

Characterization Timescales

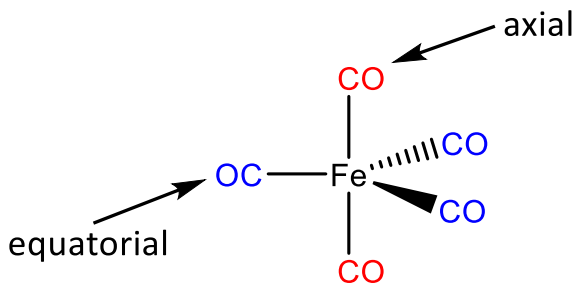
- Approximate timescales of common structural characterization techniques:

Technique	Timescale/s
Electron diffraction*	10^{-20}
Neutron diffraction*	10^{-18}
X-ray diffraction*	10^{-18}
Ultraviolet spectroscopy	10^{-15}
Visible spectroscopy	10^{-14}
Infrared spectroscopy	10^{-13}
Vibrational Raman spectroscopy	10^{-13}
Electron paramagnetic resonance	10^{-4} to 10^{-8}
Nuclear magnetic resonance	10^{-1} to 10^{-9}
Mössbauer spectroscopy	10^{-7}
Chemical separation of isomers	10^2 and longer

- *In a number of cases, particularly diffraction, the observation times are so long (typically hours) that the image obtained is an envelope spanning all atomic locations, and the theoretical timescale are not particularly relevant.

Isomerization and Rearrangement

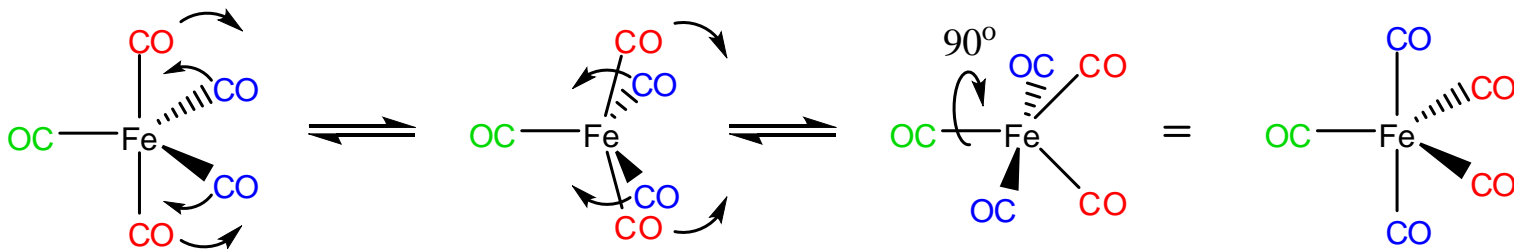
C.N. = 5 → Trigonal Bipyramidal Complexes:



- Crystal Structure → trigonal bipyramidal (2 different types of CO)
- Solution IR spectroscopy → 2 different types of CO
- Solution NMR spectroscopy → Only one ^{13}C NMR signal!

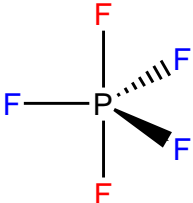
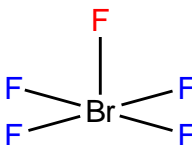
Explanation:

- Rapid rearrangement occurs at room temperature, leading to transposition of the axial and equatorial CO groups.
- IR spectroscopy occurs on a much faster timescale than NMR spectroscopy. NMR can be used to distinguish between interconverting species with lifetimes of > 1 to 10^{-6} s versus $> 10^{-13}$ to 10^{-15} s for IR. Therefore, two different CO environments are observed in the IR spectrum, while NMR spectroscopy shows only an averaged picture.
- Isomerization in trigonal bipyramidal complexes occurs by **Berry pseudorotation**:

