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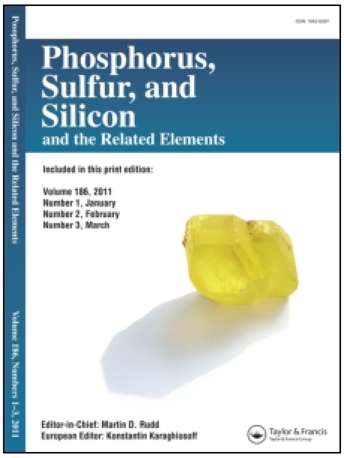

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NMR STUDIES OF P—N BOND ROTATION IN SOME PHOSPHORUS(III) AND PHOSPHORUS(V) COMPOUNDS CONTAINING A DIETHYLAMINO GROUP

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Compounds of the type $R'P(X)NEt_2$ ($R' = Bu^t$, $OCH(CF_3)_2$; $X = F$, $OCH(CF_3)_2$, Cl) and $Bu^tP(Y)(X)NEt_2$ ($Y = S$, Se; $X = F$, $OCH(CF_3)_2$, Cl) were synthesised and investigated in solution by variable temperature NMR spectroscopy. Barriers to rotation about the P—N bond are essentially determined by steric factors and increase with increasing size of the substituents on the phosphorus atom.

INTRODUCTION

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The investigation of stereochemical processes in aminophosphines has stimulated much work in the past decade, the bulk of which has concentrated on chiral phosphorus(III) compounds containing nitrogen donor ligands.[1–13] Attention has centred on the detection of P—N rotational barriers, and rigorous NMR studies have been carried out by several workers to determine the size of the barrier and to what extent it is influenced by the substituents on the phosphorus and nitrogen centres.[1,4,7,10,11]

The possibility of observing other processes, such as pyramidal inversion, has been considered[1,5,7] but in general, phosphorus inversion is slow (on the NMR timescale)[12,14] and thus not observed, whilst nitrogen inversion remains rapid even at low temperatures.[7,12]

Studies on compounds of the type $R'P(X)NR''_2$ (X = halogen; R′ = alkyl, aryl; R″ = alkyl) have shown rotational barriers[2] to be in the range of 42–63 kJ mole^{-1}. Varying the groups R′, R″, X has a dramatic effect on the rotational barrier and experimental evidence suggests that increasing the size of substituents on nitrogen increases the rotational barrier[1,11] whilst increasing the size of substituents on phosphorus decreases the barrier.[11]

The occurrence of this barrier has been attributed either to repulsive interactions between vicinal lone pairs of electrons[1,5,6] or to the involvement of (p–d)π bonding in the tortional process,[3] or to a combination of both.[7]

In an effort to further investigate these conformational processes we have synthesized the compounds, $R'P(X)NEt_2$, ($R' = Bu^t$, $OCH(CF_3)_2$; $X = F$, $OCH(CF_3)_2$, Cl) with emphasis on phosphines containing the hexafluoroisopropoxy group ($OCH(CF_3)_2 = OR_f$). Interest in this ligand is due to its large size and strong electron withdrawing properties which should have considerable influence on the P—N rotational barrier. Phosphorus(V) compounds of the series $Bu^tP(Y)(X)NEt_2$ ($Y = S$, Se; $X = F$, OR_f, Cl) were also investigated and the results compared with data for the phosphorus(III) series. We now report the synthesis and NMR study of these systems.

RESULTS AND DISCUSSION

Three and four coordinate phosphorus compounds

Compounds of the type $R'P(X)NEt_2$ ($R' = Bu^t$, OR_f; $X = F$, OR_f, Cl) were prepared in high yields, as described in the experimental section. Phosphorus-31 NMR was used as a quantitative measure of the purity of the compounds (Table I). Variable temperature Carbon-13 NMR was used to study the stereochemistry of the above compounds and the Carbon-13 chemical shifts are tabulated in Table II.

