

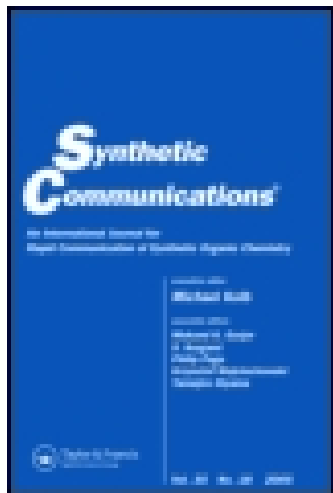
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### Chemoselective Transfer Hydrogenation of Carbonyl Compounds Catalyzed by Macrocyclic Nickel (II)Complex

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**CHEMOSELECTIVE TRANSFER HYDROGENATION OF  
CARBONYL COMPOUNDS CATALYZED BY  
MACROCYCLIC NICKEL (II) COMPLEX**

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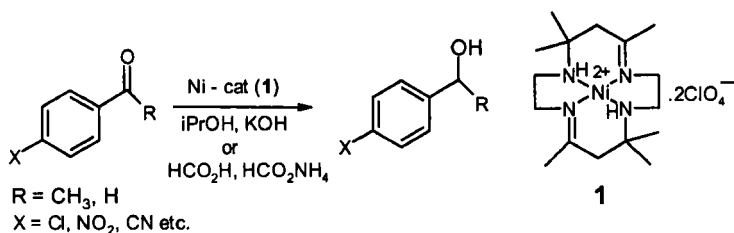
**Abstract:** Macrocyclic Ni(II) complex, **1**, catalyzes efficiently the chemoselective transfer reduction of carbonyl compounds in presence of propan-2-ol / KOH or HCO<sub>2</sub>H / HCO<sub>2</sub>NH<sub>4</sub> as hydrogen donors to produce the corresponding alcohols in high yield.

The chemoselective reduction of organic compounds is synthetically important, both in the laboratory and in industry. In comparison with catalytic reduction using molecular hydrogen,<sup>1</sup> catalytic transfer hydrogenation using hydrogen donors, such as propan-2-ol, has real and potential advantages because neither hydrogen containment nor a pressure vessel is required. Chemoselective reduction of the organic functional groups can be accomplished by classical Meerwein-Ponndorf-Verley reduction. However, the use of aluminium isopropoxide in stoichiometric amounts under drastic conditions often leads to many side products. Raney nickel has been extensively used using hydrazine

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hydrate or propan-2-ol as a hydrogen source for reductions. However, Raney nickel is pyrophoric and does not show any selectivity towards functional reduction of C-X, C=O and NO<sub>2</sub> groups, reducing all of them simultaneously. Further, it has been observed that the use of Raney Ni for the reduction of aromatic ketones leads to hydrogenolysis of alcohols quite easily at the benzylic position.<sup>2</sup> Transfer hydrogenation of ketones using homogeneous complexes of Ru, Rh, Ir, Pd, and Ni with propan-2-ol has been reported.<sup>3-5</sup> Use of acetic acid and ammonium formate in presence of Ni (PPh<sub>3</sub>)<sub>4</sub> is also reported recently.<sup>6</sup> Also, we have reported the chemoselective transfer hydrogenation of nitroarenes and carbonyl compounds using Ni-stabilized zirconia.<sup>7</sup> Most of the catalysts exhibit poor selectivity in product distribution. Therefore, it assumes great importance to have effective control over selectivity in such reactions. Herein, we report the potential application of macrocyclic Ni(II) complex **1** as an active catalyst for chemoselective reduction of carbonyl functions using propan-2-ol or formic acid along with ammonium formate as hydrogen source (**Scheme 1**).



**Scheme 1**

Nickel complex **1** was synthesized according to procedure reported in the literature.<sup>8</sup> Initially, a systematic study for the catalytic evaluation of complex **1** was undertaken using propan-2-ol because of its potential advantages over other H-donors (**Table 1**).

