Main Group Chemistry
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Lecture - 46
Chemistry of Group 15 Elements

Welcome to MSB lecture series on main group chemistry, this is going to be the last lecture on group 15 elements. Once after completing this one I will move on to the chemistry of group 16 elements. Today, let me look into group 15 halides to start with l.

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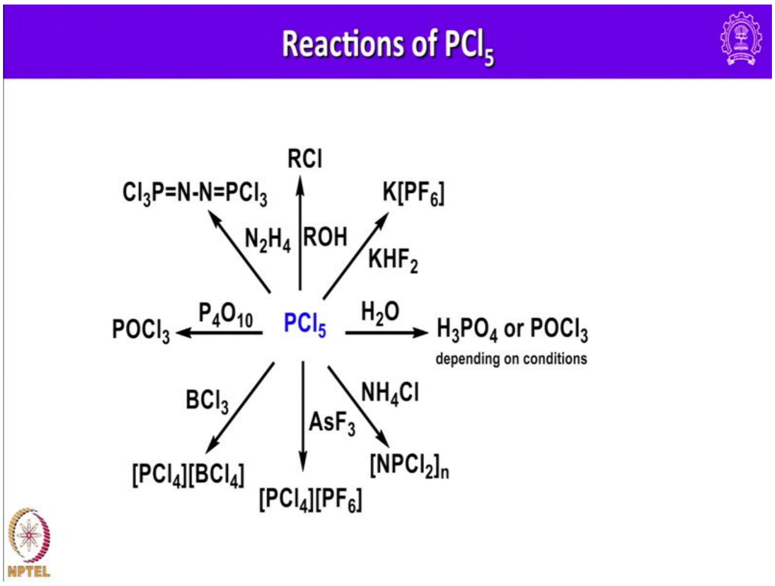

Reactions of PCl_5

$PCl_5 \xrightarrow{ROH} RCl$

$PCl_5 \xrightarrow{KHF_2} K[PF_6]$

$PCl_5 \xrightarrow{N_2H_4} Cl_3P{=}N{-}N{=}PCl_3$

$PCl_5 \xrightarrow{P_4O_{10}} POCl_3$

$PCl_5 \xrightarrow{H_2O} H_3PO_4$ or $POCl_3$ depending on conditions

$PCl_5 \xrightarrow{BCl_3} [PCl_4][BCl_4]$

$PCl_5 \xrightarrow{AsF_3} [PCl_4][PF_6]$

$PCl_5 \xrightarrow{NH_4Cl} [NPCl_2]_n$

Ets look into the reactions of phosphorus pentachloride, in fact phosphorus pentachloride is a very useful reagent, we can see in the reaction scheme I have given in the slide PCl 5 when its treated with alcohols leads to the formation of chlorides, similarly when PCl 5 is treated with fluorinating agents such as KHF 2, it leads to the formation of potassium hexafluorophosphate. When it is treated with water depending upon the reaction condition that leads to the formation of either phosphoric acid or phosphoryl chloride or POCl 3 PCl 5 on treatment with phosphorus pentoxide leads to the formation of same POCl 3.

Similarly, PCl 5 when its treated with AsF 3 a good fluorinating agent, leads to the formation of ionic complex having PCl 4 plus and 6 minus, and treatment of PCl 5 with BCl 3 leads to the formation of PCl 4 plus Bcl 4 by the (Refer Time: 01:55). PCl 5 reacts with hydrogen to form this phosphine imine here I have shown, and similarly when PCl 5 is reacted with ammonium chloride in chlorinated solvent such as symmetric tetrachloroethane leads the formation of phosphazenes with N equals 3 4 up to 8 with trimeric and tetrameric cyclotriphossines being major products. So, let us look into some aspects concerned around POCl3 among the phosphorous oxihalides the most important one is POCl3.

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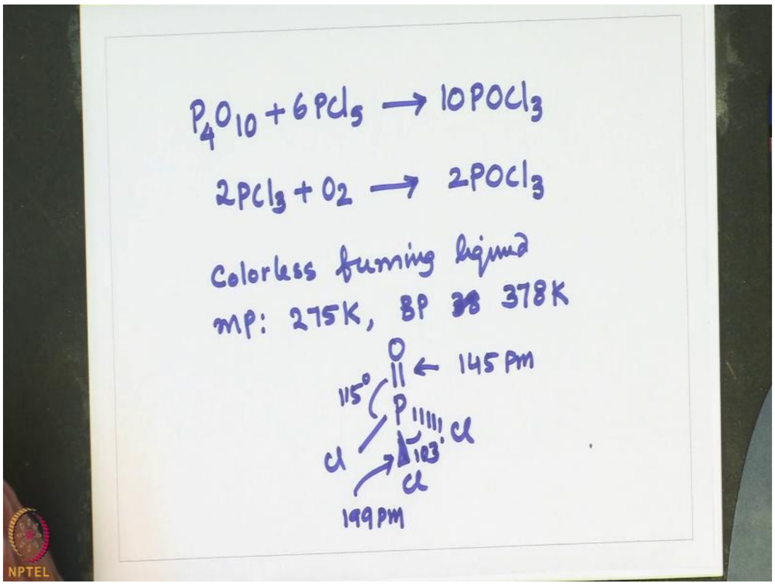

$P_4O_{10} + 6PCl_5 \rightarrow 10POCl_3$

$2PCl_3 + O_2 \rightarrow 2POCl_3$

Colorless fuming liquid

mP: 275K, BP ~~38~~ 378K

This can be prepared by reaction of PCl 3 with O 2 or one can also prepare starting from P4O10. So, P4O10 when it is reacted with PCl 5 gives as I mentioned directly PCl 3 can be reacted with oxygen to form POCl 3.

So, phosphoryl trichloride is a colorless fuming liquid and melting point is 275 kelvin and boiling point is 378 kelvin and of course, this undergoes readily hydrolysis by water liberating Hcl some of the many uses of POCl3 or as phosphorylating and tonlating agents and also as a reagent in the preparation of phosphate esters. If you want to know little bit about the bond parameters, this P O bond distance is 145 picometer and this angle is 115 whereas, this angle is 103 and PCl bond distance is 199 picometre. So, similarly arsenic forms halides As X3 trivelant halides as well as pentavelant halides as As X5.

