in native laccase. The similar optical absorption spectra associated with the two intermediates (vide supra) despite the difference in their reduction state suggests that the absorption features are not directly associated with the oxygen intermediates per se but arise from a similarly perturbed trinuclear Cu site, i.e., with respect to Cu oxidation states or ligand binding mode.

Another difference between the two intermediates is that native but not T1Hg laccase exhibits a broad EPR signal observable at liquid He temperature. This is consistent with the extra reducing equivalent derived from the type 1 Cu(I) in native laccase. The signal is further broadened when reduced laccase is oxidized by [^{17}O]dioxygen,[10b] suggesting that it is associated with an oxygen radical, and it has been assigned to O$^{•-}$ on the basis of its rapid electron spin relaxation, the assumed transfer of three electrons to dioxygen,[8] and the uptake of two protons concomitant to its formation.[36] However, note that the significant divergence of the lowest *g* value of this signal (1.7) from 2.0 is not consistent with this assignment to an O$^{•-}$ species, which would not have sufficient orbital angular momentum due to the low spin-orbit coupling constant of oxygen. Also it cannot arise from a magnetically isolated tetragonal Cu(II) ion,[37] because a system with a $d_{x^2-y^2}$ ground state cannot exhibit *g* values below 2.0. However, it does show some similarity to the triplet state EPR spectra associated with a pair of dipolar-coupled $S = ^1/_2$ centers;[38] such signals can arise from Cu(II) dimers and have been observed upon N$_3^-$-induced uncoupling of the type 3 site in native[4] and met T2D laccase.[24] Thus, although the absence of the EPR signal in T1Hg is consistent with the formulation of this intermediate as an even-electron species, the assignment of the intermediate EPR

signal in native laccase to O$^{•-}$ requires detailed spectral study.

In summary, it is clear that the type 2 Cu is required for dioxygen reactivity in laccase and that dioxygen reduction occurs in the absence of the type 1 Cu. This demonstrates that the type 2-type 3 trinuclear Cu site represents the active site for the binding and multielectron reduction of dioxygen. Previous observation that N$_3^-$ can bind as a bridging ligand between the type 2 and type 3 sites[4] suggests that a similar binding mode may be relevant to the reactivity of the trinuclear site with dioxygen. The type 1 Cu is clearly not necessary for reactivity with dioxygen, and in its absence, an intermediate is formed that shares some properties with the oxygen intermediate previously described in native laccase. Spectroscopic characterization of the oxygen intermediates in native and T1Hg laccase and X-ray edge determination of the associated Cu redox states should provide a detailed description of the mechanism of the irreversible multielectron reduction of dioxygen to water catalyzed by the multicopper oxidases.

(36) Reinhammar, B. *Chem. Scr.* **1985**, *25*, 172-176.
(37) MCD and CD studies of T1Hg laccase in the ligand field region indicate that the type 2 and type 3 sites in T1Hg have tetragonal effective geometries.[22]
(38) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173-278.

Heterocyclic 1,2,4,6-Thia- and 1,2,4,6-Selenatriazinyl Radicals. Spin Distributions and Modes of Association

Ketut Bestari,[1a] **A. Wallace Cordes,**[*,1b] **Richard T. Oakley,**[*,1a] **and Kelly M. Young**[1a]

Contribution from the Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, 72701. Received August 14, 1989

Abstract: Synthetic routes to the heterocyclic 1-chloro-1,2,4,6-thia- and -selenatriazines [(Ph$_2$P)$_{2-x}$(PhC)$_x$N$_3$ECl] (*x* = 0, 1; E = S, Se) have been developed. For *x* = 0 the method involves the coupling of [ClPh$_2$PNPPh$_2$Cl]$^+$Cl$^-$ with the N,N'-disilylated diimides Me$_3$SiNENSiMe$_3$ (E = S, Se), while for *x* = 1 the preparation uses the condensation of (Me$_3$Si)$_2$NPN(Ph)CNSiMe$_3$ with either SCl$_2$ or SeCl$_4$. Reduction of the 1-chloro derivatives with triphenylantimony affords the thia- and selenatriazinyl radicals [(Ph$_2$P)$_{2-x}$(PhC)$_x$N$_3$E]$^•$, all of which have been characterized by ESR spectroscopy. Hyperfine coupling constant data are interpreted in the light of MNDO calculations on model structures. X-ray structural analysis of the radical dimers [Ph$_2$(tol)PCN$_3$S]$_2$ and [Ph$_3$PCN$_3$Se]$_2$·CH$_3$CN reveals significantly different modes of association; for the sulfur-based radical, association occurs through a long (average (range) = 2.489 (9) Å) sulfur–sulfur bond, while in the selenium species the dimer pair is coupled by a selenium–nitrogen linkage, the structural parameters within the two rings resembling those expected for a charge-transfer interaction.
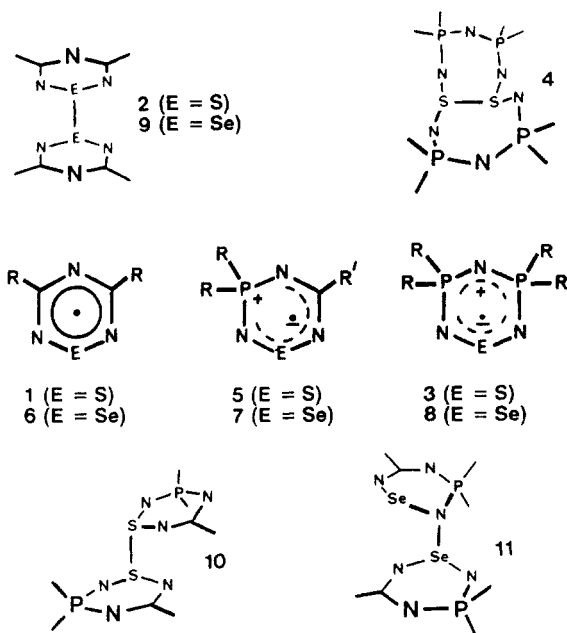
Many of the recent advances in the chemistry of sulfur nitrogen compounds have stemmed from the study of radical species.[2]

Interest has focused on the use of such compounds in the design of synthetic metals,[3] and also on how radical association can

(1) (a) University of Guelph. (b) University of Arkansas.

(2) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.

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Chart I

Table I. Hyperfine Coupling Constants (mT) and g Values in Thia- and Selenatriazinyls

	$[Ph_2C_2N_3E]^{\cdot}$		$[Ph_3PCN_3E]^{\cdot a}$		$[Ph_4P_2N_3E]^{\cdot}$	
E	S^b	Se^c	S	Se	S	Se
g	2.0059	2.0169	2.0064	2.0171	2.0058	2.0156
$a(N2)$	0.397	0.430	0.555	0.630	0.410	0.480
$a(N4)$	0.397	0.380	0.111	0.141	0.000	0.000
$a(N6)$	0.397	0.430	0.187	0.186	0.410	0.480
$a(P)$			0.420	0.544	0.050	0.259

[a] Data obtained from 5-C_6D_5 derivative. [b] Data from ref 6. [c] Data from ref 13.

