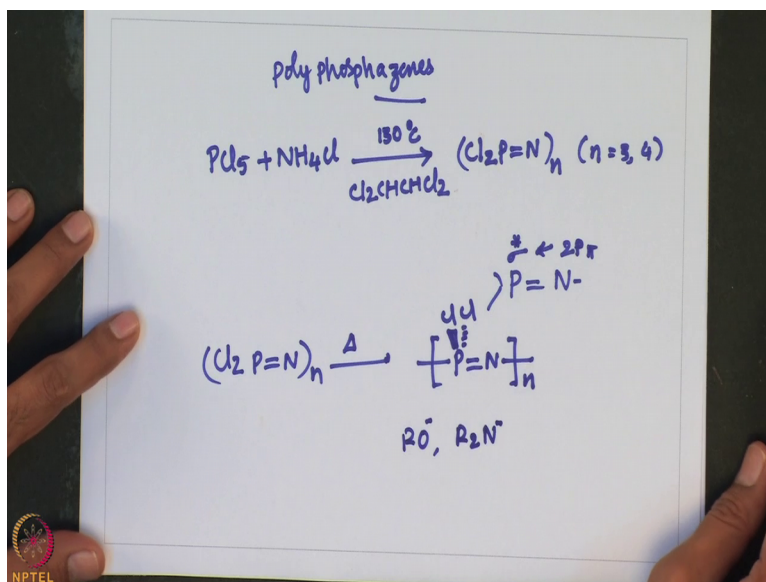


Main Group Chemistry
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Lecture - 45
Chemistry of Group 15 Elements

Welcome to MSB lecture series on the chemistry of main group elements. In my previous lecture I was discussing about various type of phosphates and oxiacids of phosphorus. So, let me discuss today another important class of compounds of phosphorus called poly phosphazenes.

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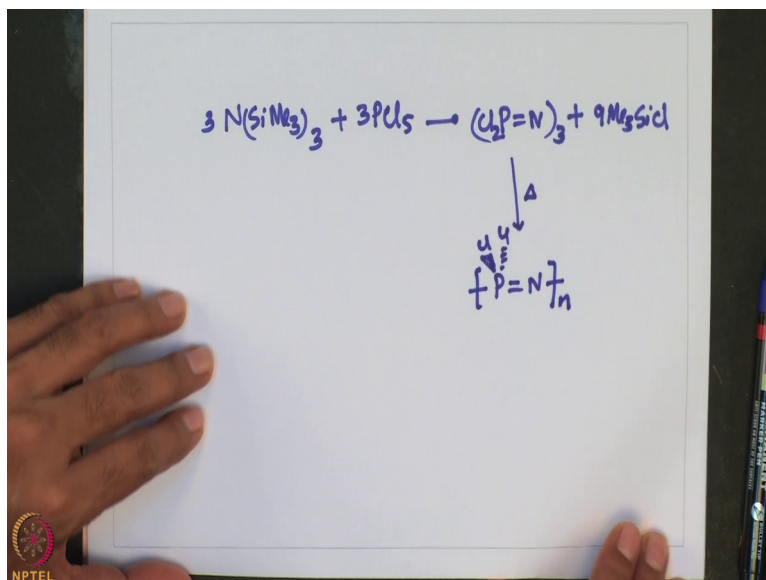
So, azenes indicates that we have a double bond between phosphorus and nitrogen. Essentially these poly phosphazenes can be prepared by mixing finely powdered PCl_5 and ammonium chloride in a chlorinated solvent heated to 130 degrees centigrade. Here preferred solvent is tetrachloroethane, so it leads to the formation of chlorophosphazenes where n can be 3 or 4 major products of course, up to n equal to 7 and 8 are also obtained in this reaction, but in very trace quantities.

The cyclic trimer I will be showing the structure later cyclic trimer has a plane or 6 membered ring structure in both side cyclic trimer and tetramer the P N bonds are all same indicating that delocalized pi bonding occurs between the filled N 2 P pi orbitals and the empty empty or orbitals and the phosphorus atom. So, here essentially if what

one can see is this sigma star and here 2 P essentially pi. So, this donation is there that delocalizes the pi system orient tyre ring making it planar. This we also call it as negative hyper conjugation. So, this triphosphazene or tetraphosphazene on further heating give polymer of this type.

