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Nickel-Catalysed anti-Markovnikov Hydroarylation of Unactivated Alkenes with Unactivated Arenes Facilitated by Non-**Covalent Interactions**

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Nickel-Catalyzed anti-Markovnikov Hydroarylation of **Unactivated Alkenes**

$$R^{1} \stackrel{\text{[L-Ni(η^6-C_6H_6$)] (3 mol\%)}}{\text{NaH (2.0 mol\%)}} \\ \text{Na(acac) (5 mol\%)} \\ \text{Na(acac) (5 mol\%)} \\ \text{neat, 120 °C, 24 h} \\ \text{(9.0 equiv)} \\ \text{(1.0 equiv)} \\ \text{(1.0 equiv)} \\ R^{1} \stackrel{\text{[L-Ni(η^6-C_6H_6$)] (3 mol\%)}}{\text{Na(acac) (5 mol\%)}} \\ \text{Na(acac) (5 mol\%)} \\ \text{Na(acac)} \\ \text{Na(acac) (5 mol\%)} \\ \text{Na(acac)} \\ \text{Na(acac)}$$

Proposed mechanism:

Significance: Nakao, Hartwig and co-workers report a novel nickel-catalyzed undirected hydroarylation reaction between unactivated alkenes and unactivated arenes. The reaction proceeds in excellent yields with high selectivity for the anti-Markovnikov product. These products are distinct from those accessed through acid-catalyzed processes.

Comment: The authors characterized the catalytically relevant substrate bound nickel complexes and identified the reductive elimination step forming the C-C bond as the rate-limiting step. They also note that differences in the activity between catalysts with large/small carbenes are more dependent on the stabilizing intramolecular noncovalent interactions in the secondary coordination sphere, than steric hindrance.

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Metals in Synthesis

Key words

nickel catalysis C-H activation hydroarylation unactivated alkenes anti-Markovnikov reaction