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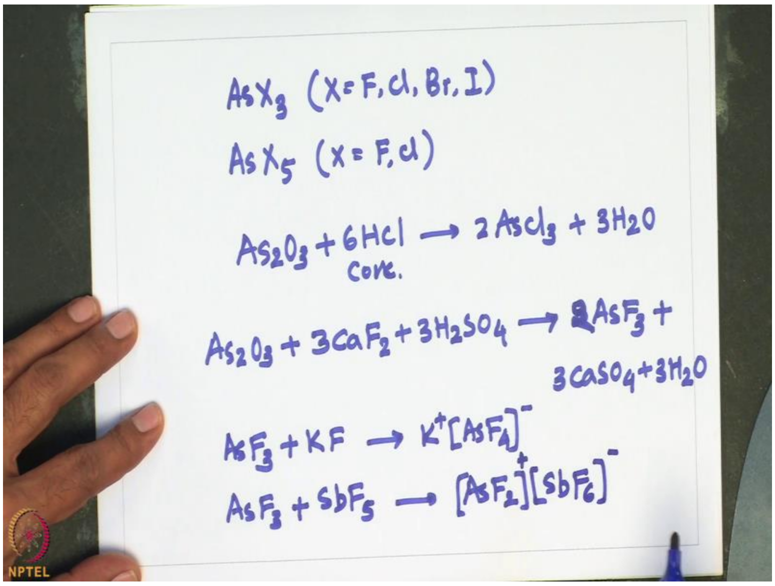

AsX_3 $(X = F, Cl, Br, I)$

AsX_5 $(X = F, Cl)$

$$As_2O_3 + \underset{\text{Conc.}}{6HCl} \longrightarrow 2AsCl_3 + 3H_2O$$

$$As_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2AsF_3 + 3CaSO_4 + 3H_2O$$

$$AsF_3 + KF \longrightarrow K^+[AsF_4]^-$$

$$AsF_3 + SbF_5 \longrightarrow [AsF_2]^+[SbF_6]^-$$

For example As X3 and As X5 both are known with respect to x equals fluorine, chlorine, bromine and iodine and when it is penta its only x equals fluorine and chloride are known and trihalides can be prepared by direct combination of the elements or one can also use ascidium oxide for example, As2 O3 when its treated with concentrated hydrochloric acid it gives ok.

Similarly treatment of As2O3 with calcium fluoride in presence of sulphuric acid leads to the formation of. In the solid liquid and gas state AsF 3 and A s c l 3 have molecular trigonal pyramidal structures very similar to PCl 3. Of course, with appropriate reagent AsF 3 may act as either fluorine acceptor or fluorine donor I will show you both of these reactions for example, ASF3 when its treated with KF which is a strong fluorinating agent leads to the formation of K plus AsF 4 minus in contrast when AsF 3 is treated with strong fluorine acceptor such as SdF 5 it forms. So, it shows the dual nature of AsF 3. So, it can act as a fluoride donor as well as fluoride acceptor.

The reaction of arsenium trichloride or Acl 3 with dimethyl amine and excess of Hcl in aqueous solution leads to the formation of As2 cl93 minus anion having this composition.

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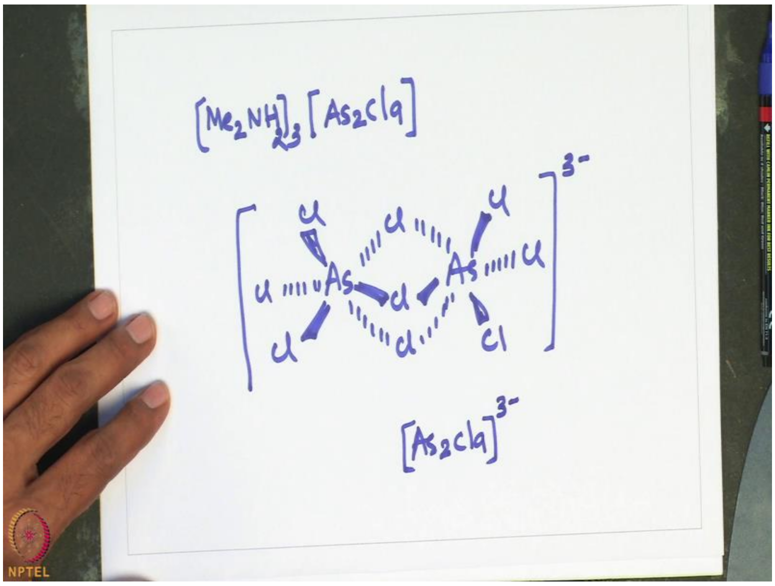

$[Me_2NH_2]_3[As_2Cl_9]$

$[As_2Cl_9]^{3-}$

All this has this is a structure of this ASC 2 l 9 is dimeric. So, AsF 5 is a colorless gas, antimony trihalides are low melting solids and although these contain trigonal pyramidal molecules each antimony centre has additional long range intermolecular SbX interactions.

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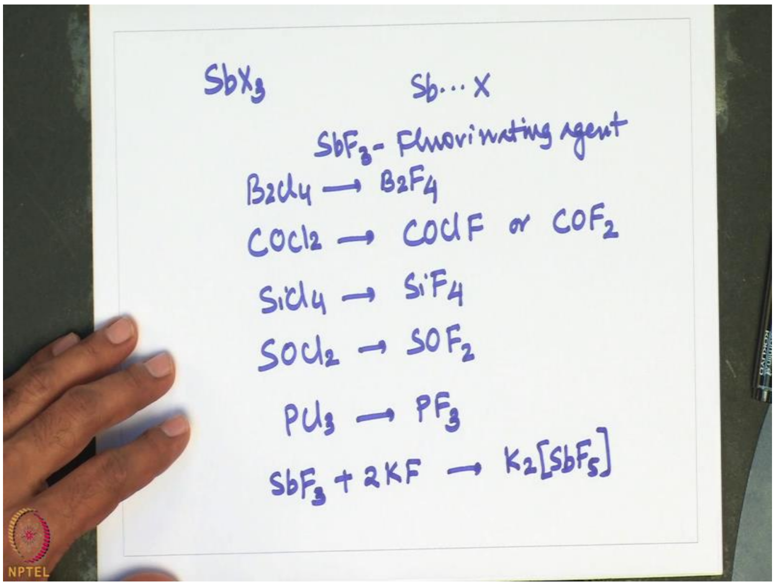

SbX_3 $Sb \cdots X$

SbF_3 - Fluorinating agent

$B_2Cl_4 \rightarrow B_2F_4$

$COCl_2 \rightarrow COClF$ or COF_2

$SiCl_4 \rightarrow SiF_4$

$SOCl_2 \rightarrow SOF_2$

$PCl_3 \rightarrow PF_3$

$SbF_3 + 2KF \rightarrow K_2[SbF_5]$

I will show you later with some structures we have we come across this kind of interactions that trifluoride and trichloride are prepared by reacting Sb2 O3 with concentrated H f and Hcl respectively very similar to I showed you in the case of As2O3.