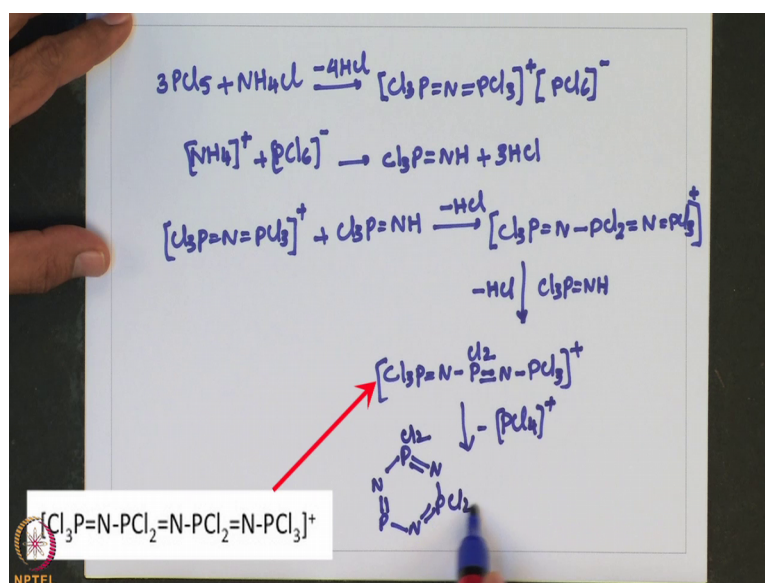
So that means, so; that means, when cyclic trimer is heated more strongly it polymerizes forming a rubbery material that TCl bonds in this one are susceptible to hydrolysis, but one can perform a series of nucleophilic substitution reactions using O R minus or R 2 N groups or one can also use a wide range of functional groups to form stable polymers with a wide range of properties; that means, improved yields of cyclic triphosphazene involves this reaction.

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That means reacting tris trimethylsilyl amine with PCl 5 of course, here we get trimethylsilyl chloride as the side product. So, yields of this trimer can be optimized by ensuring a slow rate of addition of PCl 5 to this tris(trimethylsilyl)amine and once after making this one. Of course, one can conveniently heat it further to get the poly phosphazene.

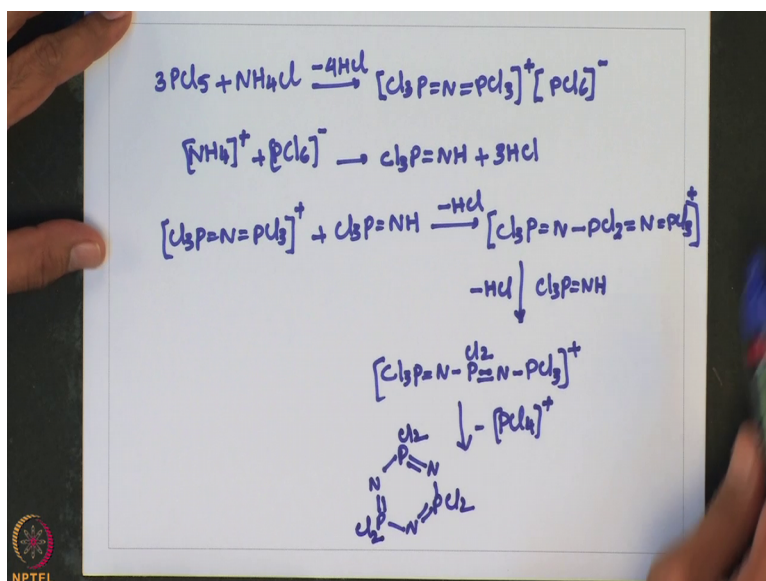
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Now, it is very interesting to analyze the reaction sequence. Let us look into the intermediates that are involved in the formation of this trimer starting from phosphorous penta chloride and ammonium chloride. Let me write some of these reactions stepwise initially it leads to the formation of an ionic compound of this type and now this ammonium plus reacts with PCl_6^- ion to form imine compound and this imine further reacts with this intermediate, it leads to the formation of. So, this essentially gives back $\text{Cl}_3\text{P}=\text{NH}$ again to form plus. So, this eliminates one molecule of PCl_4^+ to form primary species.

So this are the sequence of reactions that are involved in the preparation of trimer from PCl_5 and ammonium chloride.

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Now, so I have shown here the structures of trimer tetramer as well as polymer.