The ^{13}C—(H) NMR spectrum of $Bu^tP(OR_f)NEt_2$ at −80°C shows separate doublets for each of the methylene carbons A and A′ ($^2J_{(PC)} = 42.5$ Hz and $^2J_{(PC)} = 7.3$ Hz respectively) and singlets for each of the adjacent methyl carbons B and B′ (Figure 1). These spectral assignments are made on the basis of previous work which has shown an angular dependence of two bond coupling constants in phosphines bonded to a trigonal nitrogen.[15] On raising the temperature, the two doublets A and A′, due to the methylene carbons, collapse to a single doublet whose chemical shift and coupling to phosphorus are the average of those observed at low temperature. The resonances of the adjacent methyl carbons B and B′ collapse to a singlet at room temperature. The related compounds $Bu^tP(Cl)NEt_2$ and $Bu^tP(F)NEt_2$ show similar changes in the region of the methylene carbons (A and A′) however non-equivalence of the adjacent methyl carbons (B and B′) is not observed in these two cases.

Substituting an OR_f group for the Bu^t group i.e. $(OR_f)P(X)NEt_2$, (X = F, Cl), yields the following data. In the case of $(OR_f)P(F)NEt_2$, only broadening of the methylene carbon resonance is observed at −90°C; however, with the compound

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TABLE I

^{31}P and ^{19}F NMR data for 3 and 4 coordinate phosphorus compounds (δ ppm, J Hz) at 20°C

Compound	δP	δF		δSe
		$C\underline{F}_3$	$P\underline{F}$	
$Bu^tP(Cl)NEt_2$	156.7			
$Bu^tP(OR_f)NEt_2$	168.9	−73.4		
$Bu^tP(F)NEt_2$	181.0		−137.6; $^1J_{PF} = 937$	
$(OR_f)P(Cl)NEt_2$	172.8	−74.5		
$(OR_f)P(OR_f)NEt_2$	159.5	−74.9		
$(OR_f)P(F)NEt_2$	153.0	−75.2	−72.0; $^1J_{PF} = 1157$	
$Bu^tP(Se)(Cl)NEt_2$	118.0			−1481.5; $^1J_{PSe} = 874$
$Bu^tP(Se)(OR_f)NEt_2$	124.0	−73.3		−1678.8; $^1J_{PSe} = 866$
$Bu^tP(Se)(F)NEt_2$	130.0		−89.8; $^1J_{PF} = 1099$	−1584.5; $^2J_{SeF} = 30$; $^1J_{PSe} = 905$
$Bu^tP(Se)Cl_2$	101.0			−1209.4; $^1J_{PSe} = 928$
$NEt_2P(Se)Cl_2$	39.7			−1202.2; $^1J_{PSe} = 996$
$Bu^tP(S)(Cl)NEt_2$	117.1			
$Bu^tP(S)(OR_f)NEt_2$	112.2	−73.47		
$Bu^tP(S)(F)NEt_2$	118.7		−86.8; $^1J_{PF} = 1084$	

TABLE II

Ambient temperature ^{13}C NMR data of 3 coordinate phosphorus(III) compounds (δ ppm; J Hz)

Compound	$(\underline{C}F_3)_2CHO$	$(CF_3)_2\underline{C}HO$	$H\underline{C}H_2CH_3$	$(CH_3)_3\underline{C}$	$(\underline{C}H_3)_3C$	$NCH_2\underline{C}H_3$
$Bu^tP(Cl)NEt_2$			44.6; $^2J_{Pc} = 16.1$	37.6; $^1J_{PC} = 33.7$	26.1; $^2J_{PC} = 19.0$	14.4; $^3J_{PC} = 4.0$
$Bu^tP(OR_f)NEt_2$	122.8 $^1J_{FC} = 285.3$	76.2 $^2J_{PC} = 20.6$ $^2J_{FC} = 31.9$	44.0 $^2J_{PC} = 26.4$	35.5 $^1J_{PC} = 12.6$	25.7 $^2J_{Pc} = 22.5$	15.1
$Bu^tP(F)NEt_2$			43.2 $^2J_{PC} = 19.1$	35.1 $^1J_{PC} = 23.4$ $^2J_{FC} = 14.6$	25.6 $^2J_{PC} = 19.1$	15.6
$(OR_f)P(Cl)NEt_2$	121.6 $^1J_{FC} = 285$	71.0[a]	39.5 $^2J_{PC} = 20.7$			14.3
$(OR_f)P(F)NEt_2$			37.9 $^2J_{PC} = 22.7$			15.0
$(OR_f)P(OR_f)NEt_2$	122.7 $^1J_{FC} = 282.8$	71.8 $^2J_{PC} = 16.2$ $^2J_{FC} = 33.7$	38.9 $^2J_{PC} = 21.9$			14.7
Bu^tPCl_2				38.5 $^1J_{PC} = 44.0$	23.6 $^2J_{PC} = 20.3$	
NEt_2PCl_1			40.5 $^2J_{PC} = 25.0$			

[a] Unresolved multiplet.

