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Core Photoelectron Spectroscopy of Some Volatile Phosphorus Halides

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Core level (P_{2p}) apparent binding energies of gaseous PF_5 (144.65 eV), OPF_3 (143.30 eV), SPF_3 (142.72 eV), PF_3 (141.95 eV), $OPCl_3$ (141.3 eV), $SPCl_3$ (140.8 eV), and PCl_3 (140.1 eV) (vs. $Ar_{2p_{3/2}}$ at 248.62 eV) excited by Mg Kα radiation have been measured. Also measured were F_{1s}, O_{1s}, Cl_{2s}, Cl_{2p}, S_{2p}, S_{2s}, and some P_{2s} apparent binding energies on these same compounds. The P_{2p} binding energies display regular trends with respect to formal charge, electronegativity, and the relaxation potential model (RPM) utilizing modified CNDO potentials. The CNDO ground potential model (GPM) fails to predict the correct direction of binding energy shifts for $OPCl_3$ and $SPCl_3$. The F_{1s} peak of PF_5 shows evidence for two fluorine atom environments in this molecule.

Introduction

Core electron binding energy shifts represent changes in molecular potentials arising from chemical bonding.[2] As part of a study of simple phosphorus compounds in the gaseous state we have determined the phosphorus "core level" binding energies (the usual P_{2p} as well as some P_{2s}) of a series of halides PX_3, OPX_3 and SPX_3 (X = F, Cl), and PF_5. Also included are the core levels (Cl_{2s} and Cl_{2p}, F_{1s}, O_{1s}, S_{2s} and S_{2p}) of the substituents. The results are given in Table I.

Results and Discussion

It is interesting to note, in contrast to a previous study of solid organophosphoryl and -thiophosphoryl derivatives,[3] that there is a definite decrease in P_{2p} binding energy upon substitution of sulfur for oxygen in $EPCl_3$. Such a change is expected on the basis of Pauling charge or electronegativity correlations as well as more sophisticated analyses and it is surprising that such differences were not observed in the organophosphorus compounds. Variation in sample charging characteristics may explain the lack of observable effect in the previous study and the difference emphasizes the value of making measurements in the gas phase.

In all cases, P_{2p} and P_{2s} binding energy differences were relatively constant. Because the former is the stronger and sharper line, measurements of its energy are more reliable; therefore we will discuss binding energy shifts in terms of P_{2p} values only. It is interesting to note however that P_{2p} and P_{2s} energies are affected equally by valence-shell perturbations and that either can be used as a "core level" probe.

In no case were the $2p_{1/2}$–$2p_{3/2}$ doublets of phosphorus resolved with the Mg Kα excitation employed although a slightly asymmetric curve was obtained which could be separated into components by curve analysis[4] to yield a doublet spacing of approximately 0.9 eV. The $2p_{1/2}$–$2p_{3/2}$ doublet of Cl was also not resolved although the lines were more asymmetric that those for either phosphorus or sulfur.

As might be expected, P_{2p} (and P_{2s}) binding energies increase with oxidation state of phosphorus. Notable also is the greater P_{2p} binding energy of PF_5 relative to both OPF_3 and SPF_3 although all three compounds have the same formal valence. This difference is expected from simple charge analysis such as that due to Pauling[5] and a plot of the binding energies vs. Pauling charge (Figure 1) yields a smooth curve which connects all points except those of $SPCl_3$ and SPF_3 with a nearly linear correlation existing between PCl_3, $OPCl_3$, and PF_3. The two thiophosphoryl compounds can be placed on the curve only if the ionic character of the P=S bond is increased to 25% from the accepted value of 10% which is equivalent to increasing the electronegativity of sulfur from the accepted value of 2.75 to a new value of 3.15. While such a revision may be warranted, the present data do not provide sufficient support for such a change and in fact the electronegativity correlation (vide infra) refutes such an adjustment.

