki, R. A.; McPartlin, M.; Steiner, A.; Wright, D. S. *Chem. Commun.* **2005**, 3733. (e) Garcia, F.; Goodman, J. M.; Kowenicki, R. A.; McPartlin, M.; Riera, L.; Silva, M. A.; Wirsing, A.; Wright, D. S. *Dalton Trans.* **2005**, 1764. (f) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Organometallics* **2005**, *24*, 3780. (g) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2005**, *44*, 7925. (h) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2005**, *44*, 275. (i) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, *45*, 6678. (j) Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *Polyhedron* **2007**, *26*, 883.

(15) (a) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Inorg. Chem.* **1997**, *36*, 2044. (b) Kumaraswamy, S.; Senthil Kumar, K.; Raja, S.; Kumara Swamy, K. C. *Tetrahedron* **2001**, *57*, 8181.

(16) This compound does catalyze the formation of the Baylis−Hillman adduct (~60% yield) from 4-nitrobenzaldehyde and cyclohexenone in the presence of titanium tetrachloride. Phani Pavan, M. (University of Hyderabad), Unpublished data.

(17) For some interesting systems on isostructurality, see: Anthony, A.; Kaskólski, M.; Nangia, A. *Acta Crystallogr.* **2000**, *B56*, 512.

(18) Kumara Swamy, K. C.; Kumaraswamy, S.; Kommana, P. *J. Am. Chem. Soc.* **2001**, *123*, 12642.

(19) Volume/molecule was calculated by dividing the unit cell volume by the number of molecules. It may be noted that the cell volume for [**11**+**13**] is slightly more than that for **13** alone. Hence, caution is required while correlating the volume with the number of atoms present in the molecule when small relative differences are involved.

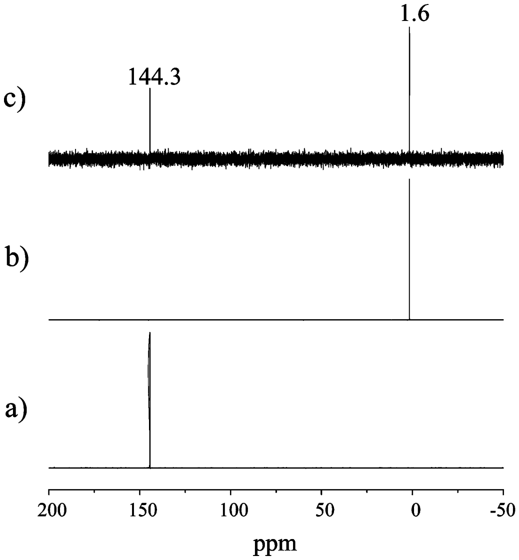

Figure 2. ^{31}P NMR spectra of crystals (a) **11**, (b) **13**, and (c) **[11+13]**.

(Figure 2) of the *as-obtained crystals*, which shows peaks at δ(P) 144.3 (compound **11**) and δ(P) 1.6 (compound **13**) in the ratio of ~1:2, consistent with the X-ray structure. This shows that a single crystal may not necessarily consist of a pure compound.

