Heteroatom Chemistry
Volume 3, Number 2, 1992

(2,4,6-Tri-tert-butylphenylimino)thioxo- and -selenoxophosphoranes. Synthesis and Structural Characterization*

Vadim D. Romanenko,[1] Alexander V. Ruban, Andrei B. Drapailo, Alexander N. Chernega, and Eduard B. Rusanov

Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Kiev 94, 252660, Ukraine

Received 9 August 1991.

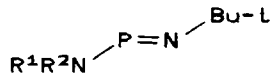
ABSTRACT

*A series of stable imino(chalcogeno)phosphoranes R — P(=X) = NAr, R = Ph, 2, 4, 6-$Me_3C_6H_2$, 2, 4, 6-i-$Pr_3C_6H_2$; Ar = 2, 4, 6-t-$Bu_3C_6H_2$; X = S, Se (**5b-d, 6b,c**), has been prepared by the oxidation of λ^3-imino-phosphines R — P = N — Ar (**4b-d**) with sulfur and selenium. When P — (tert-butyl)iminophosphine, t-Bu — P = N- — Ar (**4a**), was reacted with S_8 and Se_n, the corresponding oligomeric metaphosphonimidates 7, 8 were obtained. All new compounds are characterized by their NMR spectra. The constitution of the imino(thioxo)phosphorane **5d** is proved by X-ray crystal structure determination.*

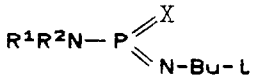
INTRODUCTION

By analogy to the synthesis of other types of three-coordinate pentavalent phosphorus compounds, imino(chalcogeno)phosphoranes, $R^1 — P(=X) = NR^2$ (X = S, Se), may be obtained from low-coordinated phosphorus precursors by oxidation reactions. Thus, the first imino-(thioxo and selenoxo)phosphoranes **2a,b** were prepared by action of sulfur or selenium on the aminoiminophosphine **1** [1,2]. Nevertheless, although $\sigma^3\lambda^5$-phosphoranes have commanded a fair amount of attention in the past decade, the number of stable compounds $R^1 — P(=S \text{ or } Se) = NR^2$ remains very limited [3,4]. Moreover, no crystal structure determinations of monomeric imino(chalcogeno)phosphoranes are known. Although the monomeric nature of **2a** in solutions was unequivocally characterized by means of NMR spectroscopy, this compound in the crystalline state was shown to adopt a dithiadiphosphetane structure **3** [5].

We report here the synthesis of (2,4,6-tri-*tert*-butylphenylimino)thioxo- and -selenoxo -$\sigma^3\lambda^5$ -phosphoranes starting from λ^3-imino phosphanes R — P = N — Ar, Ar = 2,4,6-t-$Bu_3C_6H_2$. Since the

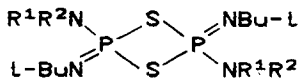


1



2a, X = S

2b, X = Se



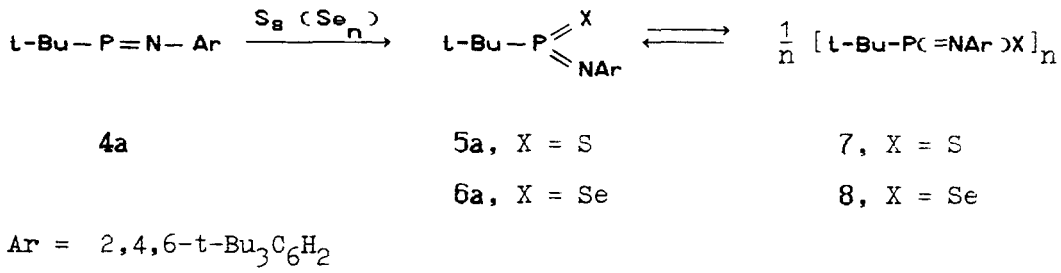
3

R^1 = t-Bu, R^2 = Me_3Si

[1]To whom all correspondence should be addressed.

*This paper is dedicated to Academician of the Ukrainian Academy of Sciences Prof. Alexander V. Kirsanov on the occasion of his 90th birthday.

1042-7163/92/$3.50 + .25



SCHEME 1

bulky 2,4, 6-tri-*tert*-butylphenyl group effectively stabilizes structures with low-coordinated phosphorus atoms [4, 6–9], the higher kinetic stability of the compounds R — P(= S or Se) = NAr in comparison with previously studied N-(*tert*-butyl)-substituted phosphoranes R — P(= S or Se) = NBu-t [1, 2, 10] might be expected.

