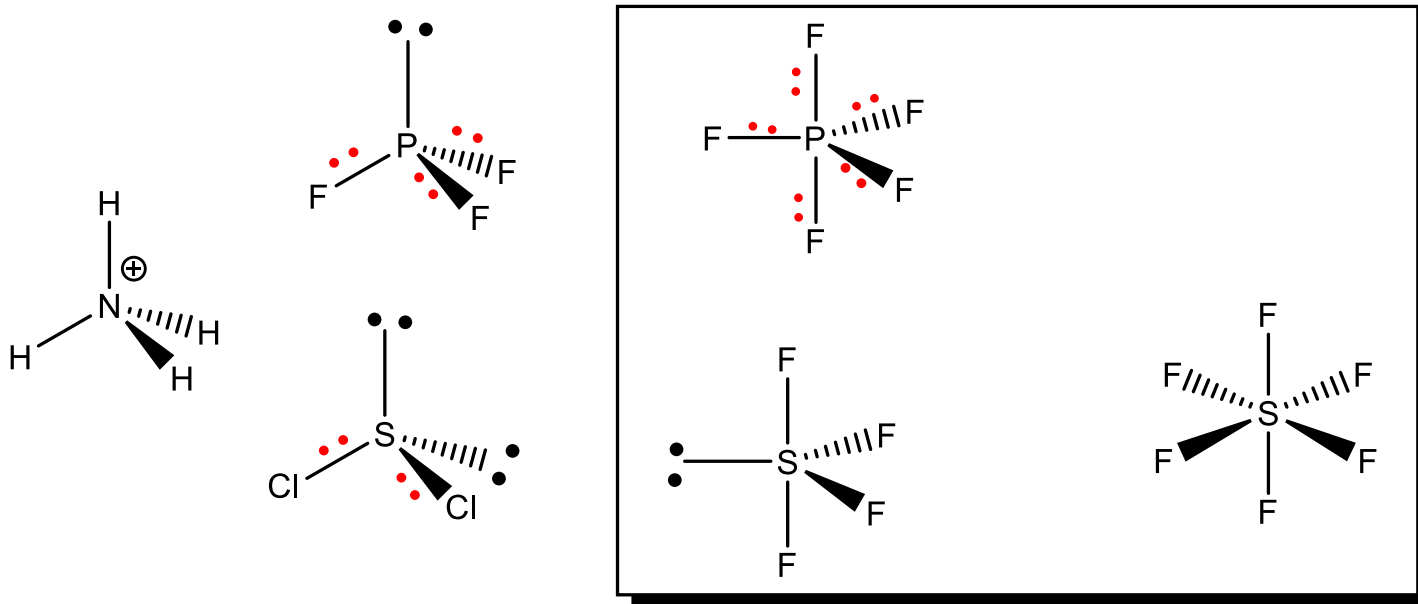


Hypervalency

The ability of an atom in a molecular entity to expand its valence shell beyond the limits of the Lewis octet rule. Hypervalent compounds are common for the second and subsequent row elements in groups 14–18 of the periodic table. A description of the hypervalent bonding implies a transfer of the electrons from the central (hypervalent) atom to the nonbonding molecular orbitals which it forms with (usually more electronegative) ligands. A typical example of the hypervalent bond is a linear three-centre, four-electron bond, e.g. that of $F_{ap}-P-F_{ap}$ fragment of PF_5 .



Hypervalent

What molecule are considered hypervalent and what are not?

The concept of hypervalency in p block compounds

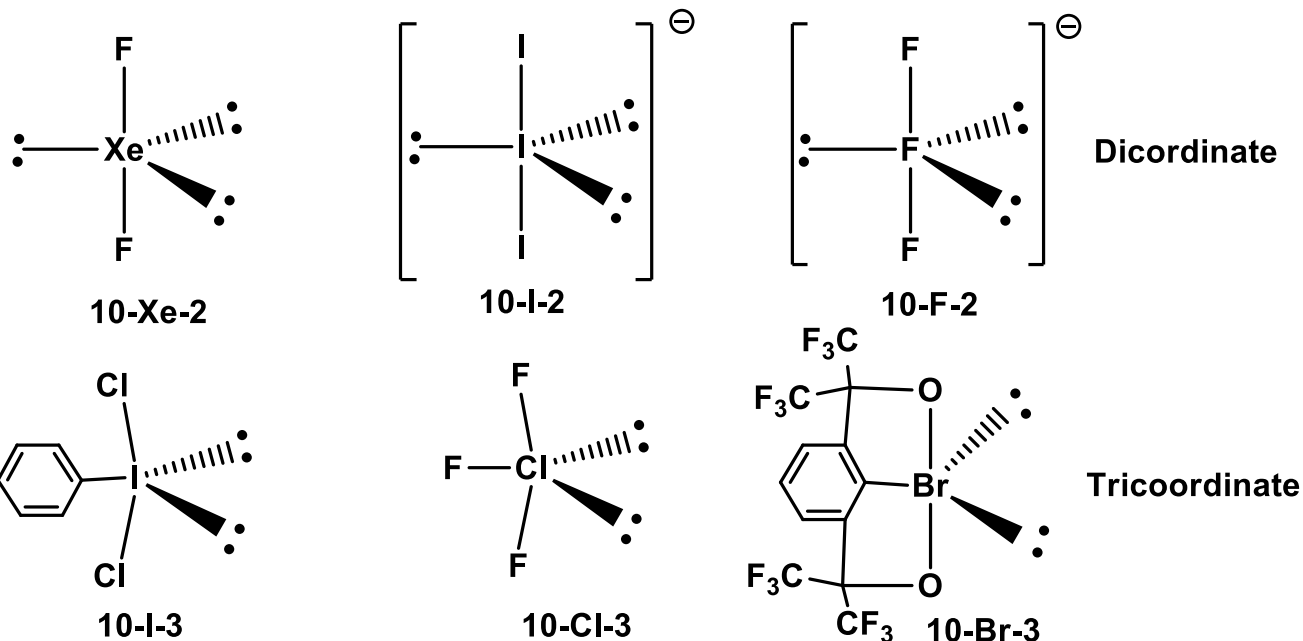
A hypervalent molecule may be defined as a molecule in which there are **more than four pairs of electrons** around the central atom in the conventional Lewis diagram of the molecule.

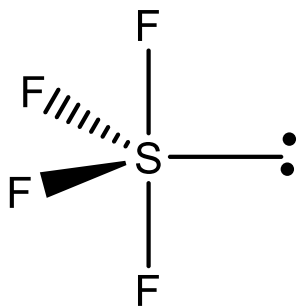
J. I Musher in 1969 originally defined hypervalent molecules as those formed by the nonmetals of groups 15-18 in any of their stable valence states higher than 3, 2, 1, and 0, respectively.

*“We refer to these molecules as **hypervalent** (or HV) since they involve atoms, called donor atoms, which exceed the number of valences allowed them by the traditional theory, and thus utilize more electron-pairs of bonding than provide stability in the Lewis-Langmuir theory. As hypervalent molecules have chemical formulas, and often the molecular structure, of the addition product of a stable molecule with two monovalent ligands or a single divalent ligand they could also be called hypermolecules or “molecules made out of molecules”*

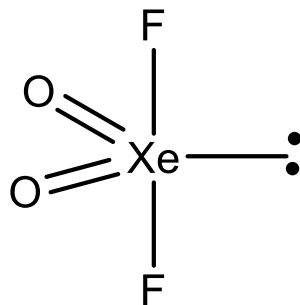
The N-X-L designation

The N-X-L designation is used to describe hypervalent molecules where **N is the number of formally assignable valence electron to the central atom**, **X is the symbol of the central atom** and **L is the number of ligands /substituents directly bonded to the central atom**. The compounds can have coordination numbers from two to six. All the known compounds of rare gases **as central atom** come under the category of hypervalent molecules. Most of the hypervalent compounds have their structure derived from a trigonal bipyramid or octahedral geometry.

