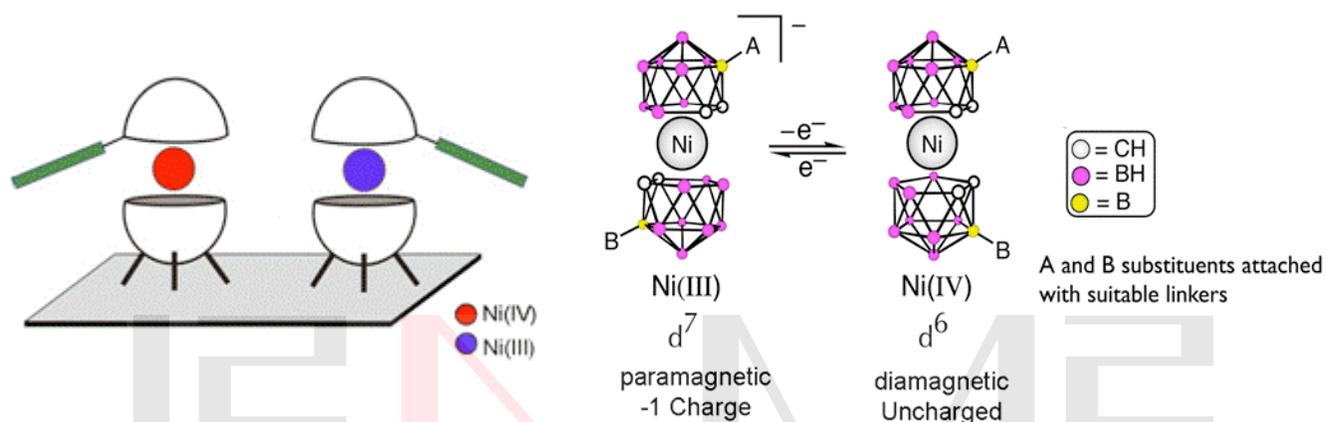


Rotary Molecular Motors

The search has intensified for molecular motors and actuators capable of delivering useful work to nanodevices for electrochemical or photochemical power sources. While many of these man-made molecular machines are designed to deliver rectilinear motion, very few are proposed for the controlled delivery of rotary motion. The adaptation of metallocarborane structures to the design and synthesis of such rotary molecular motors is now under investigation. Among the possible candidates are the nickel bis-7,8-dicarbollide structures having nickel oxidation states of +3, and +4. It appears feasible to consider the *transoid* Ni(III)/*cisoid* Ni(IV) redox transformation as the basis of such a motor which rotates through approximately 180°.



The paramagnetic d^7 Ni(III) (*transoid*) and the diamagnetic d^6 Ni(IV) (*cisoid*) species were originally reported in 1970 by Hawthorne to be interconvertible by a variety of redox reactions. The rotational confirmation for each of these two oxidation states was confirmed by molecular orbital and DFT calculations. The first step in the demonstration of a rotary motor of the type described above involves the syntheses of substituted 7,8-dicarbollide ligands, allowing the attachment of desired motor components for the rotation of the molecular motor both in solution and on a solid surface.

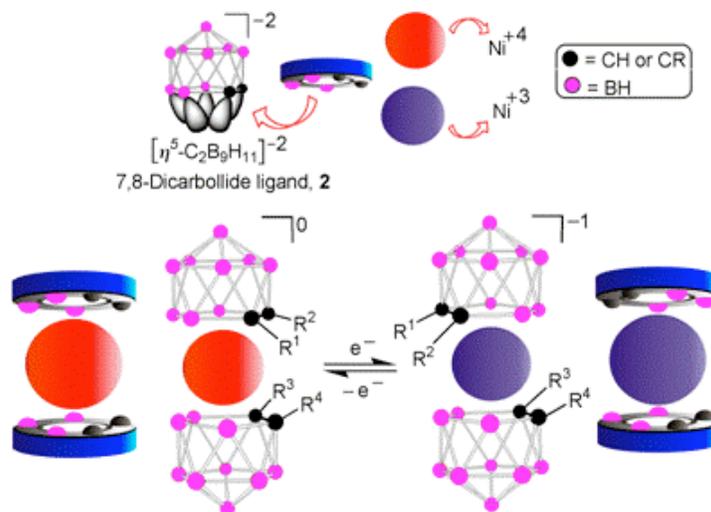
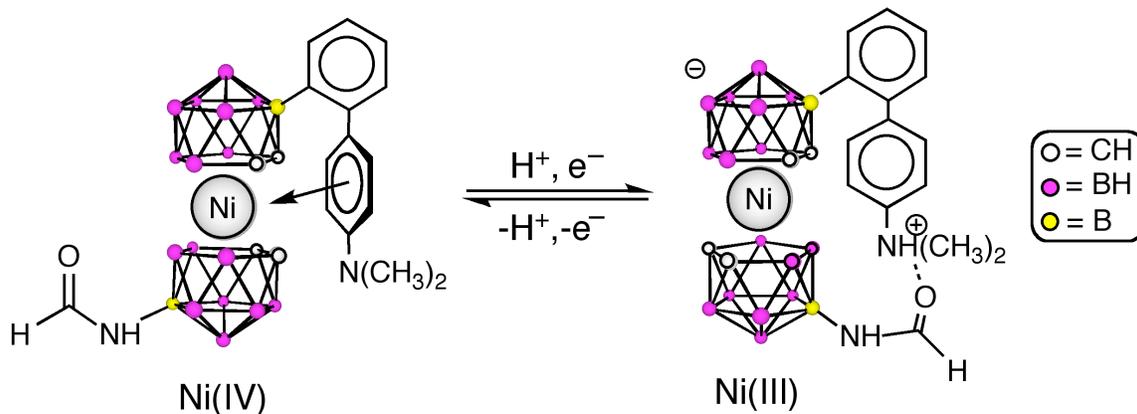


Illustration of rotor configurations of Ni(IV) and Ni(III)

Currently, work is directed towards the synthesis of the advanced version of the metallocarborane motor, which has non-covalent orthogonal bond stabilization of both the *cisoid* and *transoid* motor positions. The basis of this advanced motor is the orthogonal chemical stabilization of the Ni(III) and Ni(IV) rotamers. The Ni(IV) rotamer is stabilized by the well-known charge-transfer interaction of the p-dimethylaminophenyl ring with the Ni(IV) center. One electron reduction of the Ni(IV) rotamer in the presence of an acid produces the *transoid* Ni(III) rotamer, protonated at nitrogen and hydrogen bonded to the amide substituent located on the corresponding dicarbollide ligand.



Intramolecular charge transfer stabilization
No intramolecular H-bond possible

Intramolecular hydrogen bond stabilization
No intramolecular charge transfer possible

The rotary molecular motors have wide range of applications in biomedical and material sciences. For example, these rotary motors can be used to control fluids in a nano-valve as shown below. They can also be used to activate or inhibit chemical or biological catalysts or to regulate immunological processes.