In order to probe the generality of the above phenomenon, we first determined the X-ray structures of the sulfur- and selenium-oxidized products **14** and **15**, respectively. As can be seen from Table 1, the pure compounds **14** and **15** crystallize in the same space group ($P2_12_12_1$) with essentially identical cell dimensions. The molecule does not have a chiral center, but the structure is noncentrosymmetric. Statistics on achiral molecules crystallizing in noncentrosymmetric space groups, as are available in the Cambridge Structural Database, show that the space group $P2_12_12_1$ is one of the five most populated space groups (these are often racemically twinned).[20] Packing is fairly efficient (filled space: **14**, 64.2%; **15**, 63.9%; using *PLATON* software[21]) in both cases, with no space for any solvent molecule. The van der Waals volumes (calculated) for sulfur and selenium are respectively 24.4 and 28.7 Å^3 (the van der Waals radius for sulfur is 1.8 Å, and that for selenium is 1.9 Å).[22] Thus, the difference in volume occupied by them is only around 4.3 Å^3, and, hence, the positions of the two atoms can get interchanged in the crystal. Keeping this in mind, we mixed compounds **14** and **15** in a 1:1 molar ratio and crystallized it from a dichloromethane/hexane mixture. X-ray structural analysis of the resulting crystal is done in two ways: (a) by keeping the X in P═X as selenium and refining its occupancy and (b) by keeping both sulfur and selenium in the P═X part and refining their occupancies. An ORTEP drawing for **[14+15]** so obtained is shown in Figure 3; the labeling is identical with that of **14** and **15** except that they contain fully P═S or P═Se bonds.[23] In method a, the crystal (space group $P2_12_12_1$) shows a selenium occupancy of ~0.7 when analyzed by considering only the P═Se bond; this suggests that if the crystal is a mixture, it would have **14**/**15** in the ratio of ~56:44. Indeed, convergence is better if we refine after keeping the sulfur/selenium ratio as ~0.56:0.44 (method b). Refinement did not converge by maintaining only sulfur. The ^{31}P NMR spectra (Figure 4) of the *as-obtained* crystals of **[14+15]** clearly show the presence of both **14** and **15** in the ratio of ~4:5, corroborating the results obtained by X-ray analysis.

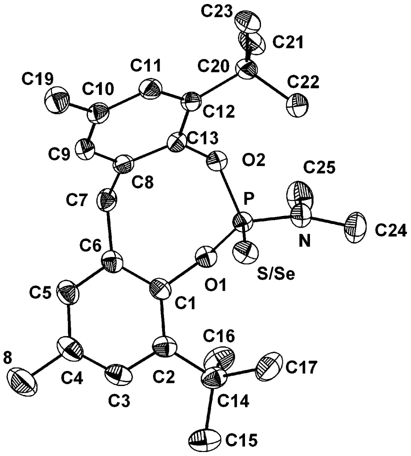

Figure 3. ORTEP drawing of **[14+15]** (hydrogen atoms are omitted).

The bis-oxidized cyclodiphosph(III)azane product **16** (Figure 5), obtained by complete oxidation of **12**,[11] crystallizes in space group $Pca2_1$, and the packing motif is different from that in **12**; the difference in volume per molecule between the two is ~34 Å^3, which becomes 17 Å^3 per extra oxygen because **16** has two more oxygen atoms than **12**. Thus, in terms of both crystal parameters and the extra volume occupied by oxygen atoms, we may expect that **12** and **16** will not form mixed crystals. This was indeed the case (at least in our hands) despite different crystallization conditions and solvents used. We always obtained **12** or **16** as individual crystals (evidence: ^{31}P NMR; cell dimensions). Thus, this case is different from that of **1** and **2** alluded to in the Introduction but is similar to that normally observed for compounds like Ph$_3$P and Ph$_3$P(O).[24]

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(23) In **15**, there is Se···H24C short contact [C24−H24C···Se′ 0.96, 2.93, and 3.783(3) Å, 148.3°; symmetry code, $-0.5 + x, 1.5 - y, 2 - z$], but a similar contact is missing in **14**. Although **13** has a disordered structure, the P═O bond has short contacts (O2···C14 3.027 Å), which obviously are absent in **11**. However, in both sets **[11+13]** and **[14+15]**, the packing and crystal dimensions are essentially unaffected by these weak interactions. Between **12** and **16**, the latter has some short contacts involving the phosphoryl oxygen [C21−H21−O7 0.93, 2.68, and 3.338(4) Å, 128.0°; symmetry code, $-1 + x, y, z$; C13−H13−O8′ 0.93, 2.69, and 3.452(4) Å, 139.6°; symmetry code, $1 - x, 2 - y, -\frac{1}{2} + z$; C36−H36−O4′ 0.93, 2.62, and 3.511(4) Å, 159.5°; symmetry code, $\frac{1}{2} + x, 1 - y, z$], but it is likely that the significant difference in the volume/molecule resulted in different structural motifs here. Thus, the interactions involving the P═X bond are not used as a guiding motif in the present series. Relevant packing diagrams are available in the Supporting Information.

(24) The compounds Ph$_3$P and Ph$_3$P═O crystallize with different unit cell dimensions. In this case, also our attempts to get mixed crystals were not successful. For selected data on their crystal structures, see: Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 6964 and references cited therein.