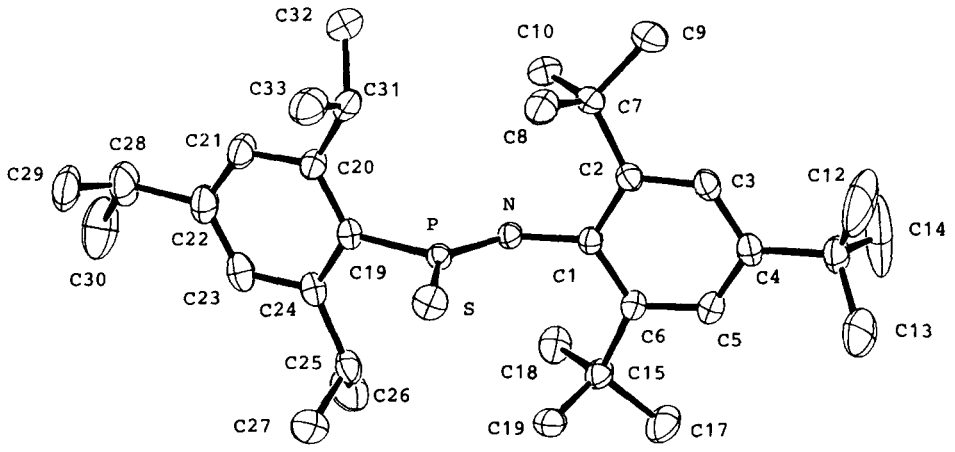
RESULTS AND DISCUSSION

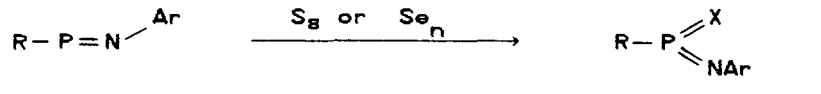
Treatment of P-(*t*-butyl)iminophosphine **4a** with 1 equivalent of sulfur or selenium in benzene at 20°C results in the quantitative formation of the addition products. The latter, in contrast to previously reported $\sigma^3\lambda^5$-phosphoranes, are high-melting (> 190°C), air-stable amorphous yellow powders, practically insoluble in common organic solvents. The NMR chemical shifts of the phosphorus atoms in the products (δP *ca.* −15 ppm) are markedly different from those in the compounds **2a, b** (δP = 110–170 ppm) and fall in the region typical of 4-coordinate P^V compounds. Microanalysis data, however, are in good agreement with the compositions $(C_{22}H_{38}NPS)_n$ and $(C_{22}H_{38}NPSe)_n$. Heating the reaction products of **4a** with S_8 and Se_n in aprotic solvents such as toluene from 20°C to 110°C leads to gradual passing of the solid into solution and appearance of the yellow-orange coloration. On increasing the temperature, the ^{31}P NMR signal of the starting material disappears, while a new one grows in the region (δP = 200–210) expected for $\sigma^3\lambda^5$-phosphoranes. This phenomenon is reversible; a return to room temperature completely restores the initial spectrum. The foregoing data can be explained assuming that the products formed by the reaction of **4a** with sulfur and selenium are oligomers which, at higher temperatures, dissociate into monomeric $\sigma^3\lambda^5$-phosphoranes (Scheme 1) [7].

In contrast to **4a**, P-aryl-substituted iminophosphines **4b-d** react with elemental sulfur and selenium to give the monomeric compounds **5b-d** and **6b,c** (Scheme 2). The new imino (chalcogeno)phosphoranes were isolated in good yields as highly air- and moisture-sensitive yellow crystalline solids readily soluble even in nonpolar organic solvents. In the ^{31}P NMR spectra they show a signal in the expected lowfield region (δP = 155–162); the coupling constants with ^{77}Se (**6b**, 964 Hz; **6c**, 927 Hz) are usual for a double bond between phosphorus and selenium [11] and comparable to that observed for **6a** (916 Hz), formed *via* dissociation. Imino(chalcogeno) phosphoranes **5b-d** and **6b,c** are completely stable in an argon atmosphere and can be stored for long periods (Table 1).

The $\sigma^3\lambda^5$-phosphorane structure **5d** has been established by a single crystal X-ray diffraction study

FIGURE 1 Crystal structure of the imino(thioxo)phosphorane **5d** showing the atom numbering scheme.





4b-d

5b-d, X = S

6b, c, X = Se

R = Ph (b), 2,4,6-$Me_3C_6H_2$ (c), 2,4,6-i-$Pr_3C_6H_2$ (d)

Ar = 2,4,6-t-$Bu_3C_6H_2$

SCHEME 2

(Figure 1 and Table 2). The PSNC (1)C(19) unit is planar—the atom deviations from the least-squares plane don't exceed 0.020(2) Å. Due to the steric conditions C(1–6) and (C19–24) phenyl rings are orthogonal to this plane, the corresponding dihedral angles being 88.24(7) and 89.66(7)°. Between these rings, the dihedral angle is 13.2(1)°. Atom P has a planar bond configuration—the bond angles sum is 360.0(2)°. It is noteworthy that the SPN bond angle 131.26(6)° is essentially larger than those of SPC(19) and NPC(19). These results are in good agreement with quantum chemical calculations on the model systems X — P(=NH)$_2$, X = H, F Cl, Me, NH_2 SiH_3 [12, 13], and X — P(=S)$_2$, X = Cl [14]. The bond angle between double bonds is a feature of the $\sigma^3\lambda^5$-phosphoranes molecular structure [15–17] and obviously is connected with peculiarities of the three-center four electron π-system. The P=S bond in **5d** (1.910(1) Å) is much shorter than the single P — S bond in the dimer **3** (2.160(1) and 2.128(1)Å) [5], whereas the P=N bond lengths in these two molecules coincide within the error limits (1.530(1) and 1.529(2) Å respectively). The C(1) — N=P — C(19) fragment in **5d** has the *trans*-configuration (the corresponding torsion angle being 177.3(2)°). The bond lengths and bond angles distribution observed for this group is usual for $\sigma^3\lambda^5$-iminophosphoranes [9,18]. The geometry of the C(1–6) and C(19–24) benzene rings is unexceptional for the *t*-$Bu_3C_6H_2$- and *i*-$Pr_3C_6H_2$-substituents [19].

