A Quantum Chemistry Simulation Strategy for Dynamic Network Polymers

Multiscale Mechanochemistry and Mechanobiology (2019)

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Organometallic Crosslinking Compounds

Dynamic crosslinking structures such as organometallic compounds can be used in place of covalent bonds in order to retain considerable crosslinking strength, while enabling improved material properties such as increased toughness and processability. In order to tailor or predict mechanical properties of the bulk material, the dynamic crosslinks must be understood at a fundamental level.

Presented here is a step-by-step density functional theory simulation-based strategy we use to quantify the mechanics of a particular organometallic complex, nickel(II) acetate hydrate, that can be used as a polymer crosslinker. The complex is analyzed before and after adding ligands, and while varying the ligand number and type. The mechanical stiffness and free energy barrier to breaking the complex change dramatically when differing the ligand amount, but the two change less when varying the ligand type.

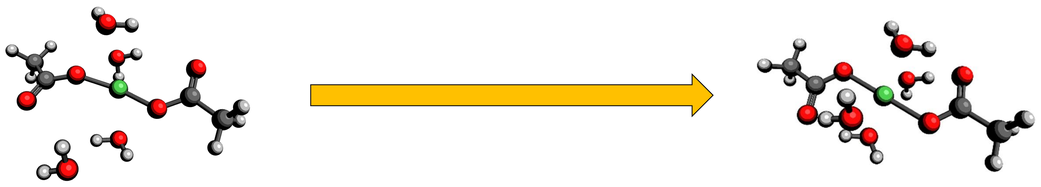
Simulation Details

Functional: ωB97X-V **Basis Set:** def2-TZVPP

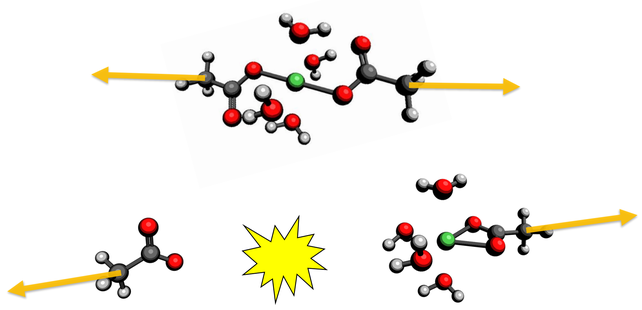
Atom Legend: Hydrogen Carbon Nitrogen Oxygen Nickel

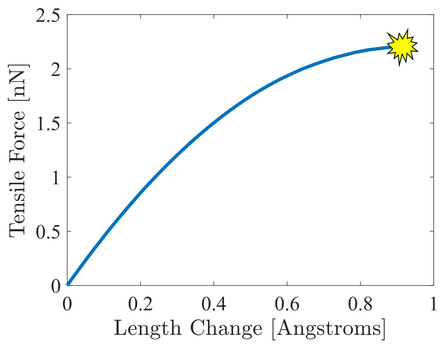
Mechanical Response

Atomic Force Equilibrium (OPT) and Hessian Diagonalization (FREQ)



Application of External Forces (EFEI)

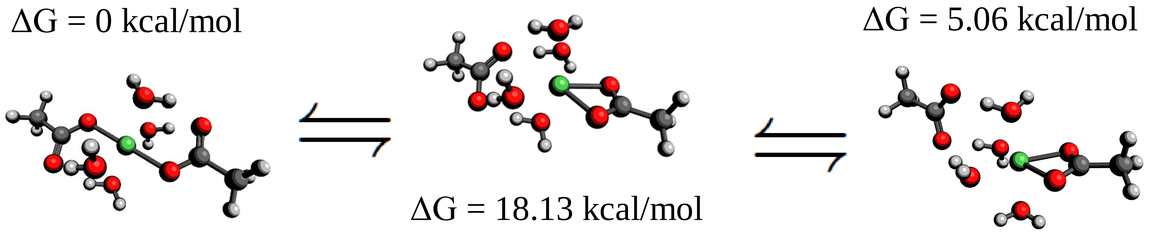




Free Energy Barriers

Reaction Pathway (FSM) and Transition State Identification (TS)

