Breaking Chemical Bonds by Force: A Computational Investigation of Metal-C-H Interaction Under High Pressure

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Activation of C-H bonds is at the center of chemical transformations of hydrocarbons, which are primary products of the petroleum industry. However, efficient C-H bond activation remains an outstanding challenge in synthetic chemistry due to the bond’s nonpolar nature and its large dissociation energy, necessitating the development of new catalysts. This work investigates pressure-driven C-H activation through the anagostic mechanism, i.e., the non-bonding interactions between a C-H bond and a late transition metal (TM), thereby expanding the scope of catalyst design for C-H functionalization. Since the first report in the early 1990s, anagostic interactions have remained largely unstudied because they are considered too weak to induce a chemical reaction, let alone activate a strong C-H bond. Utilizing two model nickel compounds, (N,N'-Di(2-aminoethyl)malondiamidato) nickel(ii) trihydrate (AEMANI) and (1,4,8,11-Tetra-azacyclotetradecane-5,12-dionato)-nickel(ii) tetrahydrate (QANQOM), we conducted energy decomposition analysis computations, natural orbitals for chemical valence deformation density visualizations, and reduced electron density gradient/non-covalent interaction index analyses. We have found that anagostic interactions can be used to activate C-H bonds under mechanical pressure and consist of competing repulsive and attractive interactions, with the net effect highly sensitive to local molecular geometry. The closer the nickel-C-H bond angle is to 180 degrees, the more C-H activation. This knowledge will be used to design energy efficient C-H activation catalysts that are capable of transforming abundant hydrocarbons into functional materials under mechanical pressure.

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