An Acyclic Nitrogen–Phosphorus–Selenium Anion: Preparation, Structure, and Reactions of (K[$Ph_2P(Se)NSiMe_3$]·THF)$_2$ with Iodine and Chlorodiphenylphosphine Sulfide

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The reaction of $Ph_2P(Se)N(SiMe_3)_2$ with potassium *tert*-butoxide in a 1:1 molar ratio in THF at room temperature produces (K[$Ph_2P(Se)NSiMe_3$]·THF)$_2$ (**5**) in excellent yields. An X-ray structural determination of **5** reveals a dimeric step-shaped structure involving two four-membered NPSeK rings fused to a central K_2Se_2 ring. The P–Se bond lengths are *ca.* 2.18 Å while the P–N bond distances are 1.556(13) and 1.594(12) Å. The value of $^1J(^{31}P–^{77}Se)$ for **5** is 604 Hz and the stretching frequency ν(P=Se) occurs at 546 cm^{-1}. Crystals of **5** are monoclinic, space group $P2_1/c$, with a = 9.643(2) Å, b = 16.500(5) Å, c = 29.366(7) Å, B = 91.34(2)°, V = 4671(1) Å^3, and Z = 8, with final R and R_w values of 0.076 and 0.081, respectively. The reactions of **5** with I_2 or $Ph_2P(S)Cl$ occur at the selenium sites to give (Me_3SiN)$Ph_2PSeSePPh_2$($NSiMe_3$) and (Me_3SiN)$Ph_2PSePPh_2$(S), respectively, which were identified by ^{31}P and ^{77}Se NMR spectroscopy.

Introduction

The coordination chemistry of dithiophosphinates ($R_2PS_2^-$) has been studied extensively because of the ability of these anionic ligands to chelate and/or bridge metal centers.[1] In contrast, metal complexes of diselenophosphinate anions (**1**) have been less well investigated owing to their tendency to decompose with the formation of elemental selenium.[1] The related diiminophosphinate anions (**2**) have received considerable attention recently and the solid-state structures of all the alkali metal derivatives have been elucidated.[2] Interestingly, the lithium and potassium compounds are monomeric, whereas the rubidium and cesium derivatives adopt dimeric, step-shaped structures.[2] The lithium reagent has been used to form chelated complexes with a variety of metals, including lanthanides and actinides.[3] The hybrid anion **3**, which combines soft (Se) and hard (N) coordination sites, is a potentially interesting ligand, and ^{77}Se NMR spectroscopy should facilitate investigations of its reactions. However, this acyclic anion is unknown.[4]


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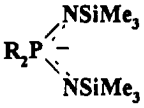
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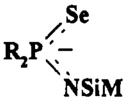
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We report here the synthesis and X-ray structural determination of the potassium derivative of **3** (R = Ph) and investigations of the reactions of this novel anion with iodine and chlorodiphenylphosphine sulfide, which give rise to new P–Se systems containing Si–N bonds.

Experimental Section

General Procedures. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen gas using freshly distilled anhydrous solvents. Chlorodiphenylphosphine, hexamethyldisilazane, n-butyllithium, iodine, and selenium (all from Aldrich) were used as received. Celite 545 and sea sand (Fisher Scientific) were dried at 110 °C before use. Potassium *tert*-butoxide (Aldrich) was purified by sublimation at 180–190 °C (0.075 Torr) $Ph_2PN(SiMe_3)_2$ was prepared from Ph_2PCl and $LiN(SiMe_3)_2$ by the method reported for $Me_2PN(SiMe_3)_2$.[5] Chlorodiphenylphosphine sulfide was prepared by heating Ph_2PCl with elemental sulfur at reflux in toluene. $\delta(^{31}P)$ (in THF): 80.5 (cf. lit. δ 79.9 in toluene).[6]

Infrared spectra were recorded as Nujol mulls with KBr plates on a Mattson 4030 FT-IR spectrometer. ^1H NMR spectra were obtained on a Bruker ACE 200 spectrometer using various deuterated solvents as internal references. ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker AM400 spectrometer using 85% H_3PO_4 or Ph_2Se_2 in $CDCl_3$ (+461 ppm relative to Me_2Se) as the external reference.