SbF3 is a widely used fluorinating agent and is a very powerful fluorinating agent it converts for example, B2cl4 to B2F4 and COCl 2 (Refer Time: 10:58) to either COClF or COF 2 can also convert SiCl4 to SiF4 or SOcl2 to SOF 2. So, here fluorinating agent depends and of course, one can also convert Pcl 3 to PF 3 as well ok.

So, reactions between SbF3 and m f gives salts which include K2 sbF5 also for example, S b F 3 if it is treated with 2 KF it forms K2 S bF 5 something like this I will show you structures of some of those things in the next slide.

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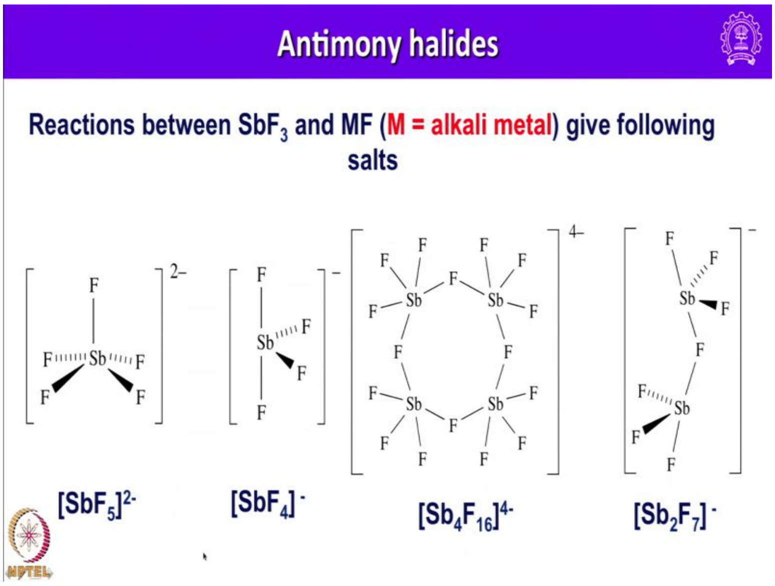

Antimony halides

Reactions between SbF_3 and MF (M = alkali metal) give following salts

$[SbF_5]^{2-}$ $[SbF_4]^{-}$ $[Sb_4F_{16}]^{4-}$ $[Sb_2F_7]^{-}$

You can see here this is for SbF 5 anionic di ionic and this is for SbF 4 minus and this is for SbF 4 F 164 minus and this is for S b 2 F 7 minus.

So, the depending upon this (Refer Time: 12:39) of SpF 3 and mf one can get the following salts antimony penta fluoride can be prepared by treating Sb cl 5 with hydrogen fluoride ok.

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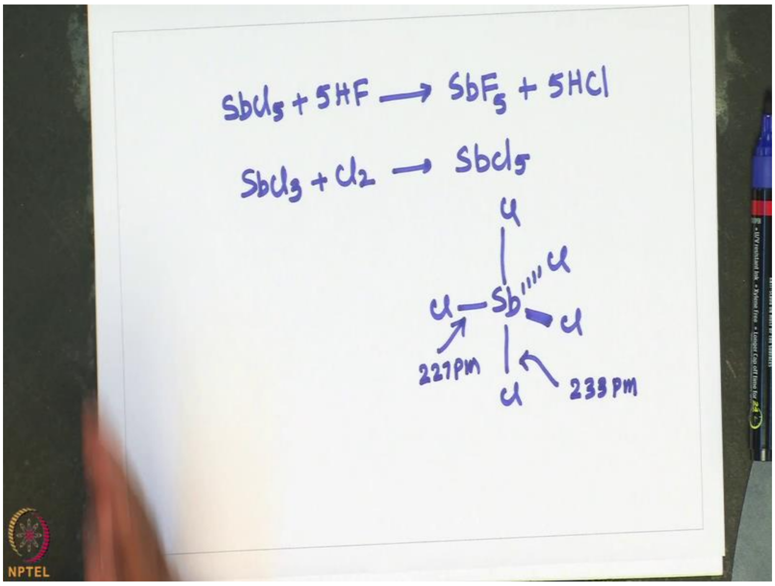

So, in the solid state SbF 5 is tetrameric and the presence of SbF b bridges account for the very high viscosity of a liquid, antimony pentachloride can be prepared from the elements or by reacting Sbcl 3 with cl 2 liquid Sbcl 5 contains discrete trigonal bipyramidal molecules having 2 longer axial bonds. So, like phosphorus pentachloride arsenium pentachloride, the axial bonds ins PCl 5 are little longer than the equatorial bonds for example. So, they are 227 picometre whereas, axial ones are little longer 233 picometre

So, below 219 kelvin the solid undergoes a reversible change involving dimerization of the Sbcl 5 molecule.

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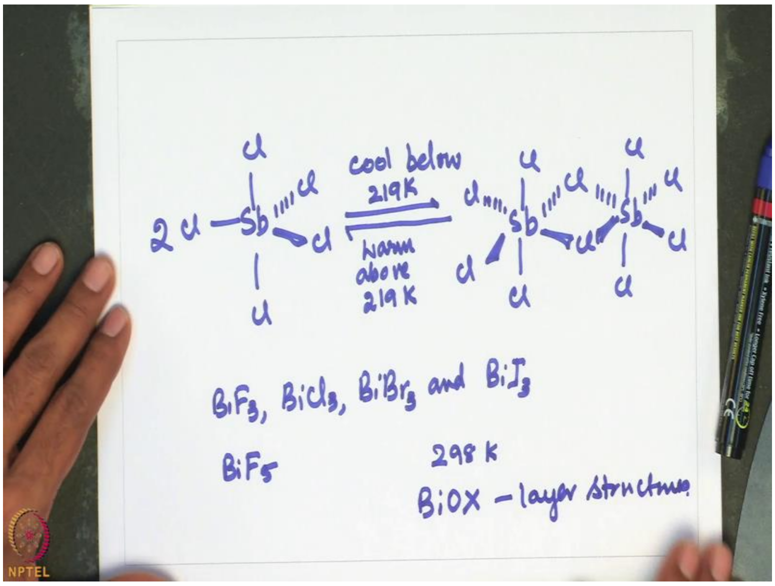

BiF_3, $BiCl_3$, $BiBr_3$ and BiI_3

BiF_5

298 K

BiOX – layer structures

So, if Sbcl 5 is cooled below 219 kelvin it forms a dimer on the other hand the dimer on the warming above 219 kelvin it gives back the monomer. So, similar to trihalides of antimony with respect to the bismuth BiF3, BiCl3, BiBr3 and BiI3 are all well characterized, but in case of pentavalent only BiF5 is known. So, others are not known. So, all are solids at 298 kelvin, in the vapor phase trihalides all trihalides have trigonal pyramidal structure which trihalide is hydrolyzed by water to give BiOx species which are insoluble compounds with layer structures.

