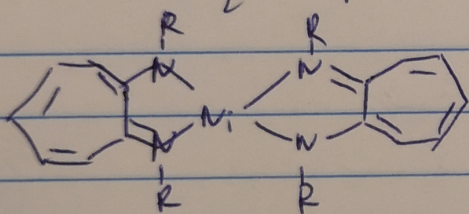


Lecture XXXI: Stereoselectivity in Transition Metal Reactions 04-17-2020

This area of dynamic stereochemistry is not as developed as its organic counterpart. We will talk about two broad classes of reactions.

Isomerizations and Substitutions

$Ni^{2+}$  complexes are some of the rare ones that can be either tetrahedral or square planar

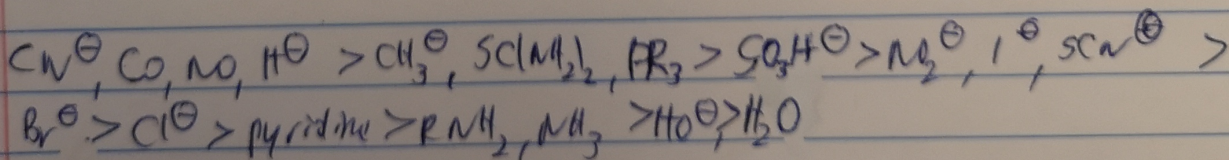


R = H 0% tetrahedral  
R = n-Pr 98% "

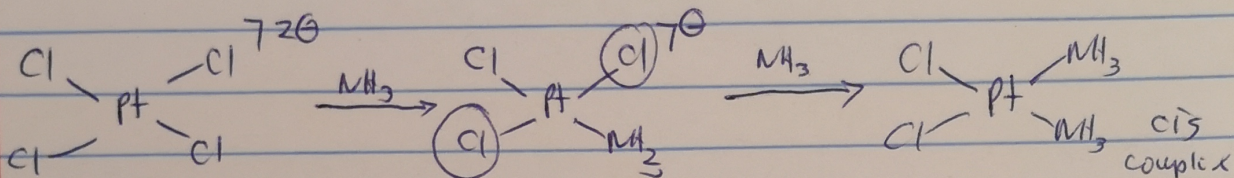
Prog. Inorg. Chem.  
1971, 41, 241

trans-effect:

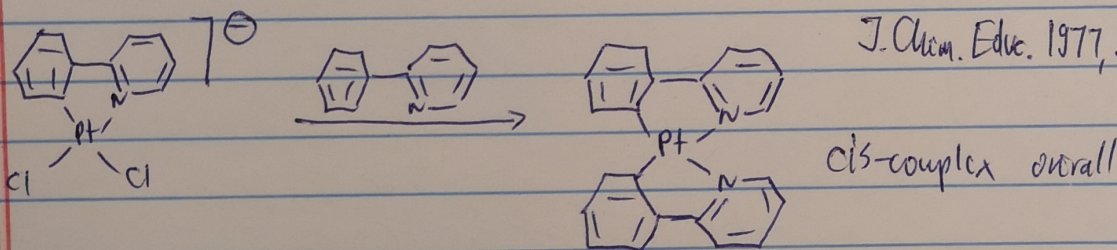
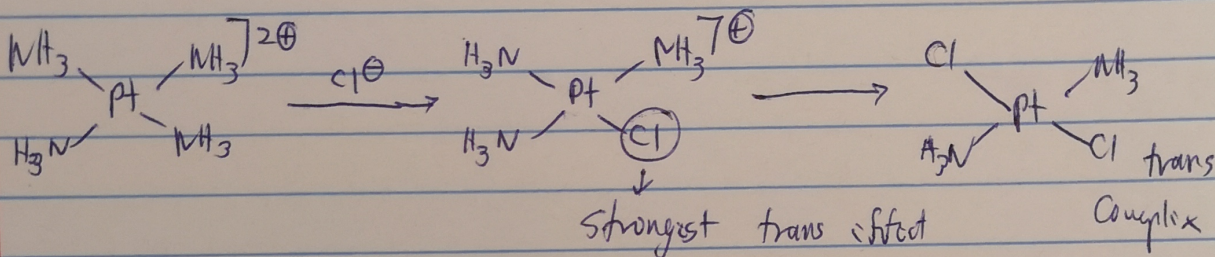
In his attempt to prepare square planar complexes of the general structural type  $Ma_2b_2$ , Russian chemist Cherrayev did a very large number of ligand substitutions on  $Pt^{2+}$  complexes. He noticed that ligands drive the incoming ligand into the trans position, but to a different extent:



The existing ligands compete on a  $d^8$  complex; the one with the strongest trans-effect will drive the incoming ligand trans to it:



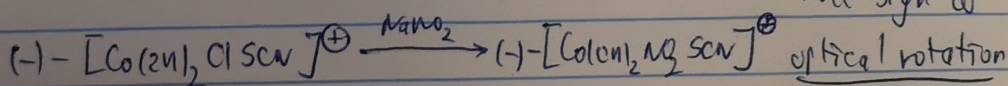
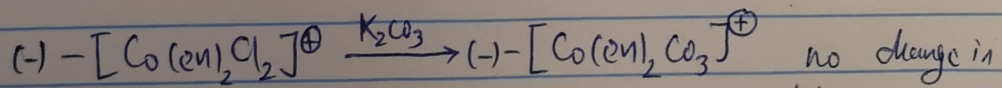
Cl stronger trans-effect than NH<sub>3</sub>



Trans-rule is probably the most general rule guiding the reactions of transition metal complexes.

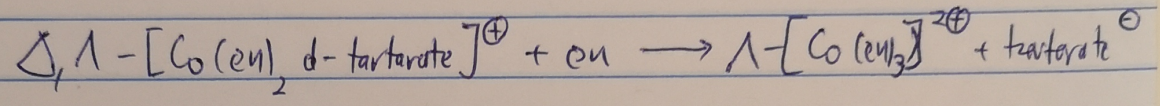
As we have seen before for trigonal bipyramidal complexes, their stereochemistry is labile because of the Berry pseudo rotation.

In octahedral complexes (CN=6), first studies of diastereoselectivity were conducted by Werner:

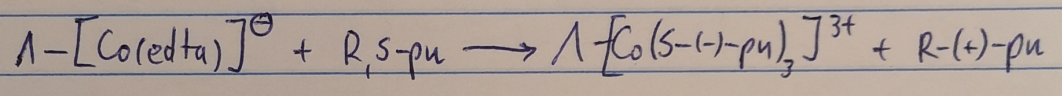


no change in the sign of optical rotation  
a little shaky argument today

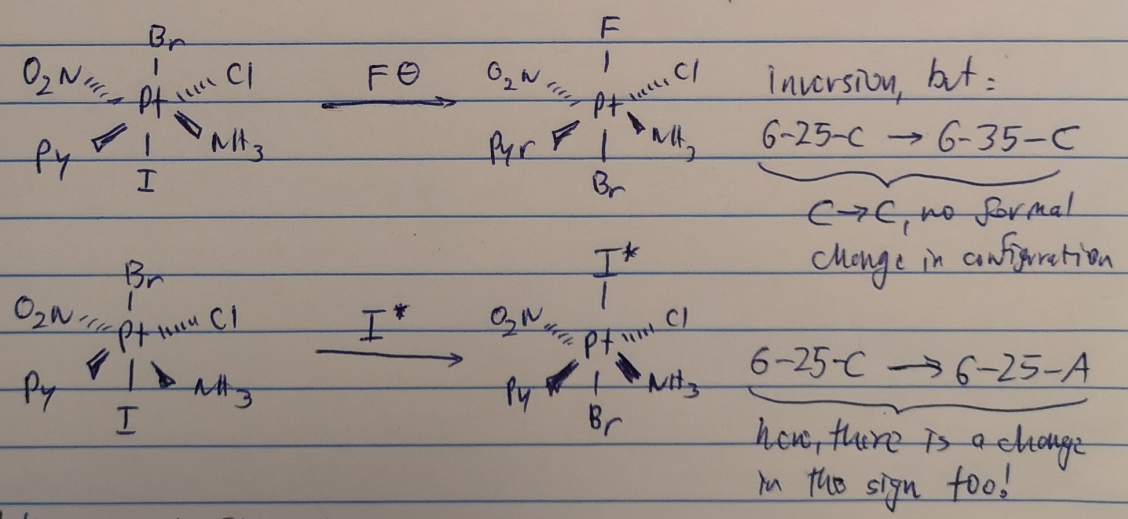
This is not happening always, though. However, this retention of configuration can be used to prepare enantiopure complexes of achiral ligands:



Or vice versa, to prepare an enantiopure ligand:

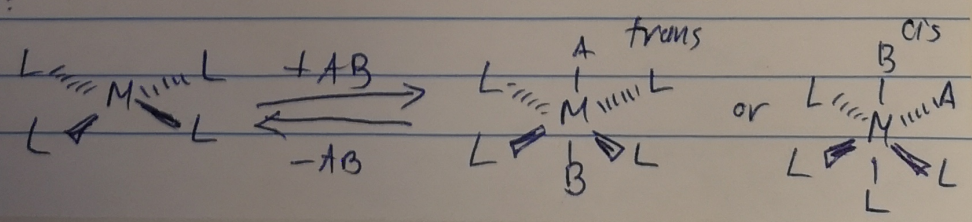


Some reactions proceed with an inversion on the octahedral center. These are called Bailar inversions (JACS, 1934, 56, 774):

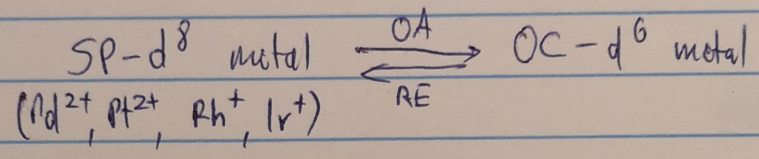


Additions and Eliminations

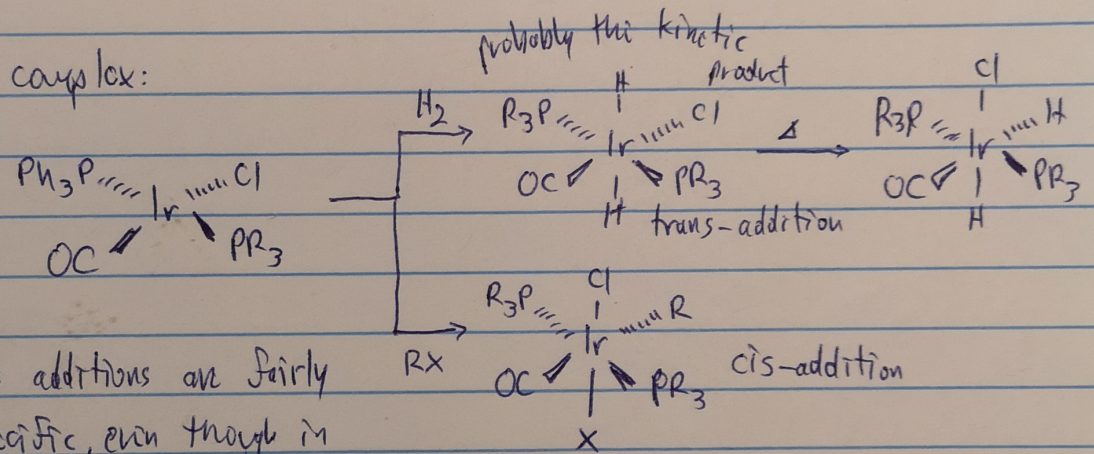
These reactions are very important now in the field of transition metal catalysis:



In the forward direction, this reaction is called oxidative addition while in the backward direction it is reductive elimination. Most of the time, we are looking at:



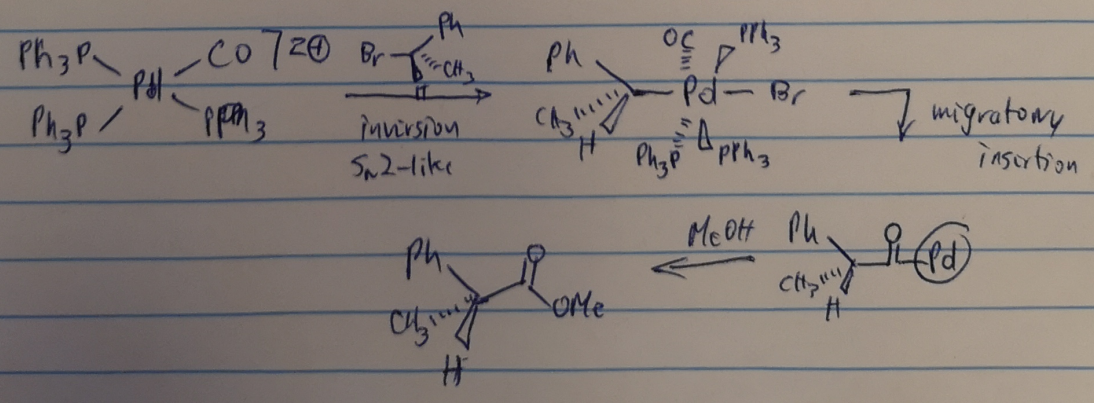
Vaska complex:



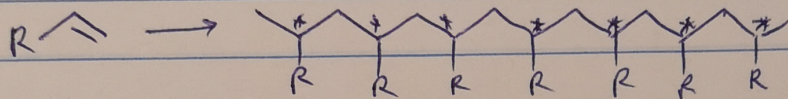
Oxidative additions are fairly stereospecific, even though in theory they could produce 15 stereoisomers—remember how rich the stereoisomerism is on an octahedral center!

Cis-addition with nonpolar reagents such as H<sub>2</sub> and trans- with alkyl/aryl halides. However, there are exceptions, [Pt(ene)<sub>2</sub>]<sup>2+</sup> will react with Cl<sub>2</sub> to only yield trans-isomer.

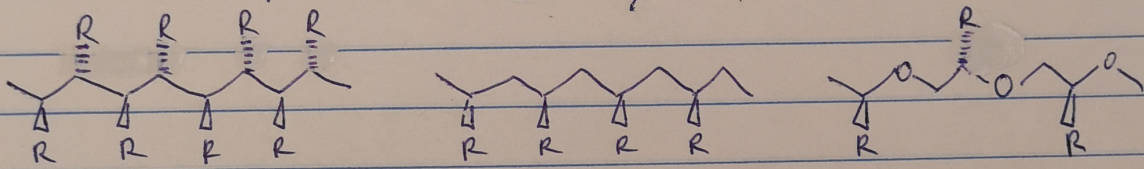
From the perspective of an organic molecule:



Let's switch gears here and talk about polymer stereochemistry. Polymerization of vinyl monomers generates a stereocenter:



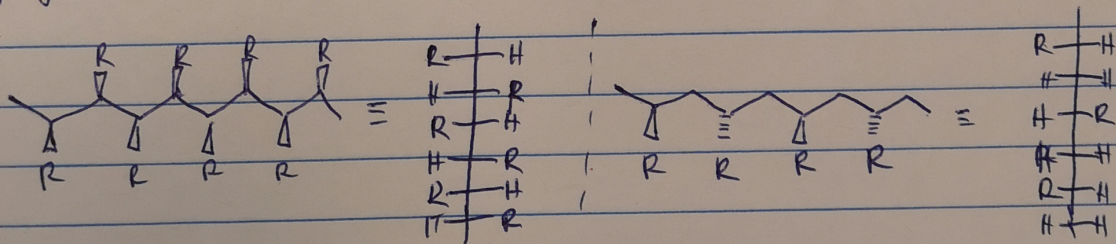
Their relationship is called tacticity - polymer version of diastereomers.



Isotactic polymers

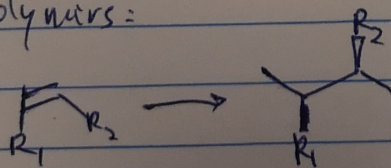
all stereocenters point in the same direction in their Fischer formulas

In syndiotactic polymers, stereocenters will alternate in the Fischer projection formulas



Atactic polymers show no ordering among stereocenters. All of the three examples apply to polymers with just one prochiral center in the monomer - these are all monotactic polymers.

Ditactic polymers:



diisotactic } smaller number of diastereomeric possibilities.  
disyndiotactic }