The identity of imino(chalcogeno)phosphoranes **5** and **6** was also corroborated by their chemical behavior (Scheme 3). The compounds **5b-d** react in refluxing benezene with hexaethylphosphorus triamide to afford quantitatively the λ^3-iminophosphines **4b-d** and thio-phosphoryl triamide, $(Et_2N)_3PS$, characterized in solution by their NMR data. An analogous reaction with formation of **4a** and $(Et_2N)_3P$ was observed when the oligomer **7** was treated with $(Et_2N)_3P$. Methanol adds quantitatively across the P=N double bond of **5b-d** and **6b,c** to form, respectivly, phosphonothioates **10** or phosphonoselenoates **11**. Oligomers **7** and **8** behave in a similar manner; however, their reactivity strongly depends on the temperature. Thus, the reactions between **7, 8** and protic reagents (methanol, piperidine) at room temperature take place very slowly. However, at higher temperatures (>80°C), reactions are completed within 1 hr. The conversions proceed probably *via* **5a, 6a**. Analytical data of the reaction products are given in Table 3.

In conclusion, it should be noted that the ability of the air- and moisture-stable oligomers **7** and **8** to dissociate into monomers at higher temperatures

TABLE 1 N-(2, 4, 6-Tri-*tert*-butylphenylimino)thioxo- and -selenoxophosphoranes /**5b-d, 6b,c**/

Compound	R	Yield (%)	mp (°C)	^{31}P NMR δ, ppm	Formula [b]	Found (%) calculated) C	H	P
5b	PH	53	185–187	158	$C_{24}H_{34}NPS$	72.12	8.51	7.52
						(72.14	8.58	7.75)
5c	Mes[c]	72	197–197	162	$C_{27}H_{40}NPS$	73.63	9.23	7.90
						(73.40	9.10	7.70)
5d	Tip[c]	60	151–153	163	$C_{33}H_{52}NPB$	75.20	9.78	5.91
						(75.34	9.97	5.88)
6b	Ph	59	181–185	161[d]	$C_{24}H_{40}NPSe$	64.78	7.70	6.89
						(66.41	8.25	6.34)
6c	Mes	85	151–152	156[e]	$C_{27}H_{40}NPS3$	66.63	8.23	6.48
						(66.41	8.25	6.34)

[a] Yields refer to purified products.
[b] *M*, Cryoscopy in C_6H_6, measured (calculated): **5b**, 392 (399.5); **5c**, 435 (441.7); **5d**, 512 (525.9); **6b** 431 (446.5); **6c**, 480 (488.6).
[c] Mes = 2, 4, 6-$Me_3C_6H_2$, Tip = 2, 4, 6-i-$Pr_3C_6H_2$.
[d] 1J(PSe) = 964 Hz.
[e] 1J(PSe) = 927 Hz.

TABLE 2 Important Bond Lengths (Å) and Angles (degrees)

P — S	1.9098(6)	S — P — N	131.26(6)
P — N	1.530(1)	S — P — C(19)	115.86(6)
P — C(19)	1.815(2)	N — P — C(19)	112.89(7)
N — C(1)	1.435(2)	P — N — C(1)	132.2(1)
C(1) — N — P — C(19)	177.3(2)		
C(1) — N — P — S	-2.5(2)		

renders them suitable for the preparative application as masked forms of imino(calcogeno)phosphoranes.

EXPERIMENTAL

All manipulations were carried out under a purified Ar atmosphere. Solvents were dried over CaH_2 (benzene, toluene) or sodium-benzophenone ketyl (ethers) and distilled under argon before use. Known methods were used for the preparation of the λ^3-iminophosphines **4a-c** [6].

^1H NMR spectra were performed on a Gemini-200 spectrometer. ^{31}P NMR spectra were recorded at 80 MHz with a Bruker WP-200 spectrometer using 85% H_3PO_4 as an external reference. Infared spectra were obtained on a Specord M80 instrument.