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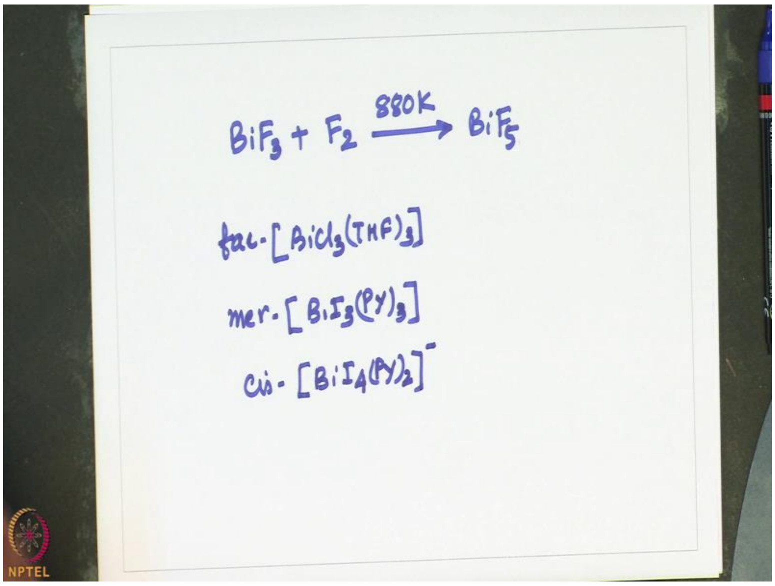

$BiF_3 + F_2 \xrightarrow{880K} BiF_5$

fac-$[BiCl_3(THF)_3]$

mer-$[BiI_3(Py)_3]$

cis-$[BiI_4(Py)_2]^-$

So, the reaction of BiF3 with fluorine at 880 kelvin yields BiF5. So, this is a very powerful fluorinating agent and trihalides are essentially Lewis acids very similar to PCl 3 PF 3 and form donor acceptor complexes with a number of ethers and also Lewis bases.

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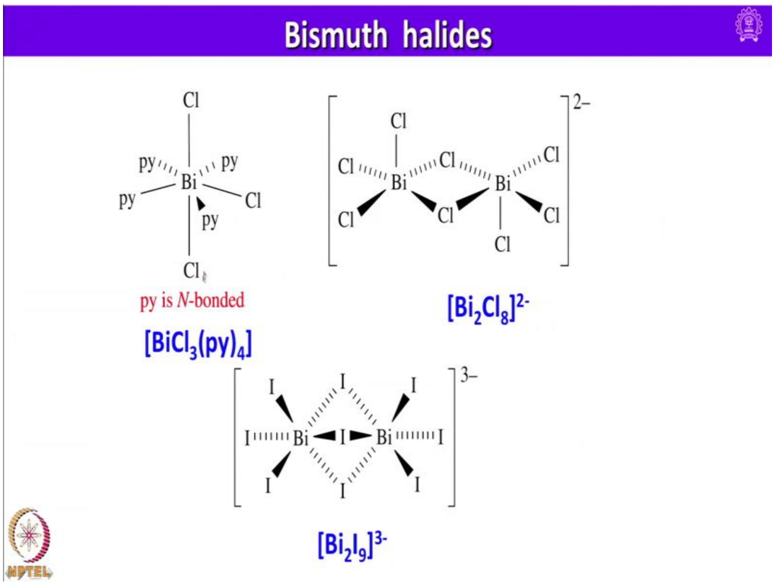

Bismuth halides

py is *N*-bonded

$[BiCl_3(py)_4]$

$[Bi_2Cl_8]^{2-}$

$[Bi_2I_9]^{3-}$

For example you can see here what we have is a (Refer Time: 18:13) BCl 3 compound. So, it is a 7 coordinated one we have 4 periodal groups N is coordinated to bismuth and here in this one BiCl 2 Cl 8 2 minus is there and this is Bi2 I 93 minus is there. So, other important compounds are facial BiCl 3 THF thriceand merid meridional Bi I3 where b I is perioding and also Cis Bi i4. So, these are some of examples of aducts which shows Lewis acid behavior of trihalides readily forming complexes with appropriate Lewis bases preferably (Refer Time: 19:31) donors.

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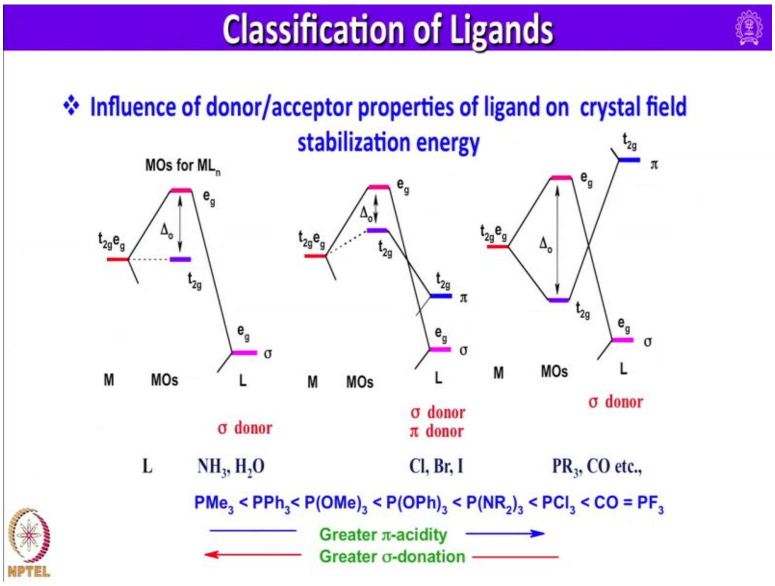

Classification of Ligands

- Influence of donor/acceptor properties of ligand on crystal field stabilization energy

σ donor

σ donor
π donor

σ donor

L NH_3, H_2O Cl, Br, I PR_3, CO etc.,

$PMe_3 < PPh_3 < P(OMe)_3 < P(OPh)_3 < P(NR_2)_3 < PCl_3 < CO = PF_3$

Greater π-acidity →

← Greater σ-donation

Let us look into the classification of ligands now of course, phosphines are widely used as ligands both in coordination chemistry and organometallic chemistry, and also in homogeneous catalysis. Phoshphines have remarkably ability to stabilize (Refer Time: 19:56) in the lower end states and also in unusual oxidized states. This diagram what I have given here essentially shows the influence of donor and acceptor properties of ligands on crystal field stabilization energy.

