

**TRANSFER HYDROGENATION OF KETONES CATALYZED BY
(PHENOXY)IMINO/AMINO NICKEL(II) COMPLEXES**

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ABSTRACT

Alcohols are important intermediates in pharmaceuticals, fine chemicals, solvent industries, cosmetics, and fuels. Alcohols have traditionally been synthesized by methods like direct hydrogenation, the addition of water to alkenes, reduction of carbonyls using metal hydrides, hydrolysis of alkyl halides, and addition of Grignard reagent to carbonyls. However, these methods have not been effective in meeting the demand of alcohol. This is due to several drawbacks such as complex synthetic routes, most reagents being sensitive to moisture or air, poor selectivity, harsh reaction conditions, and expensive reagents. Catalytic Transfer hydrogenation (CTH) of ketones, which involves the reduction of ketones using hydrogen donors and a metal-based catalyst, is a better alternative route with high percentage enantiomeric excess (ee) and good percentage yields. CTH has been utilizing precious metal-based catalysts like Ir, Ru, Rh, and Pd. However, due to the harmfulness, expensiveness, and scarcity of these precious metals, the field of CTH is turning to non-precious first-row transition metals (TM). In this work, the phenolate ligands 2-[(2-hydroxyethyl)-imino]methyl]phenol (**TL1**) and 2-[1-{2-(diethylamino)ethylimino}ethyl]phenol (**TL2**) were synthesized by condensation reactions between the appropriate aldehydes/ketones and the corresponding amines. Successive reduction of **TL1** and **TL2** with sodium borohydride resulted to formation of amino analogues 2-[(2-hydroxyethyl)-amino]methyl]phenol (**TL3**) and 2-[1-{2-(diethylamino)ethylamino}ethyl]phenol (**TL4**), respectively. Treatment of ligands **L1-TL4** with NiCl₂ afforded complexes [Ni(**TL1**)Cl₂] **C1**, [Ni(**TL2**)Cl₂] **C2**, [Ni(**TL3**)Cl₂] **C3** and [Ni(**TL4**)Cl₂] **C4**, respectively. These compounds were characterized using ¹H NMR, ¹³C NMR, FT-IR, and MS. Upon activation with ^tBuOK, these complexes displayed high catalytic activities (up to 96% conversion) in transfer hydrogenation of ketones (THK) within 6 h at 100 °C. Notably, the imine-based complexes (**C1** and **C2**) displayed higher activity (69.50% and 69.93% conversions, respectively) compared to the amine analogues (**C3** and **C4**) (63.97% and 62.66% conversions, respectively) indicating the influence of electronic effect in catalytic activity. More importantly, the nature of base, hydrogen donor and substrate employed played an essential role in the catalytic performance of these complex