X-ray Structural Analysis of the Imino(thioxo)phosphorane ***5d***

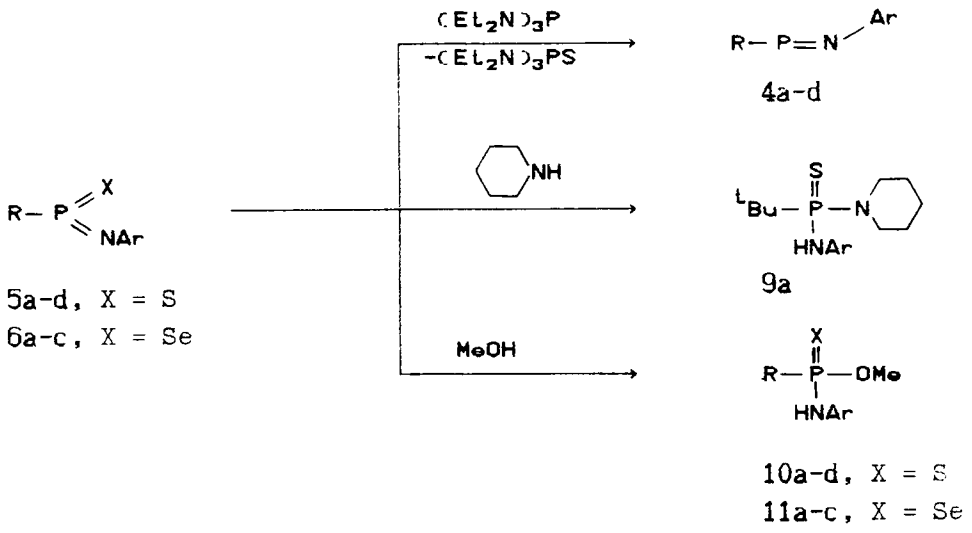
Crystal data: $C_{33}H_{52}NPS$, M = 525.8, monoclinic, a = 18.409(9), b = 17.625(7), c = 20.487(4) Å, β = 94.18(3)°, V = 6629.5Å^3, Z = 8, d_c = 1.05 g/cm^3, space-group C2/c (N 15), μ = 1.6 cm^{-1}, F(000) = 2304.

Crystallographic measurements were made at 18°C using the Enraf Nonius CAD-4 diffractometer operating in the ω-2θ scan mode (the ratio of the scanning rates ω/θ = 1.2). The intensity data were collected within the range $1 \leq \theta \leq 24°$ using graphite monochromated Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å). Intensities of 5230 unique relections were measured. The structure was solved by direct methods and refined by full-matrix least squares with the weighting scheme $\omega = 1/\sigma^2(F_o)$. In the refinement, 3494 reflections with $I > 4\sigma$ were used. About 70% of the hydrogen atoms were located in the difference Fourier maps, the positions of the remaining atoms were calculated. All H atoms were included in the final refinement with the fixed positional and thermal (B_{iso} = 5 Å^2) parameters. Convergence was obtained at R = 0.043 and R_w = 0.060. Corrections for Lorentz and polarization effects, but not for absorption, were applied. The calculations were performed using the SDP-PLUS program. Atomic coordinates are listed in Table 4. All crystal data are deposited at the Cambridge Crystallographic Data Centre [20].

TABLE 3 Phosphonothioates /**9a, 10a-d**/ and Phosphonoselenoates /**11a-c**/ Prepared

Compound	R	Yield[a] (%)	mp (°C)	Formula[b]	Found (%) calculated) C	H	P
9a	t-Bu	72	137–140	$C_{27}H_{49}N_2PS$	69.80 (69.78	10.67 10.63	6.68 6.66)
10a	t-Bu	66	120–122	$C_{23}H_{42}NOPS$	67.21 (67.11	10.19 10.28	7.54 7.52)
10b	Ph	76	91–93	$C_{25}H_{38}NOPS$	69.43 (69.57	8.93 8.87	7.03 7.17)
10c	Mes[b]	70	119–121	$C_{28}H_{44}NOPS$	70.50 (70.39	9.32 9.36	6.66 6.54)
10d	Tip[b]	75	110–112	$C_{34}H_{56}NOPS$	73.18 (73.20	10.11 10.12	5.63 5.55)
11a	t-Bu	70	97–1090	$C_{23}H_{42}NOPSe$	60.51 (60.25	9.32 9.23	6.63 6.75)
11b	Ph	72	84–86	$C_{25}H_{38}NOPSe$	62.70 (62.75	8.06 8.00	6.35) 6.47)
11c	Mes	56	114–116	$C_{28}H_{44}NOPSe$	64.51 (64.61	8.41 8.52	5.97 5.95)

[a] Yields of isolated pure products. Unoptimized.
[b] Mes = 2, 4, 6-$ME_3C_6H_2$, Tip = 2, 4, 6-i-$Pr_3C_6H_2$.