In fact, whatever the ligands we come across can be simply classified into just 3 categories first one is pure sigma donor ligands you can look into this example here first case where I have just given pure sigma donor ligands such as ammonia and water and the corresponding ligands, here you can see they have low lying field sigma orbitals, they interact with metal appropriate orbitals and you can see here the c f s c the magnitude of cf s c, and next we have another class of ligands they are called sigma donor and pi donor essentially all halides, they have low lying field sigma orbitals and low lying field pi orbitals because of s 2 p 6 electronic configuration.

So, in this case both are directed towards the metal, as a result what happens CFSC decreases considerably you can see here magnitude with respect to pure sigma donor ligands the third class of ligands are essentially sigma donor and pi acceptor, these type of ligands or phosphines carbon monoxide N heterocyclic carbenes (Refer Time: 21:29) ligands etcetera. So, they have low energy field sigma orbitals and higher energy MTPI orbitals, in this case what happens you can see CFSC remarkably increases. This is how the sigma donor and pi acceptor ligands stabilize metal complexes in their lower end state of course, let us look into the bonding we come across with metal carbonyls and metal phosphines. In fact, there very similar, both have low energy sigma donor orbitals and also both have appropriate MTPI orbitals for back bonding.

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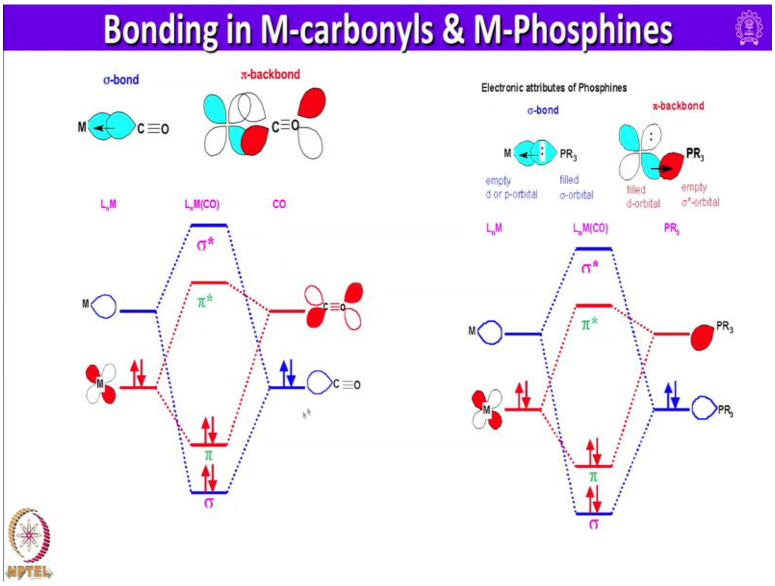
Bonding in M-carbonyls & M-Phosphines

Electronic attributes of Phosphines

So, you can see here in case of carbon monoxide, this carbon lone pair goes as sigma whereas, pi star of CO essentially combines with one of the t 2 g orbitals to form bonding and antibonding orbitals, and to the bonding orbital these electrons are coming this is called back bonding. Similarly, we can see in case of phosphines this lone pair goes as sigma towards appropriate metal eg orbitals, and phosphine sigma star energy is quite comparable to the t 2 g of metal, here this sigma star of phosphine p r 3 combines with one of the t 2 g let us say d x y, d x y z, d x z to form bonding and antibonding orbitals with pi symmetry and here these electrons are coming here. So, this essentially indicates the back donation of metal t 2 g electrons to the sigma star through back bonding.

So; that means, both are quite comparable the interesting point here is the energy of sigma star can be altered by altering the substituents on phosphorus, unlike pi star where that is not possible.

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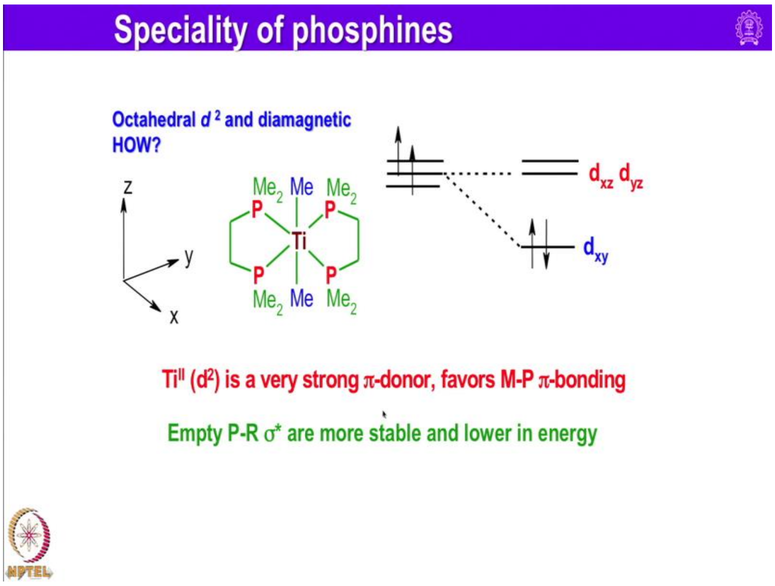

Speciality of phosphines

Octahedral d^2 and diamagnetic
HOW?

Ti^{II} (d^2) is a very strong π-donor, favors M-P π-bonding

Empty P-R σ^* are more stable and lower in energy

So, another interesting example I will show you. So, this is a titanium 2 compound. So, titanium electronic configuration is d 2 s 2, 3 d 2 4 s 2 and here in this case titanium is in plus 2 state and having 2 electrons in the d orbital, and this is an octahedral molecule surrounded by 2 this dimethyl phosphino ethane ligands and 2 methyl ligands in axial positions and strictly speaking any metal complex having up to 3 electrons in the d orbital should be paramagnetic, but interesting feature of this molecule is this is diamagnetic, let us see how that happens. You see octahedral d 2 and diamagnetic and here what happens under the influence of these bisphosphine ligands, the degeneracy of t 2 g is destroyed and dx y will become lower in energy compared to d x z and d y z these electrons now readily given to sigma star of this phosphine, this shows the diamagnetic behavior ok.

