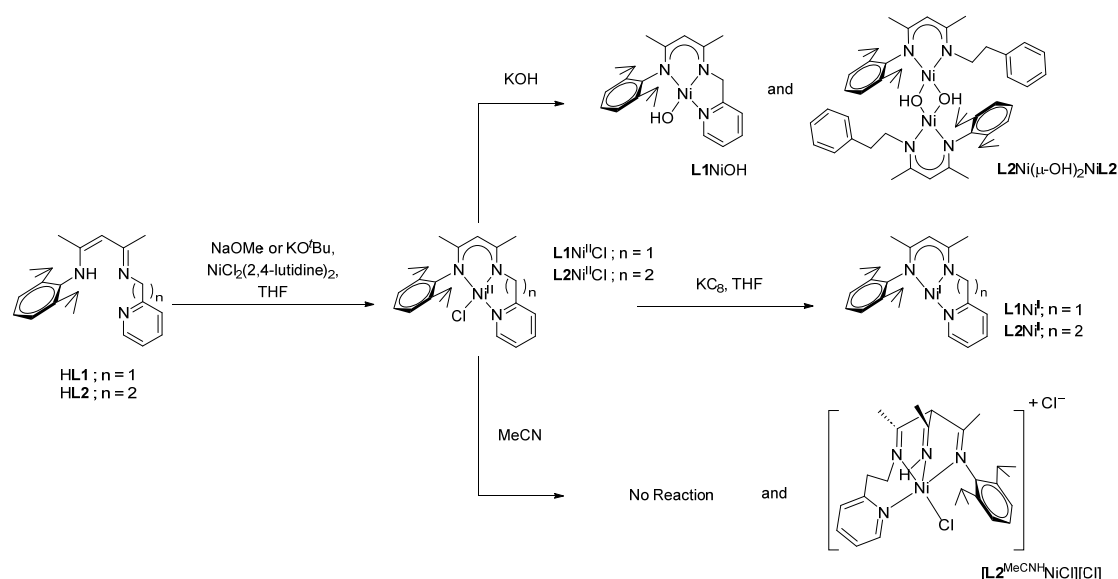


LIGAND-CONTROLLED GEOMETRY, SPIN STATE, AND REACTIVITY IN UNSYMMETRICAL β -DIKETIMINATO NICKEL COMPLEXES

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Ligand design plays a central role in determining the structure, electronics, and reactivity of transition metal complexes.¹ In this study, unsymmetrical *N*-aryl-*N'*-alkylpyridyl β -diketiminato ligands (HL1, HL2) are employed to modulate the geometry, spin state, and reactivity of nickel complexes.^{2, 3} Metallation of HL1 and HL2 with $\text{NiCl}_2(2,4\text{-lutidine})_2$ affords $\text{L1Ni}^{\text{II}}\text{Cl}$ and $\text{L2Ni}^{\text{II}}\text{Cl}$, which display distinct coordination environments. $\text{L1Ni}^{\text{II}}\text{Cl}$ adopts a diamagnetic square-planar geometry ($\tau_4 = 0.102$), while $\text{L2Ni}^{\text{II}}\text{Cl}$ exhibits a rare paramagnetic seesaw geometry ($\tau_4 = 0.299$) enabled by an extended chelating arm, as established by NMR, UV-vis, and X-ray crystallography. Chemical reduction with KC_8 generates the corresponding Ni(I) species, L1Ni^{I} and L2Ni^{I} , featuring three-coordinate T-shaped and Y-shaped geometries, respectively. Notably, $\text{L2Ni}^{\text{II}}\text{Cl}$ promotes β -C-C bond activation of acetonitrile to form a five-coordinate $[\text{L2}^{\text{MeCN}}\text{NiCl}][\text{Cl}]$ complex. Treatment with KOH yields mononuclear L1NiOH and dimeric $\text{L2Ni}(\mu\text{-OH})_2\text{NiL2}$, illustrating ligand-controlled nuclearity. These results demonstrate that unsymmetrical β -diketiminato ligands enable precise control over structure, spin state, and reactivity in nickel complexes, providing a foundation for the design of bioinspired catalytic systems.



Scheme 1. Synthesis a series of nickel complexes.

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