$(OR_f)P(Cl)NEt_2$ the methylene carbon-13 resonance begins to broaden at −60°C, and upon further cooling to −90°C coalescence occurs. Low solubility prevented further lowering of temperature.

The barriers to P—N bond rotation were calculated using the Eyring equation[6] and the values (Table III) show that the barrier increases with increasing size of the substituent X, strongly suggesting that this barrier is due to steric interactions.

The origins of P—N rotational barriers have been previously attributed to (i) steric interactions (ii) multiple bonding due to nitrogen-phosphorus (p–d)π overlap[3] and (iii) a combination of the above.[7]

Previous workers showed that P—N rotational barriers increase with increasing bulk on the nitrogen[1,11] in agreement with a simple steric interaction. DiStefano and coworkers[11] also investigated the effects on the rotational barrier of changing the phosphorus substituent in $RP(Cl)NMe_2$ (R = Me, Et, Pr^i, Bu^t), and concluded that increasing the bulk of substituents on phosphorus decreases the barrier. This latter observation is not in accordance with a simple steric interaction model. However if the amino methyl groups are replaced by isopropyl groups,[5] the reverse trend was observed. That is, the barrier again increased with the bulk of the R group, consistent with a steric effect.

The effect of multiple bonding, due to phosphorus–nitrogen (p–d)π overlap, has also been investigated by a number of workers, who concluded that this type of bonding by itself would not be expected to lead to hindered rotation.[1,17] It has been postulated that electron withdrawing groups on phosphorus enhances its behaviour as a π-acceptor, thus leading to increased (p–d)π multiple bonding.[3] Obviously any increase in P—N multiple bonding would cause the P—N bond to shorten and thereby bring the substituent on the nitrogen atom closer to the phosphorus atom thus increasing steric interactions which, in turn, would increase the P—N rotational

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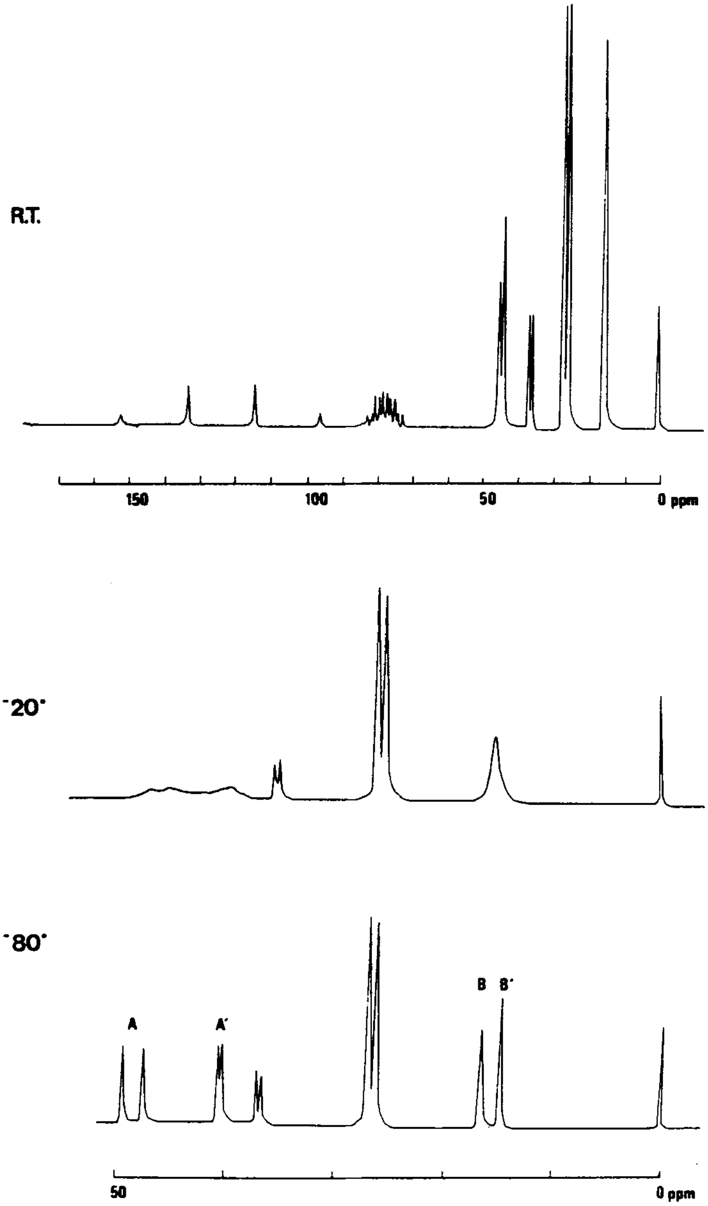