A similar correlation of P_{2p} binding energies with the total electronegativity of the substituents on phosphorus, in contrast to the success of this approach in the halogenated methane series,[6] is successful only within a very limited portion of the series investigated here. For example there is a linear relationship based on the sum of electronegativities of substituents on phosphorus which connects the P_{2p} binding energies of PF_3, OPF_3, and PF_5 (but not SPF_3), and a similar linear relationship connects the total substituent electronegativity with the P_{2p} binding energies of the chlorides PCl_3, $OPCl_3$, and $SPCl_3$ but the two lines are not coincident. Furthermore, using the higher electronegativity of S (suggested by the charge analysis above) makes the correlations worse, reinforcing our reluctance to revise the electronegativity of sulfur.

The group shift parameters of Hedman et al.[7] suffer from the same major deficiency in their inability to correlate fluorides with chlorides and also this system fails to correlate thiophosphoryl halide, SPF_3 and $SPCl_3$, P_{2p} binding energies with those of the analogous phosphino and phosphoryl halides containing the same halogen.

Two successful correlations of binding energy with molecular parameters were achieved. A thermochemically based correlation is shown by the relatively good linear relationship between the total atomization enthalpies of the compounds (Table II) and their P_{2p} binding energies (Figure 2). The predictive capability of this correlation, as suggested by the relatively large deviations from the straight line, is rather low, but it does suggest that appropriate ground-state molecular properties may provide a reasonable correlation with binding energies in these compounds. This correlation, which is suggested by the thermochemical scheme of Jolly and Hendrickson[8] and which presumably arises from similar origins, possesses an advantage over the original method since only the heat of formation of the compound and readily accessible atomization enthalpies of the elements involved are required, obviating the need for thermochemical data for the "equivalent core" isoelectronic ion[9] which may be unavailable. It is worth noting that, to date, no experimental enthalpy of formation value is available for SPF_3 and its position on the graph was deduced from an estimated value for this quantity.[10] Thus, even for simple compounds, the requisite thermochemical data may not be available.

The major disadvantage of the atomization enthalpy correlation arises from the fact that it reflects the ground-state behavior of the molecule and does not include the implicit correction for relaxation effects provided by the Jolly and Hendrickson equivalent core method. Additional investigation of the correlation of binding energies with atomization enthalpies may be warranted in systems such as the present where the lack of data prevents the employment of the equivalent core approach[8] because atomization enthalpies can be obtained

Table I. Core Electron Binding Energies of Phosphorus Compounds[a,b]

	P_{2p}	P_{2s}	F_{1s}	O_{1s}	Cl_{2p}	Cl_{2s}	S_{2p}	S_{2s}
PF_3	141.95 (1.68)^{c,d}	199.6 (2.50)	694.2 (1.59)					
OPF_3	143.30 (1.74)^d	Ni	695.8 (1.59)	539.3 (1.32)				
SPF_3	142.72^e (2.16)^d	199.75^e (2.80)	694.9^e (1.81)				170.3^e (2.39)	234.2^e (2.9)
PF_5	144.65 (1.70)^d	Ni	694.9 (2.25)^f					
PCl_3	140.1^g (1.64)^d	198.1 (2.6)			206.6^e (2.75^d)	278.2^e (2.7^d)		
$OPCl_3$	141.3^g (1.69)^d	198.8 (2.52)		538.1 (1.21)	207.4^e (2.6^d)	278.2^e (3.0^d)		
$SPCl_3$	140.8^g (1.62)^d	198.1 (2.79)			206.5^e (2.6^d)	277.6^e (2.8^d)	169.2^g (2.2^d)	233.2^e (2.9)

[a] Vs. $Ar_{2p_{3/2}}$ at 248.62 eV.[14] Values are estimated to be accurate to ±0.2 eV. Ni = not investigated. [b] Fwhm given in brackets obtained by gaussian analysis. [c] Separable by curve analysis into $2p_{1/2}$, $2p_{3/2}$ components of 0.93 eV at fwhm with energies of 141.04 and 141.97 eV, respectively. [d] Fwhm given includes both $2p_{1/2}$ and $2p_{3/2}$ components which were not experimentally resolved. [e] Value obtained only at the University of Alberta with a McPherson ESCA-36 spectrometer. [f] Average value. Gaussian analysis of the asymmetric peak gave two components of equal (fixed) fwhm (1.66 eV) with energies 695.4 (intensity 3) and 694.2 (intensity 2) eV respectively assigned to equatorial and axial fluorine environments. [g] Values obtained recently at the University of Alberta on this compound agree within 0.1 eV.