provide pathways for structural change.[2,4,5] As part of our work on both topics, we have been studying the properties of heterocyclic radicals based on the 7π-electron 1,2,4,6-thiatriazinyl framework (Chart I).[6-8] A variety of systems with similar topology, but with quite different electronic structures and chemistry, has emerged. The primary system **1** can been generated with a wide range of R groups[6,9] and is stable to oxidation to a 6π-electron cation and reduction to an 8π-electron anion.[10] ESR studies reveal a uniform spin distribution around the ring, with minimal spin leakage onto the exocyclic ligands. In the solid state, **1** (R = Ph) associates to the eclipsed dimer **2** in which the closest interannular contact is a long (2.666 Å) sulfur–sulfur "bond". Replacement of both endocyclic carbons in **1** by phosphorus affords the thiadiphosphatriazinyl system **3**. Preliminary ESR data for **3** (R = Ph) suggest a heavily localized spin distribution, indicative of the dipolar formulation shown.[8] Like **1**, **3** forms a dimer in the solid state, but the structure of dimer **4** is not the simple cofacial arrangement typified by **2**. Instead the cyclic framework of **3** is cleaved as two six-membered rings mutate into a single twelve-membered ring possessing a transannular sulfur–sulfur (2.385 (1) Å) contact.[11]

The marked structural dichotomy represented by **2** and **4** has prompted us to explore the entire range of phosphorus-containing heterocyclic radicals based on the thiatriazinyl and selenatriazinyl frameworks. Our aim has been to investigate how variations in

electronic structure (RC vs R_2P and S vs Se) and steric bulk can influence spin distributions and modes of association. In the present paper we provide a comprehensive account of the preparation and ESR analysis[12] of 1,2,4,6-thiatriazinyls **1**, **3**, and **5** (R = R' = Ph) and the corresponding 1,2,4,6-selenatriazinyls **6–8** (R = R' = Ph). Within this latter group only the purely carbon based system, i.e., **6** and its dimer **9**, have hitherto been reported.[13] The molecular structures of **10** (R = Ph, R' = tol) and **11** (R = R' = Ph), the radical dimers of **5** and **7**, are also described.

Results and Discussion

Preparation of $R_2R'PCN_3ECl$ (E = S, Se). 1-Chloro-1,2,4,6-thiatriazines can be prepared in several ways,[2] the most convenient being the condensation of an imidoylamidine, or its hydrochloride, with SCl_2.[13] 1-Chloroselenatriazines can be obtained similarly with $SeCl_4$, although more forcing conditions are required to effect complete elimination of HCl.[13] The corresponding thia- and selenatriazinyls **1** and **6** can then be generated by reduction, typically with triphenylantimony. Our proposed synthetic route to the mixed thia- and selenaphosphatriazine ring system was developed as an extension of this condensation approach, this time using the persilylated phosphimidoylamidine **12** (eq 1). Ex-

$$(1)$$
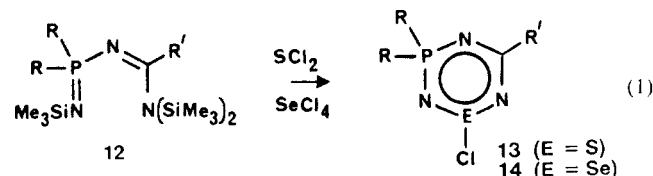
periment fulfilled expectation; the reaction of **12** (R = R' = Ph; R = Ph, R' = tol) with SCl_2 provides the required 1-chloro-1,3,2,4,6-thiaphosphatriazine **13**, while with $SeCl_4$ the corresponding 1-chloroselenaphosphatriazine **14** (R = R' = Ph) is produced. Both reactions proceed in high (>80%) yield.

Preparation of $R_4P_2N_3ECl$ (E = S, Se). 1-Chloro-1,3,5,2,4,6-thiadiphosphatriazines have been known for some time; the chloro (R = Cl) and phenyl (R = Ph) derivaties can both be prepared by the reaction of S_4N_4 with the appropriate R_2PCl compound.[14] The method, however, cannot be readily extended to selenium chemistry.[15] We have therefore sought a preparative route suitable for both $R_4P_2N_3ECl$ (**15**, E = S; **16**, E = Se). This proved to be a nontrivial task; while sulfur dichloride can be condensed with both $[NH_2(Ph_2)PN(Ph_2)PNH_2]^+Cl^-$ and $Me_3SiNPN(H)PNSiMe_3$[16] to afford $Ph_4P_2N_3SCl$ in good yield, similar condensations with $SeCl_4$ fail to give $Ph_4P_2N_3SeCl$.[17]

(3) (a) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* **1984**, 573. (b) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T.; Sutcliffe, L. H. *Synth. Met.* **1986**, *14*, 239. (c) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O., Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594. (d) Wolmershäuser, G.; Wortmann, G.; Schnauber, M. *J. Chem. Res. Synop.* **1988**, 358. (e) Del Bel Belluz, P.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276. (f) Wolmershäuser, G.; Johann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 920.

(4) (a) Burford, N.; Passmore, J.; Schriver, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 140. (b) Brooks, W. V. F.; Burford, N.; Passmore, J.; Schriver, M.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 69.

(5) (a) Bestari, K.; Cordes, A. W.; Oakley, R. T. To be published. (b) Bestari, K. M. S. Thesis, University of Guelph, 1988.

(6) Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346.

(7) Boeré, R. T.; Oakley, R. T.; Reed, R. W.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1180.
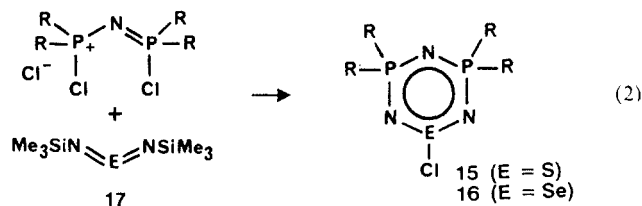
(8) Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 596.

(9) Markovskii, L. N.; Kornuta, P. P.; Katchkovskaya, L. S.; Polumbrik, P. M. *Sulfur Lett.* **1983**, *1*, 143.

(10) Boeré, R. T.; Cordes, A. W.; Hayes, P. J.; Oakley, R. T.; Reed, R. W. *Inorg. Chem.* **1986**, *25*, 2445.

(11) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

(12) For a preliminary account of part of this work, see: Cordes, A. W.; Koenig, H.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1989**, 710.

(13) Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745.

(14) (a) Chivers, T.; Rao, M. N. S. *Inorg. Chem.* **1984**, *23*, 3605. (b) Chivers, T.; Rao, M. N. S. *Inorg. Synth.* **1989**, *25*, 40.

(15) Perhaps as a result of its tendency to detonate, the chemistry of Se_4N_4 has only recently been explored. See, for example: (a) Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 408. (b) Adel, J.; El-Kholi, A.; Willing, W.; Muller, U.; Dehnicke, K. *Chimia* **1988**, *42*, 70.

(16) This compound (δ(P) = 11.3) can be made in situ by the reaction of $Ph_2PN(H)PPh_2$ with trimethylsilyl azide in toluene at 100 °C.

(17) $[NH_2(Ph_2)PNP(Ph_2)NH_2]^+Cl^-$ condenses with a variety of transition-metal halides (e.g., WCl_6) to give the heterocyclic systems (e.g., $Ph_4P_2N_3WCl_3$); see: Katti, K. V.; Roesky, H. W.; Rietzel, M. *Inorg. Chem.* **1987**, *26*, 4032.

