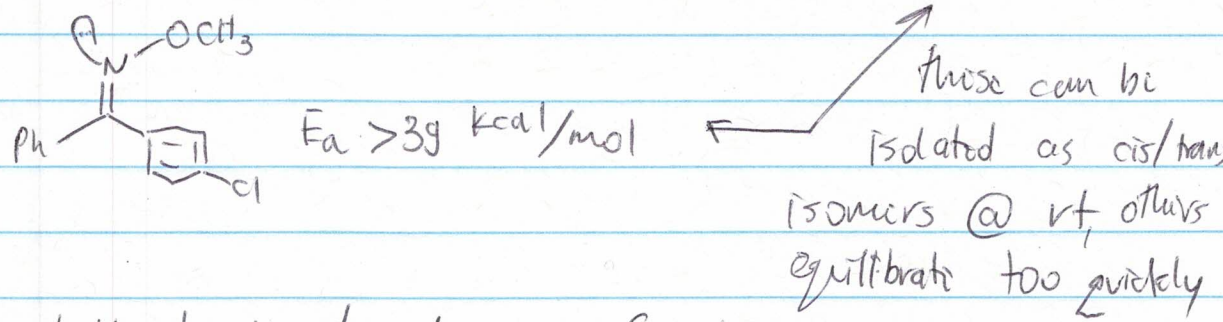
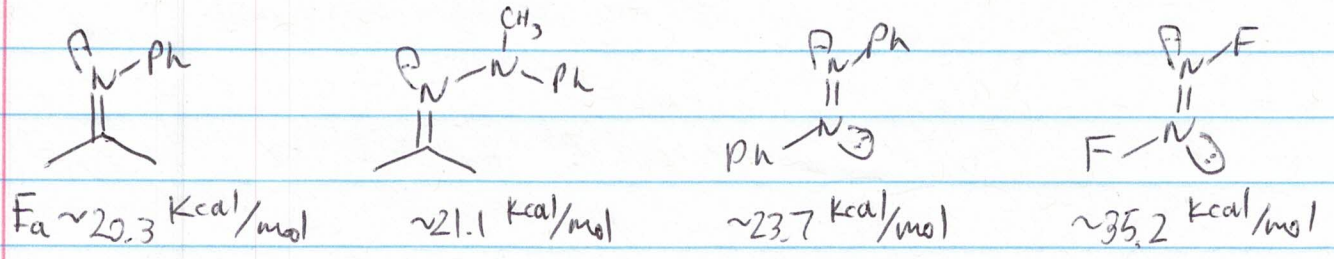


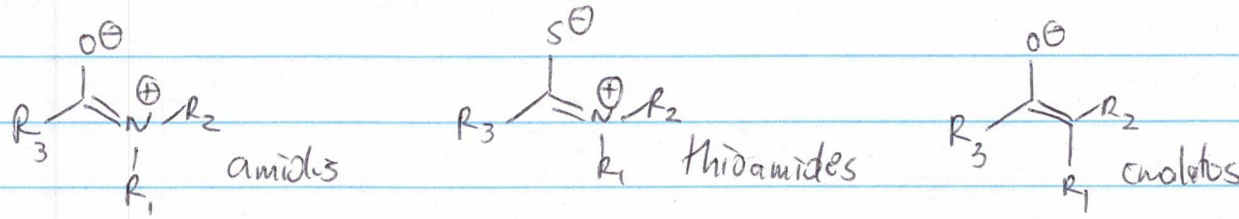
Lecture XVI: C=N, N=N Bonds & Metal Complexes

01-21-2020

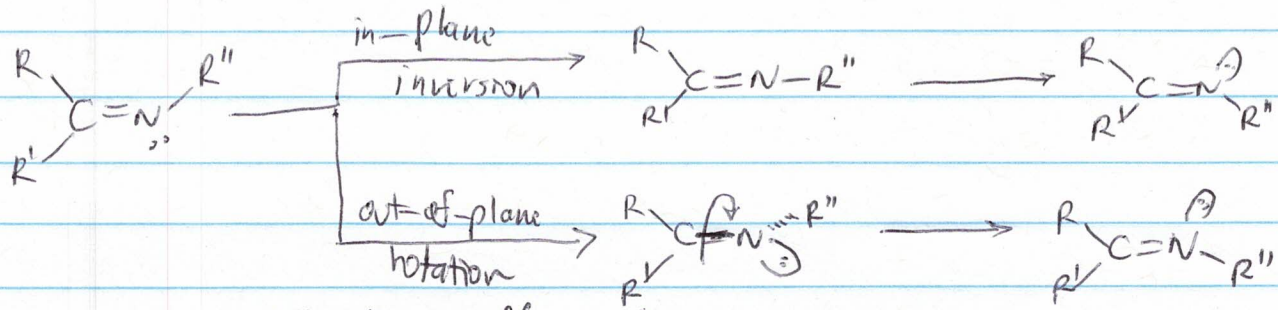
Isomerism is observable around C=N and N=N bonds too:



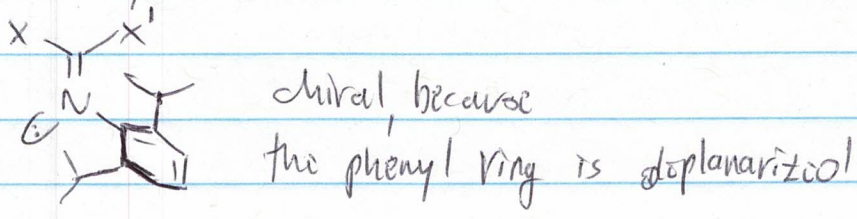
Some double bond character is found in



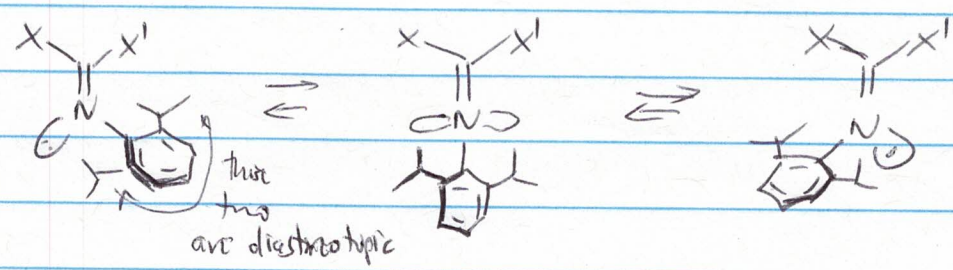
How do cis and trans isomers equilibrate? The possible mechanism



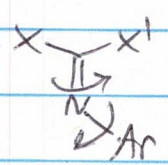
How can you tell the difference?



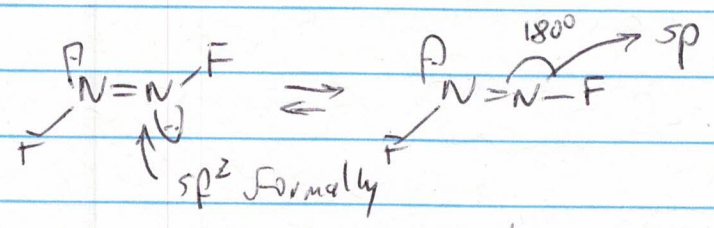
As one heats this system up, it will racemize and start converting E isomer into Z. In the case of inversion, the two processes occur concurrently:



In the case of rotation, two barriers would have been observed for rotations around two different bonds:



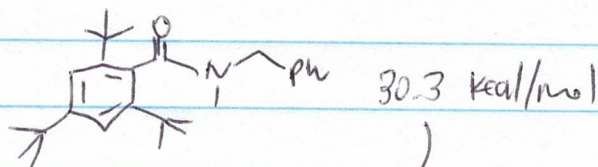
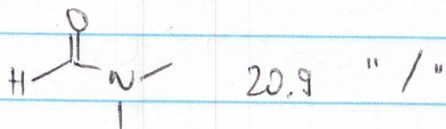
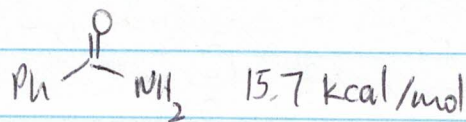
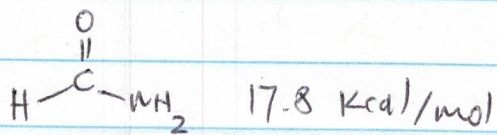
Why does F-N=N-F have much higher barrier than N=N bonds substituted with electropositive substituents?



However, with increasing electronegativity of F, the p-character increases, meaning that this angle distorts to smaller values than 120°. Increasing it even further to 180° becomes very strained.

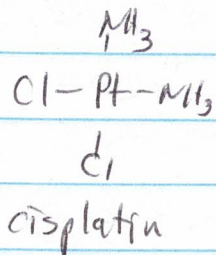
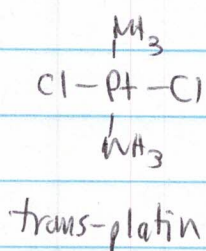
Why?
 $\text{N} \begin{matrix} \text{:} \\ \text{F} \end{matrix}$
 ↑
 much closer to F, thus better described by N's p-orbitals

In amides, resonance structures with C=N double bonded character contribute to rigidity, but barriers are generally low:



allows isolation of two diastereomers

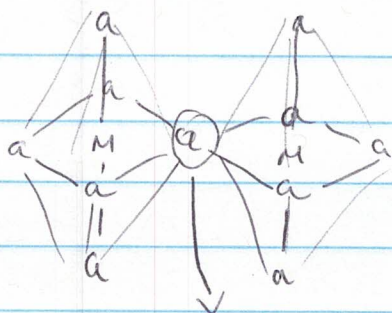
In other coordination environments, even one atom can lead to diastereomers:



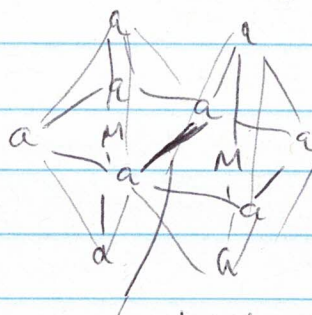
square planar geometry has no enantiomers, but yes diastereomers

We have seen many examples of this in the octahedral coordination geometry.