Table II. Formation and Atomization Enthalpy Data

	ΔH_f,[a] kcal	ΔH_{atom},[e] kcal	$E_B(P_{2p})$, eV
PF_5	−380.8[b]	363.68	144.65
OPF_3	−282	476.4	143.30
SPF_3	−250[c]	451.7	142.72
PF_3	−228.8[d]	551.9	141.95
PCl_3	−61.0	227.6	140.1
$OPCl_3$	−128.7	354.8	141.3
$SPCl_3$	−86.8	320.0	140.8

[a] Most values taken from ref 10. [b] P. A. G. O'Hare and W. N. Hubbard, *Trans Faraday Soc.*, **62**, 2709 (1966). [c] Estimated value.[10] [d] E. Rudzitis, E. H. Van Deventer, and W. N. Hubbard, *J. Chem. Thermodyn*, **2**, 221 (1970). [e] Atomic $\Delta H_f°_{298}$ values (kcal/mol) used to calculate atomization enthalpies are as follows: Cl, 28.92; S, 66.68; P, 79.8; F, 18.36; O, 59.56. These were also taken from ref 10.

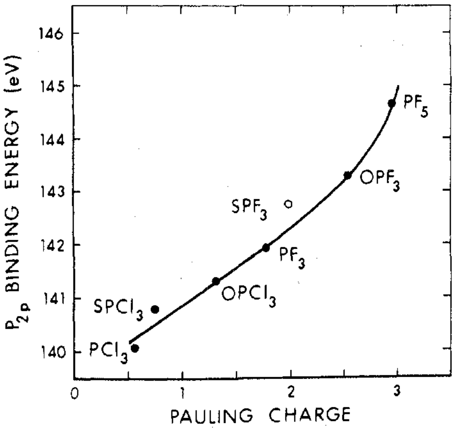

Figure 1. Correlation of P_{2p} binding energies with Pauling charge.

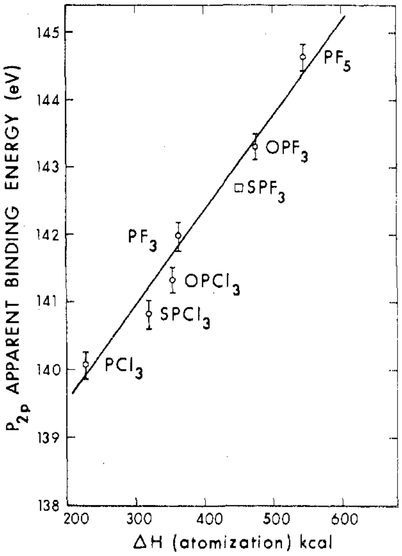

Figure 2. Comparison of P_{2p} apparent binding energy (eV) with ΔH_{atom} (kcal) of the phosphorus halides. The data used to prepare the plot are given in Table II. The square symbol used for SPF_3 serves to emphasize the use of an estimated $\Delta H_f°$ value for that compound.

from generally available formation enthalpy data and from ab initio calculations. The very limited applicability of this approach is demonstrated by a plot of the atomization enthalpies of some of the halogenated methanes against their C_{1s} binding energies which yields straight lines connecting members in a limited series (e.g., the series CH_4, CH_3F, CH_2F_2, and CF_4 and the series CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 are linearly interrelated) but the lines have slopes of opposite sense and intersect at the common (CH_4) point. It is therefore not likely that this approach will be applicable to complex molecules.

It was of interest to establish whether the CNDO-based ground state (GPM) and relaxation corrected (RPM) potential models,[11] which were rather successful with compounds of the first-row elements, could be applied to the present case. The requisite CNDO calculations[12] were performed both with and without "d" orbitals since at first it seemed reasonable to try the more limited basis set covering only the occupied orbitals. The only set of potentials which could be used for prediction of binding energy shifts were those obtained without "d" orbitals and all predictions are based on the non-"d" set of potentials. Furthermore, although the pp' model[12] gave potentials which were in reasonably good agreement with the point charge potentials (in both cases calculated with neglect of "d" orbitals), the former are not strictly correct for the second-row elements[12] and so all predictions are based on the point charge approximation included in the program.[12] The problems which arose with the extended basis set, in particular difficulties which were encountered in obtaining reasonable potentials for the $Z + 1$ ions (required for the relaxation correction) and in achieving convergence in the case of the chlorine containing molecules, appear to be computational artifacts. The fact that successful predictions were achieved with neglect of "d" orbitals cannot be taken to suggest that "d"-orbital participation in the bonding in these compounds is insignificant and we would not wish to make any such implication because the CNDO/2 computation is used herein (in a point charge approximation) to perform a rather elaborate electrostatic calculation of atomic potentials and not to derive ab initio quality results.