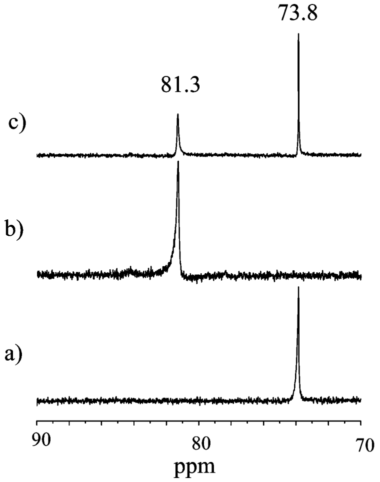

Figure 4. ^{31}P NMR spectra of (a) compound **14**, (b) compound **15**, and (c) crystal **[14+15]**.

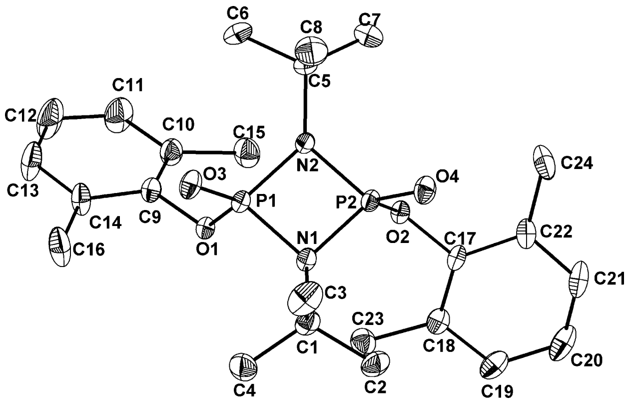

Figure 5. ORTEP diagram of **16** (hydrogen atoms are omitted). Only one of the molecules in the asymmetric unit is shown. Labeling is similar in **12**, **[16+17]a**, **[16+17]b**, and **[16+17]c**.

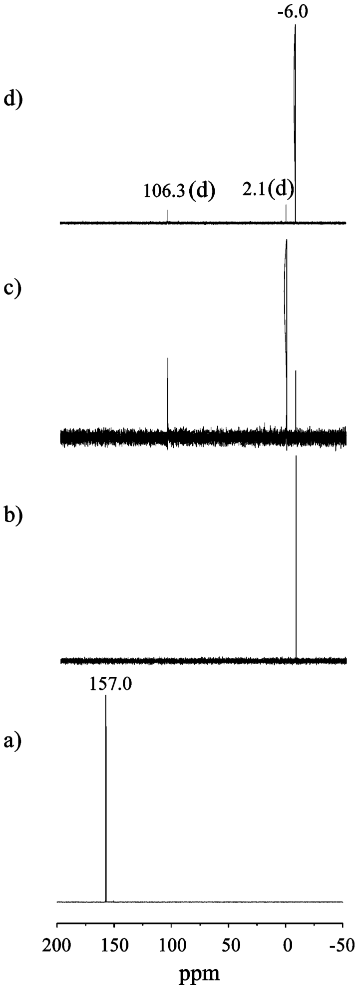

Figure 6. ^{31}P NMR spectra of (a) pure **12**, (b) pure **16**, (c) **[16+17]a**, and (d) **[16+17]c**.

In the process of crystallization after oxidation of **12** with DIAD, we noted that although the crystals contained **17** as a major component (>70%), almost always there was some bis-oxo product **16**. Thus, crystals of **[16+17]a** were obtained. These belong to the same space group $P2_1/c$ as **12**, but the crystal dimensions and the packing motifs are entirely different. The phosphoryl oxygen (P=O) at the two phosphorus centers are 0.4 and 0.7, which sums up to 1.1 oxygen atoms for two phosphorus atoms in the molecule. For pure **17**, this should have been "1". That such a thing is not an artifact is proved by the ^{31}P NMR spectrum (Figure 6d) of *as-obtained crystals*, which shows clearly that they contain both **16** and **17** in the ratio of ~1:9.[25] Thus, these crystals are also molecularly nonstoichiometric. As far as packing is concerned, the P=X (X = lone pair or oxygen) moieties pack interchangeably (Figure 7). The difference in