FIGURE 1 Variable temperature carbon-13 spectra of $Bu^tP(OR_f)NEt_2$.

barrier. Thus the unexpected decrease of the rotational barrier in the series, $RP(Cl)NMe_2$ (R = Me, Et, Pr^i, Bu^t) found by DiStefano and coworkers[11] can be explained in terms of the barrier being sensitive to the electronegativity of the phosphorus substituents, since the amine itself has little steric influence. If the phosphorus substituents are not very electronegative, it may be that the phosphorus d-orbitals are too diffuse to overlap efficiently with the nitrogen lone pair orbitals.

TABLE III

P—N rotational barriers in 3 and 4 coordinate phosphorus compounds

Compound	Coalescence temperature[a] T_c (Kelvin)	Frequency separation of resolved structure[b] $\Delta\nu$ (Hertz)	Free energy of activation[c] $\Delta G^{\neq}$ (kJ mol^{-1})
$Bu^tP(Cl)NEt_2$	238	176	46.2
$Bu^tP(OR_f)NEt_2$	268	189	52.1
$Bu^tP(F)NEt_2$	193	147	37.4
$(OR_f)P(Cl)NEt_2$	183	unresolved	< 37.4
$(OR_f)P(F)NEt_2$	< 183		
$Bu^tP(Se)(Cl)NEt_2$	< 203		
$Bu^tP(Se)(OR_f)NEt_2$	193	88	38.2
$Bu^tP(Se)(F)NEt_2$	< 183		
$Bu^tP(S)(Cl)NEt_2$	< 203		
$Bu^tP(S)(OR_f)NEt_2$	183	45	37.0
$Bu^tP(S)(F)NEt_2$	< 173		

[a] Error in coalescence temperature ±2 K.

[b] Error in frequency separation ±1 Hz.

[c] $\Delta G^{\neq} = 0.0192T_c\ (9.97 + \log_{10}T_c/\Delta\nu)$ kJ mol^{-1} estimate error ± 0.8 kJ mol^{-1}.

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This would lead to a decrease in multiple bond character and a subsequent decrease in the rotational barrier. The electron releasing power of the R groups[18] varies Me < Et < Pr^i < Bu^t which also corresponds to the direction in which DiStefano and coworkers observed a decreasing barrier. Thus the barrier in those series of compounds apparently decreases due to the electronegativity of the R group rather than due to its bulk.

Within the series of phosphines listed in Table III, the electronegativity of the X substituents increase Cl < OR_f < F so that if electronic effects alone control the barrier, the phosphine $Bu^tP(OR_f)NEt_2$ would be expected to have a lower barrier than the corresponding chloride, and a higher barrier than the fluoride. The fact that the barrier actually decreases in the order X = OR_f > Cl > F further suggests that the restricted rotation observed is largely sterically controlled.

Replacing the electron lone pair on phosphorus with a group VI atom gives compounds of type $Bu^t(P(Y)(X)NEt_2$ (Y = S, Se; X = F, OR_f, Cl) for which NMR data are presented in Table IV. The barriers to rotation in these phosphorus(V) molecules are lower than in the corresponding phosphorus(III) compounds (Table III), however it is difficult to compare the two series since the phosphorus is in different oxidation states, which in turn implies different relative energies of the d-orbitals, as well as different size phosphorus centres. The stereochemistry of these four coordinate phosphorus(V) compounds is however unchanged and a low temperature Carbon-13 study revealed similar spectral changes as observed for the phosphines described above.