Even although the point charge potentials obtained with neglect of "d" orbitals could be used to predict binding energy shifts, the predictions provided by the GPM or the RPM models,[11] in general, overestimated the magnitudes of the shifts. Furthermore, applying the GPM model with this non-"d" point charge potentials set resulted in the prediction of binding energy shifts of $OPCl_3$ and $SPCl_3$ (relative to the

Table III

	Modified central atom potentials[a]		Relaxation energy[b]	Calcd			Exptl
	V'_Z, eV	V'_{Z+1}, eV	E_R, eV	ΔE_R,[c] eV	ΔE_B(GPM),[c,d] eV	ΔE_B(RPM),[c] eV	ΔE_B,[c] eV
PF_3	33.42	41.63	4.10	0	0	0	0
OPF_3	32.20	40.41	4.10	0	1.22	1.22	1.35
SPF_3	32.06	40.93	4.44	0.34	1.36	1.03	0.9
PF_5	30.84	39.48	4.32	0.22	2.36	2.59	2.7
PCl_3	34.20	44.64	5.22	1.12	−0.8	−1.90	−1.85
$OPCl_3$	32.99	43.36	5.19	1.08	0.44	−0.65	−0.65
$SPCl_3$	32.93	43.68	5.37	1.26	0.49	−0.78	−1.15

[a] Calculated CNDO/2 (point charge) potentials[12] for phosphorus (Z) and the equivalent core (Z + 1) ion have been divided by 2. [b] $E_R = \frac{1}{2}(V'_{Z+1} - V'_Z)$. [c] Relative to PF_3 values; calculated as $\Delta X = X(\text{compound}) - X(\text{reference})$. [d] $\Delta E_B(\text{GPM}) = -\Delta V'_Z$. [e] $\Delta E_B(\text{RPM}) = -\Delta V'_Z - \Delta E_R$.

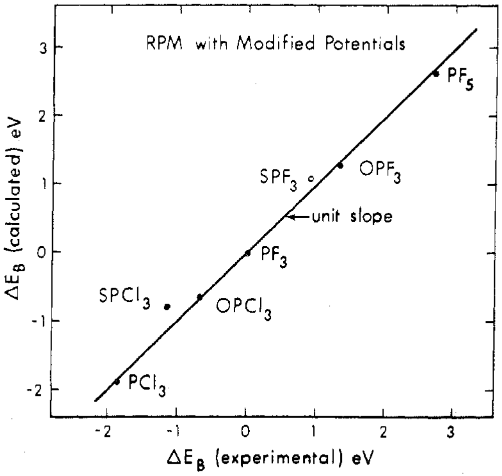

Figure 3. Comparison of experimental P_{2p} binding energy shifts (relative to PF_3) with relaxation-corrected calculated values. Note that the straight line has been constrained to unit slope. The CNDO/2 potentials used to calculate ΔE_B were divided in half before application of the RPM equations. The data used to prepare the plot are given in Table III and the open circle signifies that the data for SPF_3 were obtained only at the University of Alberta on a McPherson ESCA-36 photoelectron spectrometer; all other data were obtained on the Berkeley iron-free instrument.