Table 1. Selected Crystal Data for **11**−**16**, **[11+13]**, **[14+15]**, **[16+17]a**, **[16+17]b**, and **[16+17]c**

compd	space group	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3	occupancy[a]
			Oxygen			
11	*Pnma*	13.038(3)	22.936(3)	8.095(2)	2420.9(9)	0.0
[11+13]	*Pnma*	13.405(1)	23.054(2)	7.963(1)	2461.2(3)	0.7
13	*Pnma*	13.443(3)	23.013(3)	7.885(2)	2439.3(9)	1.0
			Selenium/Sulfur			
14	$P2_12_12_1$	10.457(1)	13.306(1)	18.114(1)	2520.4(3)	0.0/1.0
[14+15]	$P2_12_12_1$	10.540(1)	13.300(1)	18.116(1)	2539.4(3)	0.44/0.56
15	$P2_12_12_1$	10.612(1)	13.307(1)	18.117(1)	2558.3(3)	1.0/0.0
			Oxygen at P1/P2			
12[b]	$P2_1/c$	12.397(4)	10.936(4)	19.775(6)	2619.4(14)	0.0/0.0
[16+17]a[c]	$P2_1/c$	20.381(2)	8.2365(8)	16.2347(16)	2657.5(5)	0.4/0.7
[16+17]b[d]	$P2_1/c$	20.500(4)	8.225(2)	16.182(3)	2663.4(9)	0.6/0.8
[16+17]c	$Pca2_1$	16.241(2)	8.176(1)	40.054(4)	5318.9(10)	0.8/0.9[e]
16	$Pca2_1$	16.191(2)	8.159(1)	40.170(5)	5306.6(12)	1.0/1.0[e]

[a] Taken from crystal structure refinements. [b] $\beta = 102.33(3)°$. We have reported **12** before,[11] but the data were collected again. [c] $\beta = 102.806(2)°$. [d] $\beta = 102.53(3)°$. [e] Similar occupancy at P3/P4.

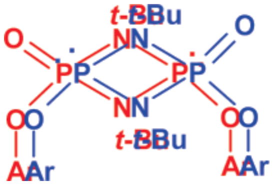

Figure 7. Drawing showing the overlap of two molecules of **17** in the crystals of **[16+17]a**, **[16+17]b**, and **[16+17]c**. It can be noted that **16** also can pack along with **17** within the same available volume.

volume per molecule in the crystals of **[16+17]a** and **16** is only ~4 Å^3, which means that interchangeability between **16** and **17** in a crystal lattice is possible despite the fact that they belong to different space groups. This assertion is amply demonstrated by the isolation of two more crystal forms, **[16+17]b** and **[16+17]c**, obtained by varying the stoichiometry of oxidizing agent *tert*-butyl hydroperoxide to the substrate **12**. Also noteworthy is the fact that when the bis-oxidized product is more, as in **[16+17]c**, the space group also changes to orthorhombic $Pca2_1$. The percentages of **16**/**17** based on oxygen occupancies are calculated to be 10:90, 40:60, and 70:30 for **[16+17]a**, **[16+17]b**, and **[16+17]c**, respectively. The ^{31}P NMR spectra for the as-obtained crystals for **[16+17]a** (Figure 6c), **[16+17]b** (not shown), and **[16+17]c** (Figure 6d) are consistent with the ratio obtained by X-ray crystallography.

With regards to interatomic distances, the P−N, P−O(ring), and P═O distances in the mixed crystal **[11+13]** are intermediate between those of **11** and **13**, respectively, as expected (Table 2). The P−N and P−O(ring) distances in the sulfur/selenium compounds **14**, **15**, and **[14+15]** are essentially the same, but the P═X (X = S, Se) distance for **[14+15]** is clearly and expectedly between those for **14** and **15**. These features also reflect the fact that, in the crystal structure of **[14+15]**, selenium and sulfur interchange their positions.