So, of course, titanium 2 plus is a very strong pi donor favors metal to phosphorous pi bonding, and empty phosphorus to alkyl group sigma are more stable and lower in energy. So, they readily overlap and take these electrons through back donation. And another important aspect with phosphines is the cone angle of course, cone angle will give you some information about steric attributes in phosphines what is this cone angle is you can see here.

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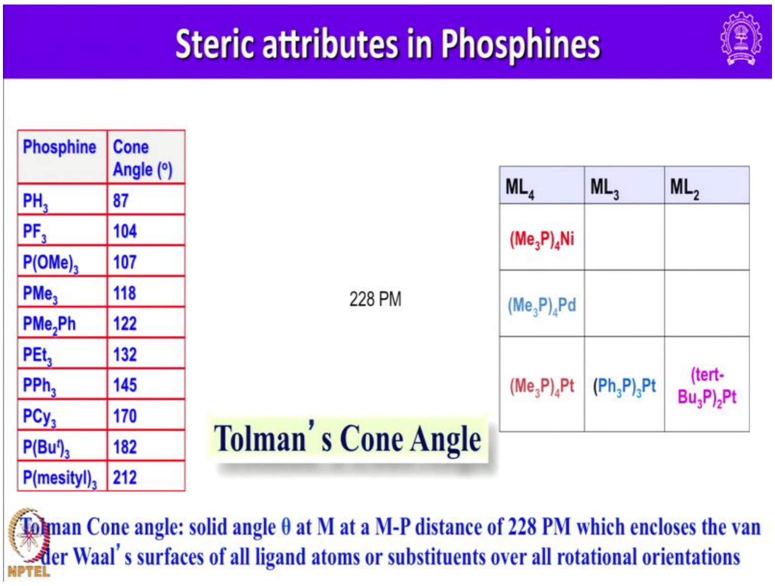

Steric attributes in Phosphines

Phosphine	Cone Angle (°)
PH_3	87
PF_3	104
$P(OMe)_3$	107
PMe_3	118
PMe_2Ph	122
PEt_3	132
PPh_3	145
PCy_3	170
$P(Bu^t)_3$	182
$P(mesityl)_3$	212

228 PM

ML_4	ML_3	ML_2
$(Me_3P)_4Ni$		
$(Me_3P)_4Pd$		
$(Me_3P)_4Pt$	$(Ph_3P)_3Pt$	(tert-$Bu_3P)_2Pt$

Tolman's Cone Angle

Tolman Cone angle: solid angle θ at M at a M-P distance of 228 PM which encloses the van der Waal's surfaces of all ligand atoms or substituents over all rotational orientations

Cone angle can be defined as a solid angle, let us assume this is a phosphine with pyramidal structure, and now this is bind into the metal and the average metal to phosphorous distance is about 228 picometre.

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So, now I will define what is cone angle. So, cone angle is nothing, but a solid angle theta at metal to phosphorous distance of 228 picometre which encloses the Vander Waal surfaces of all ligand atoms or substance or all rotational orientations.

So, basically this encloses the Vander Waal surfaces of all ligand atoms overall rotational orientations. So, this is called cone angle. So, this cone angle will vary depending upon the phosphorus substituent for example, if I take triphenyl phosphine, you can see now this cone angle increases considerably. So, this cone angle should enclose the Vander Waal surface of all ligand substance or all rotational orientations. So, this is called cone angle.

So, how this helps in determining the capability of a phosphine in homogenous catalysis. For example, let us look into the values I have given for various phosphines here, Ph 3 as 87 degree whereas, this (Refer Time: 27:16) has 2012 the maximum here and now for example, trimethyl phosphine can form tetra coordinated compound with nickel and also with palladium and also with platinum whereas, triphenyl phosphine can form a stable tri coordinated compound with platinum whereas, (Refer Time: 27:38) phosphine can form even stabilize platinum with 2 coordination number.

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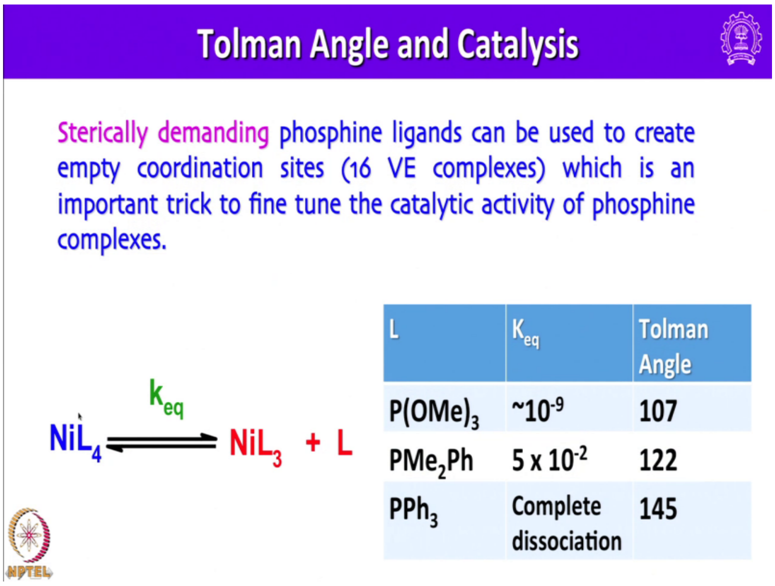

Tolman Angle and Catalysis

Sterically demanding phosphine ligands can be used to create empty coordination sites (16 VE complexes) which is an important trick to fine tune the catalytic activity of phosphine complexes.

$$NiL_4 \underset{}{\overset{k_{eq}}{\rightleftharpoons}} NiL_3 + L$$

L	K_{eq}	Tolman Angle
$P(OMe)_3$	~10^{-9}	107
PMe_2Ph	5×10^{-2}	122
PPh_3	Complete dissociation	145

So, for example, before we do any catalytic reaction if we take a compound having 18 electron, first we have to dissociate 1 or 2 ligands let us look into the dissociation of one of the phosphine from N i c l 4 to give N i L 3 plus L, here let us look into the dissociation constant for POM e 3 this is 10 to the power of minus 9, and the Tolman angle is 107. So, when this ligand is substituted with dimethylphenyl phosphine. So, dissociation rate increases and it is 5 into 10 to the power of minus 2, because the Tolman angle is 122.