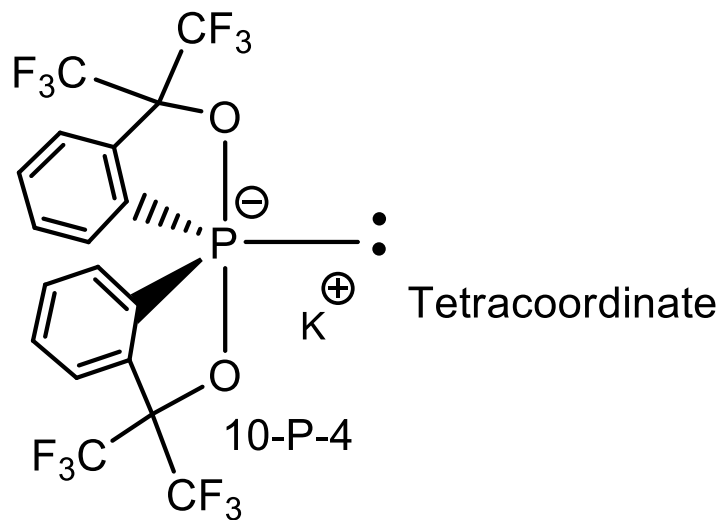




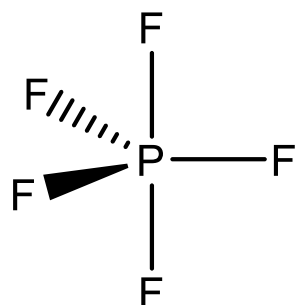
10-S-4



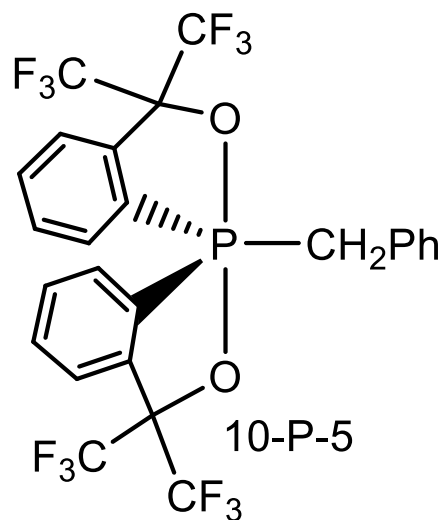
14-Xe-4



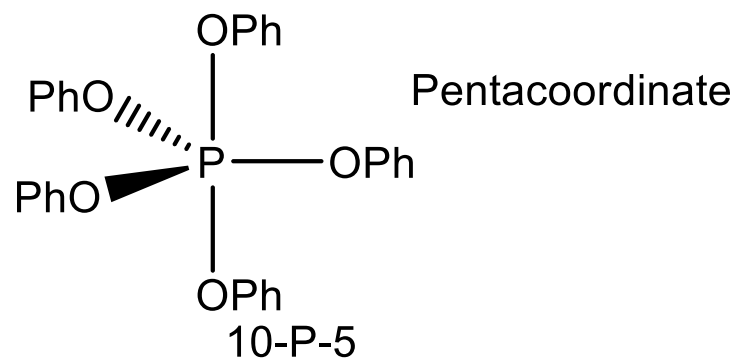
Tetracoordinate



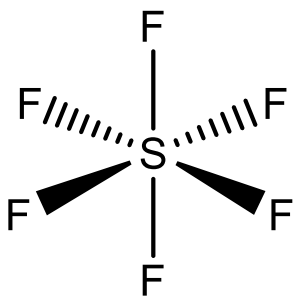
10-P-5



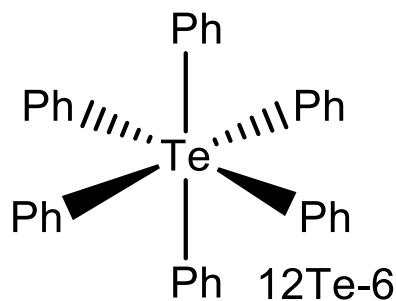
10-P-5



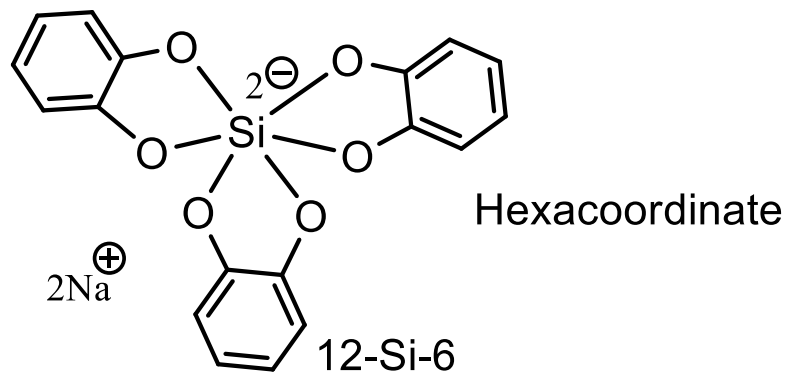
Pentacoordinate



12-S-6



12Te-6



Hexacoordinate

12-Si-6

Explaining Hypervalency

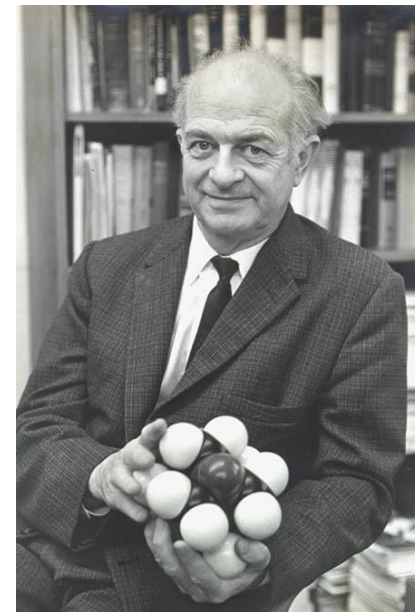
Pauling's expanded octet model

Through promotion of electrons into vacant high lying d orbitals leading to sp^3d/sp^3d^2 hybridizations

It has been shown by many theoretical researchers that even if d orbitals are necessary to provide quantitative bond energies in hypervalent species these orbitals have occupancies of only 0.3 electrons at the most .

In 2013 it was calculated that for XeF_2 the Valence bond structures corresponding to the sp^3d hybridization model account for only 11.2% of the wavefunction and brings in only stabilization energy of only 7.2 kcal/mol much less than the total binding energy (64.1 kcal/mol)

The discovery of F_3^- which has a structure same as that of I_3^- has been one of the biggest deathblows to the use of d orbitals in explaining the structure of hypervalent molecules as conventionally the central atom of I_3^- was assumed to have a trigonal bipyramid sp^3d geometry while the same fails for F_3^- since fluorine being a first row p block element is expected not to have d orbitals for invoking hybridization.

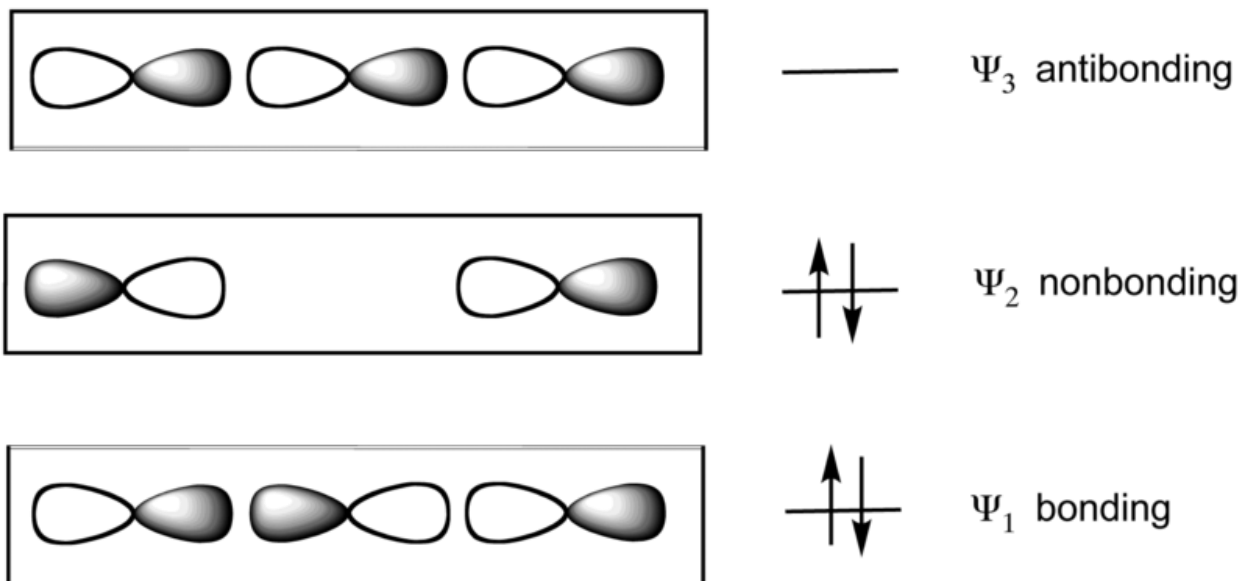


The three centre 4 electron (3c-4e) model

Proposed in 1951 by Pimental and Rundle

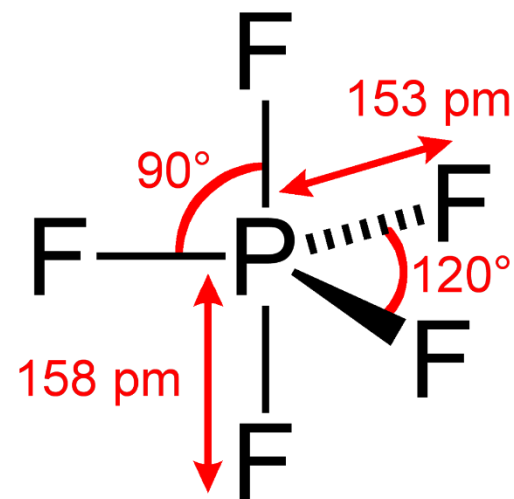
In a three centre 4 electron molecular system three atoms or fragments each contribute a single atomic orbital from which one can construct a set of three molecular orbitals (MO's) of bonding non bonding and antibonding character

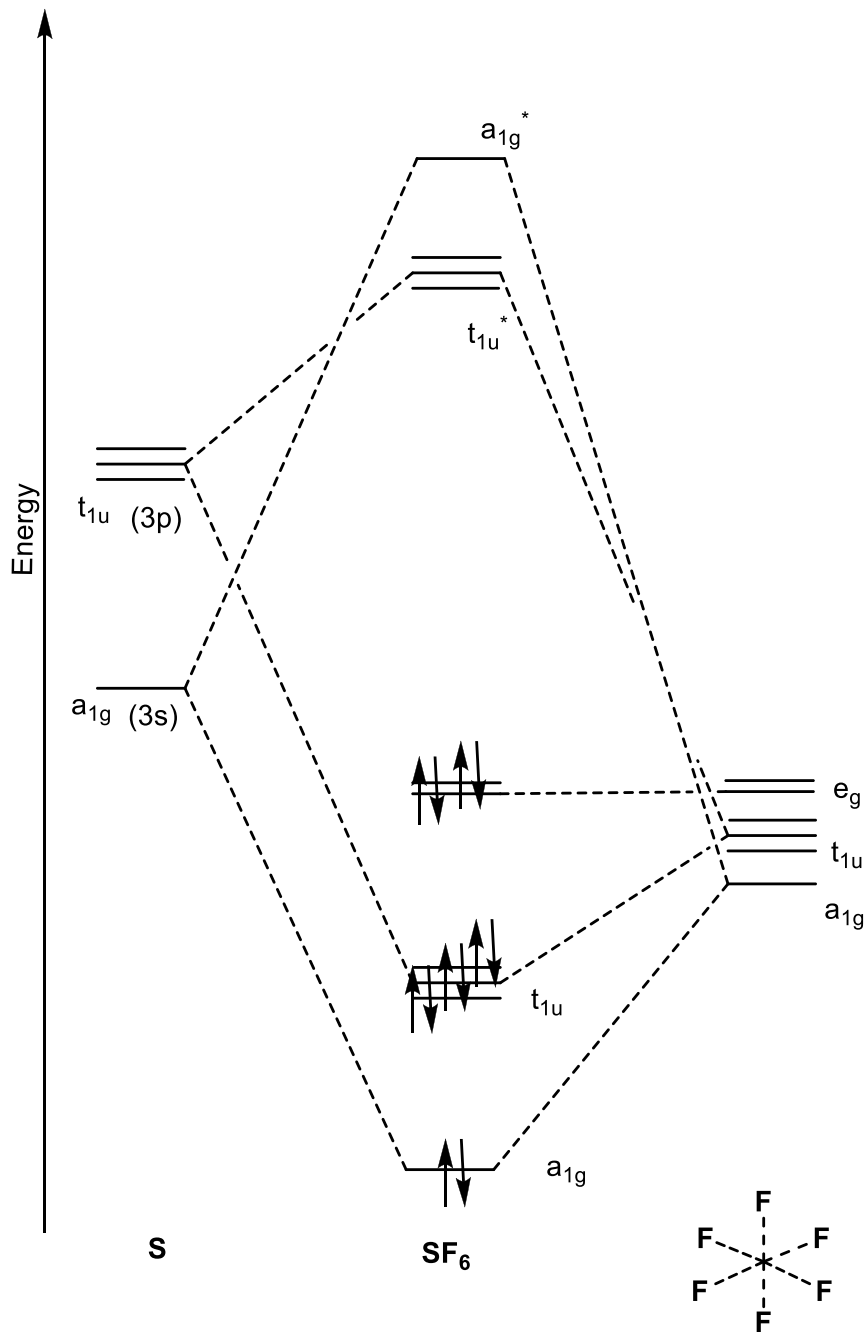
For example in the case of XeF_2 , three pure p_z orbitals combine to form a set of MO's of which only the first two are occupied giving a net bond order of 0.5.



The Xe-F bonds result from the combination of a filled p orbital in the central atom (Xe) with two half-filled p orbitals on the axial atoms (F), resulting in a filled bonding orbital, a filled non-bonding orbital, and an empty antibonding orbital. The two lower energy MO's are doubly occupied. The bond order for each Xe-F bonds is 1/2, since the only bonding orbital is delocalized over the two Xe-F bonds. A similar bonding can be envisaged for I_3^- .

