From Molecular Gyroscopes to Homeomorphic Isomerization: Molecules that Turn Themselves Inside-Out

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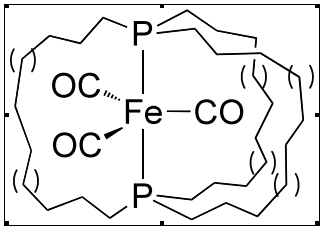
Children never cease to be fascinated by toy gyroscopes, which commonly consist of (1) a rotating axis and disk, and (2) two to four static spokes that connect the termini of the axis. This talk will briefly describe the syntheses of the first molecules that duplicate the connectivity, symmetry (D_{nh}), and rotational ability of such gyroscopes. Complexes with trans R_3P-ML_n-PR_3 linkages are first prepared, with R groups that terminate with a $CH{=}CH_2$ moiety. Then alkene metathesis is used to construct a three-spoked cage molecule. The C=C units are hydrogenated to give gyroscope-like species. Yields are highest with rotators such as $Fe(CO)_3$, which feature a three-fold symmetry axis, analogous to the phosphine ligands. However, reasonable yields can also be obtained with ML_n = $PtCl_2$, Rh(CO)Cl (square-planar geometry) and $Re(CO)_3X$ (octahedral geometry) .



Certain complexes can be dematallated to yield dibridgehead diphosphines, which can exist as three diastereomers (phosphorus lone pairs *in*/*in*, *out*/*out*, or *in*/*out*). This provides a starting point for another very interesting story. It has recently proved possible to show that these molecules rapidly turn themselves "inside-out" by a dynamic process that has only very seldom been observed previously. These topologically novel equilibria interconvert what any chemist would regard as two *configurational* diastereomers by purely *conformational* processes.

References

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