Most of these compounds required lower temperatures than were accessible to "slow" the P—N rotation on the NMR timescale. Of those that were able to be resolved it was evident that the barrier increased in the direction X = F < Cl < OR_f, as is observed with the phosphines. It was also noted that the barrier in the bulkier, $Bu^tP(Se)(OR_f)NEt_2$ ($\Delta G^{\ddagger}$ = 38.2 ± 0.8 kJ mole^{-1}) was larger than in the corre-

TABLE IV

Ambient temperature ^{13}C NMR data of 4 coordinate phosphorus(V) compounds (δ ppm; J Hz)

Compounds	$(\underline{C}F_3)_2CHO$	$(CF_3)_2\underline{C}HO$	$N\underline{C}H_2CH_3$	$(CH_3)_3\underline{C}$	$(\underline{C}H_3)_3C$	$NCH_2\underline{C}H_3$
$Bu^tP(Se)(Cl)NEt_2$			43.3	47.1 $^1J_{PC} = 71.3$	26.2	13.9 $^3J_{PC} = 4.9$
$Bu^tP(Se)(OR_f)NEt_2$	121.0 $^1J_{FC} = 282$	70.5[a]	42.4	41.8 $^1J_{PC} = 89.0$	26.1	14.3
$Bu^tP(Se)(F)NEt_2$			42.0	41.5 $^1J_{PC} = 86.8$ $^2J_{PC} = 23.5$	26.0	14.5
$Bu^tP(S)(Cl)NEt_2$			42.5	46.2 $^1J_{PC} = 85.5$	26.2	13.9 $^3J_{PC} = 3.6$
$Bu^tP(S)(OR_f)NEt_2$	120.9 $^1J_{FC} = 286$	68.1[a]	40.9	39.7 $^1J_{PC} = 101.3$	25.3	14.1
$Bu^tP(S)(F)NEt_2$			41.1	39.7 $^1J_{PC} = 98.7$ $^2J_{FC} = 28.3$	25.8	14.2
$Bu^tP(Se)Cl_2$				51.1 $^1J_{PC} = 50.8$	24.8	
$NEt_2P(Se)Cl_2$			42.9			13.45

[a] Unresolved multiplet.

sponding sulphide ($\Delta G^{\ddagger} = 37.0 \pm 0.8$ kJ mole^{-1}) which is in agreement with the hypothesis postulated earlier that the barrier is caused mainly by steric interactions.

In summary it appears that P—N rotational barriers are primarily influenced by steric factors. Electronic factors may lead to changes in P—N bond lengths which in turn are reflected by changes in steric interactions and changes in P—N rotational barriers.

EXPERIMENTAL

The normal precautions required in handling air and moisture sensitive compounds were observed. Volatile materials were handled using a conventional Pyrex-glass vacuum line fitted with Teflon taps. Phosphorus-31, Fluorine-19, and Carbon-13 spectra were recorded on a Jeol FX 100 spectrometer. Reference compounds were tetramethylsilane (internal), CCl_3F (internal), and 85% H_3PO_4 (external). High frequency positive convention is used throughout. The paramagnetic relaxant tris(acetylacetonato) chromium(III)[22] was added to the solutions to reduce relaxation times of carbon. Trichlorofluoromethane was used as a solvent in all measurements.

Reagents. The starting materials Bu^tPCl_2,[19] $Li[OCH(CF_3)_2]$,[20] $(Et_2N)_{3-n}PCl_n$ ($n = 0, 1, 2$),[13] were prepared by literature methods. The compounds $HNEt_2$, PCl_3 and PBr_3 were purified by distillation prior to use.

Preparation of Diethylamino-tert-butyl-chlorophosphine. Diethylamine (50 mmol) was condensed into a thick walled glass tube, fitted with a Teflon tap, containing tert-butyldichlorophosphine[19] (25 mmol) and allowed to warm to room temperature over a period of one hour. The product, $Bu^tP(Cl)NEt_2$, was extracted with ether and filtered, using Schlenk apparatus, to remove the solid diethylaminehydrochloride. The solution was distilled under an inert atmosphere to remove ether and then distilled in vacuo to give a colourless viscous liquid. (B.P. = 86°C/12 mmHg; Vapour pressure = 0.51 mmHg/25°C). The purity of the product was checked by ^{31}P and ^{1}H NMR.[21]

Diethylamino-1,1,1,3,3,3-hexafluoro-2-propoxy-tert-butyl-phosphine. Diethylamino-tert-butyl-chlorophosphine (25 mmol) was condensed into a thick walled glass tube, fitted with a Teflon tap, containing $Li[OCH(CF_3)_2]$ (30 mmol) and allowed to warm to room temperature over 15 minutes. To ensure complete reaction the tube was left to stand for a further 60 minutes.