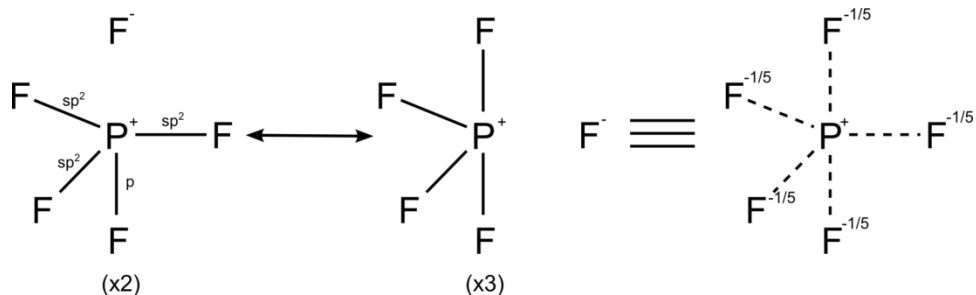
In the case of the trigonal bipyramid PF_5 , the three shorter equatorial bonds (153.4 pm) are described by localized orbitals formed by 2 center 2 electron bonds. The longer axial bonds (157.7 pm) can be described by the three molecular orbitals formed by a single p orbital on phosphorus and a p orbital on each of the fluorines. **The two electrons in the non bonding orbitals are localized on the fluorine atoms and do not contribute to the bonding and the bonding is due to the two electrons in the bonding orbital and therefore each axial P-F bond is effectively a half bond.**



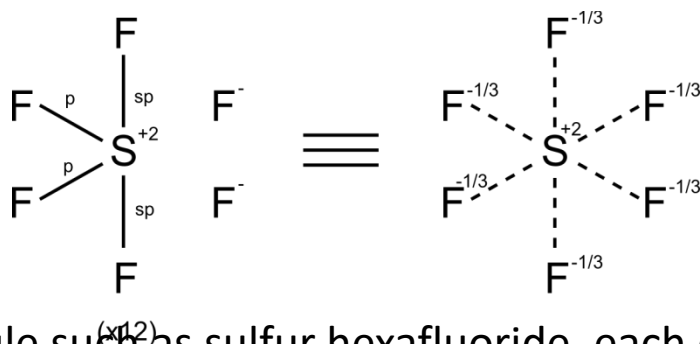


Using the group theoretical treatment and the O_h character table, one can arrive at a reducible representation and reduce this to a sum of irreducible representations for obtaining the symmetry matching orbitals. The ligand group orbitals thus obtained for the F₆ part of SF₆ are a_{1g} , t_{1u} and e_g . The qualitative molecular orbital diagram of SF₆ can be constructed by matching the symmetry of the S valence orbitals and the LGOs of the F₆ fragment. While orbital overlap occurs for the a_{1g} and t_{1u} orbitals, the e_g set remains non-bonding. There are a total of 48 valence electrons in SF₆. In addition to the molecular orbitals shown in the MO diagram there are 18 more MOs accommodating electrons which are mostly of fluorine in character. The qualitative MO picture is consistent with six equivalent S–F bonds. Since the e_g orbitals are non-bonding, there are only 4 bonding pairs of electrons and therefore the bond order for SF₆ is 2/3.

VB treatment Linus Pauling



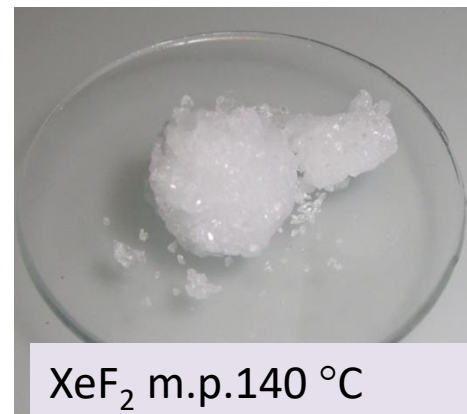
For hypervalent compounds in which the ligands are more electronegative than the central, hypervalent atom, resonance structures can be drawn with no more than four covalent electron pair bonds and completed with ionic bonds to obey the octet rule. For example, in phosphorus pentafluoride (PF₅), five resonance structures can be generated each with four covalent bonds and one ionic bond with greater weight in the structures placing ionic character in the axial bonds, thus satisfying the octet rule and explaining both the observed trigonal bipyramidal molecular geometry and the fact that the axial bond length (158 pm) is longer than the equatorial (154 pm).



For a hexacoordinate molecule such as sulfur hexafluoride, each of the six bonds is the same length. The rationalization described above can be applied to generate 15 resonance structures each with four covalent bonds and two ionic bonds, such that the ionic character is distributed equally across each of the sulfur-fluorine bonds.

The modern view of stable hypervalent molecules- charge shift bonding

Bonds in which the covalent-ionic resonance energy is the major cause for bonding have been termed **charge shift bonds**



The high stability of XeF₂ indicated by its large atomization energy cannot be ascribed to any of its individual VB structures but mostly from an exceptionally large resonance energy arising from the mixing of several VB structures which are covalent and ionic.



This model also supports that electron must be transferred from the central atom to the ligand for hypervalency to take place. Also stresses the importance of low ionization energies for the central atom and high electron affinity for the ligands. Therefore charge shift bonding along with the 3c 4e model can explain the higher stability of hypervalent molecules such as XeF₂

The essential role of charge-shift bonding in hypervalent prototype XeF₂

Benoît Braïda^{1*} and Philippe C. Hiberty^{2*}

Hypervalency in XeF₂ and isoelectronic complexes is generally understood in terms of the Rundle–Pimentel model (which invokes a three-centre/four-electron molecular system) or its valence bond version as proposed by Coulson, which replaced the old expanded octet model of Pauling. However, the Rundle–Pimentel model is not always successful in describing such complexes and has been shown to be oversimplified. Here using *ab initio* valence bond theory coupled to quantum Monte Carlo methods, we show that the Rundle–Pimentel model is insufficient by itself in accounting for the great stability of XeF₂, and that charge-shift bonding, wherein the large covalent-ionic interaction energy has the dominant role, is a major stabilizing factor. The energetic contribution of the old expanded octet model is also quantified and shown to be marginal. Generalizing to isoelectronic systems such as ClF₃, SF₄, PCl₅ and others, it is suggested that charge-shift bonding is necessary, in association with the Rundle–Pimentel model, for hypervalent analogues of XeF₂ to be strongly bonded.

Chemical Bonding in Hypervalent Molecules. The Dominance of Ionic Bonding and Negative Hyperconjugation over d-Orbital Participation

Alan E. Reed*[†] and Paul von Ragué Schleyer

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, 8520 Erlangen, Federal Republic of Germany.

Received February 2, 1989

(b) over proposal (a). Since then, more refined theoretical analyses of hypervalent molecules, employing shared electron number and occupation number analysis,¹¹ electron density analysis,¹² and natural population analysis (NPA),¹³⁻¹⁵ have been carried out. In accord with Kutzelnigg,¹⁰ these analyses¹¹⁻¹⁵ have concluded that, though d orbitals on second-row elements often give large energetic contributions in hypervalent species, the traditional dsp^3 and d^2sp^3 models are invalid: total d-orbital occupancies are at most 0.3e, and the d orbitals act primarily not as valence but as polarization functions, or, equivalently, as acceptor orbitals for back-donation from the ligands. These studies¹¹⁻¹⁵ emphasize the importance of partial ionic bonding in second-row hypervalent species (proposal (b) above) and reinforce the essential conclusions of Rundle⁷ and Musher.⁸ Due to the ionic character of the bonding, the *electronic* octet rule is far from being violated. This

No d Orbitals but Walsh Diagrams and Maybe Banana Bonds: Chemical Bonding in Phosphines, Phosphine Oxides, and Phosponium Ylides

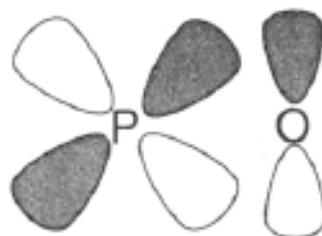
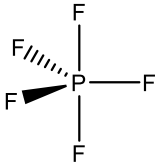
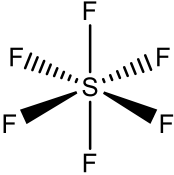
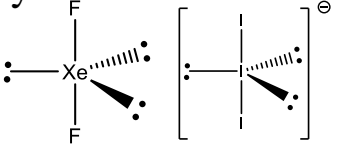
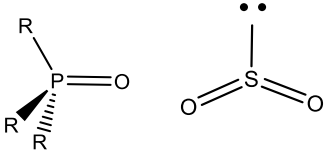
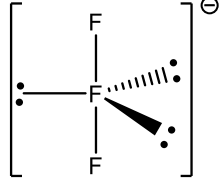


Figure 6. The now outdated and misleading view of the π -type orbital overlap in phosphine oxides.

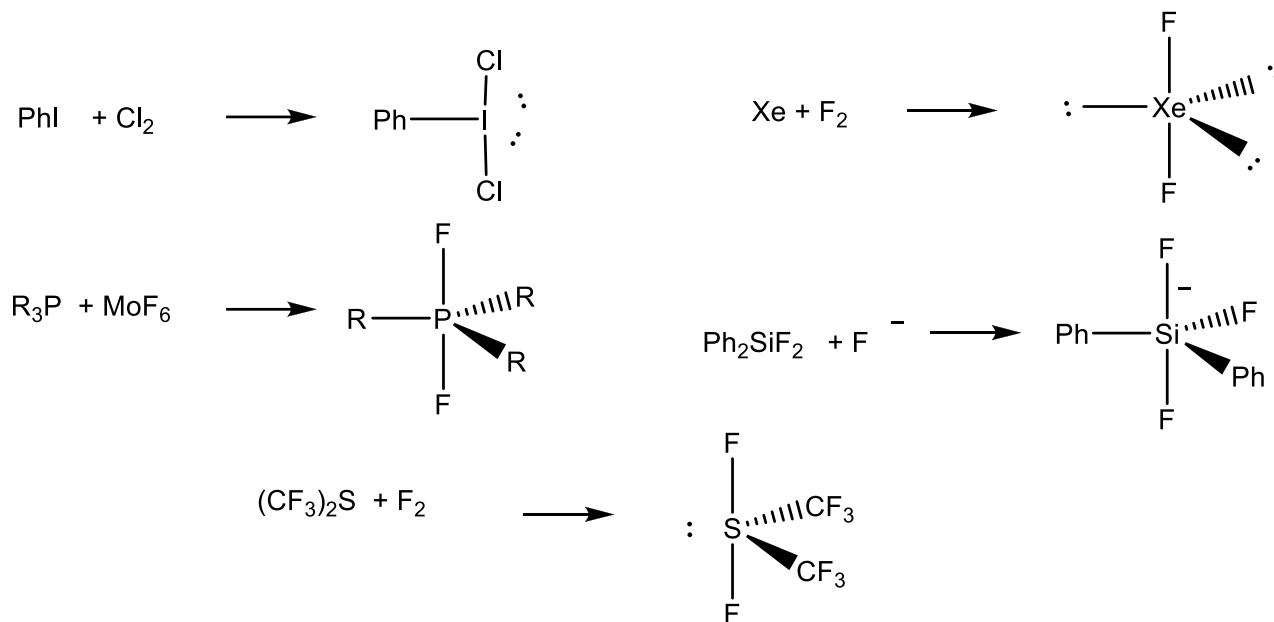
d orbitals”, a euphemism for saying that the octet rule is broken by these compounds. Also, up until recently, there was a smoothly made connection^{20,21,103–108,184–186} that this indicated that “the low-lying atomic d orbitals are involved in hybridisation at phosphorus”, in an overlap scheme like the one in Figure 6.