The formal "P═O (phosphoryl)" distances in **[16+17]a**, **[16+17]b**, and **[16+17]c** are not true "P═O" bond distances. As the proportion of **16** with respect to **17** increases, the corresponding formal P═O distance (cf. Table 3) decreases, which is reminiscent of the riddle of (nonexistent) "bond stretch isomerism" reported for transition-metal complexes in the literature.[7] This observation essentially holds good for the P−N and P−OAr distances also. The shortness of P(V)−N over P(III)−N bonds also contributes to the similarity of volumes of both compounds because the bigger P═O unit is drawn more closely into the molecule. This effect makes P═O bonds in mixed crystals appear to be shorter.

Summary

What we have described here are three sets of phosphorus compounds in which the interchangeability of the lone pair and oxygen or of sulfur and selenium allows them to crystallize in an isostructural manner and leads to nonstoichiometry. Such an exchange has earlier been described primarily for chloro/methyl groups in organic systems but not for oxygen/lone pair or sulfur/selenium types of systems presented in our work. This situation leads to a case wherein the *apparent P−X distances cannot be interpreted as true "bond lengths"*. In the oxidation of cyclodiphosphazane **12**, just by varying the stoichiometry of the oxidant, it appears that we can obtain mixed crystals with similar structures but with different P−X distances in a manner analogous to those seen in the case of so-called "bond stretch isomers". The resulting nonstoichiometric nature of partially oxidized and mixed products, as evidenced by the combined use of X-ray crystallography and ^{31}P NMR spectroscopy, is also highlighted here. These results, we believe, *must be taken note of* when we oxidize P(III) compounds and attempt to purify the products by crystallization.

Experimental Section

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[26] All reactions, unless stated otherwise, were performed under a dry nitrogen atmosphere. ^{1}H, ^{13}C, and ^{31}P{H} NMR spectra were recorded on a Bruker 200 or 400 MHz spectrometer in $CDCl_3$, with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer.

The compounds $CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2PNMe_2$ (**11**)[12] and $[(2,6\text{-Me}_2C_6H_3O)PN\text{-}t\text{-Bu}]_2$ (**12**)[13] were prepared by the following literature procedures.

(a) Synthesis of $CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2P(O)NMe_2$ (13). To a solution of *tert*-butyl hydroperoxide (0.26 g, 2.89 mmol) in toluene (5 mL) was added a solution of **11** (0.8 g, 1.93 mmol) in toluene (10 mL) dropwise at 0 °C. The mixture was heated under reflux for 24 h and allowed to cool. Removal of the solvent under reduced pressure afforded a solid that was crystallized from a hexane/dichloromethane (1:4, 6 mL) mixture. Yield: 0.498 g (60%). Mp: 252−254 °C. IR (KBr, cm^{-1}): 2953, 1604, 1467, 1267, 1217, 1134, 927, 883. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 18H, *t*-Bu−*H*), 2.30 (s, 6H, Ar−C*H*$_3$), 3.02 (d, *J*(PH) = 10.4 Hz, 6H, N(C*H*$_3$)$_2$), 3.52 (d, *J*(HH) = 13.3 Hz, 1H, C*H*$_A$H$_X$), 4.32 (dd, *J*(PH) ~ 2.2 Hz, *J*(HH) ~ 13.0 Hz, 1H, CH$_A$*H*$_X$), 7.07−7.28 (m, 4H, Ar−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (s, Ar−*C*H$_3$), 31.7 (s, Ar−C(*C*H$_3$)$_3$), 34.3 (s, Ar−*C*H$_2$), 34.9 (s, Ar−*C*(CH$_3$)$_3$), 37.0 (d, *J*(P−C) = 4.0 Hz, N(*C*H$_3$)$_2$), 127.5, 128.8, 132.8 (d, *J*(P−C) = 2.0 Hz), 134.2, 141.2 (d, *J*(P−C) = 5.0 Hz), 145.5 (d, *J*(P−C) = 8.0 Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ 1.6. Anal. Calcd for $C_{25}H_{36}O_3NP$: C, 69.91; H, 8.45; N, 3.26. Found: C, 70.0; H, 8.44; N, 3.22.

