

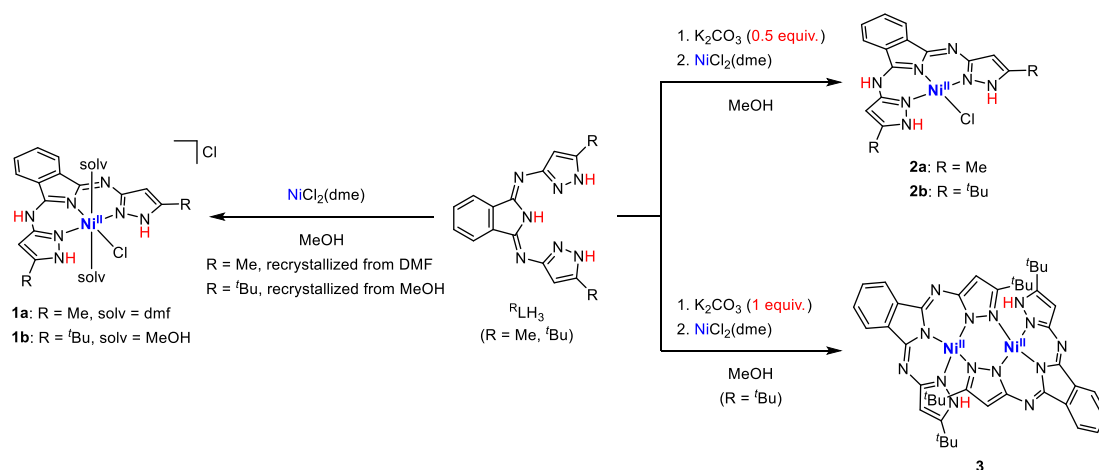
Synthesis and Reactivity of Nickel Complexes Having Isoindoline-Based Polyprotic Pyrazole Ligand

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During the past decade, isoindoline-based meridional tridentate ligand has become the subject of growing interest due to their high thermal stability, structural rigidity, and their proton response.¹ We have recently introduced two proton responsive pyrazol-3-ylimino groups in the wingtips, which gives a new type of isoindoline ligand ^tBuLH₃ having a total of three ionizable NH groups.² We have also synthesized a series of its iron complexes and explored their reactivity.² In this work, we investigated the coordination of ^tBuLH₃ as well as the methyl analogue ^{Me}LH₃ to a nickel(II) center and the Brønsted-acidity of the ligand.

Treatment of NiCl₂(dme) with ^RLH₃ in a 1:1 ratio afforded the monocationic nickel(II) chlorido complexes [Ni(^RLH₃)(solv)₂Cl]Cl (**1**) with octahedral geometry. Upon coordination, the isoindoline NH group in the free ligand migrates to the pincer backbone in the paramagnetic complexes **1**. In contrast, pre-deprotonation of the ligand by K₂CO₃ resulted in the formation of the diamagnetic and neutral complexes [Ni(^RLH₂)Cl] (**2**) with square-planar geometry. When the amount of the base was increased in the reaction of ^tBuLH₃, the pyrazolato-bridged dinuclear complex [^tBuLH] (**3**) was obtained. The products **1–3** were fully characterized by ESI-MS and ¹H NMR spectroscopy and X-ray analysis, which highlight the multiproton-responsive nature of the pincer-type ^RLH_n ligands.



- 1) R. Csonka, G. Speier, J. Kaizer, *RSC Adv.* **2015**, 5, 18401.
- 2) T. Toda, S. Kuwata, *Z. Anorg. Allg. Chem.* **2021**, 647, 1471.