Preparation of $Ph_2P(Se)N(SiMe_3)_2$. A slurry of grey selenium (1.11 g, 14.06 mmol) and $Ph_2PN(SiMe_3)_2$ (4.85 g, 14.05 mmol) in toluene (70 mL) was stirred vigorously for 2 days. Unreacted selenium was removed by filtration and the filtrate was reduced in volume to 50 mL and then cooled to 10 °C to give colorless, cubic crystals of $Ph_2P(Se)N(SiMe_3)_2$ (4.11 g, 9.68 mmol, 69%). Anal. Calcd. for $C_{18}H_{28}NPSeSi_2$: C, 50.93; H, 5.78; N, 3.82. Found: C, 51.16; H, 5.65; N, 3.30. ^1H NMR (in $CDCl_3$): δ 7.43–7.97 ppm (m, C_6H_5, 10H), 0.18 ppm (s, $SiMe_3$, 18H). $^{31}P\{^1H\}$ NMR (in THF): δ 56.2 ppm [s, $^1J(^{31}P–^{77}Se)$ = 765 Hz]. ^{77}Se NMR (in THF): δ –153 ppm [d, $^1J(^{31}P–^{77}Se)$ = 765 Hz. IR (Nujol): ν(P=Se) 567 cm^{-1}.

Preparation of (K[$Ph_2P(Se)NSiMe_3$]·THF)$_2$. A solution of $Ph_2P(Se)N(SiMe_3)_2$ (1.582 g, 3.73 mmol) in THF (25 mL) was added dropwise (10 min) to a slurry of freshly sublimed potassium *tert*-butoxide (0.412 g, 3.67 mmol) in THF (25 mL) at –78 °C. The reaction mixture was allowed to warm to 23 °C, and then the volume of the solution was reduced to 5 mL. Hexanes (45 mL) were layered onto the concentrate, which was stored at –13 °C to give colorless crystals of K[$Ph_2P(Se)NSiMe_3$]·THF (1.560 g, 3.38 mmol, 92%). Anal. Calcd for $C_{19}H_{27}KNOPSeSi$: C, 49.34; H, 5.88; N, 3.03. Found: C, 48.69; H, 5.87; N, 3.14. ^1H NMR (in $CDCl_3$): δ 7.19–7.99 ppm (m, C_6H_5, 10H), 3.54 ppm (q, ~3.5, CH_2), 1.45 (q, ~3.5, CH_2), 0.06 (s, $SiMe_3$, 9H). $^{31}P\{^1H\}$ NMR (in THF): δ 22.0 ppm [s, $^1J(^{31}P–^{77}Se)$ = 604 Hz]. ^{77}Se NMR (in THF): δ –81 ppm [d, $^1J(^{31}P–^{77}Se)$ = 604 Hz). IR (Nujol): ν(P–Se) 546 cm^{-1}.

Reaction of (K[$Ph_2P(Se)NSiMe_3$)·THF)$_2$ with $Ph_2P(S)Cl$. A solution of (K[$Ph_2P(Se)NSiMe_3$]·THF)$_2$ (0.619 g, 0.67 mmol) in THF (20 mL) was added slowly (10 min) to a solution of $Ph_2P(S)Cl$ (0.304 g, 1.20 mmol) in THF (20 mL) at 23 °C. The reaction mixture was heated at reflux for 1 h to give a cloudy solution. The volume of the solution was reduced by half at room temperature, and then the solution was passed through a filter stick containing layers of Celite and sea sand to remove

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Table 1. Crystallographic Data for $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ (**5**)

chem formula: $C_{19}H_{27}OPNSeSiK$	fw = 462.55
$a = 9.643(2)$ Å	space group: $P2_1/c$ (No. 14)
$b = 16.500(5)$ Å	$T = 150$ K
$c = 29.366(7)$ Å	$\lambda = 0.71069$ Å
$\beta = 91.34(2)$ Å	$\rho_{calcd} = 1.315$ g cm^{-3}
$V = 4671(1)$ Å^3	$\mu = 1.913$ mm^{-1}
$Z = 8$	$R = 7.64$
	$R_w = 8.11$

the precipitate of KCl. The removal of solvent produced $Me_3SiNPPh_2SePPh_2S$ as a colorless oil, which was identified on the basis of ^{31}P and ^{77}Se NMR data (see Results and Discussion section).