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Polyphosphazenes

- The P=N group is isoelectronic with the Si—O group, so the phosphazene materials are isoelectronic with the siloxanes.
- Thus, the trimer $(\text{Cl}_2\text{P}=\text{N})_3$ is isoelectronic with $(\text{Me}_2\text{SiO})_3$.
- Polyphosphazene polymers, like their siloxane counterparts, contain flexible rubbery properties even at low temperatures.

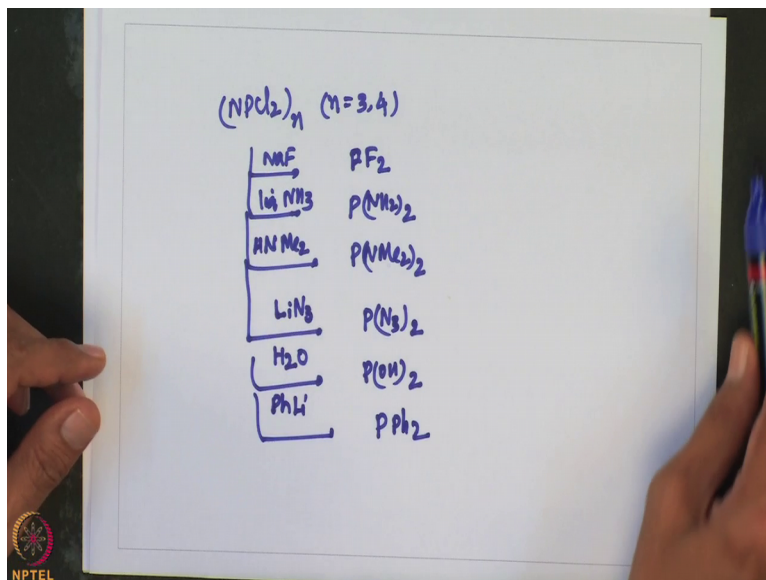
The diagram shows three structures: a trimer with three phosphorus atoms in a ring, each double-bonded to a nitrogen atom and single-bonded to two chlorine atoms; a tetramer with four phosphorus atoms in a ring; and a polymer chain with a repeating unit of $-\text{P}(\text{Cl})_2=\text{N}-$.

Of course, here if you just look into these structures P double bond N groups are isoelectronic with the SiO group. So, phosphazene materials are also isoelectronic with siloxanes. So, trimer is isoelectronic Me 3 SiO 3 times.

Poly phosphazene polymers like their siloxanes counterparts contain flexible rubbery properties even at lower temperature this is where the importance of this in organic polymers comes into picture in various applications. The chlorines atoms of these trimers

and tetramers really undergo nucleophilic substitution as I had mentioned you can introduce a variety of groups here.

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for example, if we take $NPCl_2$ n where n equals 3 or 4 we can replace Cl by performing nucleophilic substitution reaction for example, with sodium chloride we can get fluorinated compounds and we can have NH_2 using liquid ammonia and we can add NMe_2 groups by starting from H . So, we can add here F can be added that is it becomes PFF simply I write PF_2 here and here I put NH_2 two times and here I will put $P(NMe_2)_2$ two times.


Similarly, if we use lithium nitride we can add PN_3 twice. If we use water we can add POH twice and if we use phenyl lithium you can have PPh_2 . So, this is how one can perform a series of reaction to generate substituted cyclo tri or tetraphosphazenes. Of course, one can also perform some of those reactions prior to or after polymerization reaction like silicon rubber poly phosphazenes remain rubbery at very low temperature because of the PNP linkage this has delocalized electrons and similar to $SiOSi$ where we have oxygen electrons are associated with silicon sigma* orbitals. So, the molecules are alicyclic and the PNP groups are highly flexible.