Eventually we pursued the use of the well-known N,N'-bis(trimethylsilyl)sulfur diimide ($Me_3SiNSNSiMe_3$ (17, E = S)) and its recently reported[18] selenium analogue $Me_3SiNSeNSiMe_3$ (17, E = Se) as coupling reagents with the bis(chlorodiphenylphosphine)iminium salt [ClPh$_2$PNPPh$_2$Cl]$^+$Cl$^-$ (eq 2). This

$$
\begin{array}{c}
\text{[structure: R—P}_+\text{ with R, N, P—R, Cl}^-, \text{Cl, Cl, +]} \\
\text{Me}_3\text{SiN}\diagdown_E\diagup\text{NSiMe}_3 \\
\text{17}
\end{array}
\longrightarrow
\begin{array}{c}
\text{[ring structure: R—P, N, P—R, N, N, E, Cl]} \\
\text{Cl 15 (E = S)} \\
\text{16 (E = Se)}
\end{array}
\qquad (2)
$$

approach proved to be surprisingly effective for both the sulfur and selenium systems 15 and 16, the latter preparation working in spite of the thermal instability of $Me_3SiNSeNSiMe_3$ and the consequent need to use (impure) material prepared in situ.[19] In view of the success of this particular reaction, it is interesting to speculate to what extent the extensive chemistry of $Me_3SiNSNSiMe_3$ can be replicated by $Me_3SiNSeNSiMe_3$.

Generation and ESR Spectra of Radicals. All of the thia- and selenatriazines 13–16 described above can be reduced by triphenylantimony in oxygen-free methylene chloride to give strong and persistent ESR signals of the correponding thia- and selenatriazinyls 3, 5, 7, and 8.[20] There are some systematic variations in signal intensity, g value, and line width as a function of electronic structure. Thus, replacement of carbon by phosphorus and of sulfur by selenium both lead to weaker ESR signals, presumably as a result of stronger radical/radical interactions. In an earlier paper we assessed this trend quantitatively for 1 and 6.[13] Replacement of sulfur by selenium also has the predictable effect of increasing line widths and g values (Table I).

Initial attempts to analyze the ESR spectra of [Ph$_3$PCN$_3$E]$^\bullet$ 5 and 7 (R = R′ = Ph) were hindered by slight spin leakage onto the C-phenyl group, which led to additional hyperfine splitting of an already complex spectrum.[12,21] In order to simplify the spectrum, we prepared (starting from C_6D_5CN, see Experimental Section) samples of 5 and 7 in which the 5-phenyl group (R′) was fully deuteriated. The ESR spectra of these deuteriated derivatives are shown in Figure 1. Hyperfine coupling constants (Table I) to phosphorus $a(P)$ and nitrogen $a(N)$ were obtained by full spectral simulation. Analysis of the ESR spectra of [Ph$_4$P$_2$N$_3$E]$^\bullet$ 3 and 8 (Figure 1) was more straightforward. The presence of a molecular plane of symmetry and the apparent lack of coupling to N4 reduced the simulation problem to only two variables; the hyperfine coupling data provided in Table I for these two radicals were nonetheless confirmed by spectral simulation.

Spin and Charge Distributions in [(Ph$_2$P)$_{2-x}$(PhC)$_x$N$_3$E]$^\bullet$ (E = S, Se; x = 0–2). ESR hyperfine coupling constant data for both the sulfur (1, 3, 5) and selenium (6–8) based radicals are compiled in Table I. Interpretation of the data in terms of variations in electronic structure is facilitated by comparison with spin densities (ρ) and net ($\sigma + \pi$) atomic charges (q) obtained from restricted Hartree–Fock (RHF) MNDO calculations on a series of model thiatriazinyl radicals (R = R′ = H). The results (Figure 2), particularly the differences in the charge densities at carbon and phosphorus, illustrate how the delocalized [H$_2$C$_2$N$_3$S]$^\bullet$ radical evolves to the highly polarized zwitterionic structure of [H$_4$P$_2$N$_3$S]$^\bullet$. Consistent with the internal salt description for the latter species, the $a(N)$ values are of the same magnitude as those found in simple acyclic sulfur diimide radical anions [RNSNR]$^{\bullet-}$.[22]

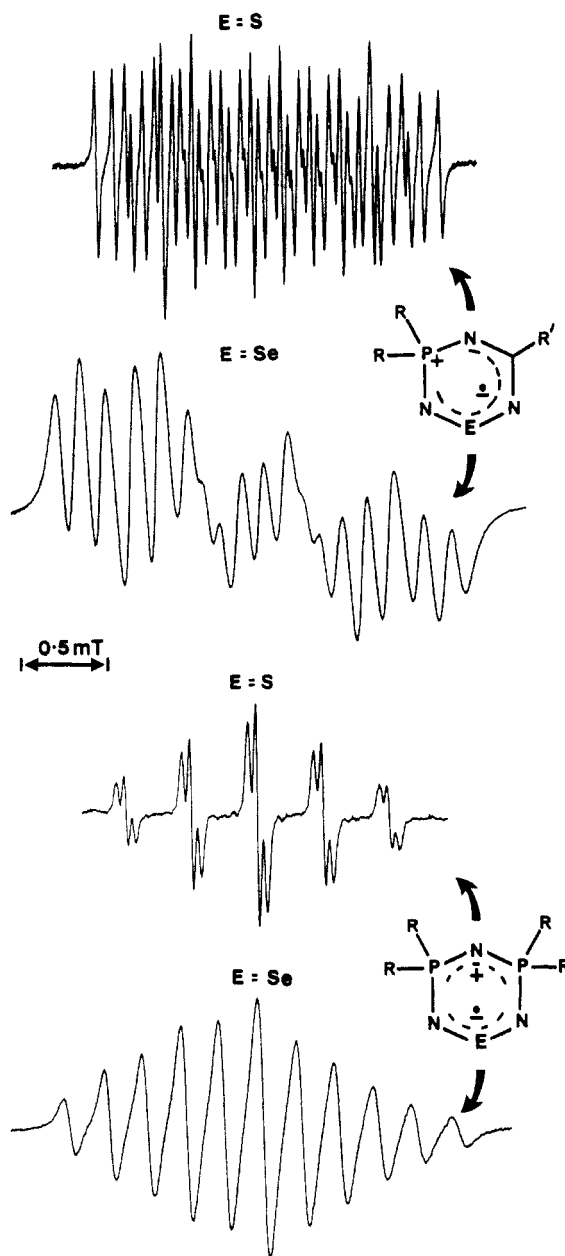Figure 1. ESR spectra of 5 and 7 (R = C_6H_5, R′ = C_6D_5) and 3 and 8 (R = C_6H_5).

In the hybrid system [H$_3$PCN$_3$S]$^\bullet$ both the spin densities and atomic charges suggest a saltlike formulation, with spin density increasing along the nitrogen sites from N4 to N6 to N2; indeed, given the limited capability of the MNDO method to model hypervalent phosphorus, the calculated spin densities concur remarkably well with the observed nitrogen hyperfine coupling constants, $a(N)$. The high spin densities at sulfur are likewise reflected in the deviation of the g values from the free-electron value. The calculated spin density at carbon in [H$_3$PCN$_3$S]$^\bullet$ is significantly greater than in [H$_2$C$_2$N$_3$S]$^\bullet$, thus accounting for the more extensive spin leakage onto the C-phenyl groups of 5 and 7.

We have been unable, within the confines of the MNDO method, to examine in detail the electronic effects of replacement of sulfur by selenium. The ESR data can nonetheless be interpreted qualitatively with simple perturbation arguments based on the expected differences in electronegativity of sulfur and selenium. In short, sulfur appears to be a better acceptor of spin density than selenium; as a result, the coupling constants $a(N)$

(18) Fockenberg, F.; Haas, A. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1986, 41b, 413.

(19) The structural parameters of Ph$_4$P$_2$N$_3$SeCl have been determined by X-ray crystallography. See: Cordes, A. W.; Bestari, K.; Oakley, R. T. Acta Crystallogr., in press.

(20) The selenium-based radical 8 is the least stable. Solutions of this radical slowly deposit a red precipitate of amorphous selenium. Attempts to isolate a dimer of this species were unsuccessful.