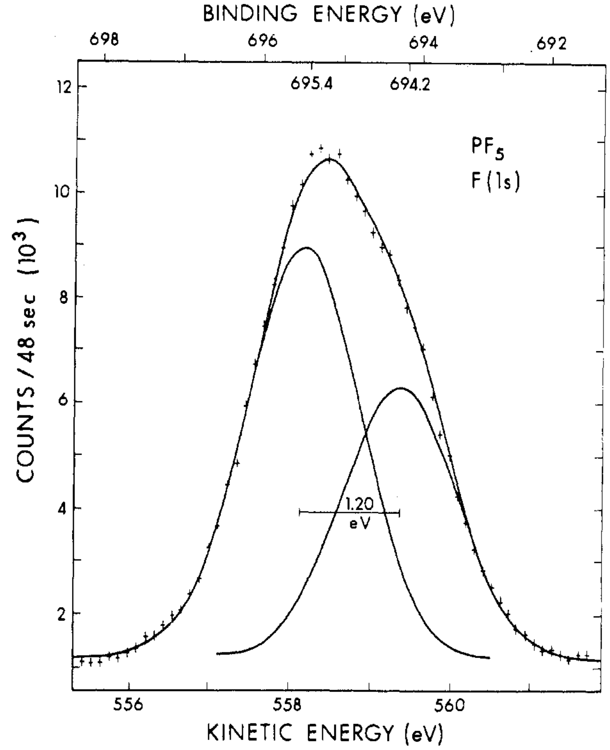

Figure 4. F_{1s} peak of PF_5 decomposed into two gaussian components with equal (fixed) fwhm of 1.66 eV and fixed intensity ratio of 3:2. The experimental points are designated + and the solid lines represent the component and total calculated curves. The two components have apparent binding energies of 695.4 and 694.2 eV, with the more intense appearing to higher binding energy, for a separation of 1.2 eV. The weighted average F_{1s} apparent binding energy is 694.9 eV.

arbitrary PF_3 reference) in the opposite sense of the observed shift. The RPM model gave, with the same non-"d" point charge set of potentials, the correct signs (but overly large magnitudes for these same relative shifts) emphasizing, as before,[11,13] the importance of adiabatic electron reorganization ("relaxation") effects (which are included in the RPM treatment and neglected in the GPM treatment) in the prediction of binding energy shifts.

Much improved prediction of the binding energy shifts can be achieved if we recognize that the CNDO/2 computation assigns $n = 2$ and $n = 1$ quantum shell electron density to the core charge and thus assigns a constant potential to the electrons within the "core" shells which appears to be overestimated. True Hartree–Fock potentials for the $n = 2$ electrons will however be different from the nuclear potentials and an appropriate value appears to be about half the nuclear potential.[14,15] Accordingly the CNDO/2-computed point charge potentials (neglecting "d" orbitals) were divided by 2 and the resultant values were used to calculate binding energy shifts relative to PF_3 as the arbitrary standard.

With these modified potentials the GPM approach continues to predict shifts for $OPCl_3$ and $SPCl_3$ which are in the opposite direction to those observed. The RPM approach (Figure 3) gave excellent agreement, as shown by the correspondence to a line of unit slope, with the largest deviation (0.35 eV) being exhibited by $SPCl_3$. The failure of the GPM approach to predict correct signs for shifts of $OPCl_3$ and $SPCl_3$, as before, again emphasizes the need for relaxation corrections in order to compare molecules of different size. The larger deviations exhibited by Cl and S compounds may indicate that the approach is still inadequate.

Estimates of relaxation contributions based on the modified potentials are given in Table III. If the numerical values correctly indicate the trends of relaxation energies then, it is clear that they change substantially throughout the series (the maximum change being about 20%) and that the relaxation contribution is larger for chlorides than fluorides in keeping with the greater number of electrons in molecules containing the former and the greater polarizability of chlorides.

An additional feature of note in the present set of results is the observation of a broad and unsymmetrical F_{1s} line for PF_5 in contrast to the narrower, symmetric F_{1s} lines obtained from PF_3 and OPF_3. Good fit was achieved with two gaussian components with an intensity ratio of 3:2 which are separated by 1.20 eV (see Figure 4). The line widths of the two components (which are defined to be equal in the fitting procedure) are similar to those experimentally obtained for

PF_3 and OPF_3 suggesting that each F_{1s} component in PF_5 arises from a chemically distinct fluorine type.[16] The two components are reasonably assigned to equatorial and axial fluorine atoms in keeping with the established trigonal-bipyramidal molecular structure of PF_5.[17] That the greater component (3 units) which arises from the equatorial fluorine atoms lies to higher binding energy of the lesser intensity (2) component due to the axial fluorine atoms is consistent with the shorter P–F bond distance (and therefore stronger binding) in the equatorial plane. Recent calculations[18] on PF_5 and related molecules confirm the expectation of stronger and shorter equatorial bonds.