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Halides of group 15 Elements



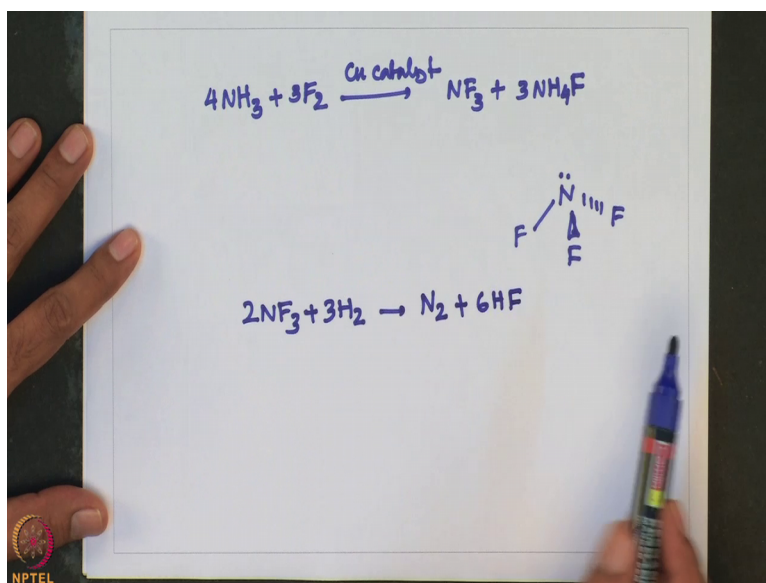
- ❑ All the elements form a trihalide with at least one halogen.
- ❑ Nitrogen is restricted to an octet of valence electrons and does not form pentahalides.
- ❑ Important nitrogen halides are NX_3 ($X = F, Cl$), N_2F_4 and N_2F_2
- ❑ Except for NF_3 , nitrogen trihalides have limited stability and nitrogen triiodide is dangerously explosive.
- ❑ Phosphorus, arsenic, and antimony form stable pentahalides.



So, with this let us move on to the halides of group 15 elements all the elements form trihalides with at least one halogen. So, nitrogen is restricted to an octet of valence electrons and does not form pentahalides. Important nitrogen halides are NX_3 where X is fluorine or chlorine and also we know besides NX_3 that is NF_3 and NCI_3 N_2F_4 and N_2F_2 are also known, except for NF_3 nitrogen trihalides have limited stability and nitrogen triiodide is dangerously explosive and phosphorus arsenic and antimony form stable pentahalides like PCl_5 , $AsCl_5$ and $SbCl_5$.

Nitrogen trifluoride is made either by the reaction which must be carried out in a very controlled manner or by electrolysis of anhydrous NH_4F and HF mixtures.

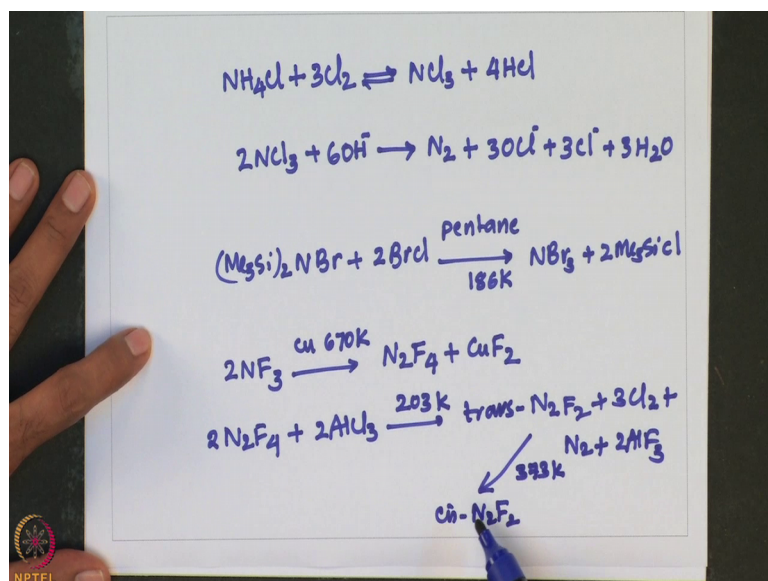
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For example when NH_3 is treated with fluorine where a copper catalyst NF_3 is formed. So, NF_3 is the most stable halides of nitrogen and it has a pyramidal structure ok. And it is a colorless gas which is resistant to attack by acid and alcohols, but is decomposed by reacting with H_2 . So 2NF_3 where it is kept along with H_2 it gives N_2 through the formation of HF .

And nitrogen tri chloride is an oily yellow liquid at 289 Kelvin, but it is highly endothermic and dangerously explosive nitrogen tri chloride can be prepared by the following reaction simply by treating ammonium chloride with chlorine.