(21) Proton ENDOR spectroscopy and ESR simulation experiments for 5, R′ = C_6H_5, revealed coupling to three exocyclic protons with $a(H) = 0.035$ mT.

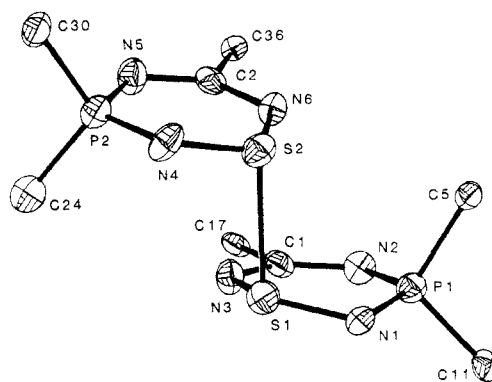(22) Hunter, J. A.; King, B.; Lindsell, W. E.; Neish, M. A. J. Chem. Soc., Dalton Trans. 1980, 880.
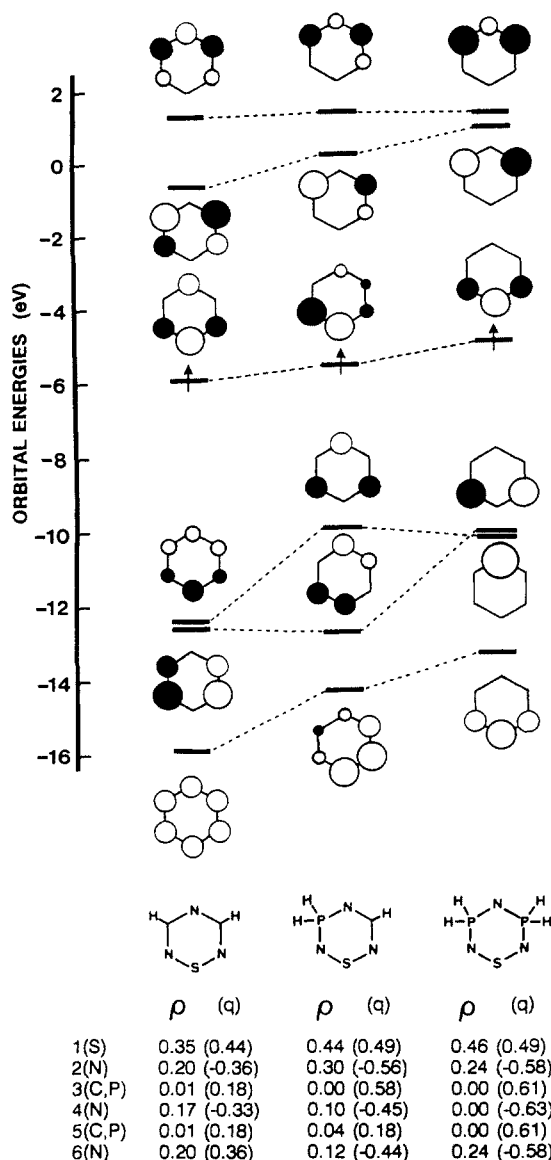
Figure 2. MNDO π-molecular orbital energies and distributions for **1, 5,** and **3** (R = R′ = H). Hyperconjugative out-of-phase PH$_2$ σ-combinations are not shown. Spin (ρ) and total ($\sigma + \pi$) charge (q) densities shown below.

	ρ	(q)	ρ	(q)	ρ	(q)
1(S)	0.35	(0.44)	0.44	(0.49)	0.46	(0.49)
2(N)	0.20	(-0.36)	0.30	(-0.56)	0.24	(-0.58)
3(C,P)	0.01	(0.18)	0.00	(0.58)	0.00	(0.61)
4(N)	0.17	(-0.33)	0.10	(-0.45)	0.00	(-0.63)
5(C,P)	0.01	(0.18)	0.04	(0.18)	0.00	(0.61)
6(N)	0.20	(0.36)	0.12	(-0.44)	0.24	(-0.58)

for nitrogens adjacent to selenium are raised relative to the a(N) values found in the corresponding sulfur-based radicals. The effect is least apparent in delocalized radicals **1** and **6**, as expected.

The relatively small a(P) values observed are typical of those found for four-coordinate phosphorus-containing radicals in which the phosphorus center represents a phosphonium cation rather than a neutral phosphoranyl unit.[23] For radicals such as **18**, which
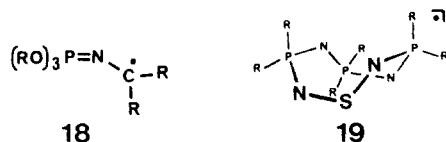
bear a close structural resemblance to those reported here, it is well recognized that the value of a(P) can be influenced by several factors, including (i) spin polarization in the P–N σ-bond, (ii) π-spin density at phosphorus, and (iii) torsional motion about the C–N bond leading to hyperconjugation with the P–N σ-bond. The

(23) See, for example: (a) Hay, R. S.; Roberts, B. P.; Singh, K.; Wilkinson, J. P. T. *J. Chem. Soc., Perkin Trans. 2* **1979,** 756. (b) Scheffler, K.; Hieke, S.; Haller, R.; Stegman, H. B. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1975,** *30a,* 1175. (c) Davies, A. G.; Parrot, M. J.; Roberts, B. P.; *J. Chem. Soc., Chem. Commun.* **1974,** 973.

Figure 3. ORTEP drawing of one (of two unique) molecule of **10** (R = C$_6$H$_5$, R′ = C$_6$D$_5$) showing the atom-numbering scheme.
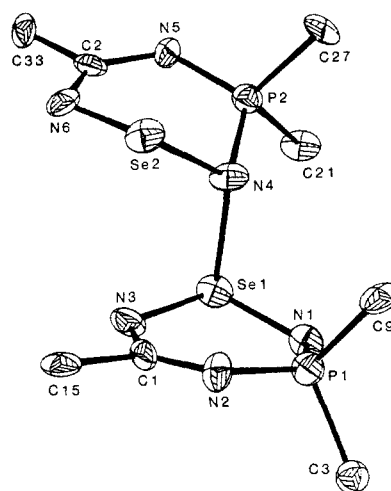
Figure 4. ORTEP drawing of **11** (R = R′ = C$_6$H$_5$) showing the atom-numbering scheme.

significant variation in the a(P) value in the present systems is most probably a result of changes in the degree of hyperconjugation rather than polarization or π-effects; in essence, the value of a(P) can be viewed as a measure of the distortion from planarity of the heterocyclic ring. Consistently, the a(P) value found in the puckered eight-membered heterocyclic radical **19**, in which spin polarization and π-effects are expected to be similar to **3**, is much larger (2.45 mT) than those of any of the six-membered radicals.[24]

In summary, the extent of spin delocalization in heterocyclic thia- and selenatriazinyl radicals is restricted to the CNS backbone. Conjugation to include phosphorus is severely limited, the observed spin distributions giving little direct evidence of a genuine π-effect.[25]

Solid-State Structures of [Ph$_2$(tol)PCN$_3$S]$_2$ and [Ph$_3$PCN$_3$Se]$_2$·CH$_3$CN. Attempts to obtain crystallographic data from the dimer of [Ph$_3$PCN$_3$S]* (**5,** R = R′ = Ph) were fruitless; the compound was amorphous to X-rays. We therefore prepared (see the Experimental Section) a modified derivative with a tolyl group rather than a phenyl group at the 5-position. This slight change afforded a crystalline dimer, the structure of which has been determined by X-ray diffraction. Compound **10** crystallizes in the triclinic space group $P\bar{1}$ with two dimers per asymmetric unit. The conformational and structural features of these two dimers, however, are very similar, and for present purposes we restrict our discussion to the average of these units. A compilation of pertinent bond lengths and angles is provided in Table II. Structural data for the other dimer are deposited with the sup-

(24) Bestari, K.; Cordes, A. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1988,** 1328.