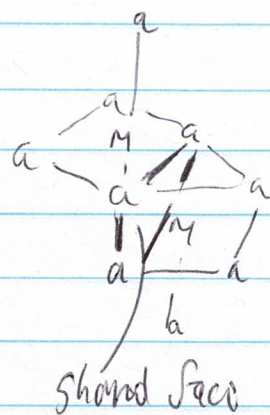
This ~~chem~~ stereochemistry becomes even richer when we consider ~~dim~~ dinuclear and other oligonuclear complexes:



bridging ligand
 $O^{2-}, S^{2-}, X^-, CN^-, OH^-, CO$

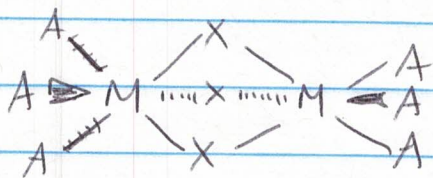


shared edge

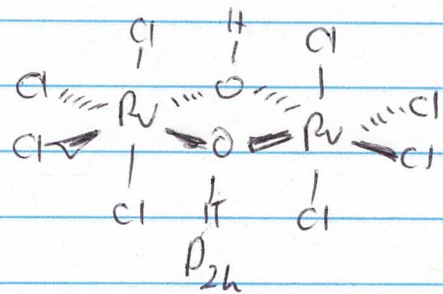
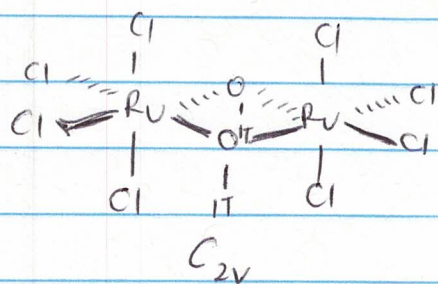


shared face

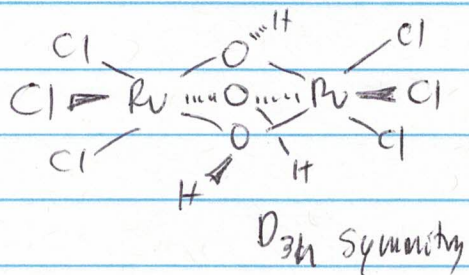
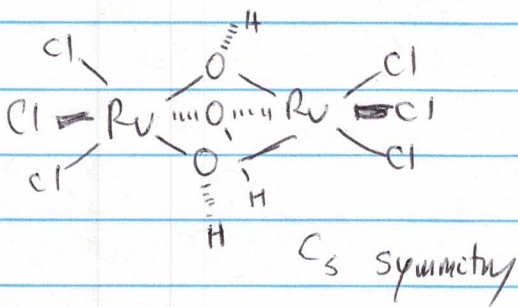
This last type is perhaps more easily represented as:



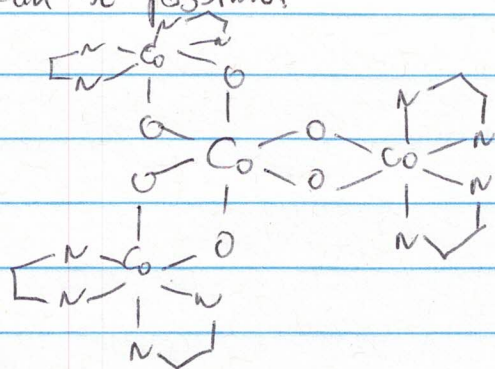
If the bridging ligands X are diatomic, there is a possibility of having diastereomers:



Triply bridged complexes can also exist as stereoisomers:



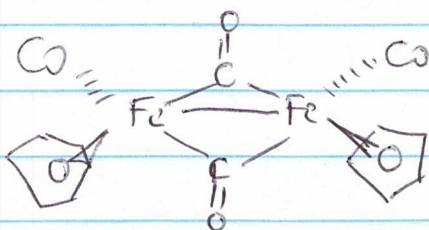
With chiral (axially) chiral species, a bewildering array of stereoisomers can be possible.



can have 208 isomers, if one considers conformations of the $N-N-N$ bridges!

This is why synthesis of stereochemically well-defined complexes which are polynuclear parallels biochemistry: stereochemically pure building blocks are used, rather than starting with random racemates. This is not too far-fetched as many polynuclear complexes are being studied as models for biochemical systems too!

For a nice personal account of the interplay between bonding and stereochemistry in:



see: Labinger
Inorg. Chim. Acta

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