Nickel-Catalyzed anti-Markovnikov Hydroarylation of Unactivated Alkenes

**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.

**Selected examples:**
- PhC8H17, L1: 96% yield, L2: 92% yield
- PhC8H17Me, L1: 92% yield, L2: 90% yield
- PhC8H17OTMS, L1: 96% yield, L2: 96% yield
- F3CPh, L1: 95% yield, L2: 96% yield
- CF3Ph, L1: 96% yield, L2: 91% yield

**Proposed mechanism:**
1. Resting state is concentration-dependent for hindered alkenes.
2. C6H6 • + alkene – alkene, N2
3. C6H5(CH2)2R • + alkene – PhH, – 2 alkene
4. C6H5(CH2)2R • + PhH, – 2 alkene
5. Rate-limiting reductive elimination
6. Ligand–ligand H-transfer
7. Isomerization
8. Resting state for unhindered alkenes

**Proposed mechanism equation:**
- [L-Ni(η6-C6H6)] (3 mol%) NaH (2.0 mol%) Na(acac) (5 mol%) neat, 120 °C, 24 h

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