(25) There is some ESR evidence for spin delocalization across a spirocyclic four-coordinate phosphorus atom. See: Haddon, R. C.; Mayo, S. L.; Chichester, S. V.; Marshall, J. L. *J. Am. Chem. Soc.* **1985,** *107,* 7585.

**Table II.** Selected Bond Lengths (Å) and Angles (deg) with Esd's

[Ph$_2$(tol)PCN$_3$S]$_2$		[Ph$_3$PCN$_3$Se]$_2$·CH$_3$CN	
		Distances	
S(1)-S(2)	2.481 (3)	Se(1)-N(4)	1.990 (13)
S(1)-N(1)	1.611 (5)	Se(1)-N(1)	1.736 (15)
S(1)-N(3)	1.606 (6)	Se(1)-N(3)	1.743 (15)
S(2)-N(4)	1.600 (5)	Se(2)-N(4)	1.888 (13)
S(2)-N(6)	1.588 (6)	Se(2)-N(6)	1.83 (2)
P(1)-N(1)	1.614 (5)	P(1)-N(1)	1.628 (13)
P(1)-N(2)	1.611 (6)	P(1)-N(2)	1.594 (15)
P(2)-N(4)	1.633 (6)	P(2)-N(4)	1.654 (14)
P(2)-N(5)	1.604 (6)	P(2)-N(5)	1.565 (15)
N(2)-C(1)	1.32 (2)	N(2)-C(1)	1.340 (8)
N(3)-C(1)	1.36 (2)	N(3)-C(1)	1.331 (8)
N(5)-C(2)	1.36 (2)	N(5)-C(2)	1.322 (8)
N(6)-C(2)	1.31 (2)	N(6)-C(2)	1.348 (8)
		Angles	
S(1)-S(1)-N(1)	102.82 (3)	N(4)-Se(1)-N(1)	101.7 (7)
S(2)-S(1)-N(3)	96.15 (3)	N(4)-Se(1)-N(2)	89.4 (7)
S(1)-S(2)-N(4)	102.50 (3)	Se(1)-N(4)-P(2)	118.7 (8)
S(1)-S(2)-N(6)	96.75 (3)	Se(1)-N(4)-Se(2)	118.4 (7)
N(1)-S(1)-N(3)	114.4 (3)	N(1)-Se(1)-N(3)	111.5 (7)
N(4)-S(2)-N(6)	115.4 (3)	N(4)-Se(2)-N(6)	103.4 (6)
N(1)-P(1)-N(2)	115.8 (3)	N(1)-P(1)-N(2)	117.5 (9)
N(4)-P(2)-N(5)	115.4 (3)	N(4)-P(2)-N(5)	115.7 (8)
S(1)-N(1)-P(1)	114.9 (3)	Se(1)-N(1)-P(1)	112.9 (8)
P(1)-N(2)-C(1)	120.1 (5)	P(1)-N(2)-C(1)	123 (1)
S(1)-N(3)-C(1)	122.1 (5)	Se(1)-N(3)-C(1)	117 (1)
S(2)-N(4)-P(2)	115.7 (3)	Se(2)-N(4)-P(2)	103.6 (7)
P(2)-N(5)-C(2)	121.4 (5)	P(2)-N(5)-C(2)	124 (1)
S(2)-N(6)-C(2)	122.4 (5)	Se(2)-N(6)-C(2)	115 (1)
N(2)-C(1)-N(3)	131 (2)	N(2)-C(1)-N(3)	128.9 (7)
N(5)-C(2)-N(6)	131 (2)	N(5)-C(2)-N(6)	128.3 (6)

plementary material. The structure of **11**, the dimer of [Ph$_3$PCN$_3$Se]$^\bullet$ (as its CH$_3$CN solvate), has also been determined, and pertinent positional and structural data for this compound are available in Table II. ORTEP drawings of the dimer units in [Ph$_2$(tol)PCN$_3$S]$_2$ (**10**) and [Ph$_3$PCN$_3$Se]$_2$·CH$_3$CN (**11**) are shown in Figures 3 and 4.

In the sulfur-based dimer **10**, the mode of association, i.e., through sulfur, is similar to that observed for **2**,[6] although the interannular S–S contact (the average of S1–S2 and S3–S4 is 2.489 Å) is somewhat shorter (2.666 Å in **2**). Also in contrast to **2** the two rings are not eclipsed. Instead, and probably to alleviate steric interactions caused by the presence of the phenyl groups on phosphorus, one ring rotates with respect to the other around the S–S contact to make an NSSN torsion angle of 84° (average of four values). Within the two PCN$_3$S rings the bond lengths and angles are comparable and similar to those found in the parent chloro derivative **10**.[12]

The structure of the selenium-based dimer **11** is markedly different, both from its sulfur analogue described above and dimer **9**,[13] which adopts a cofacial Se–Se structure similar to **2** with d(Se–Se) = 2.792 (3) Å. In **11** there is no formal Se–Se bond; instead the two rings are linked by a Se–N bond (Se1–N4 = (1.990 (13) Å). The mutual disposition of the rings, illustrated in Figure 4, is such that the four-atom sequence Se1–N4–Se2–N3 is almost coplanar (to within 0.06 Å). Within this sequence, the remaining interannular contact (Se2–N3) is 3.106 (15) Å. Both rings show marked deviations from planarity. Within the Se-bonding ring, the five-atom N–C–N–P–N sequence is planar to within 0.05 Å, with the selenium atom lying 0.410 Å out of this plane (toward N4). In the N-bonded ring the Se–N–C–N–P unit forms a near-planar sequence (to within 0.12 Å), with N4 tipped 0.82 (1) Å away (toward Se1). The geometry at the three-co-oordinate nitrogen N4, i.e., $\sum$(bond angles) = 340.7°, deviates substantially from sp^2 hybridization, but the extent of puckering falls short of that expected for a pure sp^3 configuration.

The two PCN$_3$Se rings in **11** have totally different structural features. The Se–N bonds of the N-bonded ring are much longer than in the Se-bonded ring, and the C=N(Se) bond is much shorter. Taken collectively, the endocyclic structural parameters are broadly consistent with electron transfer from one PCN$_3$Se

Scheme I
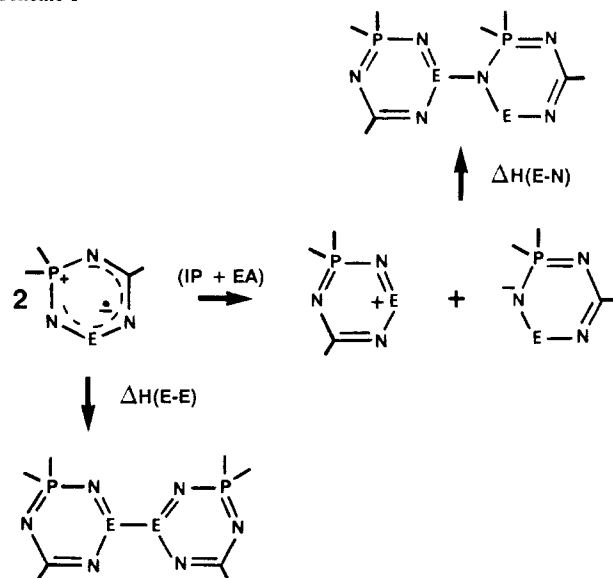
ring (Se-bonded) to the other (N-bonded); instead of the dimer unit being two loosely connected radicals, it more nearly resembles a cation/anion pair. In molecular orbital terms the gross structural features can be rationalized in terms of a simple model in which the SOMO of one ring is oxidized (to give a 6π-cation) while that of the other is reduced (to give an 8π-anion). In valence bond parlance, the resonance formulations shown in Scheme I reflect the observed endocyclic bond length variations surprisingly well. Similar structural differences have been observed between the 6π-cation **20** and the 8π-imide **21** (the disproportionation products of **1**).[10]