R = t-Bu (a), Ph (b), 2,4,6-$Me_3C_6H_2$ (c), 2,4,6-i-$Pr_3C_6H_2$ (d)

SCHEME 3

*Preparation of P-(2,4,6-Tri-isopropylphenyl)-N-(2, 4,6-tri-tert-butylphenyl)iminophosphine (**4d**)*

To a stirred solution of 2,4,6-tri-isopropylphenyl-dichlorophosphine (8.3 g, 27 mmol) in a mixture of diethyl ether (25 mL) and THF (75 mL) at −78°C was added dropwise lithium N-trimethylsilyl-N-(2, 4, 6-tri-*tert*-butylphenyl)amide (27 mmol; prepared from $ArNHSiMe_3$ in 60 mL THF and 13.5 mL of a 2.0 M solution of BuLi in hexane). The solution was slowly warmed to r.t. and stirred for 8 hr. Then the mixture was filtered, the filtrate was evaporated under reduced pressure, and hexane (150 mL) was added. Filtration, followed by solvent removal, and recrystallization of the residue form hexane afforded N-trimethylsilyl-N-(2,4,6-tri-*t*-butylphenyl)-amino (chloro)-2,4,6-tri-isopropylphenylphosphine as a colorless crystalline solid. Yield 8.8 g (54%), mp 115–117°C. ^1H NMR ($CDCl_3$/TMS): δ = 0.49 (d, $^4J_{PH}$ 2.2 Hz, 9H, Me_3Si); 0.98 (s, 9H, o-(*t*-Bu)); 1.05 (d, $^3J_{HH}$ 6 Hz, 6H, p-$(CH_3)_2CH$); 1.17 (d, $^3J_{HH}$ 6Hz, 12H, o-$(CH_3)_2CH$); 1.24 (s, 9H, o-(*t*-Bu)); 1.66 (s, 9H, p-(t-Bu)); 2.85 (m, 1H, o-$(CH_3)_2CH$); 4.15 m, ^1H, p-$(CH_3)_2CH$); 6.85 (d, $^2J_{PH}$ 0.6 Hz, 2H, C_6H_2); 7.55 (d, $^2J_{HH}$ 1.2 Hz, 2H C_6H_2). ^{31}P NMR (in C_6H_6): δ = 132. Anal. Calc. for $C_{33}H_{55}ClNPSi$: C 71.78; H 10.21; P 5.14; Si 4.66. Found: C 71.93; H 10.23; P 5.13; Si 4.81. The product was then dissolved in toluene (80 mL) and the solution was refluxed for 1 hr. After removal of the solvent and Me_3SiCl under reduced pressure, the iminophosphane **4d** remained as viscous, dark blue liquid of good purity. Yield 7.2 g (53%). ^1H NMR (C_6D_6/TMS): δ=1.18 (d, $^3J_{HH}$ 6.7 Hz, 6H, p-$(CH_3)_2CH$); 1.30 (d, $^3J_{HH}$ 6.5 Hz, 12H, o-$(CH_3)_2CH$); 1.42 (s, 9H, p-(t-Bu)); 1.53 (s, 18H, o-*t*-Bu)): 2.73 (m, ^1H, p-$(CH_3)_2CH$); 4.61 (m, 2H, o-$(CH_3)_2CH$); 7.20 (s, 2H, C_6H_2); 7.62 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6): δ = 465. Anal. Calc. for $C_{33}H_{52}NP$: C 80.27; H 10.62; P6.27. Found: C 80.35, H 10.55, P 6.35.

*Reaction of Iminophosphine **4a** with Sulfur and Selenium*

To a red-violet solution of iminophosphine **4a** (3.47 g, 10 mmol) in 15 mL benzene was added, at room temperature, an equivalent of sulfur (0.32 g, 10 mmol). The reaction mixture becomes yellow after 48 hr of stirring and the product precipitates as an amorphous, yellow solid. Filtration and drying *in vacuo* gave pure **7**. Yield 2.71 g (71%), mp 216–220°C (dec.). IR (KBr): 1592 (m), 1476 (m), 1456 (m), 1424 (vs), 1392 (m), 1358 (s), 1316 (vs) 1270, 1240, 1224, 1204, 1184, 1128 (m), 1056, 936, 880, 808, 788, 718, 676 (s), 644, 614 (s), 658 (m), 516 (m), 500, 456 (m), 500, 456 (m) cm^{-1}. ^{31}P NMR (C_6H_6): δ = −11. Anal. Calc. for $(C_{22}H_{38}NPS)_n$: C 69.61; H 10.09; P 8.16. Found: C 69.80; H 9.78; P 8.17.

Similarly, the reaction of **4a** with selenium leads to the formation of **8**. Yield 80%, mp 193–198°C (dec.). IR (KBr): 2970 (vs), 2912 (m) 2878 (m), 1480 (m), 1430 (s), 1398, 1365, 1310 (vs), 1246, 1185, 1130, 1060, 883, 775, 682, 680, 610, 510, (m), 455 cm^{-1}. ^{31}P NMR (C_6H_6): δ = −18 Anal. Calc. for $(C_{22}H_{38}NPSe)_n$: C 61.95; H 8.98; P 7.26. Found: C 62.92; H 8.72; P 8.17.