Reaction of $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ with Iodine. A solution of iodine (0.121 g, 0.477 mmol) in THF (25 mL) was added dropwise (15 min) to a solution of $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ (0.429 g, 0.464 mmol) in THF (25 mL) at −78 °C. The reaction mixture was allowed to warm to 23 °C over a period of 1 h to give an orange solution of a white precipitate of KI, which was removed by filtration through a filter stick containing layers of Celite and sea sand. Removal of the solvent under vacuum produced $Me_3SiPPh_2SeSePPh_2NSiMe_3$ as an orange oil, which was identified on the basis of ^{31}P and ^{77}Se NMR data (see Results and Discussion section). Attempts to crystallize this product using a variety of solvent combinations were unsuccessful.

X-ray Structure of $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ (5). A colorless block-shaped crystal of **5** with dimensions 0.30 × 0.43 × 0.50 mm was mounted on a glass fiber. Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 20 reflections. Crystallographic information is given in Table 1. The data were corrected for Lorentz, polarization and absorption effects;[7] transmission factors were in the range 0.5771 to 1.2578.

The structure was solved by direct methods using SAPI91.[8] Refinement of the structure was by full-matrix least-squares calculations using SHELX-76.[9] Se, K, P, Si, and O atoms were allowed anisotropic temperature factors while N and C atoms were allowed isotropic thermal parameters. At an intermediate stage in the refinement, a difference map revealed maxima consistent with the positions of hydrogen atoms which were included in the refinement at geometrically idealized positions (C–H 0.95 Å) with overall isotropic temperature factors for different types of hydrogens. Refinement converged with $R = 0.076$ and $R_w = 0.081$. In the refinement cycles, weights were derived from the counting statistics. Atomic scattering factors were taken from ref 10, and allowance was made for anomalous dispersion.[11] A difference map calculated at the conclusion of the refinement had no chemically significant features. The computer programs used for data reduction were part of TEXSAN.[12] The final positional and thermal parameters for non-hydrogen atoms are given in Table 2.

Results and Discussion

Preparation and Spectroscopic Characterization. Herberhold and Ehrenreich have prepared $K_2[SN_2]$ by the reaction of $Me_3SiNSNSiMe_3$ with potassium *tert*-butoxide (1:2 molar ratio) in boiling dimethoxyethane (DME).[13] We have adopted a similar approach for the synthesis of the potassium derivative of **3** (R = Ph) (eq 1).

$$Ph_2P(Se)N(SiMe_3)_2 + KOBu^t \rightarrow K[Ph_2P(Se)NSiMe_3] + Me_3SiOBu^t \quad (1)$$

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^3 Å^2) for Non-Hydrogen Atoms of $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ (**5**)

atom	x	y	z	U_{eq}[a]
Se(1)	9208(2)	213(1)	8041(1)	26(1)
Se(2)	6088(2)	2087(1)	6977(1)	25(1)
K(1)	5965(4)	959(3)	7951(1)	38(2)
K(2)	9410(4)	1444(2)	7109(1)	33(2)
P(1)	9277(4)	1301(3)	8463(1)	20(3)
P(2)	6115(4)	929(3)	6620(1)	21(2)
Si(1)	7049(5)	2094(3)	9044(2)	35(3)
Si(2)	8480(5)	37(3)	6149(2)	25(3)
O(1)	4860(13)	−50(8)	8548(5)	60(10)
O(2)	10598(13)	2262(8)	6467(4)	53(9)
N(1)	7826(14)	1643(8)	8582(4)	26(3)
N(2)	7624(12)	565(7)	6546(4)	20(3)
C(1)	10243(15)	2035(9)	8118(5)	16(3)
C(2)	9560(16)	2743(9)	7990(5)	21(4)
C(3)	10201(18)	3260(11)	7675(6)	35(5)
C(4)	11527(19)	3103(11)	7522(6)	39(5)
C(5)	12218(16)	2418(9)	7682(5)	23(4)
C(6)	11607(17)	1882(10)	7956(5)	29(4)
C(7)	10428(15)	1120(9)	8975(5)	14(3)
C(8)	11273(18)	1712(11)	9152(6)	38(5)
C(9)	12096(19)	1570(12)	9555(6)	42(5)
C(10)	12003(21)	831(12)	9768(7)	50(5)
C(11)	11140(17)	257(11)	9613(6)	32(4)
C(12)	10347(18)	381(10)	9191(6)	34(4)
C(13)	7859(29)	3071(16)	9211(9)	114(11)
C(14)	6951(25)	1445(15)	9555(8)	86(8)
C(15)	5216(25)	2341(16)	8864(9)	99(9)
C(16)	5831(23)	−631(13)	8712(7)	66(7)
C(17)	5149(21)	−975(13)	9132(7)	63(6)
C(18)	3608(22)	−956(13)	8991(7)	62(6)
C(19)	3507(21)	−157(12)	8728(7)	53(6)
C(20)	5042(16)	247(9)	6955(5)	19(4)
C(21)	5596(18)	−493(10)	7105(5)	30(4)
C(22)	4823(19)	−1025(11)	7382(6)	38(5)
C(23)	3503(18)	−797(10)	7502(5)	31(4)
C(24)	2947(19)	−59(11)	7370(6)	38(5)
C(25)	3710(17)	441(10)	7074(5)	32(4)
C(26)	5110(18)	1021(10)	6085(6)	32(4)
C(27)	4295(17)	398(11)	5915(6)	34(5)
C(28)	3682(20)	449(12)	5451(6)	46(5)
C(29)	3939(22)	1115(13)	5166(7)	57(6)
C(30)	4748(21)	1733(13)	5329(7)	56(6)
C(31)	5383(18)	1681(11)	5768(6)	33(4)
C(32)	7881(19)	−1017(11)	6081(6)	42(5)
C(33)	8390(20)	500(12)	5558(6)	52(6)
C(34)	10371(20)	1(12)	6335(7)	59(6)
C(35)	9657(26)	2852(15)	6222(8)	86(8)
C(36)	9997(26)	2899(16)	5736(8)	83(8)
C(37)	11372(30)	2597(19)	5747(10)	119(11)
C(38)	11848(24)	2317(15)	6181(8)	76(7)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. Nitrogen and carbon atoms were allowed isotropic temperature factors.