ΔG = 0 kcal/mol

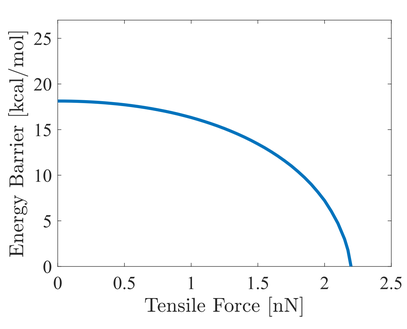


ΔG = 18.13 kcal/mol

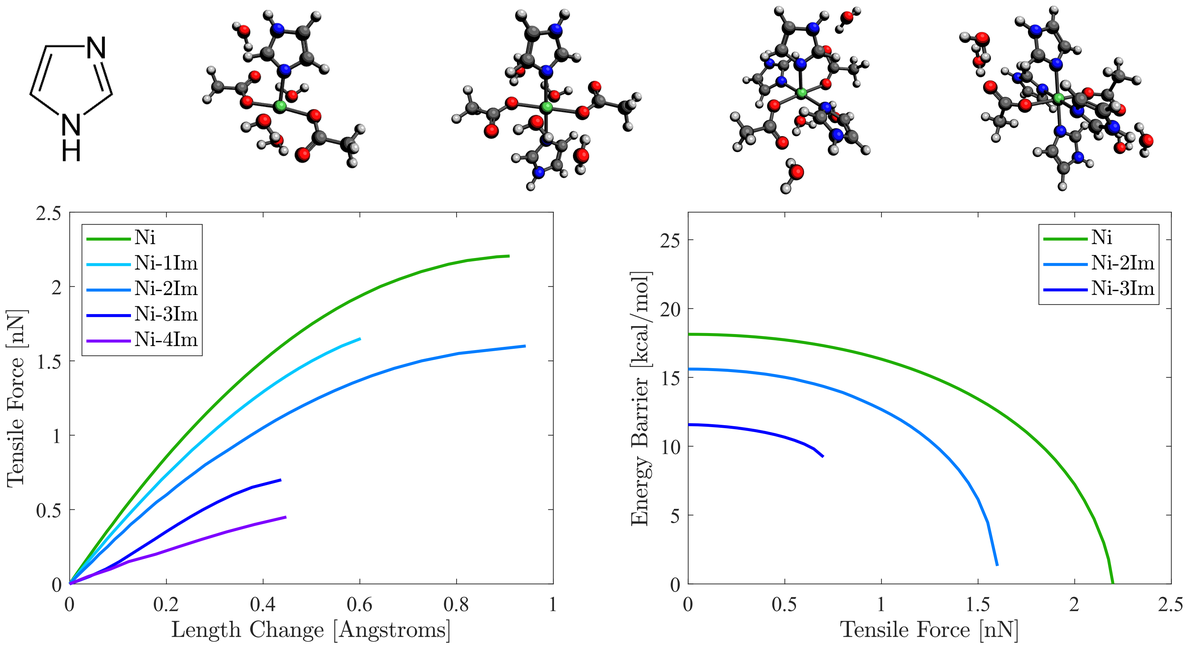
ΔG = 5.06 kcal/mol

Mechanochemical Activation

$$\Delta G_f = \Delta G_f^0 - \int \mathbf{F} \cdot d\mathbf{r}$$



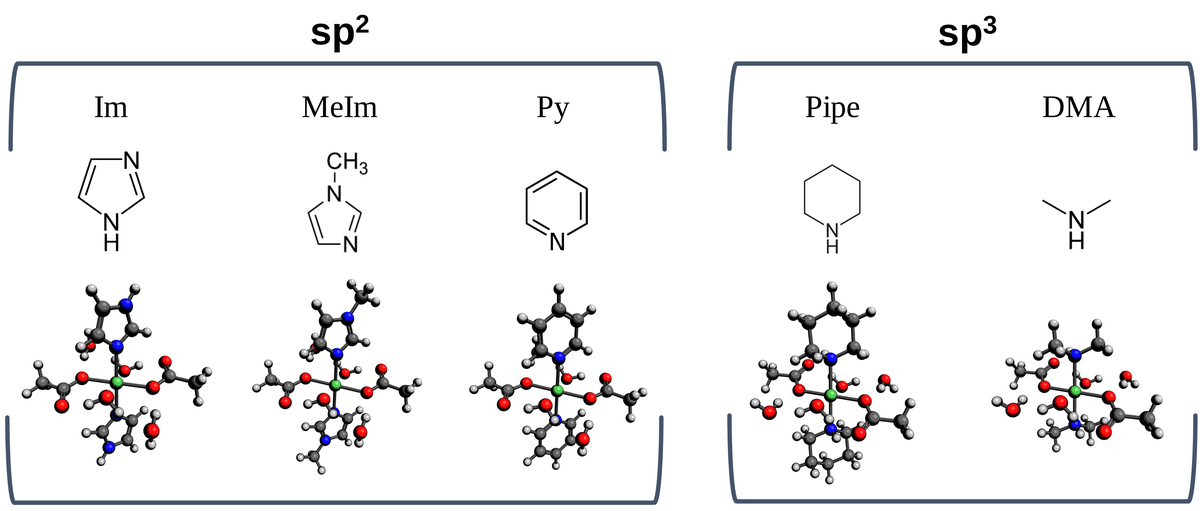
Differing Ligand Amount

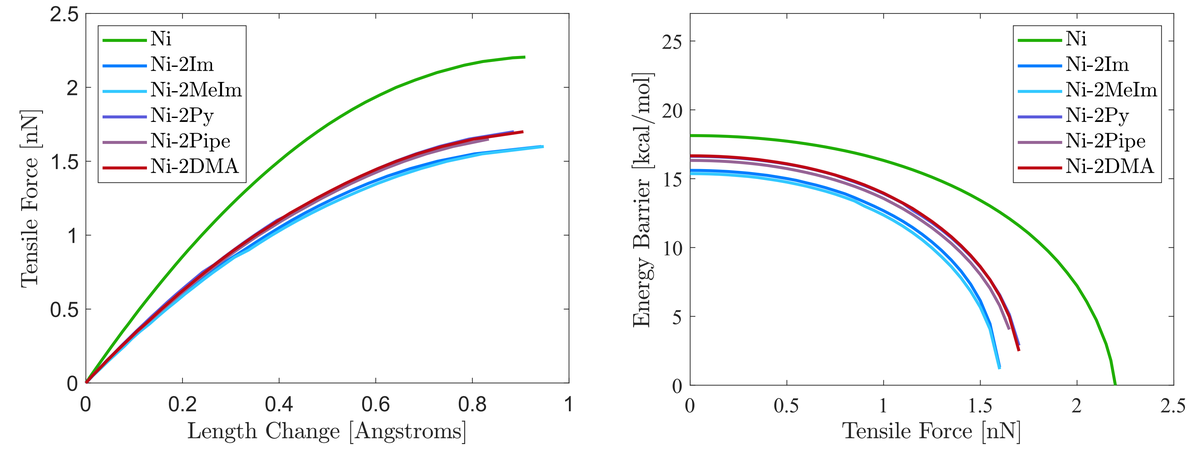


Differing Ligand Type

sp² **sp³**

Im MeIm Py Pipe DMA





Conclusion

- A step-by-step quantum chemistry simulation method was presented to analyze the mechanics of dynamic crosslinking structures.
- The analysis predicts that each ligand added to the crosslinking structure will significantly diminish both its mechanical response and energy barrier to breaking.
- The same analysis predicts more subtle changes in the mechanical response and energy barrier of the structure when changing the type of ligand.
- Further analyses may be necessary if non-bonded interactions of the complex with the polymer dominate and change appreciably between different ligands.

Acknowledgment

This research is funded by the National Science Foundation (CMMI-1653059) and the Office of Naval Research (N00014-17-1-2989), and used computational resources provided by the Extreme Science and Engineering Discovery Environment (XSEDE) and the Department of Defense High Performance Computing Modernization Program (DOD HPCMP).