Work over the last 10–15 years has rendered this description untenable. First we have already seen in section II that the d-orbitals concept is now redundant at best, inaccurate and misleading at worst. Secondly, at a deeper level, doubt has been cast on the description of the PO bond as a single bond with some backbonding, the rival description being a formal triple bond. As we shall see in section IV.E.3, this latter issue is not yet settled and is part of a developing general controversy about the nature of multiple bonding.

| P block compound and its property | Earlier explanation suggested based of participation of empty d orbitals | Modern explanation supported by theoretical studies where d orbitals are not used. |
|--|--|--|
| PF ₅  | Assuming promotion of electrons to vacant higher energy d orbitals resulting in sp ³ d hybridization. | Invoking 3c-4e bonding of the axial bonds: wavefunctions described as superpositions of resonance structures some of which obey the octet rule (ionic) and some break the octet rule (covalent). |
| SF ₆  | Assuming promotion of electrons to vacant higher energy d orbitals resulting in sp ³ d ² hybridization | Invoking two 3c-4e bonds involving delocalization of one of the two bonding pairs on to the substituents and resulting in a charge distribution of +1 on the central atom and -0.5 on each of the substituents |
| XeF ₂ structure and unusual stability  | Sp ³ d hybridization with equatorial positions of the trigonal bipyramid occupied by lone pairs | 3 centre 4 electron bonding along with charge shift bonding. Extra stability due to charge shift bonding (Bonds in which the covalent-ionic resonance energy is the major cause for bonding) |

| | | |
|---|---|--|
| <p>Phosphine oxide, sulfur dioxide</p>  | <p>Covalent compounds having $p\pi$- $d\pi$ bonds resulting in shorter P-O and S-O bonds</p> | <p>Covalent bonds but not involving d orbitals. The back bonding of electron density to the σ^* acceptor orbitals of phosphorus or sulfur which are the LUMO. An example of negative hyperconjugation effect (n to σ^*)</p> |
|  | <p>No explanation possible based on d orbitals since fluorine, a first row p block element has no d orbitals</p> | <p>3 center - 4 electron bonding</p> |
| <p>General lack of hypervalency among the first row p block elements</p> | <p>Absence of d orbitals of lower energy</p> | <p>Higher electro negativity of the first row p block elements and smaller size of these elements</p> |
| <p>$H_3SiOSiH_3$ and $N(SiH_3)_3$ structures have large bond angles around oxygen/nitrogen, structures not predicted by VSEPR rules</p> | <p>$p\pi$- $d\pi$ bonds between silicon and oxygen/nitrogen reduces effect of lone pair on geometry</p> | <p>VSEPR rules are applicable only if substituents have higher or comparable electronegativity as the central atom. Large bond angles are due to weak pairing of electrons on oxygen as a result of weakly electronegative SiH_3 group as well as electrostatic repulsions between bulky SiH_3 groups.</p> |

Primary factors stabilizing a hypervalent bond: Electronegative substituents



Electronegative groups stabilizes hypervalent bonds in main group compounds

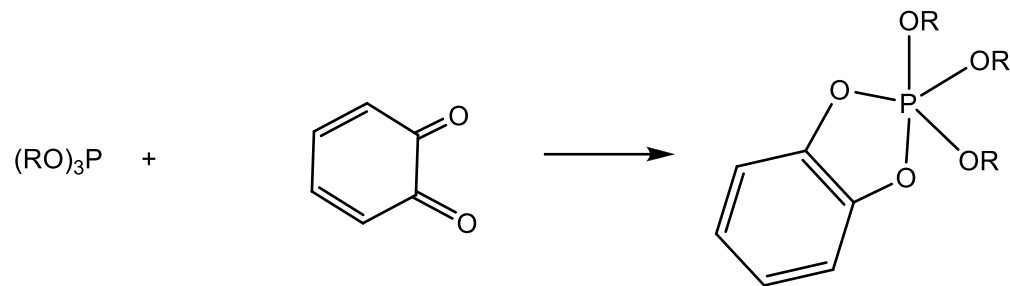
Apicophilicity: Tendency of a substituent to prefer axial positions in TBP

Experimentally observed apicophilicity of selected substituents in TBP:

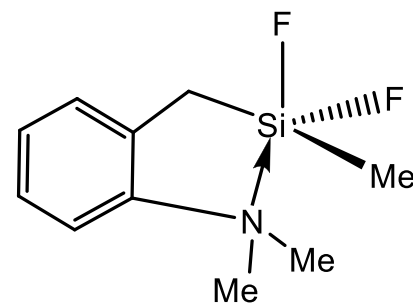
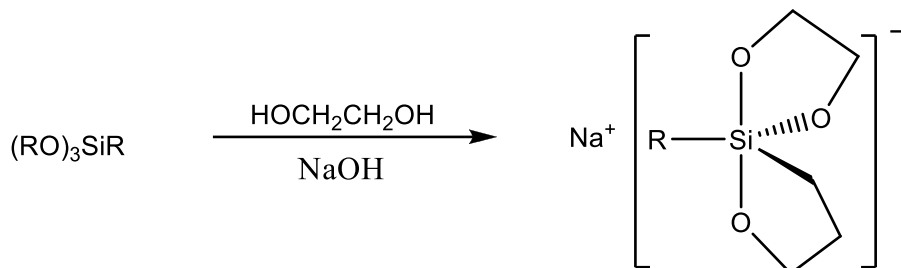


The apicophilicity of a substituent mainly depends on its electronegativity, but some other factors can also have an effect. A bulky substituent prefers equatorial positions, which are more distant from other substituents. A substituent with π -bonding ability also prefers equatorial positions.

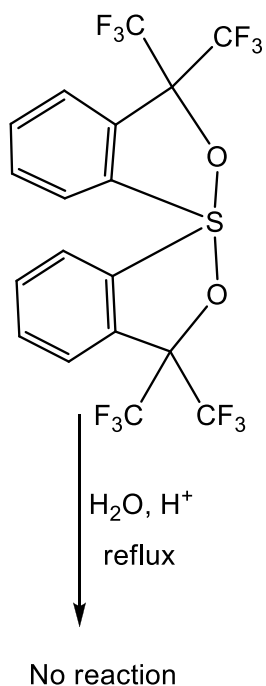
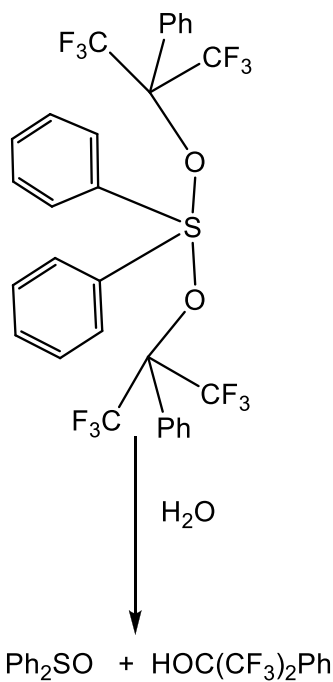
Primary factors stabilizing a hypervalent bond: Steric constraints on small rings



Small rings (5-6 mem) prefer axial/equatorial orientation than eq-eq or ax-ax.



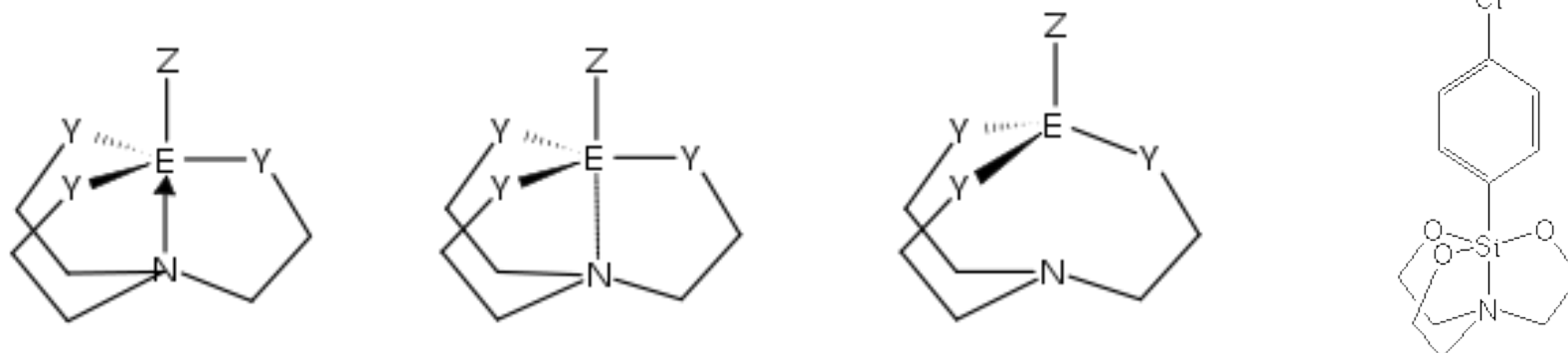
Strategic choice of substituents can even overcome the apicophilicity preference of electronegative substituents



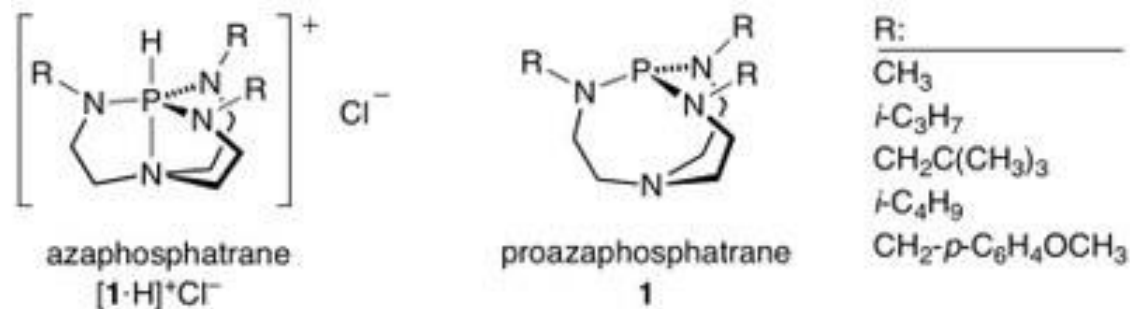
Small rings impart stability to molecules unlike their acyclic analogues