The neutral ligand $Ph_2P(Se)N(SiMe_3)_2$ (**4**) was obtained as white crystals in 65% yield by the reaction of $Ph_2PN(SiMe_3)_2$ with grey selenium in toluene at 65 °C for 2 days. The reaction of **4** with an equimolar amount of potassium *tert*-butoxide in dry THF occurs readily at room temperature. White crystals of $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$ (**5**) were obtained in *ca.* 90% yield by layering a concentrated THF solution of the product with a large volume of hexane. The dianion $PhP(Se)N^{2-}$ could not be generated by changing the stoichiometry in eq 1 to 1:2 even in boiling DME.

The NMR and IR spectroscopic data for **5** indicate a substantial decrease in the phosphorus–selenium bond order in the anion **3** (R = Ph) compared to that in the neutral compound **4**. The coupling constant $^1J(^{31}P-^{77}Se)$ decreases from 765 Hz in **4** to 604 Hz in **5** and the IR stretching frequency $\nu(P{=}Se)$ undergoes a corresponding decrease from 567 to 546 cm^{-1}.

Crystal Structure. The structure of **5** was established by X-ray crystallography. The molecular geometry and atomic numbering scheme for **5** are shown in Figure 1, and pertinent structural

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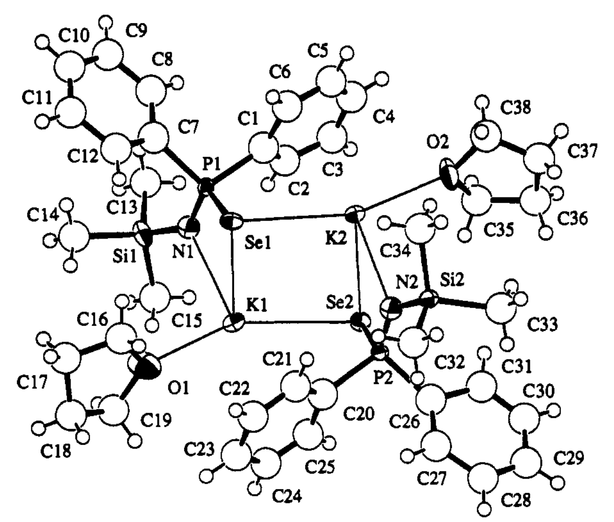
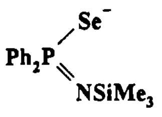


Figure 1. ORTEP diagram for (K[Ph$_2$P(Se)NSiMe$_3$]·THF)$_2$, **5**.