(b) Mixed Crystal [11+13]. This was obtained from a 1:1 (molar ratio) mixture (total 0.200 g) of **11** and **13** in a toluene/hexane mixture (5:1, 7 mL) at 0−5 °C. Mp: 218−220 °C. The ^{1}H NMR spectrum showed a mixture of **11** and **13** and was complex, as expected. ^{31}P NMR (160 MHz, $CDCl_3$): δ 144.3 and 1.6 (cf. Figure 2c).

(c) Synthesis of $CH_2(6\text{-}t\text{-Bu-4-MeC}_6H_2O)_2P(S)NMe_2$ (14). Elemental sulfur (0.019 g, 0.592 mmol) was added to a solution of **11** (0.244 g, 0.590 mmol) in dry toluene (10 mL), and the solution was heated under reflux for 24 h. After removal of toluene, the solid obtained was crystallized from dichloromethane/hexane (1:1; excess sulfur could be removed by hand-picking). Yield: 0.176 g (67%). Mp: 188−190 °C. IR (KBr, cm^{-1}): 2961, 1615, 1472,

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(25) It should be noted that the peaks due to **17** are two doublets over which integration is taken.

(26) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, U.K., 1986.

Table 2. P−N and P−X Distances (Å) in **11**, **13**, **[11+13]**, **14**, **15**, and **[14+15]**

crystal	**11**	**13**	**[11+13]**	**14**	**15**	**[14+15]**[a]
P−N	1.640(2)	1.596(3)	1.608(3)	1.623(2)	1.620(2)	1.623(2)
P−O(ring)	1.659(1)	1.585(2)	1.615(2)	1.609(1) 1.615(1)	1.609(2) 1.615(2)	1.611(2) 1.615(2)
P═X		1.440(2)	1.402(4)	1.910(1)	2.059(1)	2.013(1)

[a] The corresponding distances (Å) when analyzed by keeping both sulfur and selenium in the P═X part and refining their occupancies (method b) are P−N 1.621(2) Å, P−O(ring) 1 1.612(2) and 1.614(2) Å, P−S 2.012(7) Å, and P−Se 2.013(3) Å.

Table 3. P−N and P−O Distances (Å) in **12**, **[16+17]a**, **[16+17]b**, **[16+17]c**, and **16**

crystal	**12**	**[16+17]a**	**[16+17]b**	**[16+17]c**	**16**
P1−N1	1.694(2)	1.684(3)	1.683(2)	1.674(6)	1.666(2)
P3−N3				1.691(6)	1.676(2)
P1−N2	1.715(2)	1.700(3)	1.692(2)	1.680(6)	1.681(2)
P3−N4				1.684(6)	1.669(2)
P1−O1	1.658(2)	1.627(2)	1.613(2)	1.597(5)	1.578(2)
P3−O5				1.591(5)	1.584(2)
P1−O3		1.337(6)	1.387(4)	1.434(6)	1.448(2)
P3−O7				1.441(6)	1.450(2)
P2−N1	1.701(2)	1.680(3)	1.679(2)	1.674(6)	1.672(2)
P4−N3				1.665(6)	1.669(2)
P2−N2	1.713(2)	1.768(3)	1.670(2)	1.676(5)	1.668(2)
P4−N4				1.680(6)	1.673(2)
P2−O2	1.656(2)	1.607(2)	1.601(2)	1.597(5)	1.583(2)
P4−O6				1.595(5)	1.583(2)
P2−O4		1.426(3)	1.436(3)	1.438(6)	1.450(2)
P4−O8				1.452(6)	1.453(2)

1364, 1262, 1211, 1134, 1109. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 18H, *t*-Bu−*H*), 2.32 (s, 6H, Ar−C*H*$_3$), 3.12 (d, *J*(PH) = 11.4 Hz, 6H, N(C*H*$_3$)$_2$), 3.46 (d, *J*(HH) = 13.3 Hz, 1H, C*H*$_A$H$_X$), 4.15 (dd, *J*(PH) ~ 3.6 Hz, *J*(HH) ~ 13.0 Hz, 1H, CH$_A$*H*$_X$), 7.08−7.10 (m, 4H, Ar−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (s, Ar−*C*H$_3$), 31.7 (s, Ar−C(*C*H$_3$)$_3$), 34.9 (s, Ar−*C*H$_2$), 35.2 (s, Ar−*C*(CH$_3$)$_3$), 37.7 (d, *J*(PC) = 4.4 Hz), 127.7, 128.9, 133.3 (d, *J*(PC) = 3.4 Hz), 134.0, 141.3 (d, *J*(PC) = 5.4 Hz), 146.5. ^{31}P NMR (160 MHz, $CDCl_3$): δ 73.8. Anal. Calcd for $C_{25}H_{36}O_2NPS$: C, 67.38; H, 8.14; N, 3.14; S, 7.19. Found: C, 67.38; H, 8.18; N, 3.24; S, 7.17.