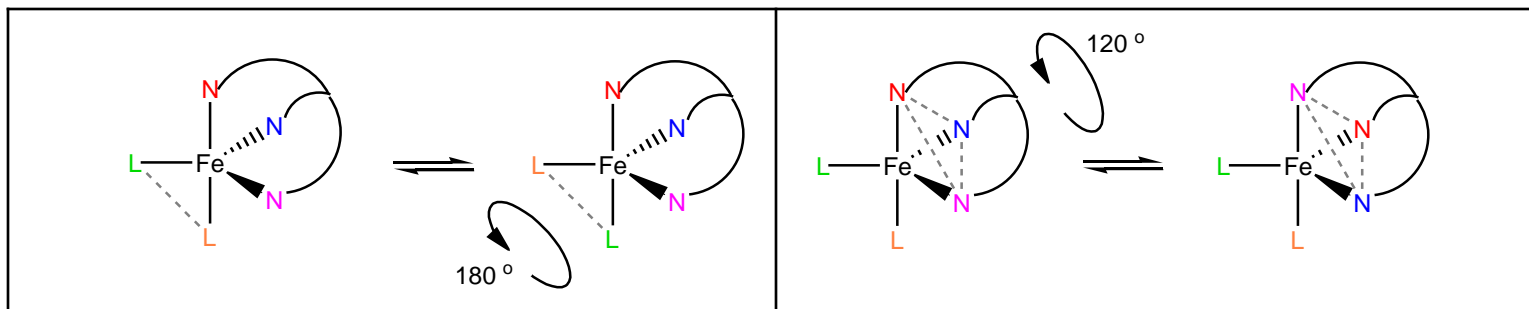


Isomerization and Rearrangement

- Berry pseudorotation is the same process responsible for the dynamic behaviour of familiar main group compounds such as PF_5 (trigonal bipyramidal by VSEPR) and BrF_5 (square pyramidal by VSEPR).

		
Solution ^{19}F NMR Spectroscopy:	<ul style="list-style-type: none"> 1 signal between 25 °C and -96 °C (a doublet due to ^{31}P coupling) 	<ul style="list-style-type: none"> 2 signals (4:1 doublet and quintet) at 25 °C. As the temperature is raised, these signals coalesce to a single resonance (a well-defined singlet at 180 °C).

- When three of the donor atoms are part of a moderately rigid tridentate ligand, Berry pseudorotation is often disfavoured, and **turnstile rotation** (an alternative process that is usually considerably higher in energy than Berry pseudorotation) becomes operative:

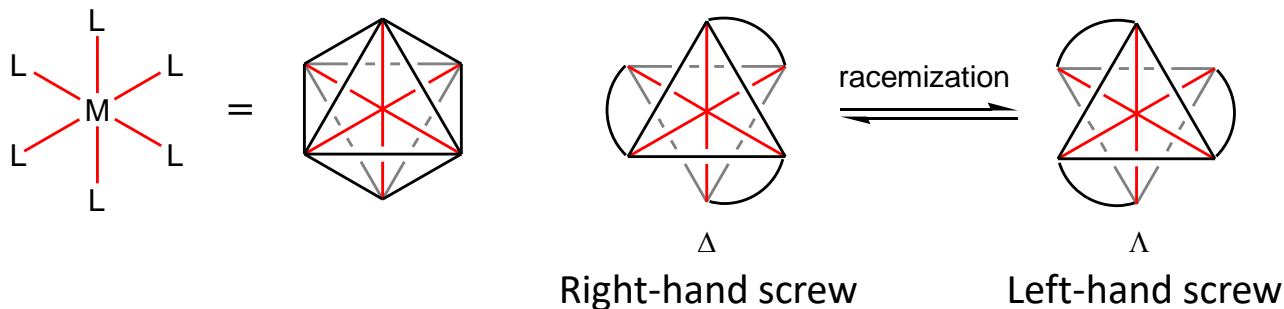


- Turnstile rotation involves either (1) rotation of one axial and one equatorial ligand by 180°, or (2) rotation of the tridentate ligand (one axial and two equatorial binding sites) by 120°.