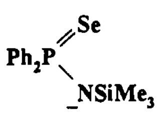
Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for (K[Ph$_2$P(Se)NSiMe$_3$]·THF)$_2$ (**5**)

P(1)–Se(1)	2.181(5)	P(2)–Se(2)	2.180(5)
P(2)–N(2)	1.594(12)	P(1)–N(1)	1.556(13)
N(1)–K(1)	2.789(14)	N(2)–K(2)	2.770(12)
Se(1)–K(2)	3.416(4)	Se(1)–K(1)	3.366(5)
Se(2)–K(2)	3.389(4)	Se(2)–K(1)	3.418(4)
N(1)–P(1)–Se(1)	114.3(5)	N(2)–P(2)–Se(2)	114.4(5)
P(1)–Se(1)–K(2)	88.0(1)	P(2)–Se(2)–K(1)	85.7(1)
N(1)–K(1)–Se(2)	107.6(3)	N(2)–K(2)–Se(1)	97.0(3)
Se(1)–K(2)–Se(2)	101.9(1)	Se(1)–K(1)–Se(2)	102.4(1)
K(1)–Se(1)–K(2)	77.9(1)	K(1)–Se(2)–K(2)	77.5(1)
P(1)–N(1)–Si(1)	137.7(9)	P(2)–N(2)–Si(2)	138.8(8)

parameters are summarized in Table 3. In contrast to the potassium derivative of **2** (R = Ph), which is monomeric,[2] compound **5** has a dimeric, step-shaped structure reminiscent of the type of coordination observed for Rb and Cs derivatives of **2** and alkali metal sulfinimidamides of the type M[RNS(Ph)NR] (M = Na, K; R = ^{t}Bu; M = Rb, Cs; R = SiMe$_3$).[14] The structure of **5** consists of two four-membered KNPSe rings fused above and below a central K$_2$Se$_2$ ring. Each potassium is coordinated to the nitrogen and selenium atoms of one ligand (**3**, R = Ph) and the selenium of the second NPSe ligand. A THF molecule is also attached to each potassium. In addition, one of the phenyl groups on each phosphorus is oriented so that the π-electron cloud interacts with potassium. The distances between the center of the C$_6$H$_5$ rings and potassium are 3.128 and 3.341 Å. These separations are significantly smaller than the value of 3.698 Å found for the related compound (K[^{t}BuNS(Ph)NBu^t]·THF)$_2$.[14] No close contact between the phenyl group and potassium was observed for the monomeric derivative K[Ph$_2$P(NSiMe$_3$)$_2$(THF)$_4$].[2] The central K$_2$Se$_2$ ring is a distorted square with K–Se bond distances in the range 3.366(5)–3.418(4) Å and bond angles at potassium and selenium of *ca.* 102° and *ca.* 78°, respectively. The K–N distances of 2.770(12) and 2.789(14) Å in **5** are similar to those found in (K[^{t}BuNS(Ph)NBu^t]·THF)$_2$.[14] The P–Se bond distances are 2.180(5) and 2.181(5) Å. These values should be compared to single and double phosphorus–selenium bond distances of 2.238 and 2.093 Å, respectively.[15,16] The phosphorus–nitrogen bond lengths of 1.556(13) and 1.594(12) Å suggest substantial double bond character for these bonds. Taken together, these structural data and the spectroscopic parameters for **5** indicate a significant contribution from the resonance structure **3a** for the monoanion.


Ph$_2$P(Se$^-$)=NSiMe$_3$

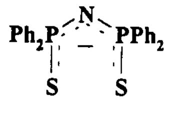
3a


Ph$_2$P(=Se)$\underline{N}$SiMe$_3$

3b

The bite angle (∠NPSe) in **5** of 114.3(5)° and the angles at nitrogen (∠PNSi) of 137.7(9) and 138.8(8)° are very similar to the values reported for the potassium derivative of the symmetrical ligand **2** (R = Ph)[2] despite the difference in degree of association.

Reactions with Electrophiles. Metal complexes of the chelating monoanion [Ph$_2$P(S)]$_2$N$^-$ (**6**) are well-known.[1b,17] In an attempt to generate the mixed chalcogen ligand **7**, the reaction of **5** with chlorodiphenylphosphine sulfide was investigated. However, in this instance, electrophilic attack occurs at selenium in preference to nitrogen[18] to give compound **8** as a colorless oil which was identified by ^{31}P and ^{77}Se NMR spectroscopy.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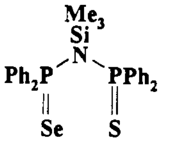
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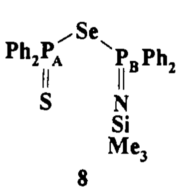
8

