

**NUCLEOPHILICITY INDICES AS DESCRIPTORS
FOR BOTH THERMODYNAMIC FEASIBILITY AND REACTIVITY
OF C-ELECTROPHILES OXIDATIVE ADDITION TO Pt(II) SPECIES**

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Oxidative addition (OA) is a crucial step in numerous C-C coupling reactions catalyzed by transition metals [1]. The efficiency of this process depends on the nucleophilicity of the metal donating electron pairs, as well as on the nature of the substrate and the reaction conditions. An appreciation and prediction of nucleophilic reactivity are of paramount importance for controlling the course of chemical reactions, understanding their mechanisms, and creating new approaches to the synthesis of organic compounds.

Recently, we developed a model cross-electrophile coupling reaction between methyl iodide and vinyl iodide to form propylene in a Pt(II)–NaI–acetone system [2; 3]. The key intermediate in the reaction is a methyl-vinyl derivative of Pt(IV), generated by the sequential oxidative addition of these electrophiles to Pt(II) iodo complexes. However, the sequence in which methyl iodide and vinyl iodide molecules bind to $[PtI_4]^{2-}$ remains unclear. A step toward resolving this issue could be comparing the reactivity of the $[Pt(CH_3)I_3]^{2-}$ and $[Pt(CH_2CH_3)I_3]^{2-}$ complexes in OA reactions with vinyl iodide and methyl iodide, respectively.

The results of DFT-modeling the energy profiles of OA reactions, along with correlations between the free Gibbs energies/barriers of the reactions and the calculated values of the condensed-to-atom (Pt) nucleophilicity indices will be presented and discussed.

1. Bavi M., Nabavizadeh S. M., Hosseini F. N. [et al.]. Ligand-Mediated C–Br Oxidative Addition to Cycloplatinated (II) Complexes and Benzyl-Me C–C Bond Reductive Elimination from a Cycloplatinated(IV) Complex // ACS omega. 2020. Vol. 5, №. 44. P. 28621–28631. <https://doi.org/10.1021/acsomega.0c03573>

2. Krasnyakova T. V., Nikitenko D. V., Gogil'chin A. S. [et al.]. Reductive Cross-Electrophile C(sp²)-C(sp³) Coupling Catalyzed by PtI₂: In Situ Structural Determination of the Intermediates by X-ray Absorption Spectroscopy and Multinuclear NMR // Organometallics. 2024. Vol. 43, № 1. P. 55–67. <https://doi.org/10.1021/acs.organomet.3c00400>

3. Krasnyakova T. V., Nikitenko D. V., Mitchenko S. A. Catalytic C(sp²)-C(sp³) Cross-Electrophile Coupling in the Pt^{II}-NaI-C₂H₃I-CH₃I-Acetone System // Kinetics and Catalysis. 2024. Vol. 65, № 1. P. 30–39. <https://doi.org/10.1134/S002315842401004X>

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