20   **21**
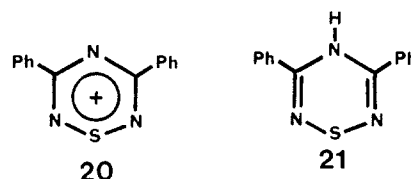
The above electronic description of the selenium-based dimer as a cation/anion pair allows some qualitative insight into the reason for the structural dichotomy observed for **10** and **11**. As illustrated in Scheme I, the energetics of heteronuclear association of two radicals (**5** or **7**) can be viewed as the net result of two steps, (i) the disproportionation of two radicals, i.e., the sum of the ionization potential (IP) and electron affinity (EA), and (ii) the subsequent formation of a donor–acceptor (E–N) bond between the cation and anion, here denoted by ΔH(E–N). This process must then be compared with the simple homonuclear association enthalpy ΔH(E–E). The strong ESR signals observed for both **5** and **7** indicate that ΔH(E–E) and [ΔH(E–N) + IP + EA] are small.

While the overall balance between the two modes of association clearly depends on several variables, the easiest to specify, and certainly the largest, is the IP of the radical.[26] On the basis of the ESR evidence outlined above, which suggests that selenium is slightly more electropositive than sulfur, we anticipate that **7** should have a slightly lower IP than **5**. The preference for the Se–N dimerization mode for **7** can then be viewed as a result of a more favorable (less endothermic) disproportionation energy. Increasing the IP of **7**, through judicious modification of the exocyclic R groups, may allow isolation of a Se–Se-coupled system. Reciprocally, decreasing the IP of **5** may favor a charge-transfer (S–N) dimer. Experiments to test this hypothesis are in progress.

(26) MNDO calculations on **1** (R = H)[10] indicate that the IP is the major contributor to the disproportionation energy. Measurements on the dissociation constants for **1** and **6**[13] suggest that, entropy effects notwithstanding, the Se–Se bond is very slightly stronger than the S–S bond.
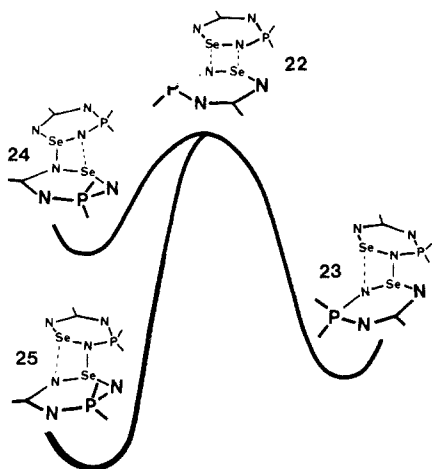
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Figure 5. Qualitative potential energy hypersurface for Se–N-bonded dimers of **7**.

Radical Association and Rearrangement. One of the major objectives of our ongoing studies of thia- and selenatriazinyl radicals has been to map out the relationships between electronic structure and mode of association. Our initial efforts were prompted in part by the early report of the structure of the dimer of **3**, which revealed the possibility of association with rearrangement (to **4**).[11] The result provided a direct analogy with the scrambling reaction of sulfur diimide radical anions (eq 3)[2,5]
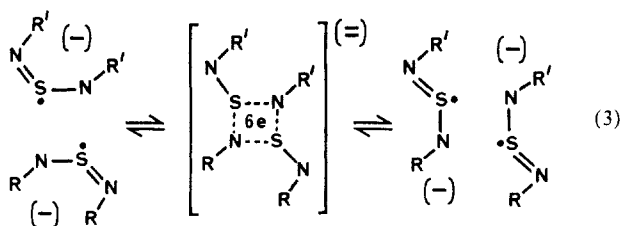
and further substantiated the description of **3** as an internal salt of a radical anion. In the case of the acyclic radical anion scrambling, the position of the equilibrium is determined by the nature of the groups R and R', while the expansion **3** to **4** is most probably driven by a release of ring strain.

In the present work we have sought to isolate and characterize dimers of the novel radicals **5**, **7**, and **8**. Our initial hope was to find a radical dimer whose structure mimicked to some degree the putative head-to-tail four-center transition state in eq 3. While the instability of the [Ph$_4$P$_2$N$_3$Se]$\cdot$ radical (with respect to decomposition to selenium) and the consequent difficulties in isolating a radical dimer for this species precluded completion of the desired "hat-trick", characterization of the two dimers **10** and **11** has successfully demonstrated how sensitive the preferred mode of binding for two radical units can be to minor electronic changes. In the context of the rearrangement shown in eq 3, the selenium dimer can be viewed as an example of a severely distorted four-center interaction between two radical anions. Qualitative consideration of the global potential energy hypersurface available to the undistorted arrangement **22** (Figure 5) reveals, however, several other distorted Se–N-bonded structures, i.e., **23** and **24**. The preference for observed structure **25** can be understood in terms of the charge-transfer model developed above. Accordingly, the most stable coupling modes should be those that involve the most negatively charged nitrogen (N2) on the anion, i.e., **23** and **25** as opposed to **24**.[27] Secondary interactions in **23** and **25** between a (donor) selenium of the anion ring can take place to two different (acceptor) nitrogens of the cation, N6 in **25** and N2 in **23**. The preference for **25** over **23** stems from the relative (electrostatic) acidities of these two sites; calculated MNDO

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(27) Structure **23** is directly accessible by distortion of the centrosymmetric four-center interaction **22**. Generation of the other two structures, **24** and **25**, requires that one ring of **22** be inverted with respect to the other.

charge densities on a model [H$_3$PCN$_3$S]$^+$ cation[28] confirm that N6 ($q = -0.45$) rather than N2 ($q = -0.56$) is the better acceptor.

