

surfaces and electric field lines are drawn and discussed in some cases of chemical reactivity prediction for molecules in the solid state. The topology of the electrostatic potential exhibits novel atomic basins where the total charge is zero. The quantum theory of Bader is used to establish the atomic bonding structures and chemical reactivity relationship. Finally, the interatomic force (pressure) [3] concept is introduced: the Ehrenfest and Feynman forces are computed for a set of chosen molecules to emphasize their contributions for a better molecular reactivity understanding.

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Keywords: molecular reactivity, electrostatic potential and electric field, ehrenfest & feynman forces.

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Structural chemistry of 2-aza-1,3-dienes

Marek M. Kubicki

University of Burgundy, Chemistry, 9, Avenue Alain Savary, Dijon, Bourgogne, 21000, France, E-mail: marek.kubicki@u-bourgogne.fr

Since the solution of crystal structure of leading compound 1 ($\text{Ph}_2\text{C}(1)=\text{N}-\text{C}(2)(\text{H})=\text{C}(3)\text{X}_2$, $\text{X}=\text{Cl}$) we focused our attention on its capability of acting as a target for both the nucleophilic and the electrophilic attacks. One of the phenyl groups is roughly coplanar with azadienic chain suggesting so an extended pi-conjugation. The calculated electronic structure of 1 (B3LYP/6-311G) is compatible with that of butadiene, but shows a significant contribution of Cl atoms to the HOMO. The first nucleophilic attack occurs on C(2) atom with alkoxydes, cyanide and pyrrol anion, but C(3) carbon is preferred with thiolates and OPh. Such a regio - selectivity is rationalized by the hardness of incoming nucleophile calculated with DFT (hard nucleophile attacks on C(2) and the soft one on C(3)). A mentioned pi-conjugation of one phenyl ring with azadienic chain seems to operate in several molecules with $\text{X} = \text{Cl}, \text{OPh}, \text{SPh} \dots$ where the dihedral angles $\text{Ph}/\text{C}(1)\text{NC}(2)\text{C}(3)$ fall in the range of 10 to 38 deg. This effect is much stronger for free molecules (gas phase) as calculated with DFT (range of angles is 1 to 8 deg). Thus, the packing in the crystals partially leaves this conjugation. An oxidative addition is observed. The terminal chloride in Pt sigma-alkenyl complex may be substituted with a neutral (xylyl)NC ligand rising a spectacular linear pi-system delocalized on some 20 atoms. Substituted azadienes with $\text{X} = \text{SPh}$ and SiPr act as the ligands in complexes with Re, Mn, Cu, Hg, Pt and Pd. Generally, the chelates with five membered S_2N -metallacycles are formed. Orthometallation reactions predicted by DFT calculations are also observed in some cases.

Keywords: azadienes, chemical hardness, organometallics

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Iridium catalyzed hydrogenation with chiral ferrocenyl P-S ligands. X-ray structure of precatalysts

Jean-Claude Daran, Raluca Malacea, Lucie Routaboul, Sandrine Vincendeau, Rinaldo Poli, Eric Manoury
CNRS, Laboratoire de Chimie de Coordination (LCC), 205 route de

Narbonne, Toulouse, Haute-Garonne, 31077, France, E-mail : daran@lcc-toulouse.fr

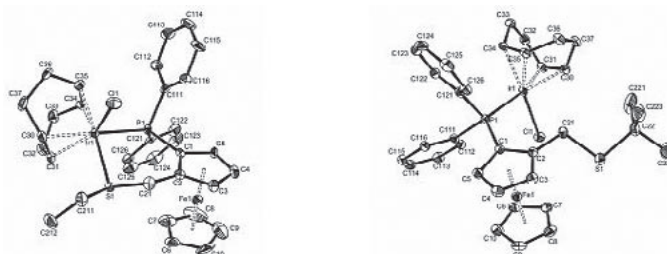
Iridium complexes of the new chiral ferrocenyl (P,SR) ligands $\text{CpFe}[1,2-\text{C}_5\text{H}_3(\text{PPh}_2)(\text{CH}_2\text{SR})]$ ($\text{R} = \text{Et}, \text{tBu}, \text{Ph}, \text{etc.}$), were successfully used in the hydrogenation of diphenylacetylene and in asymmetric hydrogenation simple ketones with high activities (turnover numbers up to 915 and global turnover frequencies up to ca. 250 h^{-1}) and enantioselectivities (ee up to 99%). The X-ray structural characterization of the precatalyst Ir complexes allowed to reveal that the coordination geometry of chlorocyclooctadieneiridium ligand adducts is delicately controlled by the nature of the R substituent, yielding five or four-coordinate complexes featuring then a dangling thioether group. Moreover, the ligand chirality controls the geometry at the sulfur and iridium atoms, producing single diastereomers.

Ref.

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Keywords: structural ferrocene chemistry, asymmetric catalysis by iridium, catalysts optimization

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Macromolecular refinement at subatomic resolution with interatomic scatterers

Paul D Adams^{1,5}, Pavel V Afonine¹, Ralf W Grosse-Kunstleve¹, Vladimir Y Lunin², Alexandre Urzhumtsev^{3,4}

¹Lawrence Berkeley Laboratory, Physical Biosciences, 1 Cyclotron Road, Berkeley, CA, 94720, USA, ²Institute of Mathematical Problems of Biology, Russian Academy of Sciences, Pushchino 142290, Russia, ³IGMBC, 1 Rue L. Fries, 67404 Illkirch and IBMC, 15 Rue R. Descartes, 67084 Strasbourg, France, ⁴Faculty of Sciences, Nancy University, 54506 Vandoeuvre-lès-Nancy, France, ⁵Department of Bioengineering, University of California Berkeley, Berkeley, CA, 94720, USA, E-mail : PDAdams@lbl.gov

The study of accurate electron-density distributions in molecular crystals at subatomic resolution (better than 1.0 \AA) requires more detailed models than those based on independent spherical atoms. We present a simple model composed of conventional independent spherical atoms augmented by additional scatterers to model bonding effects at high resolution. Refinement of these mixed models for several benchmark data sets gives results that are comparable in quality with the results of multipolar refinement and superior to those for conventional models. The application of this method to several data sets of both small molecules and macromolecules will be described as well as its implementation in the general-purpose macromolecular refinement module, phenix.refine, in the PHENIX software package.