So, when you consider phosphine triphenyl phosphine, this happens complete association the moment you put into the solution because the Tolman angle is 145; that means, as the angle increases because of steric crowding removal of 1 or 2 dissociation of 1 or 2 phosphines becomes very easy so; that means, if we make any phosphines with bulky ligands prior to the oxidative addition, it ready forms 14 or 16 electron species and this information readily comes from simply looking into the Tolman cone angle.

So, this is where Tolman cone angle assets in looking into the catalytic properties of some of these phosphines and their metal complexes. And another it aspect is bite angle. So, influence of bite angle on catholic efficiency is also very important for example, if you look into a typical square planer complex the bite angle will be 90 degree.

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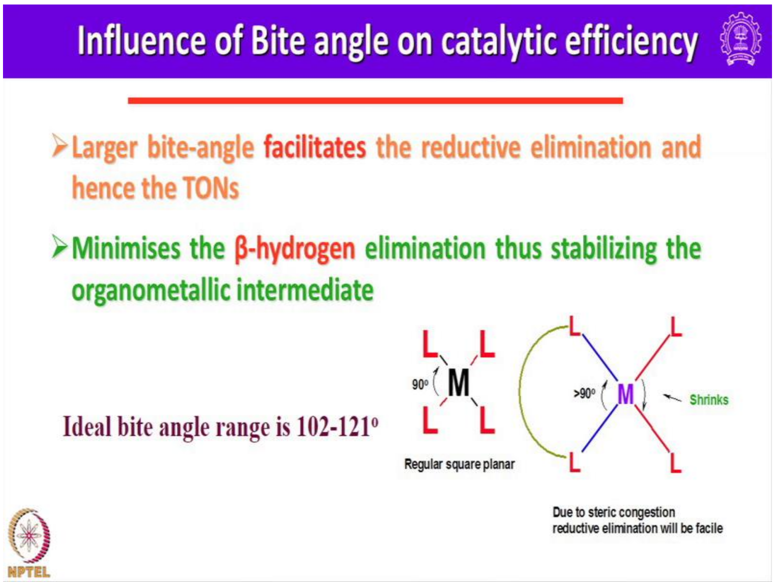

Influence of Bite angle on catalytic efficiency

- Larger bite-angle **facilitates** the reductive elimination and hence the TONs
- Minimises the β-hydrogen elimination thus stabilizing the organometallic intermediate

Ideal bite angle range is 102-121°

Regular square planar

Due to steric congestion reductive elimination will be facile

On the other hand if you take a bulky phosphines what happens? They occupy larger space as a result these 2 will come very closer to each other, you in case if there are 2 carbon fragments that have to be eliminated through consultant elimination reductive elimination this readily facilities if the angle is instead of 90, it if it is 115 or. So, these l and L if they are carbon fragments they readily come and establish a bond here and form 3 centered (Refer Time: 30:01) elimination. So, this is where the bite angle also very handy in looking into the catalytic efficiency of a bisphosphine ligand.

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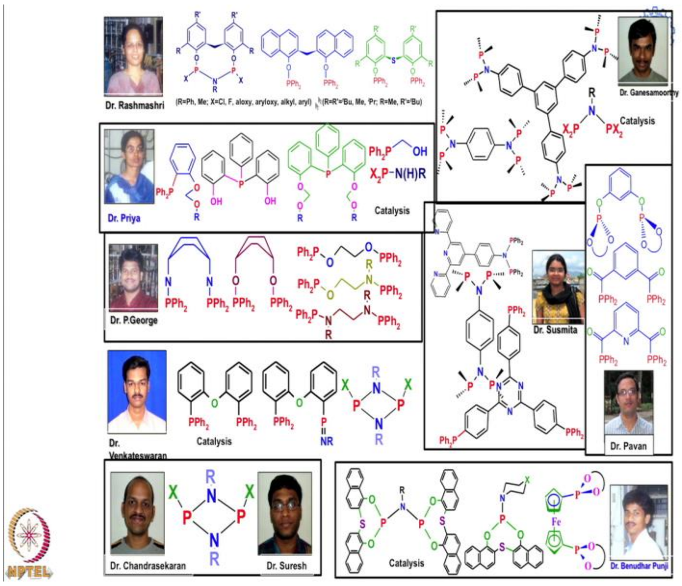

So, these are some of the ligands that are generated in my group here, for exploring their trans mettalic chemistry, coordination chemistry and catalytic applications.

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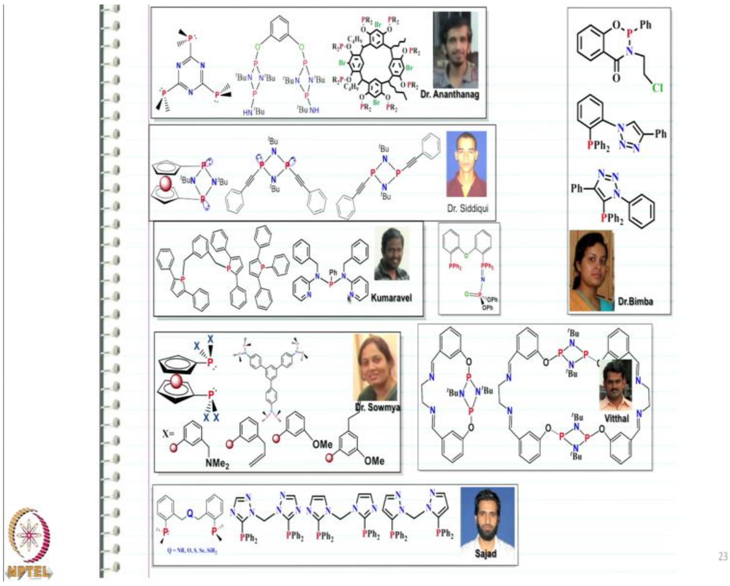

These are some more ligands I have shown here and these are some of the ligands derived from cycloidiphosphazane.