TABLE 4 Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors B_{eq} (Å^2) in structure **5d**

Atom	*x*	*y*	*z*	*B*
S	0.18005(4)	0.42320(4)	0.48904(3)	4.75(2)
P	0.17946(3)	0.43008(3)	0.58204(3)	2.97(1)
N	0.24167(9)	0.4379(1)	0.63536(9)	3.09(4)
C(1)	0.3193(1)	0.4398(1)	0.6327(1)	3.01(5)
C(2)	0.3600(1)	0.3714(1)	0.6403(1)	3.51(5)
C(3)	0.4349(1)	0.3755(1)	0.6355(1)	3.87(5)
C(4)	0.4724(1)	0.4418(2)	0.6257(1)	3.80(5)
C(5)	0.4316(1)	0.5082(1)	0.6243(1)	3.84(5)
C(6)	0.3568(1)	0.5101(1)	0.6288(1)	3.27(5)
C(7)	0.3261(1)	0.2931(1)	0.6535(1)	4.52(6)
C(8)	0.2872(2)	0.2620(2)	0.5909(2)	5.26(7)
C(9)	0.3846(2)	0.2337(2)	0.6753(2)	7.61(9)
C(10)	0.2762(2)	0.2974(2)	0.7109(2)	5.15(6)
C(11)	0.5558(1)	0.4433(2)	0.6222(1)	4.79(6)
C(12)	0.5848(2)	0.3713(3)	0.6016(3)	16.0(2)
C(13)	0.5790(2)	0.5019(3)	0.5751(2)	11.2(1)
C(14)	0.5893(2)	0.4623(4)	0.6875(2)	14.9(2)
C(15)	0.3188(1)	0.5889(1)	0.6297(1)	3.92(5)
C(16)	0.2768(1)	0.6046(2)	0.5648(1)	4.82(6)
C(17)	0.3755(2)	0.6531(2)	0.6423(2)	6.48(8)
C(18)	0.2705(1)	0.5938(2)	0.6874(1)	4.70(6)
C(19)	0.0905(1)	0.4268(1)	0.6146(1)	3.44(5)]
C(20)	0.0513(1)	0.4945(1)	0.6204(1)	3.75(5)
C(21)	-0.0199(1)	0.4891(2)	0.6399(1)	4.73(6)
C(22)	-0.0522(1)	0.4205(2)	0.6532(1)	4.98(7)
C(23)	-0.0117(1)	0.3550(2)	0.6466(1)	4.97(6)
C(24)	0.0590(1)	0.3559(1)	0.6270(1)	4.05(6)
C(25)	0.0819(1)	0.5707(1)	0.6036(1)	4.41(6)
C(26)	0.0740(2)	0.6305(2)	0.6567(2)	6.64(8)
C(27)	0.0490(2)	0.5979(2)	0.5376(2)	6.54(8)
C(28)	-0.1302(2)	0.4120(2)	0.6731(2)	6.76(9)
C(29)	-0.1788(2)	0.3825(2)	0.6159(2)	7.17(9)
C(30)	-0.1606(2)	0.4815(3)	0.7014(2)	9.4(1)
C(31)	0.0969(1)	0.2815(2)	0.6176(1)	4.72(6)
C(32)	0.0921(2)	0.2269(2)	0.6750(2)	6.64(8)
C(33)	0.0680(2)	0.2437(2)	0.5539(2)	6.32(8)

Synthesis of Imino(chalcogeno)phosphoranes ***5b-d, 6b,c.*** *General Procedure*

To a suspension of sulfur or selenium (10 mmol) in 10 mL of benzene was added at room temperature a solution of iminophosphine **4b-d** (10 mmol) in 10 mL of benzene. The initially blue solution turned yellow after 48 hr of stirring. Benzene was evaporated *in vacuo* and the residue crystallized from benzene to afford yellow crystals identified as **5b-d, 6b,c** (Table 1).

^{1}H NMR (C_6D_6, 200 MHz): **5b:** δ 1.36 (s, 9H, p-(t-Bu)), 1.62 (s, 18H, o-(t-Bu)), 6.84–7.00 (m, 5H, C_6H_5), 7.61 (d, $^5J_{HH}$ = 2.9 Hz, 2H, C_6H_2); **5c:** δ 1.36 (s, 9H, p-(t-Bu)), 1.69 (s, 18H, o-(t-Bu)), 1.94 (s, 3H, p-Me), 2.73 (d, $^4J_{PH}$ = 2.0 Hz, 6H, o-Me), 6.63 (d, $^4J_{PH}$ = 6.1 Hz, 2H, C_6H_2), 7.63 (d, $^5J_{PH}$ = 3.1 Hz, 2H, C_6H_2); **5d:** δ 1.13 (d, $^3J_{HH}$ = 7.0 Hz, 6H, p-CH(CH_3)$_2$), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 12H, 0-CH(CH_3)$_2$), 1.37 (s, 9H, p-(t-Bu)), 1.72 (s, 18H, o-(t-Bu)), 2.43 (m, $^3J_{HH}$ = 7.0 Hz, 1H p-*CH*(CH_3)$_2$), 4.27 (m, $^3J_{HH}$ 7.0 Hz, $^4J_{PH}$ 2.4 Hz, 2H, o-*CH*(CH_3)$_2$), 7.10 (s, 2H, C_6H_2), 7.68 (s, 2H C_6H_2); **6b:** δ 1.30 (s 9H, p-(t-Bu)), 1.62 (s, 18H, o-(t-Bu)), 6.90–7.06 (m, 5H, C_6H_5), 7.62 (d, $^5J_{PH}$ = 3.2 Hz, C_6H_2); **6c:** δ 1.36 (s, 9H, p-(t-Bu)), 1.95 (s, 3H, p-Me), 2.70 (s, 18H, o-(t-Bu)), 2.75 (d, $^4J_{PH}$ = 1.7 Hz, 6H, o-Me), 6.53 (d, $^4J_{PH}$ = 6.1 Hz, 2H, C_6H_2), 7.65 (d, $^5J_{PH}$ 3.2 Hz, 2H, C_6H_2). The ^{31}P NMR data are listed in Table 1.