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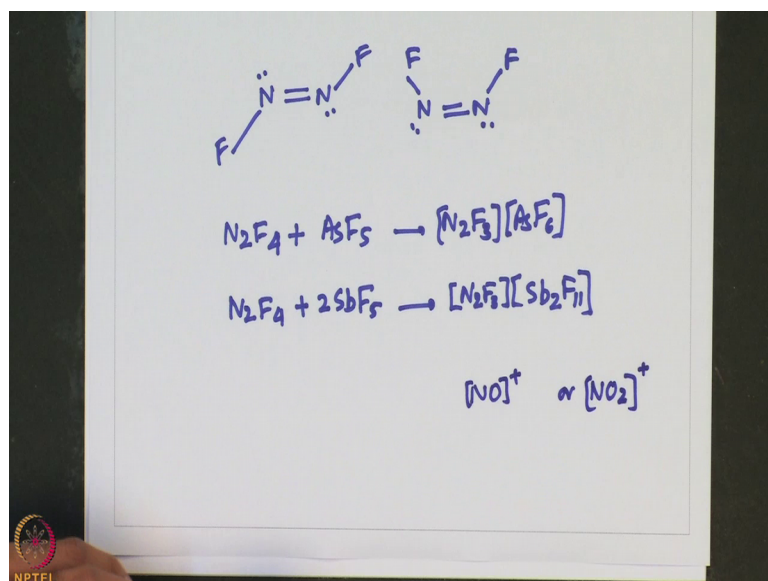


So, alkyl is hydrolyzed NCl_3 ; that means, if you take NCl_3 and treat with alkynes we get nitrogen. Of course, in case if you sodium hydroxide we get NaOCl and NaCl ok.

So, nitrogen tribromide is very reactive than NCl_3 and explodes at temperature 175.5 Kelvin that indicates how reactive it is it can be prepared by treating this trimethylsilyl bromo amine with BrCl . So, this reaction has to be carried out at very low temperature is pentane it gives NBr_3 plus we get $2\text{Me}_3\text{SiCl}$.

Nitrogen fluorides N_2F_4 and N_2F_2 can be obtained by simply creating NF_3 with copper at higher temperature. For example, if we take NF_3 and pass it over copper at 670 Kelvin it gives N_2F_4 plus CuF_2 similarly if you take N_2F_4 and treat this one with aluminum chloride at 203 Kelvin it forms trans N_2F_2 . So, this one if it is one heating to 273 Kelvin gives N_2F_2 ; that means, one can perform isomerization by heating the trans 1 to 273 Kelvin to form a cis compound.

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Of course one should be able to distinguish this as trans and this as cis. The ability of N_2F_4 to donate F^- to strong acceptors is quite known; that means, it can be used as a good fluorinating agent especially when we have strong fluorine acceptors. Let me write a couple of reactions for that N_2F_4 when it is treated with very strong fluorine acceptor such as AsF_5 it forms N_2F_3 and AsF_6^- . Similarly N_2F_4 when it is treated with antimony pentafluoride it forms a dimeric species having SbF_5 bridge.

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Oxofluorides and oxochlorides of nitrogen

	X		
	F	Cl	Br
a / pm	152	198	214
b / pm	113	114	115
α / °	110	113	117

Oxifluorides and oxychlorides of nitrogen are also known. You can see here they have a structure like this where X can be fluorine chlorine or bromine and you can see the bond distances here and of course, bond distances have to do something with the size of X here. Whereas, N O bond essentially remains very same 113 to 11 there is no dramatic increase or decrease in the N O bond distance whereas, this one is quite obvious because of the change of the halides one can expect this bond distance should change.