Experimental Section

Starting Materials and General Procedures.[29] Benzonitrile (Aldrich), benzonitrile-d_5 (MSD), tolunitrile (Aldrich), chlorodiphenylphosphine (Aldrich), butyllithium (1.6 M in hexane, Aldrich), trimethylsilyl azide (Aldrich), hexamethyldisilazane (Aldrich), selenium powder (Alfa), sulfur dichloride (Aldrich), chlorine gas (Matheson), thionyl chloride (Aldrich), triphenylantimony (Aldrich), and selenium oxychloride (Alfa) were all commercial products; all were used as received, save thionyl and sulfur dichloride, both of which were freshly distilled before use. Acetonitrile (Fisher HPLC grade) was also freshly distilled from P$_2$O$_5$ before use. LiN(SiMe)$_2$·Et$_2$O,[30] Me$_3$SiNSNSiMe$_3$,[31] and Ph$_2$PN(H)PPh$_2$[32] were prepared according to standard literature methods. The N,N,N'-tris(trimethylsilyl)phosphimidoylamidine [(Me$_3$Si)N(Ph$_2$)PN(Ph)CN-(SiMe$_3$)$_2$, δ(P) = -3.6 (lit. -4.2)] was prepared as recently described,[33] i.e., by the reaction of benzonitrile with LiN(SiMe$_3$)$_2$ with PhCN and treatment of the so-formed amidine with Ph$_2$PCl to produce Ph$_2$PN-(Ph)CN(SiMe$_3$)$_2$, followed by in situ reaction of the latter intermediate with Me$_3$SiN$_3$. The product was crystallized from acetonitrile. Deuteriation of the phenyl group (at carbon) was achieved with benzonitrile-d_5. The corresponding C-tolylphosphimidoylamidine [(Me$_3$Si)N-(Ph$_2$)PN(tol)CN(SiMe$_3$)$_2$, mp = 95 °C, δ(P) = -4.0] was made in an analogous fashion from tolunitrile. Anal. Calcd for C$_{29}$H$_{44}$N$_3$PSi$_3$: C, 63.34; H, 8.06; N, 7.64. Found: C, 63.32; H, 8.09; 7.80. [ClPh$_2$PNPPh$_2$Cl]$^+$Cl$^-$ was prepared by direct oxidation of Ph$_2$PN(H)-PPh$_2$ with chlorine; ^{31}P NMR datum (δ(P) = 44.4) of the product so obtained was in agreement with the literature (δ(P) = 44.3).[34] The selenium diimide Me$_3$SiNSeNSiMe$_3$ was prepared from SeOCl$_2$ and LiN(SiMe$_3$)$_2$[18] and used in situ. All reactions and experimental manipulations were performed under an atmosphere of nitrogen or argon. NMR spectra were recorded (in CDCl$_3$ reference H$_3$PO$_4$ unless otherwise indicated) on a Bruker WH-400 spectrometer, and infrared spectra (1600–250-cm^{-1} region, CsI optics) were obtained on a Nicolet 20SX/C FTIR instrument. Chemical analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of Ph$_3$PCN$_3$SCl (13, R = R' = Ph). An excess (2 mL) of sulfur dichloride in 20 mL of CH$_3$CN was added slowly to a stirred solution of (Me$_3$Si)$_2$N(Ph$_2$)PN(Ph)CNSiMe$_3$ (1.4 g, 2.6 mmol) in 40 mL of acetonitrile. In the course of the addition the reaction mixture turned dark red and then golden yellow. The mixture was heated at reflux for 1 h, cooled to room temperature, and filtered. The filtrate was concentrated in vacuo to a volume of ca. 20 mL and cooled to -25 °C overnight. Subsequent filtration of this mixture afforded bright yellow blocks of Ph$_3$PCN$_3$SCl (0.81 g, 2.1 mmol, 81%) that were recrystallized from acetonitrile: dec > 157 °C; ^{31}P NMR δ(P) = 10.9; IR 1494 (w), 1438 (w), 1318 (s), 1256 (m), 1179 (m), 1119 (m), 1035 (m), 1022 (m), 749 (w), 730 (s), 703 (s), 682 (s), 543 (s), 488 (w), 377 (w) cm^{-1}. Anal. Calcd for C$_{19}$H$_{15}$N$_3$PSCl: C, 59.46; H, 3.94; N, 10.95; Cl, 9.24. Found: C, 59.26; H, 4.06; N, 10.70; Cl, 9.09. A sample of this material, fully deuteriated at the 5-position, was made on a small scale from (Me$_3$Si)$_2$N(Ph$_2$)PN(C$_6$D$_5$)CNSiMe$_3$ and SCl$_2$.

Preparation of Ph$_2$(tol)PCN$_3$SCl (13, R = Ph, R' = tol). This compound was made (in 69% yield) with a procedure identical with that described above for Ph$_3$PCN$_3$SCl from the reaction of SCl$_3$ and (Me$_3$Si)N(Ph$_2$)PN(tol)CN(SiMe$_3$)$_2$. Ph$_2$(tol)PCN$_3$SCl forms pale yellow crystalline blocks from acetonitrile: mp 165–70 °C; ^{31}P NMR δ(P) = 10.3; IR 1436 (m), 1405 (w), 1314 (m), 1296 (m), 1186 (m), 1125 (sh), 1115 (m), 1035 (m), 1016 (m), 934 (w), 882 (w), 814 (m), 740 (s), 692 (m), 540 (s), 520 (m), 490 (m), 446 (w), 397 (m) cm^{-1}. Anal. Calcd for C$_{20}$H$_{17}$N$_3$PSCl: C, 60.38; H, 4.31; N, 10.56; Cl, 8.91. Found: C, 60.11; H, 4.30; N, 10.56; Cl, 9.11.

Preparation of Ph$_3$PCN$_3$SeCl (14, R = R' = Ph). Selenium tetrachloride was prepared in situ by passing chlorine gas over a slurry of selenium powder (0.59 g, 7.5 mmol) in 35 mL of acetonitrile. A solution

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(28) In the absence of MNDO parameters for selenium, the calculation was performed on the sulfur-containing cation.

(29) The health hazards of the selenium compounds prepared in this work are not known. Caution should be exercised in handling these potentially toxic materials.

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Thia- and Selenatriazinyl Radical Spin Distributions

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of $(Me_3Si)_2N(Ph_2)PN(Ph)CNSiMe_3$ (4.0 g, 7.5 mmol) in 15 mL of acetonitrile was then added dropwise to the previously generated slurry of $SeCl_4$; the $SeCl_4$ rapidly dissolved to give a bright yellow solution. When the addition was complete, the mixture was heated at reflux for 30 min and then cooled to −25 °C overnight. The canary yellow blocks of Ph_3PCN_3SeCl (2.7 g, 6.3 mmol, 85%) so obtained were filtered and recrytallized from acetonitrile: mp 147–50 °C; ^{31}P NMR $\delta(P) = 12.0$; IR 1590 (w), 1438 (w), 1423 (m), 1323 (s), 1284 (m), 1778 (m), 1129 (s), 1115 (s), 1068 (w), 1026 (w), 947 (s), 783 (w), 755 (w), 724 (s), 705 (s), 690 (s), 528 (s), 445 (w), 353 (w), 322 (w) cm^{-1}. Anal. Calcd for $C_{19}H_{15}N_3PSeCl$: C, 52.98; H, 3.51; N, 9.76; Cl, 8.23. Found: C, 53.05; H, 3.65; N, 9.85; Cl, 8.16.

Preparation of $Ph_4P_2N_3SCl$ (15, R = R′ = Ph). A solution of $Me_3SiNSNSiMe_3$ (1.3 g, 6.3 mmol) in 10 mL of acetonitrile was added dropwise to a cold (0 °C) solution of $[ClPh_2PNPPh_2Cl]^+Cl^-$ (3.0 g, 6.1 mmol) in 25 mL of acetonitrile. The mixture was stirred for 30 min at room temperature, then concentrated in vacuo to ca. 25 mL, and cooled to −25 °C overnight. Subsequent filtration affored pale yellow blocks of $Ph_4P_2N_3SCl$ (1.4 g, 2.9 mmol, 48%), the identity of which was confirmed by comparison of its infrared spectrum[14] and ^{31}P chemical shift ($\delta(P) = 8.1$, lit.[14] 7.8) with the literature data.

Preparation of $Ph_4P_2N_3SeCl$ (16, R = Ph). A solution of crude $Me_3SiNSeNSiMe_3$, prepared in situ by the reaction of $SeOCl_2$ (4.2 g, 25.5 mmol) with $LiN(SiMe_3)_2$ (8.0 g, 47.9 mmol) in 50 mL of diethyl ester, was dissolved (after removal of the ether) in 75 mL of CH_3CN. To this solution was added solid $[ClPh_2PNPPh_2Cl]^+Cl^-$ (7.0 g, 14.3 mmol). The mixture was stirred at room temperature for 30 min, then filtered, and concentrated in vacuo to a volume of ca. 40 mL, and the filtrate was cooled to −5 °C overnight. The large pale yellow blocks of $Ph_4P_2N_3SeCl$ (3.0 g, 5.7 mmol, 40% based on phosphorus) so obtained were recrystallized from acetonitrile: dec > 143 °C; ^{31}P NMR $\delta(P) = 12.5$;[19] IR 1437 (7), 199 (m), 1172 (w), 1036 (m), 1025 (m), 910 (s), 722 (s), 691 (s), 674 (m), 584 (m), 539 (s), 516 (s), 423 (m), 331 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{20}N_3P_2SeCl$: C, 54.72; H, 3.83; N, 7.98; Cl, 6.73. Found: C, 54.62; H, 4.08; N, 7.83; Cl, 6.56.

