

Muetterties E L & Schunn R A. Pentaco-ordination.

Quarterly Reviews 20:245-99, 1966.

[Central Research Dept., E.I. du Pont de Nemours & Co., Wilmington, DE]

The article comprised a summarial characterization of structure, stereochemistry, and dynamic processes in five-coordinate complexes. These complexes tend to have trigonal bipyramidal or square pyramidal form and readily undergo transitions between the two limiting forms. Stereochemical guidelines were presented for the placement of ligands at the inequivalent sites of the coordination polyhedra. [The *SCI*[®] indicates that this paper has been cited in over 450 publications since 1966.]

Earl L. Muetterties
Department of Chemistry
University of California
Berkeley, CA 94720

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"In the 1950s, I had a unique opportunity at the Du Pont central research department to apply nuclear magnetic resonance (NMR) spectroscopy to structural and dynamic properties of inorganic molecules. This research was done in collaboration with William D. Phillips, now chairman of Washington University's chemistry department. In those early days of NMR, we had no means to regulate the temperature of the sample but still managed to obtain information about temperature dependent stereochemical phenomena: we repeatedly chilled the NMR sample tube in liquid nitrogen and inserted the tube into the spectrometer probe until the more massive probe was cooled. Then, by frantic tuning and retuning, we generated NMR spectra as a function of temperature—as the probe warmed. These crude but effective studies established that many inorganic and organometallic molecules possessed structures that rapidly underwent intramolecular rearrangements through vibrationally excited states.

"Seminal to the development of our research was the proposal¹ by R. Stephen Berry, now at the University of Chicago, that rearrangement of five-coordinate complexes proceeded by a deformation that traversed trigonal bipyramidal and

square pyramidal idealized geometries. This 'Berry rearrangement' postulate in conjunction with stereochemical considerations—what type of ligands prefer equatorial over axial vertex positions of a trigonal bipyramid—ultimately provided broad generalizations about pentacoordination. Next, the development stage of five-coordination came when Reinhard Schmutzler, now at Technische Universität Braunschweig, presented me with a large series of substituted PF₅ molecules. Initially, the NMR spectra of these molecules appeared uninformative. However, a more detailed analysis proved insightful: adoption of a very simple set of stereochemical guidelines that modified the Berry postulate for intramolecular rearrangement of five-coordinate molecules provided a self-consistent rationalization of structure, stereochemistry, and intramolecular rearrangement in pentacoordination.² These studies also provided a sound experimental basis for a generalization about rearrangements in inorganic molecules ('stereochemically nonrigid molecules').³

"The summarial features of structure, stereochemistry, and dynamic stereochemistry from these earlier studies and an evaluation of the literature were presented in the *Quarterly Reviews* 'Pentaco-ordination' article by Bob Schunn and me. I believe that it became a much cited article because chemists were just then perceiving that molecular species with five ligands were not an oddity but a relatively common phenomenon. The article, because of the timing, naturally became a key reference. In addition, it was evident from reaction mechanism studies that five-coordinate species are often transition states or reaction intermediates in reactions of the more common four- and six-coordinate molecules. In fact, the stereochemical guidelines and the Berry rearrangement mechanism were later used to rationalize and systematize the vast body of kinetic data concerning the hydrolysis of phosphorus esters.⁴ Still later, Lloyd Guggenberger and I⁵ analyzed crystallographic data for five-coordinate molecules and demonstrated that these structures fell precisely on the Berry geometric path, connecting the idealized trigonal bipyramidal and square pyramidal structures. Thus, the Berry postulate was in quantitative agreement with solid-state structural data. An excellent systematic molecular orbital analysis of pentacoordination was published in 1975."⁶

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2. Muetterties E L, Mahler W & Schmutzler R. Stereochemistry of phosphorus(V) fluorides. *Inorg. Chem.* 2:613-18, 1963.
3. Muetterties E L. Stereochemically nonrigid structures. *Inorg. Chem.* 4:769-71, 1965.
4. Westheimer F H. Pseudo-rotation in the hydrolysis of phosphate esters. *Account. Chem. Res.* 1:70-8, 1968.
5. Muetterties E L & Guggenberger L I. Idealized polytopal forms. Description of real molecules referenced to idealized polygons or polyhedra in geometric reaction path form. *J. Amer. Chem. Soc.* 96:1748-56, 1974.
6. Rossel A R & Hoffmann R. Transition metal pentacoordination. *Inorg. Chem.* 14:365-74, 1975.