Action of Hexaethylphosphorus Triamide on Imino(thioxo)phosphoranes

A mixture of imino(thioxo)phosphorane **5b-d** or oligomer **7** (10 mmol and $(Et_2N)_3P$ (10 mmol) was refluxed in 20 mL of dry toluene for 1 hr. The initially colorless solution turned dark blue after 20 min. of refluxing. After evaporation of all volatiles *in vacuo* a blue, oily residue remained, which was shown to consist of a mixture of **4a-d** and $(Et_2N)_3PS$ by means of NMR spectroscopy. ^{31}P NMR (C_6D_6): δ = 490 **(4a);**

415 **(4b)**; 456 **(4c)**; 465 **(4d)**. $(Et_2N)_3PS$: ^1H NMR (CD_2Cl_2/TMS: δ = 1.10 (t, $^3J_{HH}$ 6.9 Hz, 3H, Me); 3.10 (m, $^3J_{HH}$ 6.9 Hz, $^3J_{PH}$ 11.4 Hz, 2H, CH_2); ^{31}P NMR (C_6D_6): δ = 78.

Reactions of Imino(chalcogeno)phosphoranes **5, 6** *with Methanol and Piperidine. General Procedure*

Methanol (0.35 g, 11 mmol) or piperidine (0.94 g, 11 mmol) was added from a syringe to a solution of **5b-d** (10 mmol) in benzene (15 mL at 0°C. After the solution had been stirred for 5 hr at room temperature, volatiles were evaporated *in vacuo*. Recrystallization of the residue from methanol gave analytically pure product (Table 3). In the case when oligomers **7** and **8** were used as a source of $\sigma^3\lambda^5$-phosphorane, the reaction mixture was refluxed in benzene for 1 h.

9a: ^1H NMR ($CDCl_3$): δ 1.1–1.25 (m, 10H CH_2), 1.17 (d, $^3J_{PH}$ = 16.2 Hz, 9H, t-BuP), 1.29 (s, 9H, p-(t-Bu)), 1.62 (s, 18H, o-(t-Bu)), 4.39 (d, $^2J_{PH}$ = 8.1 Hz, 1H, NH), 7.33 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 91.

10a: ^1H NMR (C_6D_6): δ 1.28 (s, 9H, p-(t-Bu)), 1.31 (d, $^3J_{PH}$ = 17.1 Hz, 9H, t-BuP), 1.248 (s, 18H o-t-Bu)), 3.46 (d, $^3J_{PH}$ = 13. Hz 3H, MeO), 4.72 (d, $^2J_{PH}$ = 10.0 Hz, 1H, NH), 7.25 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 98.

10b: ^1H NMR (C_6D_6): δ 1.26 (s, 9H, p-(t-Bu)), 1.31 (s, 18H, o-(t-Bu)), 3.37 (d, $^3J_{PH}$ = 13.2 Hz, 3H, MeO), 4.81 (d, $^2J_{PH}$ = 10.0 Hz, 1H, NH), 7.11–7.28 (m, 5H, C_6H_5), 7.42 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 79.

10c: ^1H NMR (C_6D_6): δ 1.30 (s, 9H, p-(t-Bu)), 1.54 (s, 18H, o-(t-Bu)), 1.99 (s, 3H, p-Me), 3.04 (d, $^3J_{PH}$ = 13.9 Hz, 3H, MeO), 6.67 (d, $^4J_{PH}$ = 9.6 Hz, 2H, C_6H_2), 7.47 (d, $^5J_{PH}$ = 4.8 Hz, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 81.

10d: ^1H NMR (C_6D_6): δ 1.25 (d, $^3J_{HH}$ = 7.0 Hz, 12H, o-CH(CH_3)$_2$) 1.27 (d, $^3J_{HH}$ = 7.0 Hz, 6H, p-CH(CH_3)$_2$), 1.30 (s, 9H, p-(t-Bu)) 1.40 (s, 18H, o-(t-Bu)), 2.89 (m, $^3J_{HH}$ = 7.0 Hz, 1H, p-CH(CH_3)$_2$) 3.25 (d, $^3J_{PH}$ = 14.8 Hz, 3H, MeO), 4.39 (m, $^3J_{HH}$ = 7.0 Hz, 2H, o-CH(CH_3)$_2$, 7.09 (s, 2H, C_6H_2), 7.33 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 78.