Primary factors stabilizing a hypervalent bond: Polydentate ligands

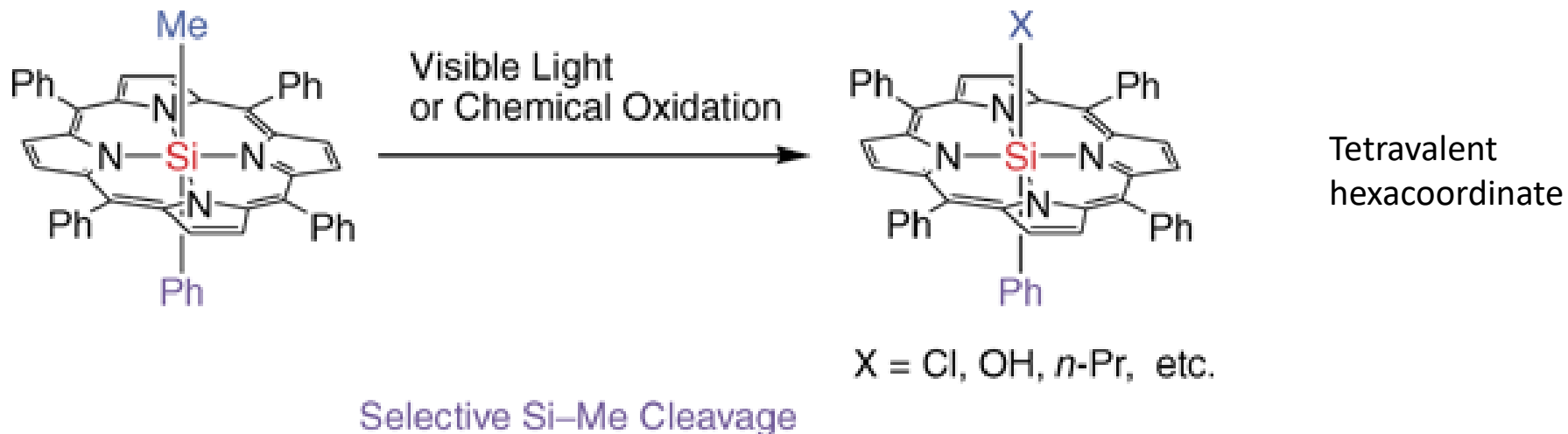
An **Atrane** is a tricyclic molecule with three five-membered rings having mostly P or Si as central atom. It has a transannular dative bond by a nitrogen atom



Silatranes exhibit unusual properties as well as biological activity in which the coordination of nitrogen to silane plays an important role. Some derivatives such as phenylsilatrane are highly toxic. The transannular coordinate bond in atranes can be stretched by controlling their stereoelectronic properties. Proazaphosphatrane, obtained from azaphosphatrane is a very strong non-ionic base and is utilized as an efficient catalyst.

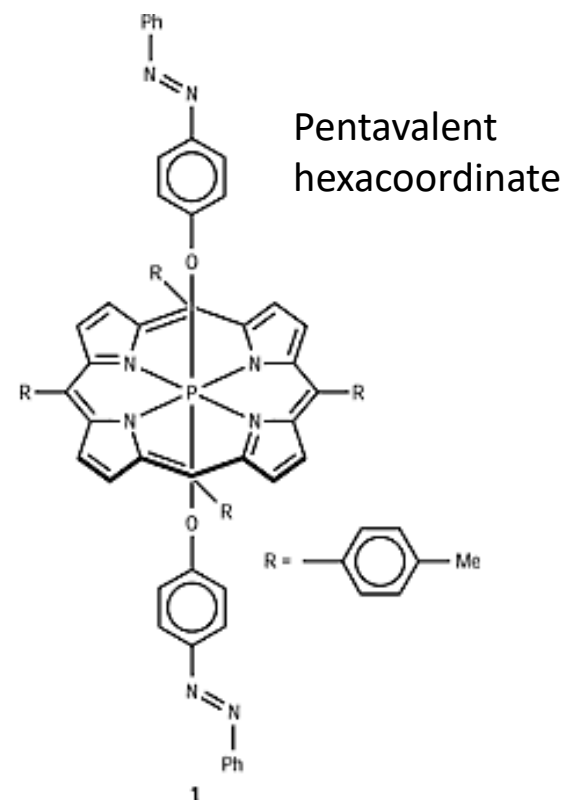


Primary factors stabilizing a hypervalent bond: Polydentate ligands; Porphyrins



A hypervalent phosphorus(V) porphyrin with axially bonded azobenzene groups functions as a molecular photoswitch.

describe the luminescent on–off behavior of an interesting metalloid porphyrin-based photoswitch they prepared using the axial-bonding capability of hexacoordinated phosphorus(V) porphyrin. The trick was to irradiate **1**, inducing E–Z isomerization of the azobenzene group to simulate an on–off switch.



Unique aspects of structure and reactivity of hypervalent compounds

Apicophilicity

Site exchange- fluxionality: pseudorotation

Stable intermediates of reaction

Increased reactivity

Stabilization of low oxidation states of p block compounds

Experimentally observed apicophilicity of selected substituents in TBP:



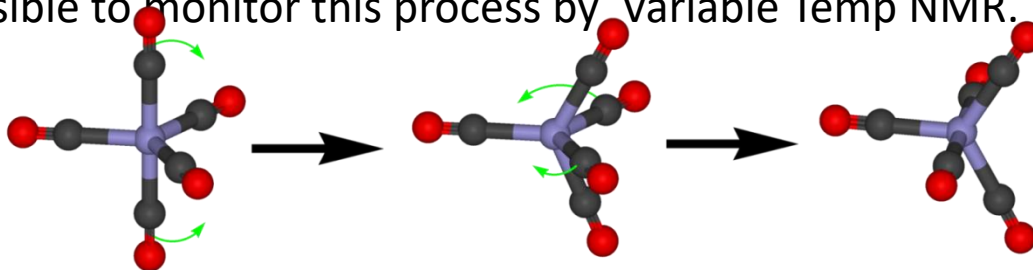
Site exchange- Fluxionality: Stereochemical non-rigidity

Fluxional molecules are molecules that undergo dynamics such that some or all of their atoms interchange between symmetry-equivalent positions.

| | |
|-----------------------------|------------------------------------|
| Berry Pseudorotation | Pentacoordinate |
| Turnstile Rotation | |
| Bailar Twist | Hexacoordinate chiral |
| Ray-Dutt Twist | |
| Ring whizzing | Organometallic Cp complexes |

In hypervalent pentacoordinate molecules, two types of bonds exist. These bonds may interconvert by an isomerization process without breaking of bonds.

In **Berry Pseudorotation** (Proposed by R Stephen Berry, Univ of Michigan 1960) the axial bonds of a TBP become equatorial and two equatorial bonds become axial- the whole process possibly through a square pyramidal intermediate situation. Although it was first proposed by Berry for PF_5 , this scrambling activity is too fast for PF_5 to be followed up by even low temp. NMR spectral studies. When one or two fluorines are replaced by chlorines, it becomes possible to monitor this process by Variable Temp NMR.



Turnstile rotation is more complex involving the simultaneous internal rotation of one axial and one equatorial bond followed by other bonds rearranging.

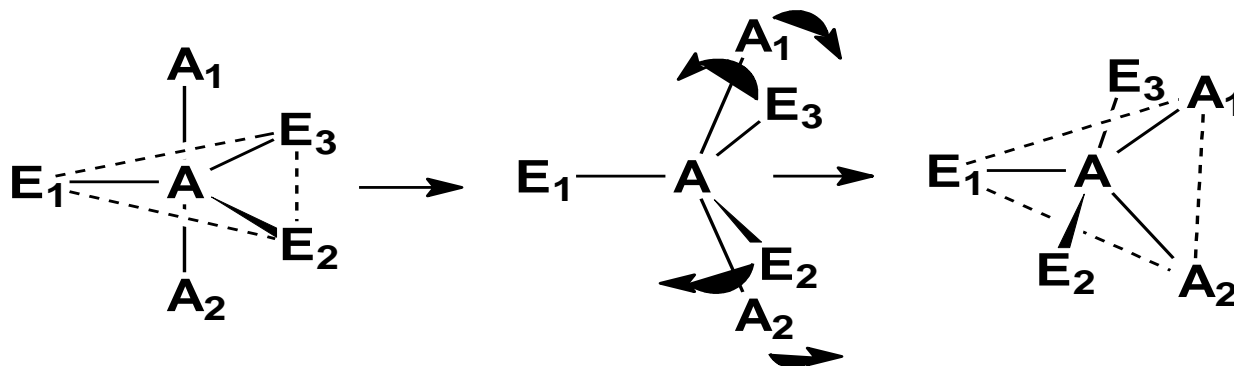
Stereochemically non-rigid structures: Berry Pseudorotation

In NMR if a spin active nucleus couples with another spin active nucleus, each with a spin quantum number I , then $2nI+1$ lines will be seen where n is the number of NMR active nuclei in the vicinity.

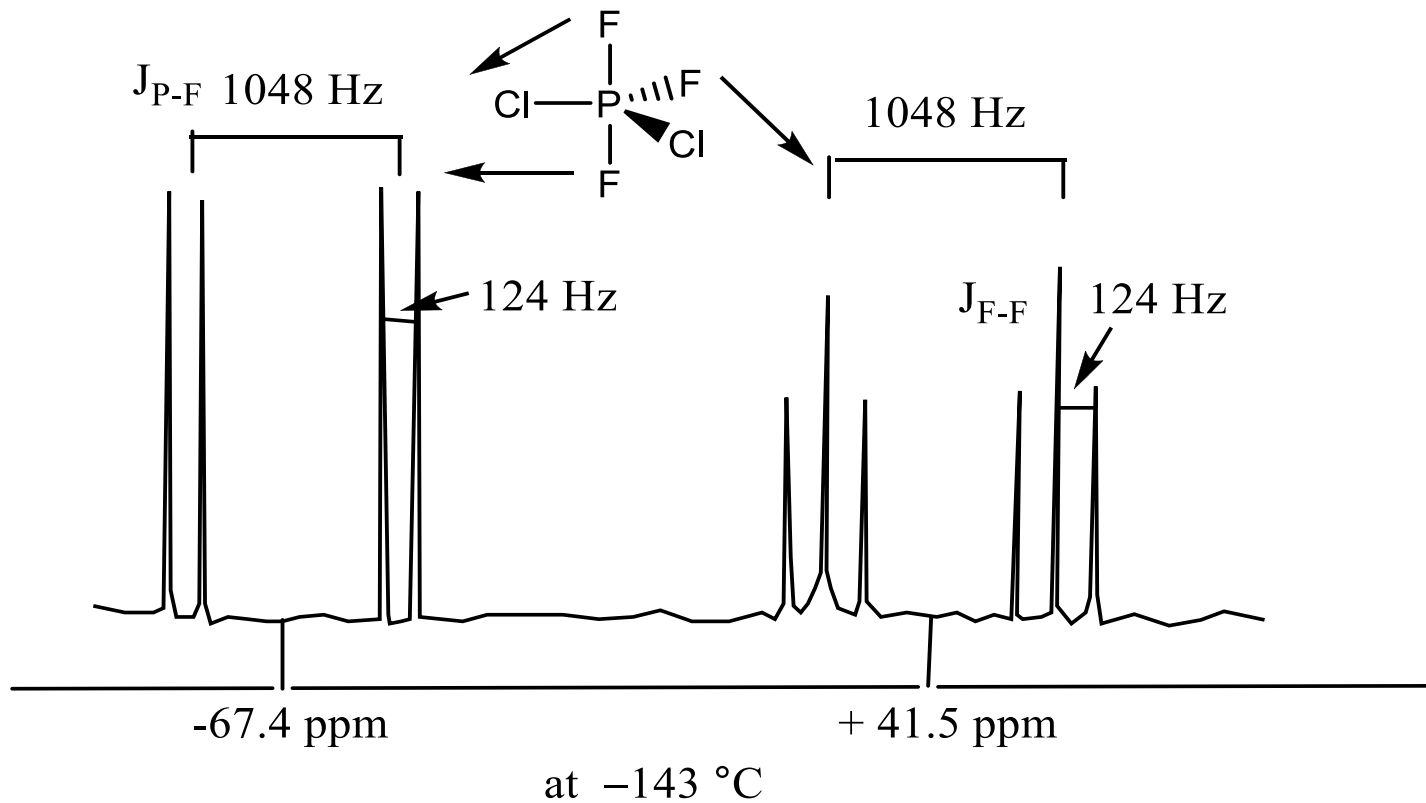
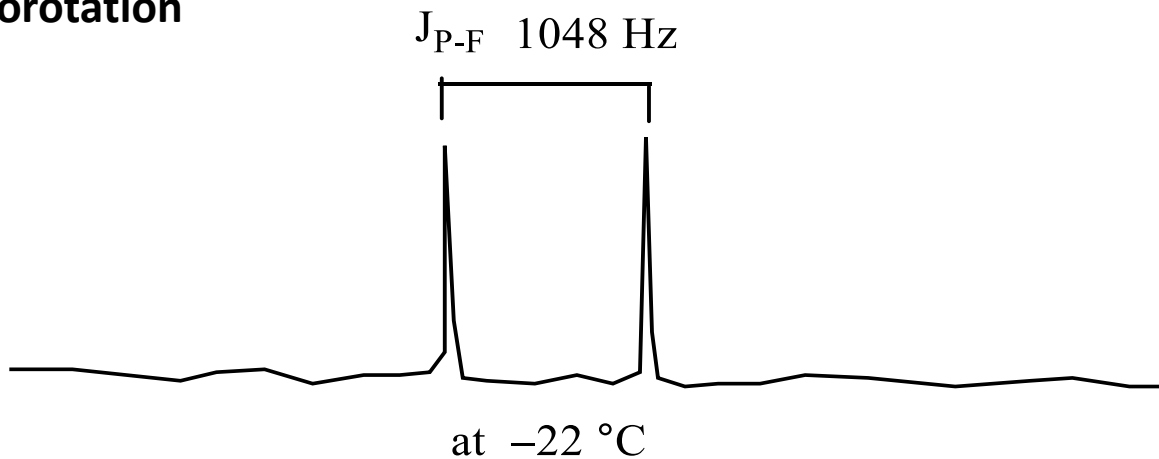
Spin quantum number I of ^{19}F , ^{31}P , ^1H and ^{13}C are $\frac{1}{2}$ while for ^{35}Cl it is $\frac{3}{2}$.

