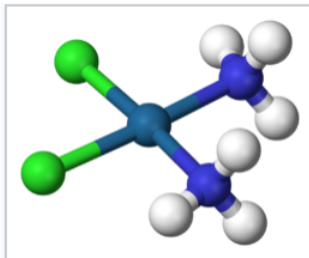


5.7: Non-octahedral Complexes

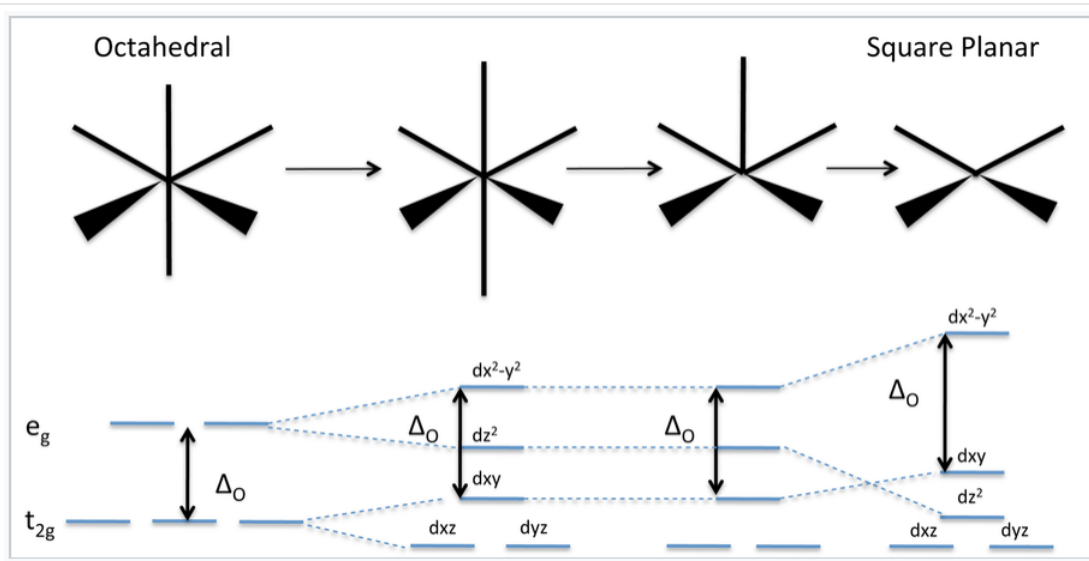
The most important non-octahedral geometries for transition metal complexes are:

4-coordinate: square planar and tetrahedral

5-coordinate: square pyramidal and trigonal bipyramidal



cis-Pt(NH₃)₂Cl₂, a 5d⁸ square planar complex



Crystal field energy diagram showing the transition from octahedral to square planar geometry

Energies of the d-orbitals in non-octahedral geometries

The figure above shows what happens to the d-orbital energy diagram as we progressively distort an octahedral complex by elongating it along the z-axis (a **tetragonal distortion**), by removing one of its ligands to make a **square pyramidal**, or by removing both of the ligands along the z-axis to make a **square planar** complex. In all cases, we keep the total bond order the same by making the bonds in the xy plane shorter as the bonds in the z-direction are stretched and/or broken.



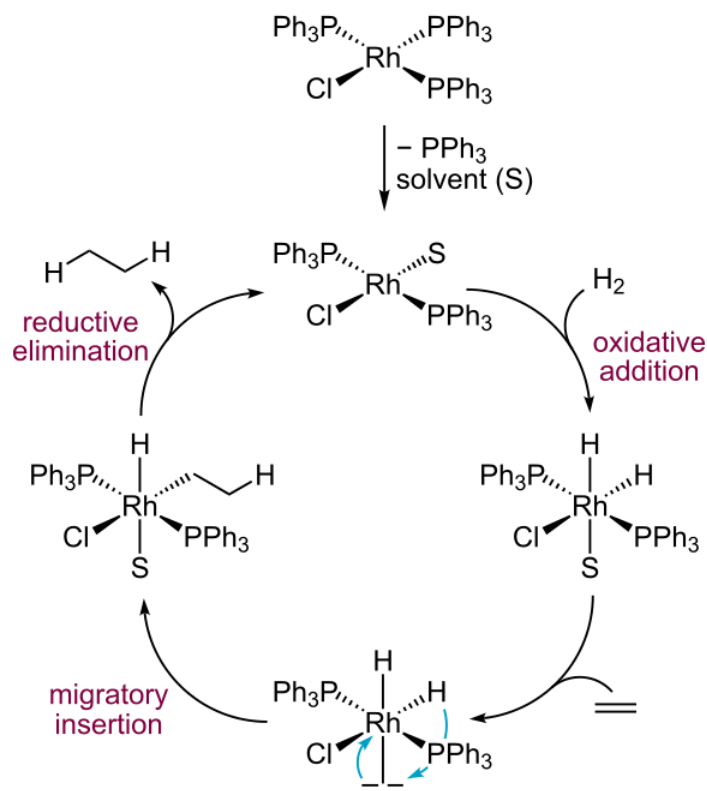
Barnett Rosenberg (Michigan State University) accidentally discovered the biological effects of square planar $\text{cis-Pt(NH}_3)_2\text{Cl}_2$ while researching bacterial growth in electric fields.^[8] The Pt electrode he used reacted with chloride and ammonium ions in the electrolyte to produce the compound at 1-10 ppm concentration. Further experiments revealed that the cis-isomer (but not the trans-isomer) is a potent anti-cancer drug which is especially effective against testicular cancer. The drug works by cross-linking guanine-cytosine rich regions of DNA, thus inhibiting cell division.