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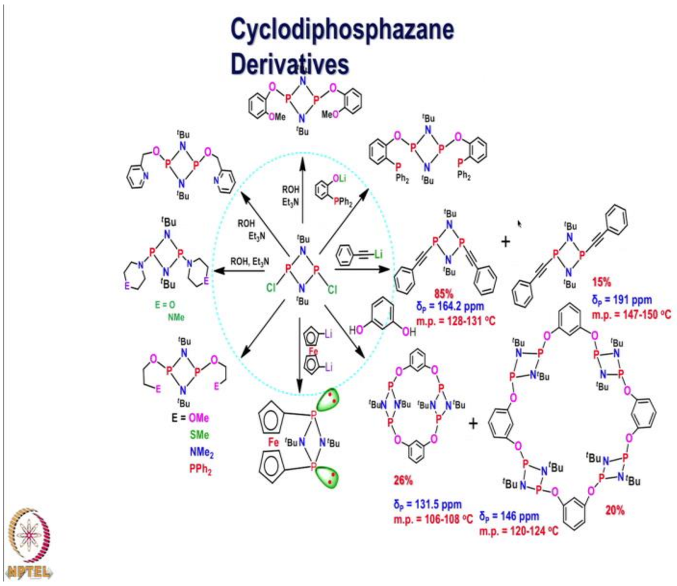

And some of these compounds also very valuable in forming metal O phosphine framework similar to metalorganic frameworks, and another important feature of phosphine is there phosphorous enamor spectroscopy.

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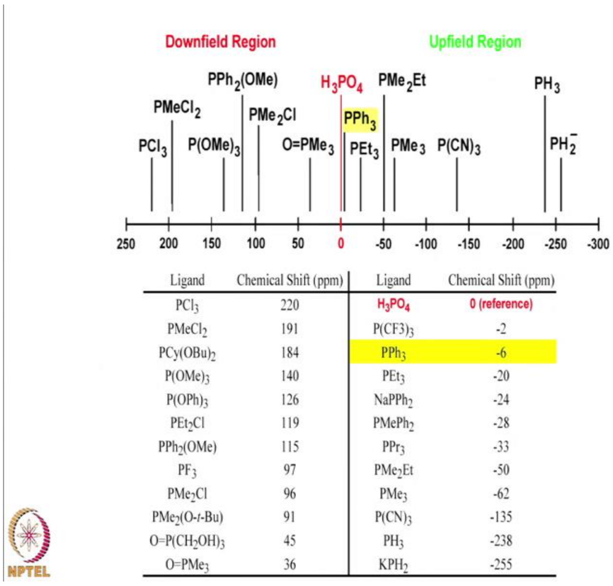

Ligand	Chemical Shift (ppm)	Ligand	Chemical Shift (ppm)
PCl_3	220	H_3PO_4	0 (reference)
$PMeCl_2$	191	$P(CF3)_3$	-2
$PCy(OBu)_2$	184	PPh_3	-6
$P(OMe)_3$	140	PEt_3	-20
$P(OPh)_3$	126	$NaPPh_2$	-24
PEt_2Cl	119	$PMePh_2$	-28
$PPh_2(OMe)$	115	PPr_3	-33
PF_3	97	PMe_2Et	-50
PMe_2Cl	96	PMe_3	-62
$PMe_2(O\text{-}t\text{-}Bu)$	91	$P(CN)_3$	-135
$O{=}P(CH_2OH)_3$	45	PH_3	-238
$O{=}PMe_3$	36	KPH_2	-255

So, these the 31 P NMR spectroscopy is as simple as proton NMR and here all phosphines have distinct chemical shift as a result what happens when we react this phosphines with metal complexes, we can (Refer Time: 31:04) the structure readily and we can look into the fate of the reaction simply by recording 31 P NMR, one can also do kinetics by doing temperature dependent or variable time NMR that helps in understanding lot of aspects revolving around metal phosphine complexes and their coordinating ability and also their ability to promote organic transformation as homogeneous getlates.

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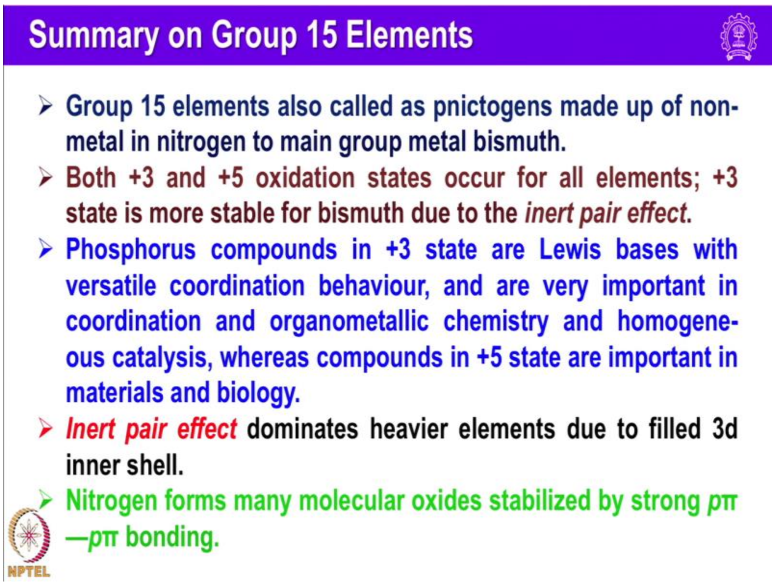

Summary on Group 15 Elements

- Group 15 elements also called as pnictogens made up of non-metal in nitrogen to main group metal bismuth.
- Both +3 and +5 oxidation states occur for all elements; +3 state is more stable for bismuth due to the *inert pair effect*.
- Phosphorus compounds in +3 state are Lewis bases with versatile coordination behaviour, and are very important in coordination and organometallic chemistry and homogeneous catalysis, whereas compounds in +5 state are important in materials and biology.
- *Inert pair effect* dominates heavier elements due to filled 3d inner shell.
- Nitrogen forms many molecular oxides stabilized by strong $p\pi$—$p\pi$ bonding.

So, let me summarize the chemistry of group 15 elements so far we have discussed in. Group 15 elements are also called as pnictogens, made up of nonmetals in nitrogen to main group metal bismuth both plus 3 and plus 5 states occur for all elements; plus 3 state is more stable for bismuth due to the inert pair effect, phosphorus compounds in plus 3 state are excellent Lewis bases with versatile coordination behavior, and are very important in coordination and organometallic chemistry and also in homogeneous catalysis whereas, compounds in plus 5 state are important in materials and biology, inert pair effect dominates heavier elements due to field 3 d inertial. Nitrogen forms many molecular oxides stabilized by strong p pi p pi bonding.

I conclude the chemistry of group 15 elements in my next lecture I will be dealing with group 16 elements until then have a pleasant reading of main group chemistry.

Thank you very much.