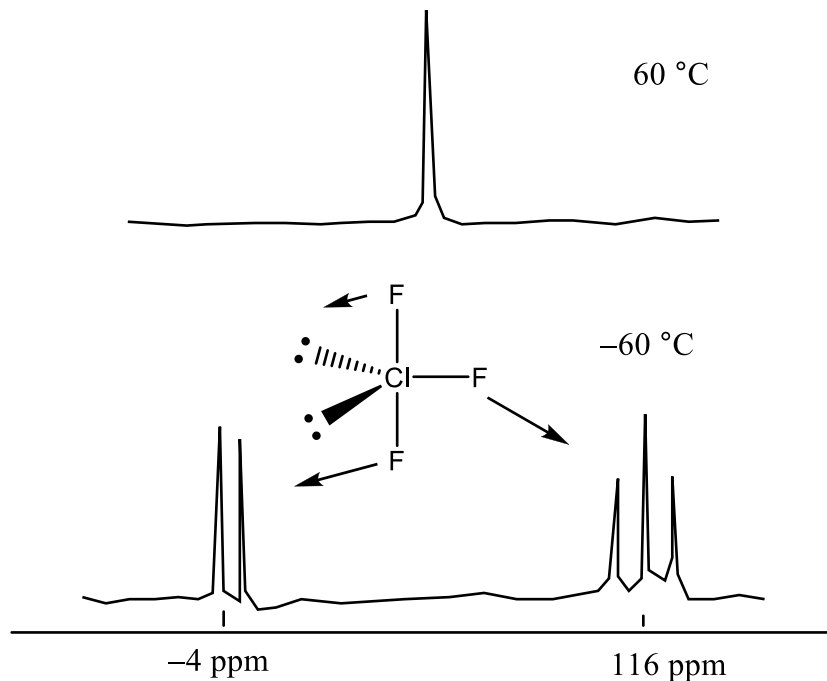
$2nI+1$; $n=2$ gives triplet $n=1$ gives doublet

For PCl_2F_3 one observes that in the fluorine NMR spectra taken at room temperature there is only one kind of fluorine's but when measured at -143°C one gets two sets of peaks (a doublet of a doublet for the two axial fluorine's and a doublet of a triplet for the equatorial fluorine at -143°C). This shows that the axial and equatorial fluorine's are exchanging positions at room temperature faster than the NMR technique can follow. One envisages the intermediate situation as a square pyramidal structure as shown. This process which does not involve bond breaking is called Berry pseudorotation

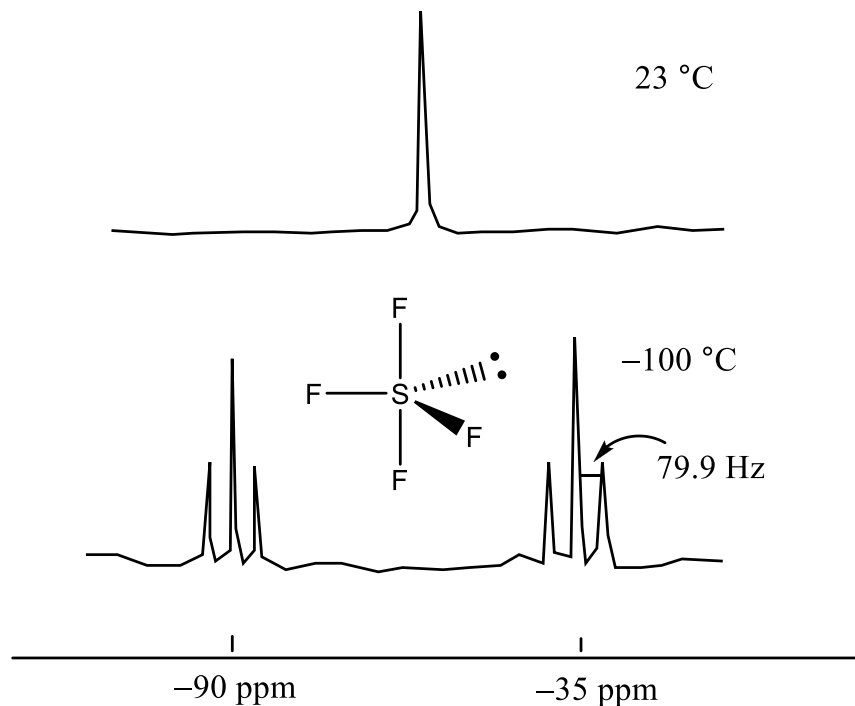


Berry Pseudorotation





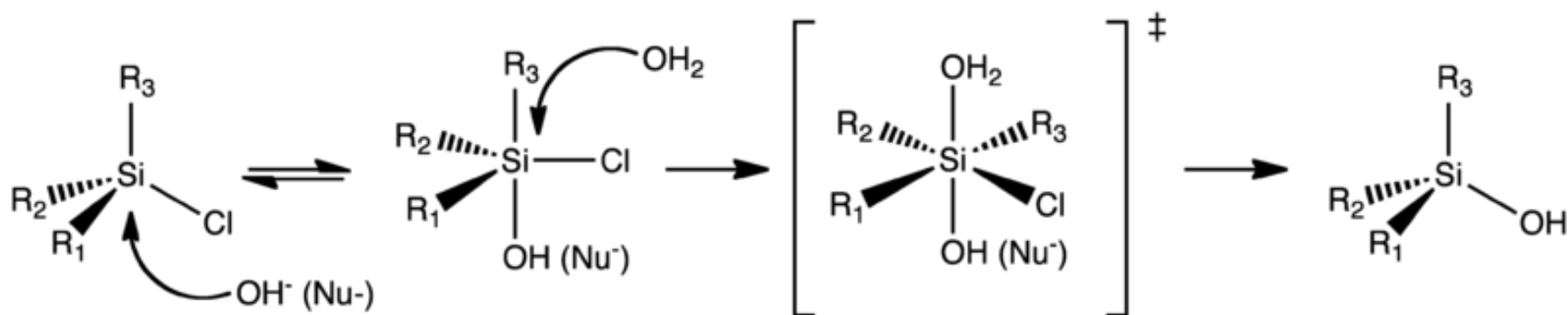
For ClF_3 , Berry pseudorotation is arrested below -60 °C and a similar spectra is obtained



For SF_4 , Berry pseudorotation is arrested below -100 °C and a spectra with equal splitting of axial and equatorial fluorines are obtained

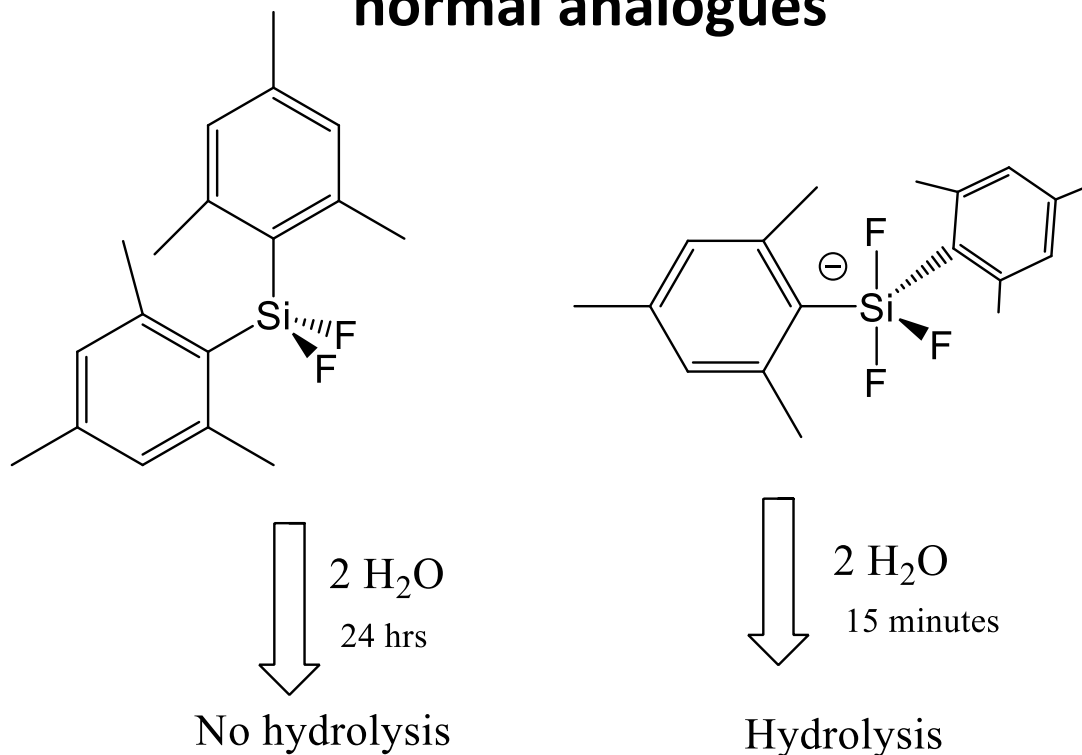
Hypervalent compounds as stable intermediates

Hydrolysis of tetravalent chlorosilanes



In the reaction mechanism proposed for the hydrolysis of trichlorosilane, there is a pre-rate determining nucleophilic attack of the tetracoordinated silane by the nucleophile (or water) resulting in a hypervalent pentacoordinated silane. This is followed by a nucleophilic attack of the intermediate by water in a rate determining step leading to a hexacoordinated species (transition state) that quickly decomposes giving the hydroxysilane.