It is evident from **Table 1** that both aliphatic and aromatic carbonyl functions are reduced without affecting C=C, C-Cl, NO<sub>2</sub>, C≡N and CO<sub>2</sub>Et groups (entries 6, 8-11). However, it takes longer time (>24 h) to achieve good yield of

**Table 1:** Transfer hydrogenation of various carbonyl compounds using catalyst 1 in propan-2-ol.<sup>a</sup>

Entry	Substrate	t/h	Product	Yield <sup>b</sup> (%)
1	Acetophenone	30	1-Phenylethanol	78
2	4-Methyl-acetophenone	24	1-(4-Methylphenyl)-ethanol	73
3	4-Chloro-acetophenone	24	1-(4-Chlorophenyl)-ethanol	71
4	Cyclohexanone	24	Cyclohexanol	56
5.	Octanal	24	1-Octanol	61
6	Cinnamaldehyde	30	Cinnamyl alcohol	53
7	Benzaldehyde	24	Benzyl alcohol	71
8	4-Chloro-benzaldehyde	24	4-Chlorobenzyl alcohol	74
9	4-Nitro-benzaldehyde	36	4-Nitrobenzyl alcohol	52
10	4-Cyano-benzaldehyde	36	4-Cyanobenzyl alcohol	56
11	Ethyl acetoacetate	30	Ethyl-3-hydroxybutanoate	60

a: Reaction conditions: Substrate, 4 mmol; Catalyst, 0.08 mmol; KOH, 0.4 mmol; <sup>1</sup>PrOH, 10 mL, 82 °C. b: Isolated yield after chromatographic purification; products were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS.

the alcohol. In order to achieve better control over rate and specificity, we have carried out reactions using various hydrogen sources. The results are summarized in **Table 2**. It is surprising to note that neither ammonium formate nor formic acid alone is useful as H-source for ketone reduction. However, a dramatic rate enhancement has been observed in the ketone reduction with excellent yield when combinations of both formic acid and ammonium formate are used together as H-source. It has been established that the addition of alkali metal formates accelerates the rate of hydrogen transfer from formic acid in the presence of various Ru-complexes.<sup>9</sup> Also, triethyl amine is well known to accelerate the rate of decomposition of formic acid.<sup>10</sup> In a similar way, it is believed that ammonium

**Table 2: Transfer hydrogenation of various carbonyl compounds using Ni-complex 1 over different hydrogen donors<sup>a</sup>**

Entry	Substrate	Hydrogen donor	Temp. (°C)	t/h	Yield <sup>b</sup> of alcohols (%)
1	Acetophenone	<sup>1</sup> PrOH + KOH	82	30	78
2	Acetophenone	EtOH + HCO <sub>2</sub> NH <sub>4</sub>	80	24	NR
3	Acetophenone	n-BuOH + HCO <sub>2</sub> NH <sub>4</sub>	117	24	NR
4	Acetophenone	98% HCO <sub>2</sub> H	100	24	NR
5	Acetophenone	98% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	2.5	94
6	Acetophenone	85% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	2.5	94
7	Acetophenone	60% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	10	NR
8	4-Methyl-acetophenone	85% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	2.5	91
9	4-Chloro-acetophenone	85% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	2.5	90
10	Cyclohexanone	85% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	7	73
11	Cinnamaldehyde	85% HCO <sub>2</sub> H + HCO <sub>2</sub> NH <sub>4</sub>	100	5	87

a: In every cases 2 mol% of catalyst is used; 5 mol and 2 mol equiv. of ammonium formate was used for entries 2-3 and 5-11, respectively in 10 ml of solvent. b: isolated yield after chromatographic purification. NR: no reaction.

formate is activating the decomposition of formic acid, so that nickel hydride formation is facilitated which in turn helps transfer of hydrogen to carbonyl compounds. Another important observation is that the reaction proceeds with excellent yield in 85% formic acid and ammonium formate. But further increase of water content (60% formic acid, entry 7, **Table 2**) led to no reaction at all. The reaction fails in the absence of catalysts for both the cases.

In conclusion, we have shown that macrocyclic nickel complex (I) acts as an excellent catalyst for the chemoselective transfer hydrogenation of carbonyl functions.

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