N. I. SAPER, A. OHGI, D. W. SMALL, K. SEMBA, Y. NAKAO*, J. F. HARTWIG*
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Nickel-Catalysed anti-Markovnikov Hydroarylation of Unactivated Alkenes with Unactivated Arenes Facilitated by Non-Covalent Interactions
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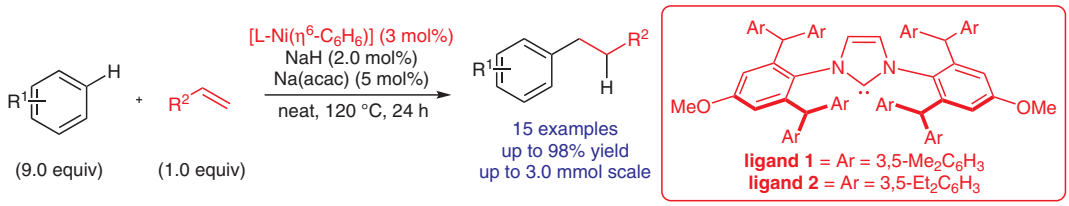
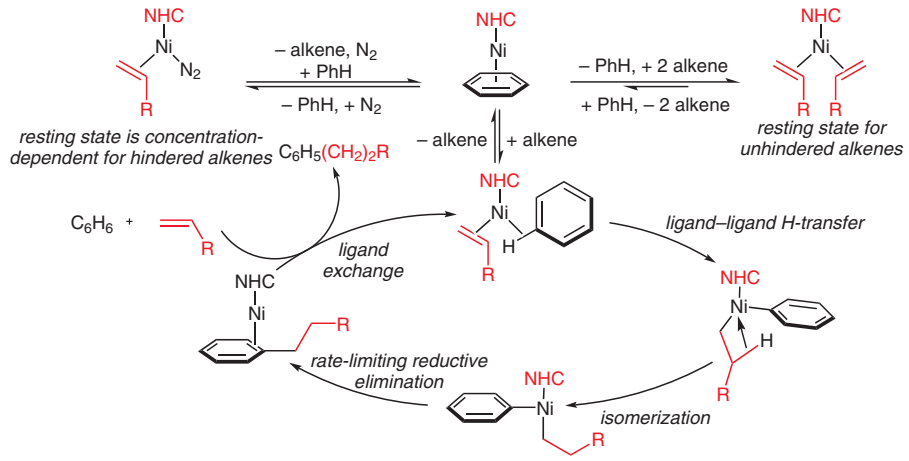
Category
Metals in Synthesis

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

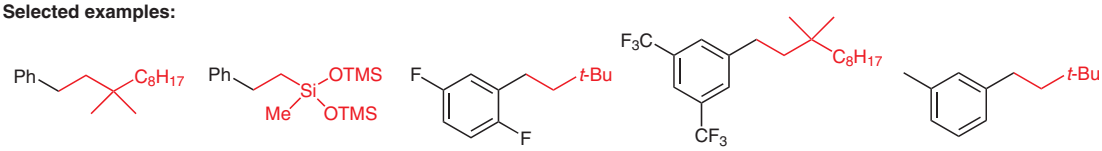
Nickel-Catalyzed anti-Markovnikov Hydroarylation of Unactivated Alkenes



Proposed mechanism:



Selected examples:



L1: 96% yield
L2: 92% yield

L1: 92% yield
L2: 90% yield

L1: 95% yield
L2: 96% yield

L1: 95% yield
L2: 96% yield

L1: 91% yield
L2: 91% yield
m/*p* = 2.2:1

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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