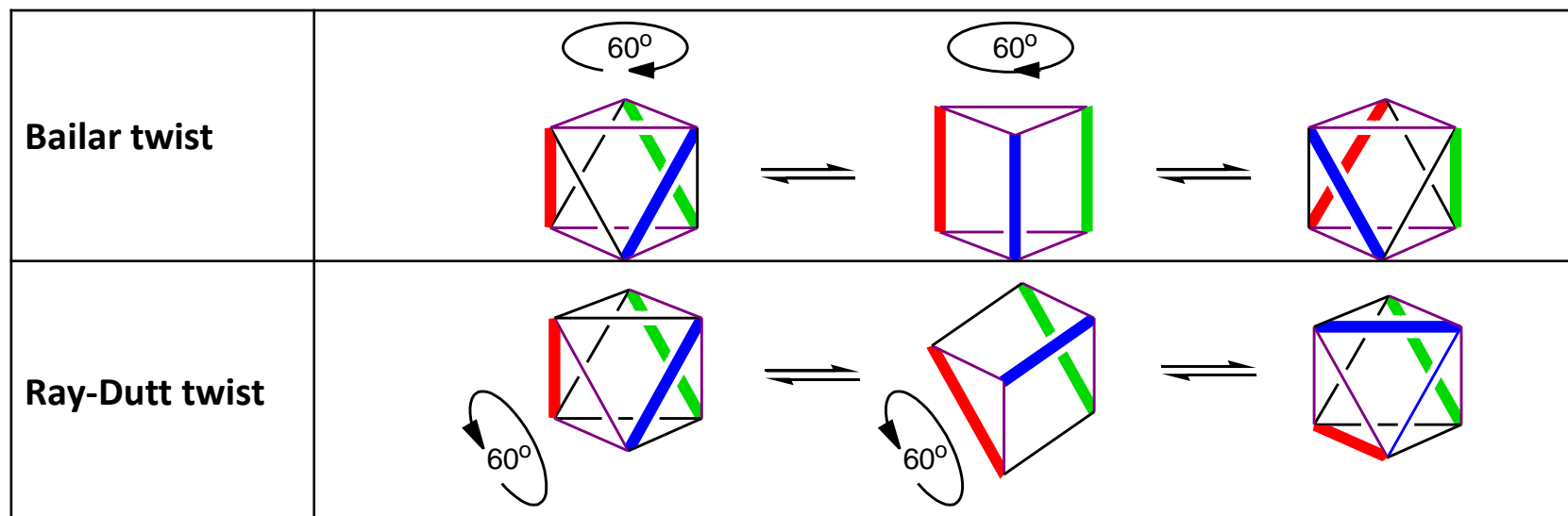
Isomerization and Rearrangement

C.N. = 6 → Octahedral Complexes:

- Octahedral complexes are generally far more stereochemically rigid than 5-coordinate complexes.
- However, chiral molecules such as $[\text{Ni}(\text{en})_3]^{2+}$, $[\text{M}(\text{bipy})_3]^{2+}$ ($\text{M} = \text{Ni}, \text{Fe}$) and $[\text{M}(\text{ox})_3]^{3-}$ ($\text{M} = \text{Ni}, \text{Cr}, \text{Co}, \text{Rh}$) do undergo racemization at temperatures between 0 °C and 200 °C.



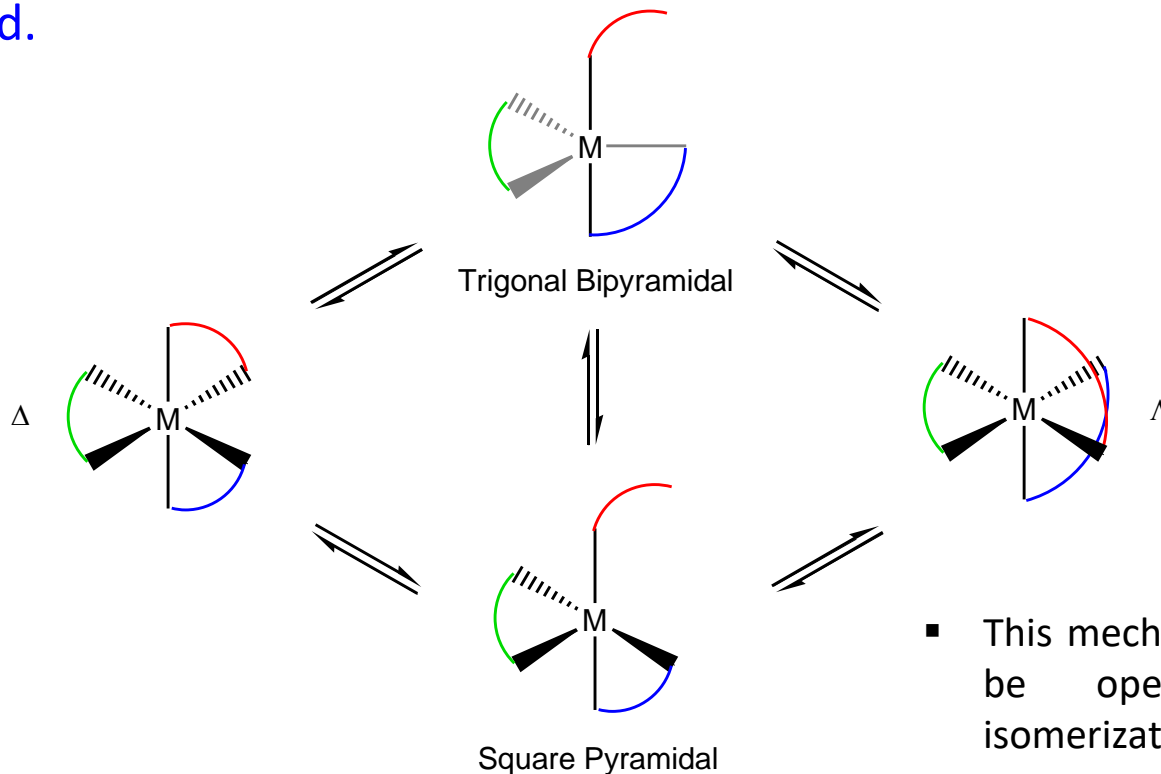
1. Trigonal Twist mechanisms (Bailar twist or Ray-Dutt twist):



Isomerization and Rearrangement

- Both the Bailar twist and Ray-Dutt twist involve two consecutive 60° rotations of a triangular face of the octahedron. For the Bailar twist, this occurs down a C_{3v} axis, while for the Ray-Dutt twist, it does not.
- A twist mechanism is thought to be operative for the racemization of $[\text{Ni}(\text{ox})_3]_{3-}$.