Experimental Section

Any physical study of reactive fluorides requires extensive precautions to ensure that hydrolysis of the compound does not occur. The present measurements were done with commercial samples of PF_3, OPF_3, and PF_5 each having a purity greater than 98% (as determined by infrared spectroscopy). The gases were introduced into the gas sample cell of the Berkeley iron-free spectrometer[19] through stainless steel tubing which had been baked (200°C) under vacuum and then repeatedly flushed with the fluorides in order to remove all traces of moisture before establishing the sample flow. The chlorides were also commercial materials and were introduced as gases into the supply lines which had been previously exposed to the fluorides and so were probably free of traces of moisture. The spectra were measured at pressures of the order of 5×10^{-2} Torr and were calibrated by introducing, simultaneously with the compound, an approximately equal pressure of gaseous Ar ($2p_{3/2} = 248.62$ eV)[20] with known binding energy. Line widths given as fwhm in Table I were determined on data obtained in the absence of calibrant. The raw data, obtained on a momentum base, were converted to a linear kinetic energy scale and the corrected data were fitted to a gaussian line shape by an iterative nonlinear least-squares curve-fitting program.[4] Additional support for the validity of the PF_5 F_{1s} data is provided by the reproducibility of the asymmetric line shape over several determinations on different occasions suggesting that impurity or decomposition is not responsible for the two-component F_{1s} line. Furthermore the F_{1s} spectrum did not change with time and, finally, monitoring the O_{1s} region during accumulation of F_{1s} data for PF_5 showed that no significant concentration of OPF_3 was present. Line shapes for F_{1s} of OPF_3 and PF_3 were symmetric which supports the proposal of two F_{1s} components in PF_5.

Data for SPF_3 and some of the other compounds mentioned herein were obtained on a McPherson ESCA-36 photoelectron spectrometer using precautions similar to those described above to prevent hydrolysis in the sample-handling system. The data, obtained in this case on a linear kinetic energy scale, were analyzed in a fashion similar to that above, using a modified version of the same least-squares fitting program.[4]

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Registry No. PF_3, 7783-55-3; OPF_3, 13478-20-1; SPF_3, 2404-52-6; PF_5, 7647-19-0; PCl_3, 7719-12-2; $OPCl_3$, 10025-87-3; $SPCl_3$, 3982-91-0; P, 7723-14-0; F, 7782-41-4; O, 7782-44-7; Cl, 7782-50-5; S, 7704-34-9.

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Mechanism of the Reactions between Ortho Dinucleophiles and Cyclophosphazenes[1,2]

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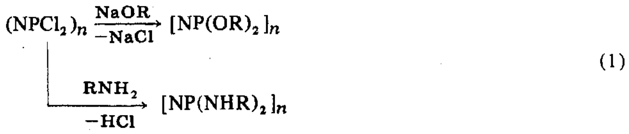
Phosphoranes are formed when halocyclophosphazenes or spiro[arylenedioxycyclophosphazenes] react with ortho dinucleophiles such as catechol and base or *o*-aminophenol. With the latter reagent, a critical intermediate in the degradation pathway, iminobis[spiro[bis(*o*-phenyleneoxyamino)phosphorane]], has been isolated. The effects of temperature, solvent, and other nucleophiles on these reactions have been analyzed, and the reaction pathways are discussed.

Introduction

Cyclic and polymeric halophosphazenes undergo a broad range of nucleophilic substitution reactions with alkoxides, aryl oxides, or amines to generate organophosphazenes by processes such as eq 1. Approximately 650 cyclic organophosphazenes ($n = 3$ or 4) have been synthesized by this route, together with more than 60 high molecular weight polymers ($n \approx 15{,}000$). The high polymers, in particular, show considerable promise for technological applications. In all of these reactions the phosphazene backbone is essentially unaffected by the halogen replacement process. However, as an outgrowth of our studies



$$(NPCl_2)_n \xrightarrow[-NaCl]{NaOR} [NP(OR)_2]_n$$
$$(NPCl_2)_n \xrightarrow[-HCl]{RNH_2} [NP(NHR)_2]_n \qquad (1)$$