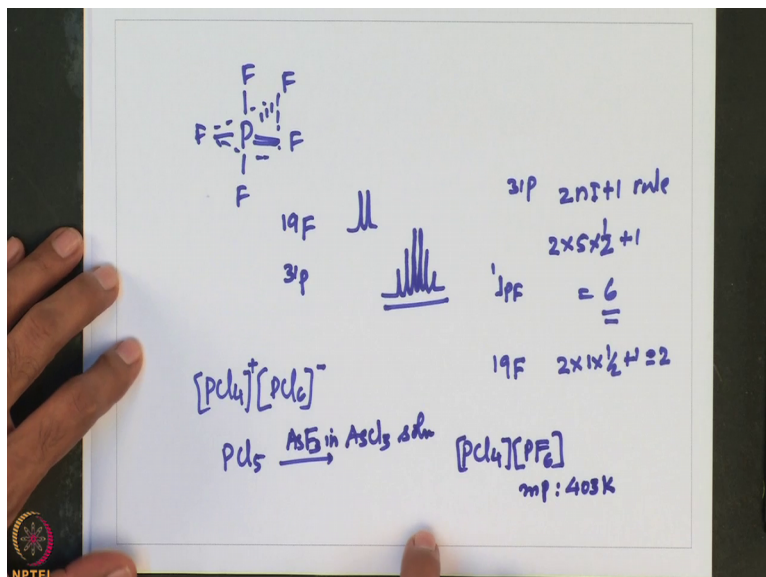
So, several oxifluorides and oxychlorides of nitrogen are quite known, but all are unstable gases or volatile liquids which are rapidly hydrolyzable and nitrosyl halides like F N O, Cl N O, P R N O are formed in reactions of N O with F₂ Cl₂ or Br₂. And nitrile fluorides like F N O₂ and nitrile chloride like Cl N O₂ can also be prepared respectively by fluorination of N₂ O₄ or chlorination. The oxyhalides such as F N O, Cl N O, F N O₂, Cl N O₂ combine with suitable fluorides or chlorides to give salts containing N O plus or N O₂ plus. So, let us now look into the phosphorous halides.

As I mentioned phosphorous forms 2 type of halides one is trivalent having P X₃ and composition and another one is pentavalent having P X₅. So, in case of halides for all the 4 halides P X₃ is known and in case of P X₅ it is only known for fluorine chlorine and chorine whereas, P I₅ is unknown. And most are made by direct combination of elements with products determined by which element is in excess the halides are all hydrolyzed by water although P F₃ reacts very slowly P F ones are much more stable for hydrolysis compared to P b l or P b r or even P I bonds. Phosphorous trifluoride is a very poisonous colorless and odorless gas, phosphorous tri chloride is a colorless liquid with melting point 179.5 Kelvin and boiling point 349 Kelvin and of course, PCl₃ emits fumes in air and stocks and PCl₃ is starting compound for many of the phosphorous derivatives and also phosphines like tertiary phosphines. They find important application as soft ligands in organometallic chemistry as well as coordination chemistry.

P O Cl₃ is an important reagent of the preparation of phosphate esters. In case of P F₅ single crystal ray diffraction carried out at very low temperature of 109 Kelvin has shown that it has trigonal bipyramidal structure. In solution the molecule is fluxional on the NMR spectroscopy time scale as a result when we do phosphorous NMR we cannot distinguish between axial and equatorial PF bonds and as a result what happens it accounts for only one type of fluorine atoms. So, when we look into the phosphorous NMR it shows only one type of fluorine atoms and of course, in case of 19 fluorine

NMR we simply get a doublet that accounts for only one type of PF coupling and it does not show any F F coupling.

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For example, if you take this is how the structure look like if you look into ^{19}F NMR all of them are equivalent because through berry pseudorotation. I had already explained what is berry pseudorotation how that proceeds via a square pyramidal intermediate in which axial bonds are changed into equatorial bonds.

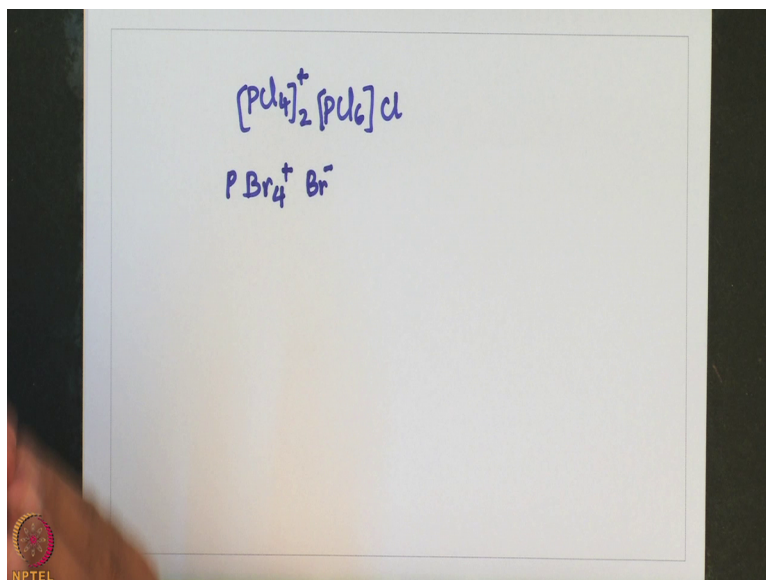
So, ^{19}F NMR it shows only a doublet something like this whereas, in case of ^{31}P NMR it shows 6 lines something like this here it indicates all P F bonds are equivalent this is because of 1 J PF coupling of course, whatever the spacing is there that is same as this one. And you may be wondering why 5 peaks are there, we use this $2nI+1$ rule here and of course, 2 into n is number of fluorine atoms 5 into its spin is half nuclear spin in this case also I equals half I equals half plus 1 this gives 6 lines. And the other hand in case of ^{19}F NMR again only one is there this is in case of ^{31}P NMR, in case of ^{19}F NMR we have only one again if we use $2nI+1$ 1 phosphorous is there and I is half plus 1. So, essentially it will give you 2 line so we get a doublet here.