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The colourless liquid, Bu^{t}P(OR$_f$)NEt$_2$, was condensed into another tube, at −196°C, in quantitative yield. Vapour pressure = 0.85 mmHg/25°C.

Diethylamino-tert-butyl-fluorophosphine. Diethylamino-tert-butyl-chlorophosphine (25 mmol) was condensed into a tube containing an excess of SbF$_3$, and allowed to reach room temperature over 15 minutes. The tube was then heated to 50°C to ensure complete reaction. The colourless volatile liquid, Bu^{t}P(F)NEt$_2$, was condensed into another tube at −196°C.

Diethylamino-1,1,1,3,3,3-hexafluoro-2-propoxy-chlorophosphine. Diethylamino-dichlorophosphine,[13] (25 mmol) was condensed into a glass tube at −196°C, containing Li[OCH(CF$_3$)$_2$] (25 mmol). The reaction tube was allowed to warm to room temperature over 15 minutes and then heated to 50°C. The product, Et$_2$NP(Cl)OR$_f$, was condensed under vacuum into another tube at −196°C, as a colourless liquid.

Diethylamino-1,1,1,3,3,3-hexafluoro-2-propoxy-fluorophosphine. Diethylamino-1,1,1,3,3,3-hexafluoro-2-propoxy-chlorophosphine (25 mmol) was condensed into a thick walled glass tube at −196°C, containing an excess of SbF$_3$, and allowed to warm to room temperature over 15 minutes. The tube was gently warmed to room temperature and the product Et$_2$NP(F)OR$_f$ was condensed as a colourless liquid into another tube at −196°C.

Diethylamino-bis-(1,1,1,3,3,3-hexafluoro-2-propoxy)-phosphine. Diethylamino-dichlorophosphine (25 mmol) was condensed into a thick walled tube, fitted with a Teflon tap, containing Li[OCH(CF$_3$)$_2$] (60 mmol). The tube was allowed to warm to room temperature over 20 minutes and the product (Et$_2$N)P(OR$_f$)$_2$ condensed into another tube at −196°C.

Preparation of Bu^{t}P(Y)(X)NEt$_2$ (*Y* = *S*, *Se*: *X* = *F*, *OR*$_f$, *Cl*). Bu^{t}P(X)NEt$_2$ (X = F, OR$_f$, Cl) was condensed into a thick walled tube, fitted with a Teflon tap, containing an excess of dry sulphur or, selenium. The tube was then placed in a water bath at 100°C for 12 hours. In all cases the products were pale yellow, involatile liquids. Excess sulphur or selenium was removed from the products by filtration under vacuum. Yields were quantitative.

Analyses:

Bu^{t}P(S)(F)NEt$_2$	$C_8H_{19}FNPS$	Calc: C, 45.50; H, 9.07
		Found: C, 45.49; H, 9.07
Bu^{t}P(S)(Cl)NEt$_2$	$C_8H_{19}ClNPS$	Calc: C, 42.21; H, 8.42
		Found: C, 41.86; H, 8.29
Bu^{t}PS(OR$_f$)NEt$_2$	$C_{11}H_{20}F_6NOPS$	Calc: C, 36.78; H, 5.61
		Found: C, 37.01; H, 5.75
Bu^{t}P(Se)(F)NEt$_2$	$C_8H_{19}FNPSe$	Calc: C, 37.22; H, 7.42
		Found: C, 37.55; H, 7.64
Bu^{t}P(Se)(Cl)NEt$_2$	$C_8H_{19}ClNPSe$	Calc: C, 35.00; H, 6.98
		Found: C, 36.00; H, 7.03
Bu^{t}P(Se)(OR$_f$)NEt$_2$	$C_{11}H_{20}F_6NOPSe$	Calc: C, 32.53; H, 4.96
		Found: C, 32.90; H, 5.12

Analyses were performed by the Australian Microanalytical Service, Port Melbourne, Victoria.

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