2. Dissociation of one end of a bidentate ligand to give a 5-coordinate species that can undergo rearrangement within the time that the donor atom remains uncoordinated.

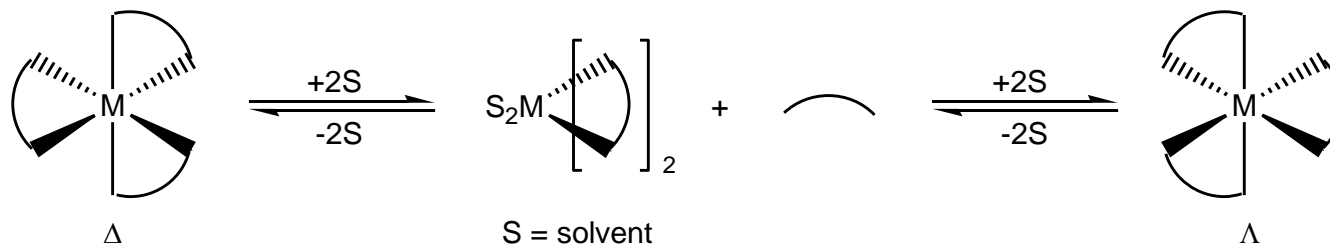


- This mechanism is thought to be operative for the isomerization of $[\text{Rh}(\text{ox})_3]^{3-}$.

Isomerization and Rearrangement

3. Full dissociation of a bidentate ligand (unusual).

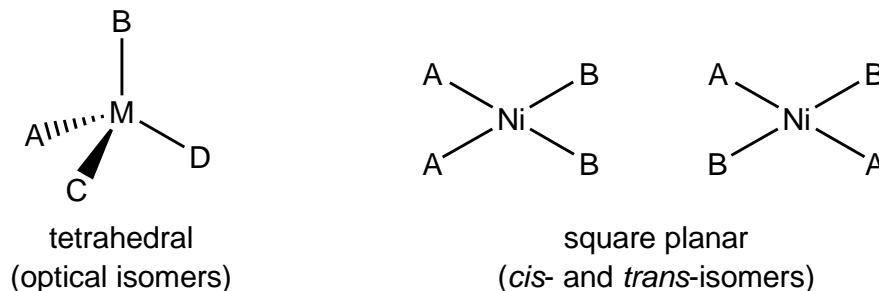
- This rare process is *intermolecular*, while the other mechanisms are strictly *intramolecular*.



- This mechanism is operative for $[\text{Ni}(\text{bipy})_3]^{2+}$ racemization.

C.N. 4 \rightarrow Tetrahedral and Square Planar Complexes

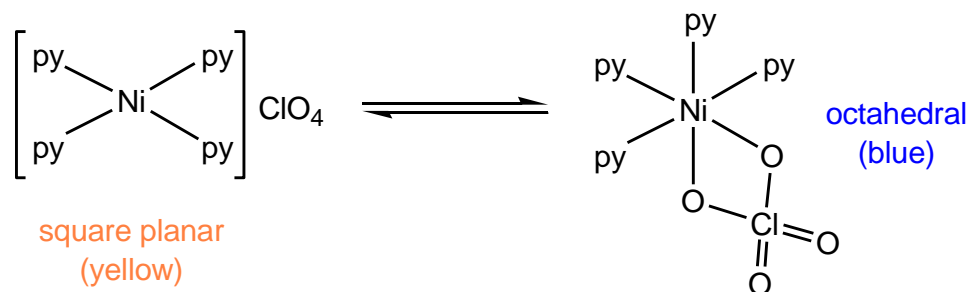
- Tetrahedral and square planar complexes are generally rigid – *i.e.* isomers (optical isomers for tetrahedral complexes, *cis*- and *trans*-isomers for square planar complexes) do not readily interconvert.



Isomerization and Rearrangement

Exceptions:

- In the presence of strongly donating solvents or suitably coordinating counter-anions, 4-coordinate complexes can sometimes undergo ligand redistribution *via* 5- or 6-coordinate intermediates.



- Most complexes are either tetrahedral (non-d⁸) or square planar (Rh^I, Ir^I, Pd^{II}, Pt^{II}, Au^{III}). However, nickel(II) complexes can be either square planar or tetrahedral, and often undergo facile square planar / tetrahedral interconversion.