The distortion away from octahedral symmetry breaks the degeneracy of the t_{2g} and e_g orbitals. d-orbitals with a z-component (d_{xz} , d_{yz} , d_{z^2}) go down in energy as orbitals that reside in the xy plane (d_{xy} , $d_{x^2-y^2}$) rise in energy. The barycenter (the weighted average orbital energy) remains constant. Also, it is important to note that the splitting between the d_{xy} and $d_{x^2-y^2}$ orbitals stays constant at Δ_O regardless of the nature of the distortion.

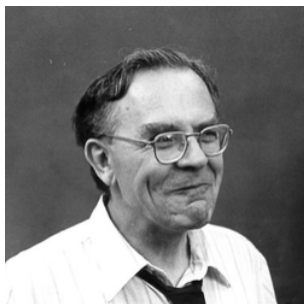
Why would a "happy" octahedral complex want to lose two of its ligands to make a **square planar** complex? This occurs frequently in d^8 and sometimes in d^9 complexes with large Δ_O , i.e., **$3d^8$ complexes with strong field ligands and $4d^8$, $5d^8$ complexes with any ligands**. Examples of such d^8 complexes are $[\text{Ni(CN)}_4]^{2-}$, the anti-cancer drug cisplatin ($\text{cis-Pt(NH}_3)_2\text{Cl}_2$), $[\text{Pd(H}_2\text{O)}_4]^{2+}$, and $[\text{AuCl}_4]^-$. At the d^8 electron count, the lowest four orbitals are filled and the highest orbital (the $d_{x^2-y^2}$) is empty, resulting in a large CFSE. These complexes are diamagnetic and tend to be quite stable. With weak field ligands, $3d^8$ complexes are octahedral and paramagnetic (e.g., $[\text{Ni(H}_2\text{O)}_6]^{2+}$, which has two unpaired electrons in the e_g orbitals).

Square planar complexes in catalysis:

Square planar d^8 complexes can be oxidized by two electrons to become octahedral (low spin) d^6 complexes, which also have a large CFSE. Because the loss of two electrons is accompanied by the gain of two ligands, this process is called **oxidative addition**. The reverse process is called **reductive elimination**. Both processes function together in catalytic cycles, such as the hydrogenation of olefins using **Wilkinson's catalyst**.^{[10][11]} The catalytic cycle is shown below.



The catalyst cycles between 4-coordinate Rh(I) ($4d^8$) and 6-coordinate Rh(III) ($4d^6$). The complex first adds H_2 oxidatively, to give a six-coordinate complex in which the hydrogen is formally H^- . An olefin molecule displaces a solvent molecule, using its π -electrons to coordinate the metal. The complex rearranges by inserting the olefin into the metal-hydrogen bond, a process called **migratory insertion**. Finally, the complex returns to the square planar geometry by eliminating the hydrogenated olefin (reductive elimination). Wilkinson's catalyst is highly active and is widely used for homogeneous hydrogenation, hydroboration, and hydrosilation reactions.^{[12][13]} With chiral phosphine ligands, the catalyst can hydrogenate prochiral olefins to give enantiomerically pure products.^[14]



Sir Geoffrey Wilkinson, an inorganic chemist at Imperial College London, developed Wilkinson's catalyst in 1966. Earlier, as an Assistant Professor at Harvard University, he had elucidated the sandwich structure of ferrocene,^[9] which had been discovered a few years before but not understood. Wilkinson was awarded the Nobel Prize in Chemistry in 1973 for his contributions to organometallic chemistry.

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