The ^{31}P NMR spectrum of **8** in THF consists of a pair of mutually coupled doublets [$^2J(^{31}P_A–^{31}P_B)$ = 13.5 Hz][19] at 50.2 and 3.3 ppm, which are tentatively assigned to P$_A$ and P$_B$, respectively.[20] These resonances exhibit ^{77}Se satellites with one-bond coupling constants of 373 and 355 Hz, respectively. The ^{77}Se NMR spectrum of **8** in THF is comprised of a doublet of doublets centered at 411.9 ppm [reference Me$_2$Se (0 ppm)] with $^1J(^{31}P–^{77}Se)$ values of 355 and 373 Hz. The $^1J(^{31}P–^{77}Se)$ value for the P–Se single bond in the related compound Me$_2$P(S)SeMe is 341 Hz.[21]

A second example of electrophilic attack at selenium in the anion **3** (R = Ph) is observed in the reaction of **5** with iodine at room temperature, which produces the diselenide **9** (eq 2) as determined by ^{31}P and ^{77}Se NMR spectroscopy.

$$[K(Ph_2P(Se)NSiMe_3)]_2 + I_2 \rightarrow (Me_3SiN)Ph_2PSeSePPh_2(NSiMe_3) + 2KI \quad (2)$$

9

The ^{31}P NMR spectrum of **9** in THF exhibits a single resonance at 0.4 ppm flanked by two sets of ^{77}Se satellites with $^1J(^{31}P–^{77}Se)$ = 354 Hz, indicative of a P–Se single bond, and $^2J(^{31}P–^{77}Se)$ = 13.5 Hz. Since the natural abundance of ^{77}Se is only 7.7%, the ^{77}Se NMR spectrum of **9** is expected to be that of an AXX′ spin system (where A represents ^{77}Se in the most abundant isotopomer and X and X′ are the magnetically inequivalent phosphorus atoms). In fact, the ^{77}Se NMR spectrum of **9** in THF consists of a doublet of doublets centered at 363 ppm with $J(^{31}P–^{77}Se)$

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(18) By contrast, the reaction of the neutral ligand Ph$_2$P(S)N(SiMe$_3$)$_2$ with TiCl$_4$ occurs at nitrogen to give Ph$_2$P(S)NTiCl$_2$, which is formally a complex of the dianion Ph$_2$P(S)N^{2-}. Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669.

(19) $^2J(^{31}P–^{31}P)$ values of *ca.* 15 Hz have been reported for the P(V)–P(V) couplings in R$_2$(S)PSP(S)R$_2$ derivatives. Harris, R. K.; McVicker, E. M.; Hagele, G. *J. Chem. Soc., Dalton Trans.* **1978**, 9.

(20) The ^{31}P NMR chemical shifts of R$_3$PS and R$_3$PNR derivatives fall within the ranges +60 to −45 ppm and +30 to −20 ppm, respectively. However, for a specific R group, the shift for the sulfide usually occurs downfield from that of the corresponding imino compound. Dixon, K. R. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 369 and references cited therein.

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values of 354 and 15.7 Hz[22] for the one-bond and two-bond couplings, respectively. The apparent first-order pattern of this spectrum suggests that the coupling between the magnetically inequivalent phosphorus nuclei in **9** is approximately zero.

The oily nature of **9** is likely caused by the presence of trimethylsilyl groups. However, attempts to prepare a crystalline potassium derivative by the reaction of **9** with two molar equivalents of potassium *tert*-butoxide in THF regenerated **5**.

Conclusion. In summary, the novel ligand **3** (R = Ph) is readily obtained as a potassium derivative and reactions of this anion with the soft electrophiles I_2 or $Ph_2P(S)Cl$ occur at the selenium center. ^{77}Se NMR spectroscopy played a decisive role in the identification of the products of these reactions and will provide an informative probe for investigations of the coordination chemistry of **3**. The combination of hard (N) and soft (Se) sites may confer flexibility in the bonding modes adopted by this ligand in metal complexes and the presence of a Si–N bond allows the possibility of further reactions once complexes of **3** have been formed. The compounds **8** and **9** are also potentially interesting ligands.

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Supplementary Material Available: Tables listing crystallographic data, and thermal parameters for non-hydrogen atoms, bond distances, bond angles, torsion angles, anisotropic thermal parameters, and parameters for hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

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(22) The disparity between the values of $^2J(^{31}P-^{77}Se)$ obtained from the ^{31}P and ^{77}Se NMR spectra is likely due to the poorer resolution of the ^{77}Se NMR spectrum.