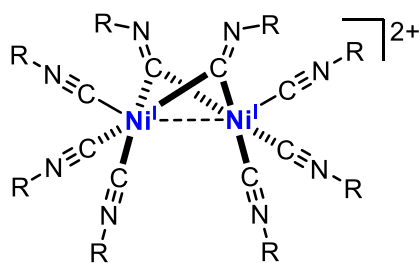
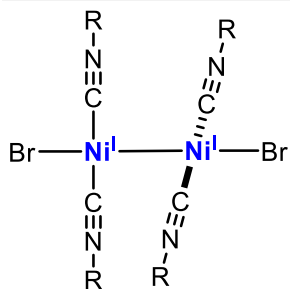


Catalytically Competent Nickel(I) Compounds with Isocyanides as Spectator Ligands

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Nickel (Ni)-catalyzed cross-coupling has emerged as a powerful strategy to construct complex molecules. A salient feature of nickel catalysis is its ability to engage in one-electron chemistry involving paramagnetic intermediates like Ni(I) and Ni(III), which has led to a tremendous growth in nickel-catalyzed cross-coupling reactions. Such reactions generally employ Ni(II) or Ni(0) complexes as pre-catalysts. Although highly desirable, well-defined, stable, and catalytically competent Ni(I) sources with exchangeable ancillary ligands are lacking. Here we report the synthesis, characterization, and catalytic activity of a family of thermally stable dinuclear Ni(I) complexes supported by commercially available isocyanides as a general solution to this problem. Two classes of Ni(I) isocyanide complexes showing unprecedented thermal and solid-state stability have been developed – coordinatively saturated homoleptic compounds and coordinatively unsaturated halide compounds. The bound isocyanides were shown to be extremely labile, which mitigates the non-innocent behavior of metal-bound isocyanides. This enabled rapid ligand substitution and productive use in Kumada, Suzuki-Miyaura, and Buchwald-Hartwig cross-coupling reactions, suggesting the potential of these compounds as Ni(I) catalysts or pre-catalysts. Spectroscopic and mechanistic studies were performed to establish the first general use of simple isocyanides as spectator ligands for cross-coupling catalysis, which represents an untapped chemical space for new reaction discovery.

Catalytically competent Ni^I Isocyanide Compounds



- Coordinatively unsaturated and thermally stable.
- Facile, rapid ligand substitution.
- Catalyzes Suzuki-Miyaura, Buchwald-Hartwig, and Kumada cross-coupling reactions.