(d) Synthesis of CH_2(6-*t*-Bu-4-MeC_6H_2O)$_2$P(Se)NMe_2 (15). Selenium powder (0.087 g, 1.1 mmol) was added to a solution of **11** (0.228 g, 0.551 mmol) in dry toluene (10 mL), and the contents were heated under reflux for 24 h. After cooling, excess selenium was separated by filtration, and toluene was removed under reduced pressure. The solid obtained was crystallized from a dichloromethane/hexane mixture (1:1). Yield: 0.215 g (80%). Mp: 176−178 °C. IR (KBr, cm^{-1}): 2957, 1736, 1601, 1456, 1360, 1262, 1190, 1105, 997. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 18H, *t*-Bu−*H*), 2.32 (s, 6H, Ar−C*H*$_3$), 3.16 (d, *J*(PH) = 12.0 Hz, 6H, N(C*H*$_3$)$_2$), 3.46 (d, *J*(HH) = 12.9 Hz, 1H, C*H*$_A$H$_X$), 4.15 (dd, *J*(PH) ~ 3.4 Hz, *J*(HH) ~ 13.1 Hz, 1H, CH$_A$*H*$_X$), 7.08−7.10 (m, 4H, Ar−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (s, Ar−*C*H$_3$), 30.0 (s, Ar−*C*(CH$_3$)$_3$), 31.9 (s, Ar−C(*C*H$_3$)$_3$), 35.2 (s, Ar−*C*H$_2$), 38.0 (d, *J*(P−C) = 3.6 Hz), 127.8, 129.0, 133.4 (d, *J*(P−C) = 3.6 Hz), 134.0, 141.2 (d, *J*(P−C) = 6.1 Hz), 147.0 (d, *J*(P−C) = 7.3 Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ 81.3 (d, *J*(PSe) = 942.8 Hz). Anal. Calcd for $C_{25}H_{36}O_2NPSe$: C, 60.97; H, 7.37; N, 2.84. Found: C, 60.91; H, 7.38; N, 2.68.

(e) Mixed Crystal [14+15]. This was obtained from a mixture of **14** (0.0117 g, 0.026 mmol) and **15** (0.013 g, 0.026 mmol) in dichloromethane/hexane (1:3, total 8 mL) by slow evaporation of the solvent. Mp: 172−174 °C. IR (KBr, cm^{-1}): 2961, 1615, 1472, 1364, 1262, 1211, 1134, 1109. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 18H, *t*-Bu−*H*), 2.32 (s, 6H, Ar−C*H*$_3$), 3.12 (d, *J*(PH) = 11.4 Hz, 6H, N(C*H*$_3$)$_2$), 3.46 (d, *J*(HH) = 13.3 Hz, 1H, C*H*$_A$H$_X$), 4.15 (dd, *J*(PH) ~ 3.6 Hz, *J*(HH) ~ 13.0 Hz, 1H, CH$_A$*H*$_X$), 7.07−7.08 (m, 4H, Ar−*H*). ^{31}P NMR: δ 73.8 and 81.3 (2 s, 1.3:1).