Preparation of $[Ph_3PCN_3S]_2$ (10, R = R′ = Ph). Solid triphenyl-antimony (0.25 g, 0.71 mmol) was added to a hot (70 °C) solution of Ph_3PCN_3SCl (0.50 g, 1.3 mmol) in 10 mL of triply degassed (freeze–pump–thaw) acetonitrile. The solution was slowly cooled to room temperature, and the bright red glassy nodules of $[Ph_3PCN_3S]_2$ (0.31 g, 0.45 mmol, 68%) were separated by filtration: dec > 90 °C; IR 1491 (m), 1435 (w), 1338 (s), 1322 (s), 1295 9s), 1180 (m), 1123 (s), 1112 (m), 853 (s), 926 (m), 884 (m), 817 (m), 743 (s), 724 (s), 686 (s), 533 (s), 528 (s) cm^{-1}. Anal. Calcd for $C_{38}H_{30}N_6P_2S_2$: C, 65.51; H, 4.34; N, 12.06. Found: C, 65.29; H, 4.54; N, 11.84.

Preparation of $[Ph_2(tol)PCN_3S]_2$ (10, R = Ph, R′ = tol). Solid tri-phenylantimony (0.38 g, 1.1 mmol) was added to hot (70 °C) solution of $Ph_2(tol)PCN_3SCl$ (0.75 g, 1.9 mmol) in 50 mL of acetonitrile. The solution was slowly cooled, and the resultant bright red crystals of $[Ph_2(tol)PCN_3S]_2$ (0.28 g, 0.4 mmol, 41%), separated by filtration: dec > 153 °C; IR 1421 (m), 1338 (s), 1315 (m), 1293 (m), 1184 (w), 1122 (m), 1115 (m), 977 (s), 926 (m), 862 (w), 811 (w), 737 (m), 722 (w), 693 (m), 535 (m), 523 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_6P_2S_2$: C, 66.28; H, 4.73; N, 11.59. Found: C, 65.40; H, 4.89; N, 11.81.

Preparation of $[Ph_3PCN_3Se]_2$ (11, R = R′ = Ph). Solid triphenyl-antimony (0.45 g, 1.3 mmol) was added to hot (70 °C) solution of Ph_3PCN_3SeCl (1.0 g, 2.3 mmol) in 25 mL of triply degassed (freeze–pump–thaw) acetonitrile. The deep red solution so formed was then filtered (to remove a trace of red selenium) and allowed to cool slowly to room temperature. The resulting deep red crystals of $[Ph_3PCN_3Se]_2 \cdot CH_3CN$ (0.56 g, 0.71 mmol, 62%) were isolated by filtration: dec > 109 °C; IR 1436 (w), 1424 (m), 1319 (s), 1293 (m), 1177 (m), 1120 (m), 1118 (m), 1067 (w), 1024 (w), 946 (m), 880 (m), 819 (w), 753 (w), 724 (s), 700 (s), 692 (s), 612 (w), 597 (s), 525 (s), 517 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{33}N_7P_2Se_2$: C, 57.77; H, 4.00; N, 11.79. Found: C, 57.49; H, 4.10; N, 11.79.

Preparation of $[Ph_4P_2N_3S]_2$ (4, R = Ph). Solid triphenylantimony (0.52 g, 1.5 mmol) was added to a hot (70 °C) solution of $Ph_4P_2N_3SCl$ (0.70 g, 1.5 mmol) in 30 mL of triply degassed (freeze–pump–thaw) CH_3CN. The orange solution was left to stand overnight, and the resulting orange crystals of $[Ph_4P_2N_3S]_2$ (0.33 g, 0.37 mmol, 51%) were isolated by filtration. The identity of this material, dec > 210 °C, was confirmed by comparison with the known IR spectrum[11] and ^{31}P chemical shift ($\delta(P) = 15.8$; lit.[11] 15.8). Anal. Calcd for $C_{48}H_{40}P_4N_6S_2$: C, 64.86; H, 4.54; N, 9.45; S, 7.21. Found: C, 64.76; H, 4.66; N, 9.57; S, 7.13.

Attempted Preparation of $[Ph_4P_2N_3Se]_2$. Repeated attempts to generate a radical dimer of $[Ph_4P_2N_3Se]^•$ by reduction of $Ph_4P_2N_3SeCl$ with Ph_3Sb with a procedure analogous to that described above for $[Ph_4P_2N_3S]_2$ were unsuccessful. Such reactions afforded pale yellow solutions (from which ESR data were obtained) that slowly deposited a red precipitate of amorphous selenium.

ESR Spectra. All ESR spectra were recorded on samples in degassed methylene chloride at ambient temperature with a Varian E109 ESR spectrometer. Samples were prepared either by in situ reduction of the corresponding chloro derivative with triphenylantimony or by dissolving the radical dimer. Spectral simulations, from which coupling constant data were extracted, were performed with the program ESR42, written by Dr. U. M. Oehler, University of Guelph.[35]

Molecular Orbital Calculations. Restricted open-shell Hartree–Fock (RHF) MNDO molecular orbital calculations were performed with the MOPAC suite of programs[36] operating on a SUN-3 workstation. Geometries of all model structures were optimized with a minimum requirement of C_s symmetry (i.e., ring planarity).

X-ray Structure Determinations. Crystals of $[Ph_2(tol)PCN_3S]_2$ and $[Ph_3PCN_3Se]_2 \cdot CH_3CN$ suitable for X-ray work were grown from acetonitrile. All X-ray data were collected on an Enraf-Nonius CAD-4 at 293 K with monochromated Mo K_α ($\lambda = 0.71073$ Å) radiation. Crystals were mounted on glass fibers coated with epoxy. Data were collected by using a $\theta/2\theta$ technique with a scan width of $(1.0 + 0.3 \tan\theta)$. Data collection, structure solution, and refinement parameters for both structures are available as supplementary material. Both structures were solved with MULTAN and refined by full-matrix least squares that minimized $\Sigma w(\Delta F)_2$. In the selenium-based dimer the solvent molecule was best modeled by five partially occupied positions centered in crystal cavities at 0.0, 0.5, 0.0 and 0.3, 0.5, 0.0. The paucity of data with $I > 3\sigma(I)$ for the sulfur dimer is apparently due to lack of long-range order; the number of reflections with $I > 3\sigma(I)$ dropped off rapidly at 19° in θ and comprised only 12% of the reflections scanned in the shell of θ from 21 to 22°. No extinction correction was applied to either structure. Atomic scattering factors and anomalous dispersion corrections were taken from ref 37. All programs used were those provided by the Enraf-Nonius Structure Determination Package.

Supplementary Material Available: Tables of crystal data, structure solution, and refinement (S1), atomic coordinates for $[Ph_2(tol)PCN_3S]_2$ (S2) and $[Ph_3PCN_3Se]_2 \cdot CH_3CN$ (S3), bond lengths and angles (S4, S5), and anisotropic thermal parameters (S6, S7) for both structures 10 and 11 (26 pages). Ordering information is given on any current masthead page.

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