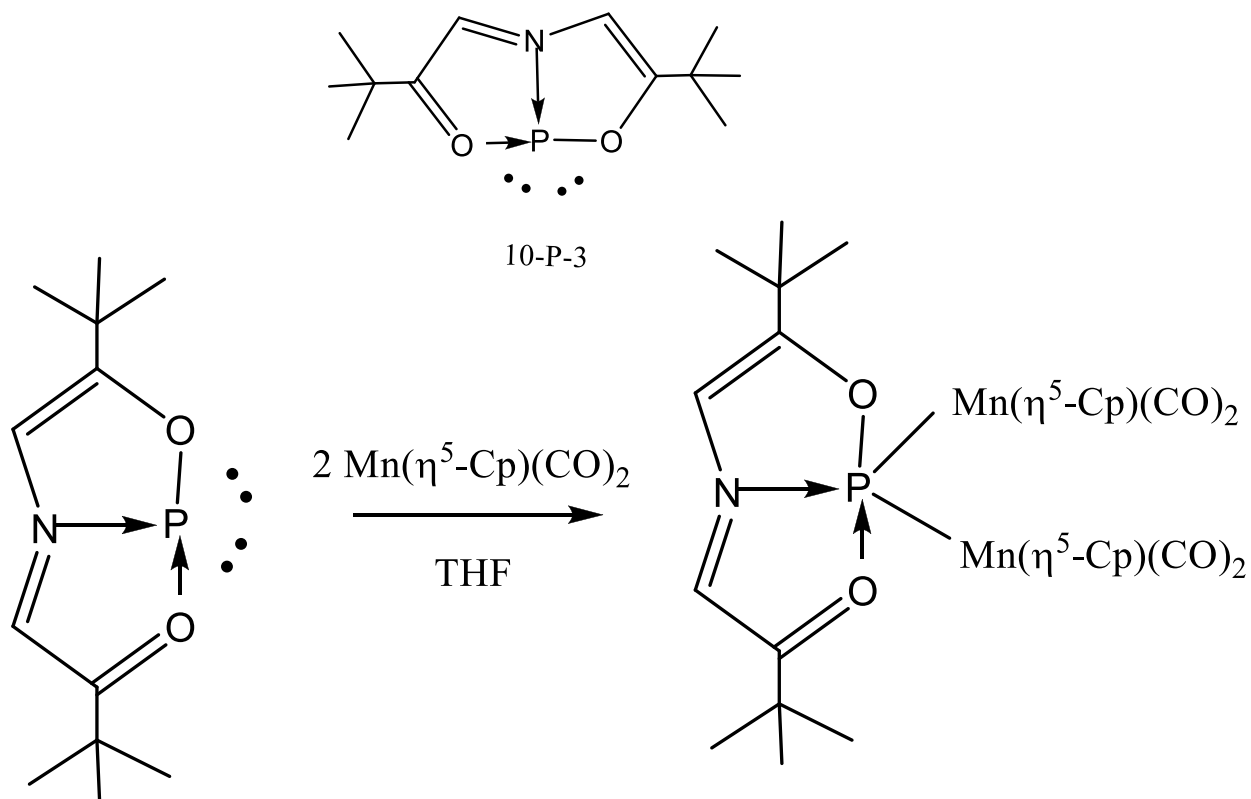
Increased reactivity of hypervalent species in comparison to normal analogues



Silane hydrolysis was further investigated by Holmes and coworkers in which tetracoordinated Mes₂SiF₂ (Mes = mesityl) and pentacoordinated Mes₂SiF₃⁻ were both reacted with two equivalents of water. Following twenty-four hours, almost no hydrolysis of the tetracoordinated silane was observed, while the pentacoordinated silane was completely hydrolyzed after fifteen minutes. This indicates increased reactivity of the hypervalent species

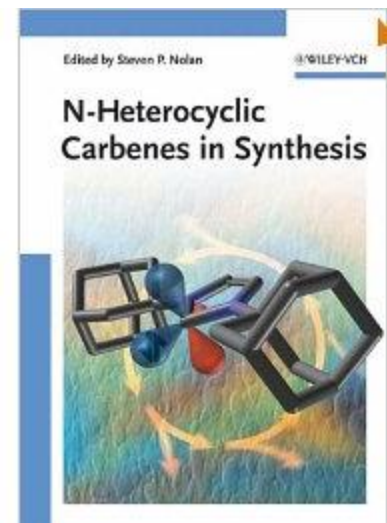
Stabilizing unusually low oxidation states of main group elements

Anthony J Arduengo (first stable NHC fame) designed and prepared a stable P(I) compound by using a specially designed ligand which by covalent and coordinate bonds formed a 10-P-3 system. The presence of two lone pairs on the phosphorus was also proved by using it as a ligand to bind two metal sites simultaneously. (while at Univ of Illinois)





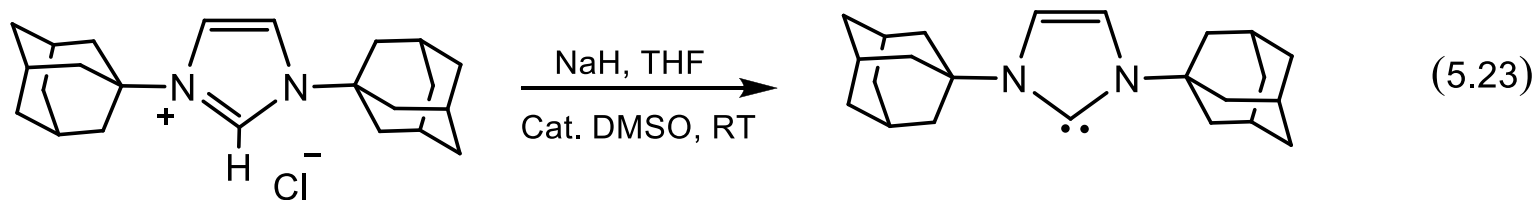
1991

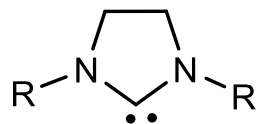


Anthony J.
Arduengo, III
U of Alabama

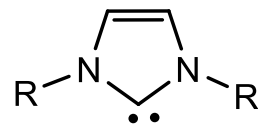
Chemists are particularly drawn to molecules that react rapidly and often violently. One such species is the carbene which is imperative for an entire framework of organic reactions thereby leading to an altogether a separate branch named---**Carbene Chemistry**.

Anthony J Arduengo III prepares the **first stable carbene** now well known as the NHC or N-Heterocyclic Carbene



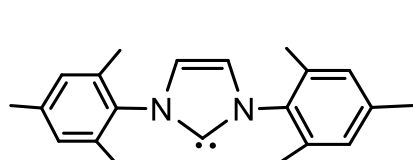


imidazolidinylidene

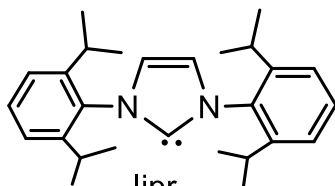


imidazolylidene

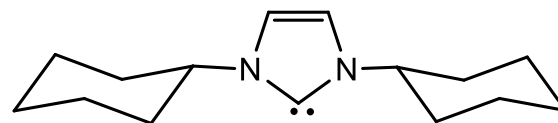
NHCs are in general defined as heterocycles containing a carbene carbon with at least one nitrogen atom as part of the ring. They generally have sterically hindered substituents on the atom adjacent to the carbene carbon which helps to provide kinetic stability. In the traditional NHCs, the HOMO has been described as a formally sp^2 hybridised lone pair and the LUMO has been described as an unoccupied p orbital on the carbene carbon. The nitrogen atoms of this heterocycle are σ -electron withdrawing and π -electron donating thus providing inductive and mesomeric stabilisation for the carbene. The cyclic structure also stabilises a singlet ground state by forcing the carbene carbon into a bent sp^2 -like arrangement. The stability of singlet carbenes results mostly from electronic effects [mesomeric (+M) as well as inductive (-I) effects], while steric bulkiness of the substituents also contributes significantly. NHCs have been described as better ligands than phosphines



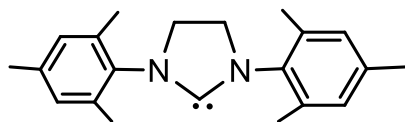
IMes



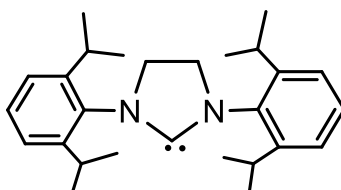
IPr



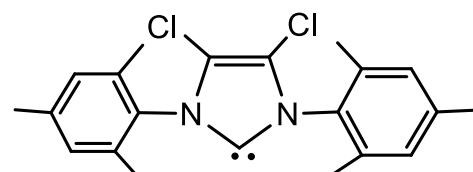
ICy



SIMes

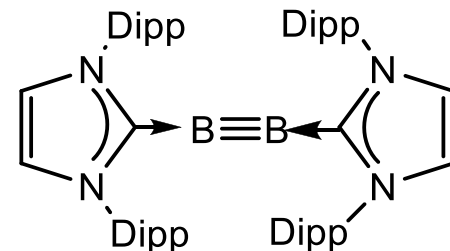
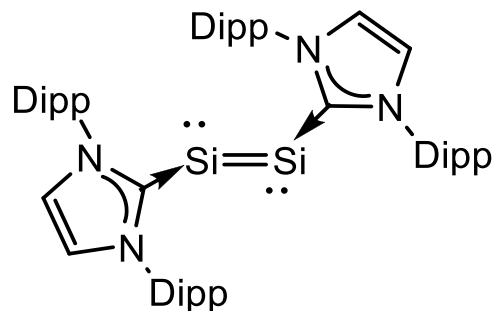
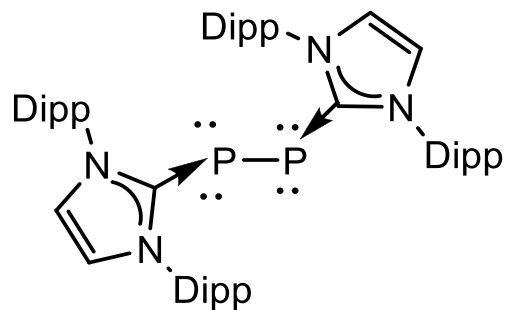