(f) Synthesis of [(2,6-$Me_2C_6H_3O$)P(O)N-t-Bu]$_2$ (16). To a stirred solution of cyclophosphazane **12** (0.44 g, 1 mmol) in toluene (10 mL) was added dropwise at 0 °C *tert*-butyl hydroperoxide (0.44 g, 5 mmol) in toluene (5 mL). The mixture was heated under reflux for 24 h and allowed to cool to room temperature. Removal of the solvent under reduced pressure afforded a solid that was crystallized from a hexane/dichloromethane (1:4, 6 mL) mixture. Yield: 0.31 g (68%). Mp: 210−212 °C. IR (KBr, cm^{-1}): 2980, 2934, 1684, 1475, 1277, 1165, 655, 949, 775. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 18H, *t*-Bu−*H*), 2.57 (s, 12H, Ar−C*H*$_3$), 7.04−7.09 (m, 6H, Ar−*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5 (s, Ar−*C*H$_3$), 30.3 (s, N−C(*C*H$_3$)$_3$), 56.6 (s, N−*C*(CH$_3$)$_3$), 125.3, 129.3, 130.4, 148.4 (d, *J*(P−C) = 9.7 Hz). Anal. Calcd for $C_{24}H_{36}O_4P_2N_2$: C, 60.23; H, 7.58; N, 5.85. Found: C, 60.15; H, 7.60; N, 5.87.

(g) Mixed Crystals [16+17]a, [16+17]b, and [16+17]c. When the tricoordinate compound **12** was treated with an equimolar quantity of DIAD in THF, the major product was **17** (^{31}P NMR) along with ca. 10% of the bis-oxidized product **16**. After removal of the solvent, the mixture was subjected to column chromatography [ethyl acetate (2%) in hexane] to separate the non-phosphorus components. The solid material obtained was crystallized from a mixture of toluene and hexane with traces of ethyl acetate to obtain crystals of **[16+17]a**.

When a 2:1 molar ratio of *tert*-butyl hydroperoxide/phosphazane was used for the reaction given in section f, mixed crystals of **[16+17]b** were obtained. ^{31}P NMR (160 MHz, $CDCl_3$): δ −6.0 (fully oxidized, **16**), 2.1 and 106.3 (d each, *J* ~ 11.5 Hz, monooxidized **17**). Use of a 3:1 molar ratio of *tert*-butyl hydroperoxide/phosphazane produced mixed crystals of **[16+17]c**.

(h) Attempted Synthesis of Mixed Crystals Containing 12 and 16. A mixture of **12** (0.446 g, 1.0 mmol) and **16** (0.478 g, 1.0 mmol) was dissolved in a set of solvents separately (dichloromethane, acetonitrile, toluene, hexane, ethyl acetate, or a combination) in an effort to get the mixed crystals of **12** and **16**. Each time, the individual compounds crystallized separately (unit cell dimensions + ^{31}P NMR).

(i) X-ray Crystallography. X-ray data were collected on an Enraf-Nonius-MACH3 at 293 K (**12**) or a Bruker AXS SMART diffractometer at 293 K (other crystals) using Mo Kα (λ = 0.710 73 Å) radiation and capillary mounting. The structures were solved by direct methods and refined by full-matrix least-squares methods using standard procedures.[27] Absorption corrections were done using the *SADABS* program, where applicable. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a difference Fourier and refined isotropically. In the structures of **11** and **13**, only a half-molecule is present in the asymmetric unit and the two methyl groups attached to the nitrogen seem to be disordered about the mirror plane; hence, a suitable disorder model was used. For the mixed crystal, the aspect

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[27] (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996. (b) Sheldrick, G. M. *SHELXTL NT, Crystal Structure Analysis Package*, version 5.10; Bruker Analytical X-ray System: Madison, WI, 1999.

regarding occupancy of oxygen was fairly clear. The refinement for **11** and **[11+13]** was carried out using the respective *hkl* files and the fixed *ins* files from **13**. For the mixed crystal **[14+15]**, refinement with the full occupancy of selenium showed a poorer result ($R = 0.0703$) than the refined occupancy of selenium ($R = 0.0377$). The occupancy assuming only the presence of selenium is 0.7. To avoid confusion regarding the presence of sulfur, we have included sulfur and refinement was carried out isotropically (to alleviate the nonpositive definite problem). We have done this after confirmation of the presence of sulfur in **[14+15]**, from our ^{31}P NMR studies.

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Supporting Information Available: X-ray crystallographic data in CIF format for all of the structures reported here, additional ORTEP drawings, and selected packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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