Organocalcium-Mediated Nucleophilic Alkylation of Benzene

Andrew Wilson, Michael S. Hill, Mary F. Mahon, Chiara Dinoi and Laurent Maron.

I. Group 2: Beyond Magnesium

- Magnesium-based Grignard reagents are ubiquitous in chemistry due to their simple synthesis, stability and reactivity.
- Heavy Grignards often lack these properties and have thus remained relatively unexplored.

Synthesis

i. Solvent-Free Calcium Hydride

- Molecular calcium hydride species have been prepared via a bond metathesis of a Ca-X bond with a hydride E-H bond.
- The reaction of [BDI]CaH(μ-Me)2 (1) with a three-fold excess of PhSiH3 afforded [BDI]CaH(μ-3SiMe2Ph)2 (2) in good yields (> 70%).

ii. n-Alkylic Species

- The insertion of C≡C bonds into Ca-H bond of 2 afforded unprecedented n-alkylcalcium species (3 – 5).\(^1\)

Reactivity

i. Nucleophilic Alkylation of Benzene

- Compounds 3 – 5 were identified by indicative upfield resonances of the α-methylene protons (ca. –0.7 ppm).

ii. DFT Calculations

- DFT supports this supposition as dissociation to a monomer (G) is the most endothermic (ΔH = +23.3 kcalmol\(^{-1}\)) step.\(^1\)
- Benzene is activated towards nucleophilic attack through its coordination to the calcium centre.
- Overall the process is exothermic (ΔH = -30.1 kcalmol\(^{-1}\)).

Isolable organocalcium species could overcome benzene’s defences.

Unprecedented n-alkylcalcium species are isolable.

References