11a: ^1H NMR (C_6D_6): δ 1.17 (d, $^3J_{PH}$ = 17.3 Hz, t-BuP), 1.28 (s, 9H, p-(t-Bu)), 1.57 (s, 18H, o-(t-Bu)), 3.31 (d, $^3J_{PH}$ = 13.8 Hz, 3H, MeO), 7.45 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 105, $^1J_{PSe}$ = 830 Hz.

11b: ^1H NMR (C_6D_6): δ 1.27 (s, 9H, p-(t-Bu)), 1.52 (s, 18H o-(t-Bu)), 3.31 (d, $^3J_{PH}$ = 14.7 Hz, 3H, MeO), 6.82–6.94 (m, 5H, C_6H_5), 7.42 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 105, $^1J_{PSe}$ = 842 Hz.

11c: ^1H NMR (C_6D_6); δ 1.28 (s, 9H, p-(t-Bu)), 1.53 (s, 18H, p-(t-Bu)), 1.99 (s, 3H, p-Me), 2.64 (s, 6H, o-Me), 2.95 (d, $^3J_{PH}$ = 14.5 Hz, 3H, MeO), 6.65 (d, $^4J_{PH}$ = 5.1 Hz, 2H, C_6H_2), 7.42 (s, 2H, C_6H_2). ^{31}P NMR (C_6H_6) δ 80, $^1J_{PSe}$ = 816 Hz.

REFERENCES

[1] O. J. Scherer and N. Kuhn, *Agnew. Chem., 86,* 1974, 899.

[2] O. J. Scherer and N. Kuhn, *J. Organomet. Chem., 78,* 1974, C17.

[3] H. Germa and J. Navech, *Phosporus and Sulfur, 26,* 1986, 327.

[4] E. Niecke and D. Gudat: Iminooxo-, Iminothioxo-, and Iminose-lenoxophosphoranes, in M. Regitz, J. O. Scherer (eds): and Iminoselenoxophosphoranes, in Regitz, J. O. Scherer (eds): *Multiplle Bonds and Low Coordination in Phosphorus Chemistry,* Thieme Verlag, Stuttgart, pp. 405–410 (1990).

[5] S. Pohl, *Chem. Ber.,* 109, 1976, 3122.

[6] L. N. Markovskii, V. D. Romanenko, A. B. Drapailo, A. V. Ruban, A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, *Zh. Obshch. Kim., 56,* 1986, 2231.

[7] L. N. Markovskii, V. D. Romanenko, A. V. Ruban, *Pure and Appl., 59,* 1987, 1047.

[8] E. Niecke, M. Lysek, E. Symalla, *Chimia, 40,* 1986, 202.

[9] A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, A. V. Ruban, V. D. Romanenko, *Zh. Strukt. Khim., 29,* 1988, 133.

[10] O. J. Scherer and N. Kuhn, *J. Organomet. Chem., 82,* 1974, C3.

[11] The coupling constant for a phosphorus-selenium double bond is generally between 750 and 1000Hz. M. Yoshifuji., K. Shibayama, N. Inamoto, *Chem. Lett.,* 1984, 603; O. J. Scherer, N. Kuhn, *J. Organomet. Chem.,* 78, 1974, C17; Th. Van der Knapp. M. Vos, F. Bickelhaupt, *J. Organomet. Chem.,* 244, 1983, 363; L. Weber, G. Meine, N. Neiderprum, R. Boese, *Organometallics, 6,* 1987, 1989.

[12] R. Ahlrichs, H. Sciffer, *J. Am. Chem. Soc.,* 107, 1985, 6494.

[13] W. W. Schoeller, C. Lerch, *Inorg. Chem.,* 25, 1986, 576.

[14] S. Mathieu, J. Navech, J. C. Barthelat, Inorg. Chem., 28, 1989, 3099.

[15] R. Appel, E. Gaitzsch, K.–H. Dunker, F. Knoch, *Chem. Ber.,* 119, 1986, 535.

[16] M. Caira, R.H. Neilson, W. H. Watson, P. Wisian-Neilson, Ze-Min-Xie, *J. Chem.Soc., Chem.Commun.,* 1984, 698.

[17] M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, T. Higuchi, J. Chem. Soc., *Chem. Commun.,* 1983, 862.

[18] A. N. Chernega, E. B. Rusanov, A. B. Ruban, V. D. Romanenko, *Zh. Strukt. Khim.,* in press.

[19] A. N. Chernega, A. V. Ruban, V. D. Romanenko, L. N. Markovski, A. A. Korkin, M. Yu. Antipin, Yu. T. Struchkov, *Heteroatom Chem.,* 2, 1991, 229.

[20] CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.