SIPr



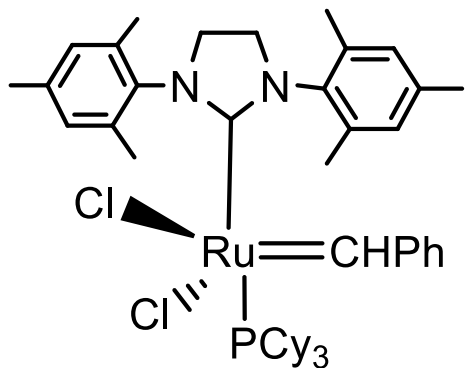
First air stable carbene

NHC's in main group chemistry: Stabilization of Low oxidation states

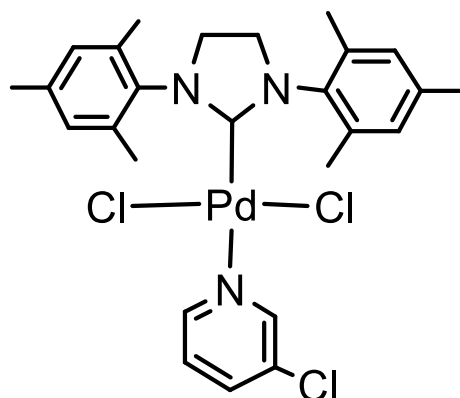


Dipp = 2,6 diisopropylphenyl

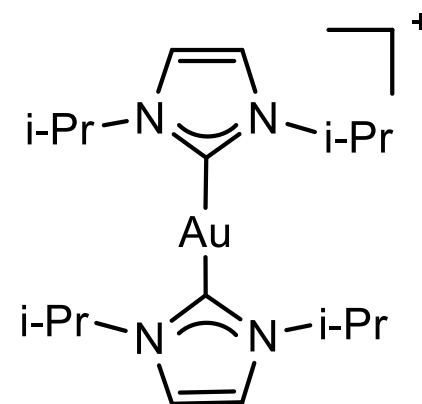
NHC's in transition metal chemistry: better σ donation, trans effect



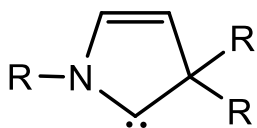
Grubbs 2nd Gen. Catalyst



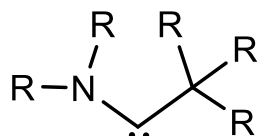
PEPPSI Catalyst



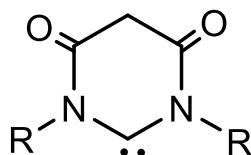
New types of carbenes : even more better σ donors



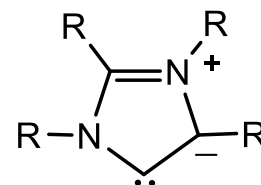
Cyclic alkyl amino carbene
cAAC or CAAC



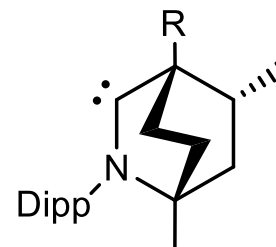
Acyclic alkyl amino carbene
aAAC



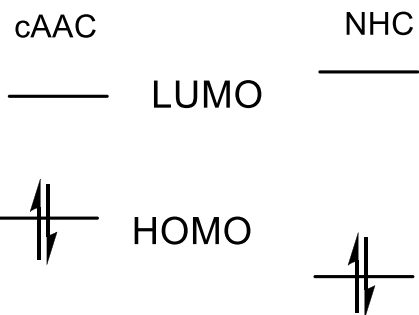
Cyclic diamido carbene
cDAC



Abnormal
N-heterocyclic
carbene
aNHC

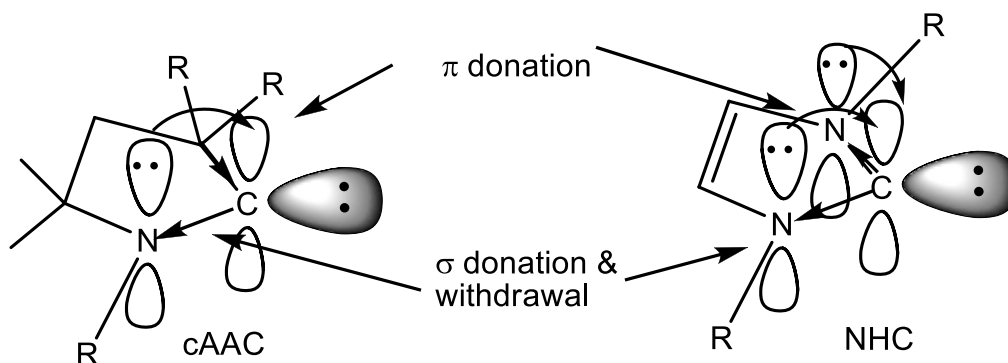


Bicyclic alkyl amino carbene
BICAAC

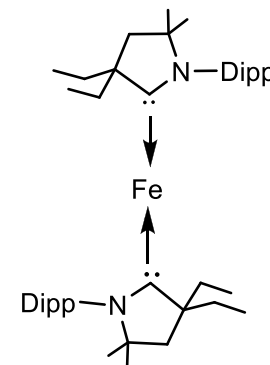
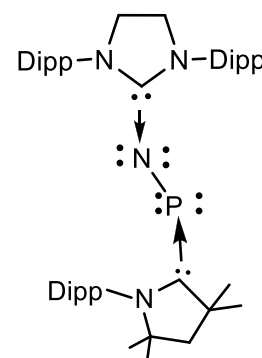
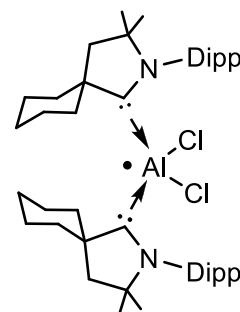
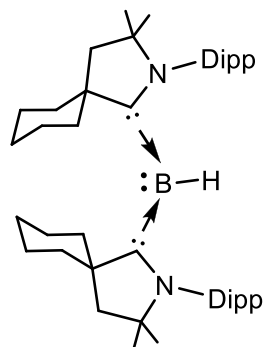


$$\Delta E = 45 \text{ kcal/mol}$$

$$\Delta E = 68 \text{ kcal/mol}$$



indicate the relatively
better σ -donating
capability of the
cAACs



Resurgence of dative bonds in *p*-block compounds

To use or not to use dative bonds ($A \rightarrow B$) in describing the structures of compounds based on *p*-block elements has been a topic under considerable discussion recently, especially after the discovery of low valent and zerovalent compounds of main group elements that are stabilised using strong σ -donors such as N-heterocyclic carbenes (NHCs) and cyclic alkyl amino carbenes (cAACs). Historically in 1929, it was Sidgwick who introduced the notation of the arrow for dative bonds or donor acceptor bonds, $A \rightarrow B$ to differentiate them from electron-sharing bonds $A-B$ (often termed covalent bonds). It was widely used in depicting metal–ligand interaction of early coordination compounds. However, Linus Pauling, in his classical book *The nature of the chemical bond*, discouraged the use of the dative bonds because it did not fit into his scheme of convenience as he preferred to depict compounds by resonance structures and use of formal charges on the atoms, wherever required.



Carbone

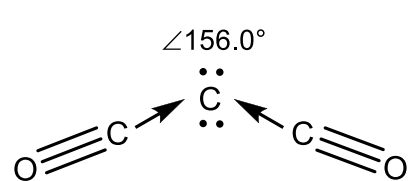


Silylone

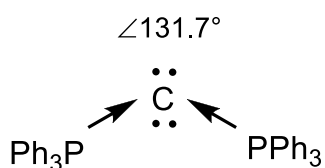


Germylone

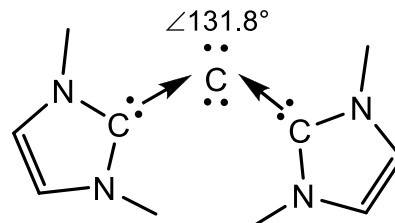
G. Bertrand and coworkers in 2008 prepared an extremely bent acyclic allene (carbodicarbene) which passes the test for zerovalent carbon compounds of the type $(L \rightarrow C^0 \leftarrow L)$ predicted earlier by G. Frenking as ‘carbene’ compounds



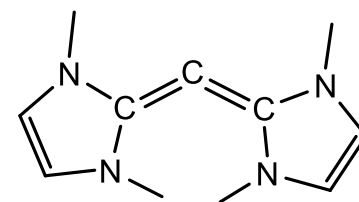
Carbon suboxide (vapour phase)



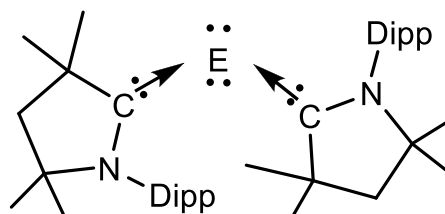
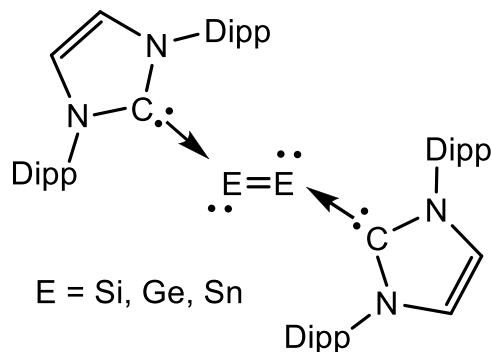
Carbodiphosphorane



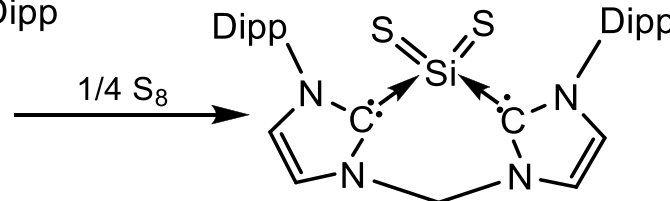
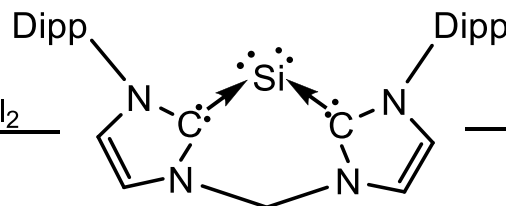
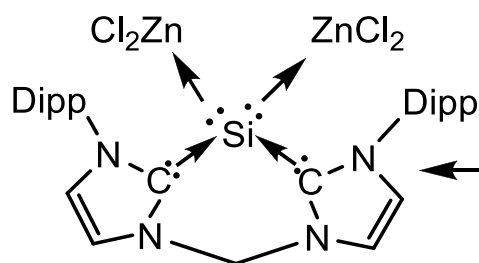
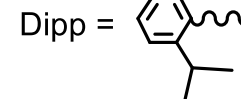
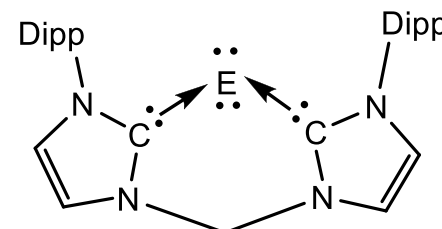
Carbene (carbodicarbene)



Carbene (bent allene format)



Silylone and Germylone



(2.1)