The stereo chemical non rigidity is another example of berry pseudorotation that we come across in case of PF₅. So, electron diffraction data show that in the gas phase PCl₅ has a molecular trigonal bipyramidal structure where the axial PCl bond distance is 214 picometer whereas, PCl equatorial is 202. You should remember always axial bonds are

little bit longer in the solid state PCl_5 has a totally different structure it is ionic and made up of PCl_4^+ plus and PCl_6^- and of course, when PCl_5 is reacted with AsF_3 fluorination occurs of the alkylal phosphorus; that means, when PCl_5 is reacted with AsF_3 in AsCl_3 solution what it gives is PCl_4^+ and PF_6^- and the melting point for this one is 403 Kelvin. So, fluorination occurs of the octa hydral phosphorous.

So, what kind of geometry is these halides prefer. So, in the gas phase NCl_5 adopt trigonal bipyrominal geometry one can derive that one using valence shell electron pair repulsion theory. In the solid state the situation is more complicated so that means, PCl_5 doesnt exist as a trigonal bipyrodal molecule instead it has a composition of PCl_4^+ plus and PCl_6^- minus, but in meta stable state it also assumes.

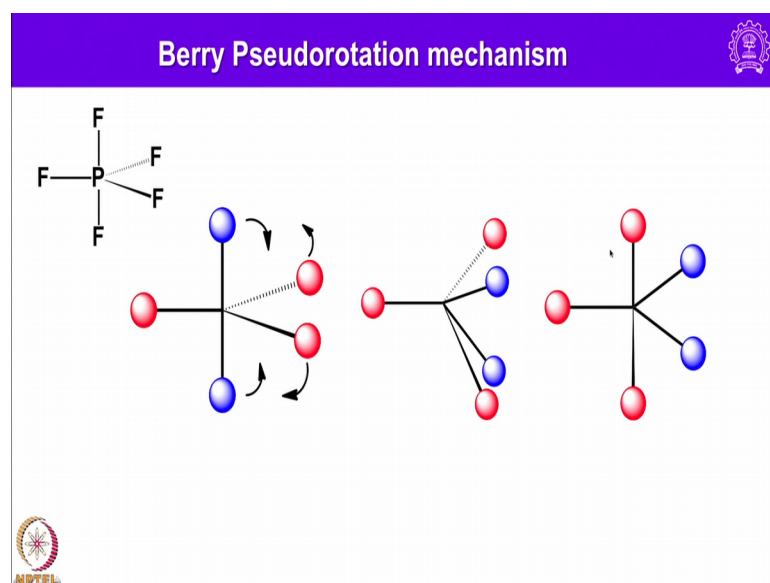
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As a composition of this type something like this. So, in contrast to PCl_5 , PBr_5 contains yeah plus and Br minus. So, this shows how different this phosphorous halides are with respect to their structures.

So, before I conclude let me show you berry pseudo rotation mechanism here.

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You can see here I have just marked in different color to denote axial and equatorial halides. So, now, basically what happens these two will be moving towards each other and then these two will be moving away from each other and we have an intermediate of this one. It resembles square pyramidal molecule and then now the exchange is complete axial has become equatorial and equatorial has become axial. So, this is very rapid at room temperature in case of PF_5 as a result what happens we cannot distinguish between equatorial and axial PF bonds.

So, let me discuss more chemistry of phosphorous halides in my next lecture. Until then have a pleasant reading of inorganic chemistry of phosphorous compounds.

Thank you very much.