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Applications of imino-pyridine Ni(II) complexes as catalysts in the transfer hydrogenation of ketones

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ABSTRACT

Five imino-pyridine Ni(II) complexes: $[\{Ni(L1)Cl_2\}_2]$ Ni1; $[\{Ni(L2)Cl_2\}_2]$ Ni2; $[\{Ni(L3)Cl_2\}_2]$ Ni3; $[\{Ni(L4)Cl_2\}_2]$ Ni4 and $[Ni(L5)_2Cl_2]$ Ni5 derived from ligands 2,6-diisopropyl-N-[(pyridin-2-yl) methylene] aniline (L1); 2,6-diisopropyl-N-[(pyridin-2-yl) ethylidene]aniline (L2); 2,6-dimethyl-N-[(pyridin-2-yl) methylene] aniline (L3); 2,6-dimethyl-N-[(pyridin-2-yl) ethylidene] aniline (L4) and N-[(pyridin-2-yl) methylene] aniline (L5) were evaluated as catalysts in the transfer hydrogenation of ketones. The Ni(II) complexes demonstrated moderate catalytic activities giving a turnover number (TON) of up to 126 at catalyst loading of 0.5 mol%. The structure of the complexes and nature of ketone substrate influenced the catalytic activities of the complexes. Deactivation studies using mercury and sub-stoichiometric poisoning experiments pointed to the presence of both Ni(0) nanoparticles and Ni(II) homogeneous as the active species.

1. Introduction

Ni(II) catalysed reactions have occupied a pivotal position in organic synthesis as supported by significant work performed on the design of efficient Ni catalysts in the last two decades [1–4]. In many instances, Ni(II) catalysts have been applied as catalysts in cross-coupling [5], hydrogenation [6], hydrosilylation [7] carbene transfer [8], dehalogenation [9] and olefin polymerisation [10–12] reactions among others. Furthermore, Ni(II) catalysts have demonstrated unique reactivity in facilitating tandem catalytic transformations [13]. Transfer hydrogenation of ketones is an important transformation, due to the production of industrially valuable feedstocks, fine chemicals and biologically active compounds [14,15]. These transfer hydrogenation reactions are traditionally catalysed using the more expensive Ru(II) complexes [16]. This has posed serious challenges in the industrial commercialization and applications of these systems due to their high level of toxicity and cost of establishment [17,18]. Thus significant amount of research efforts have been directed towards the design and development of relatively cheaper metals catalysts such as Fe(II) [19], Mn(II) [20], Co(II) [21] and Ni(II) [22]. It is therefore not surprising that Ni(II) complexes have emerged as promising catalysts in these reactions, due to their ease of preparation and relatively cheaper costs [12,22].

To date, few Ni(II)-based catalysts have been developed and applied in the transfer hydrogenation of ketones. Notable among them include the nickel complex [(dcype)Ni(COD)] derived from (1,2-bis(dicyclohexyl-phosphine)ethane and 1,5-cyclooctadiene) reported by Castellanos et al. and found to have a broad scope of substrates activity. In addition, these catalysts display moderate catalytic activities of up to 99% yield within 98 h at catalyst loadings of 2 mol% [23]. Recently, N-heterocyclic carbene Ni(II) complexes displaying catalytic activities of up to 99% within 4 h in the transfer hydrogenation of ketones have also been reported by Bala and co-workers [24]. Although appreciable efforts have been harnessed in the development of more efficient catalysts for transfer hydrogenation of ketones, it is apparent that less attention has been paid to the application of Ni(II) imino-pyridine complexes in the recent past years. Inspired by our recent reports using similar imine Ni(II) complexes in asymmetric transfer hydrogenation of ketones, [22], we herein report the applications of readily available and affordable dinuclear imino-pyridine Ni(II) complexes developed by Laine et al [25] as catalysts in the transfer hydrogenation of ketones (Fig. 1). The steric and electronic effects of the complex structure, substrate scope as well as deactivation profiles in the transfer hydrogenation of ketones are hereby discussed.

2. Results and discussion

Complexes Ni1 – Ni5 (Fig. 1) were prepared following literature procedures [22]. Detailed synthetic protocols of both the ligands, the complexes and their respective spectral data are provided

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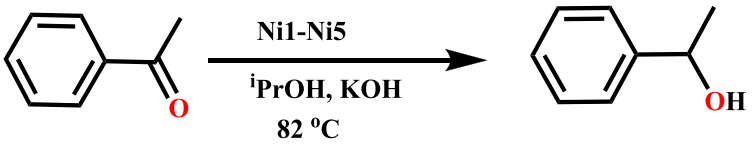
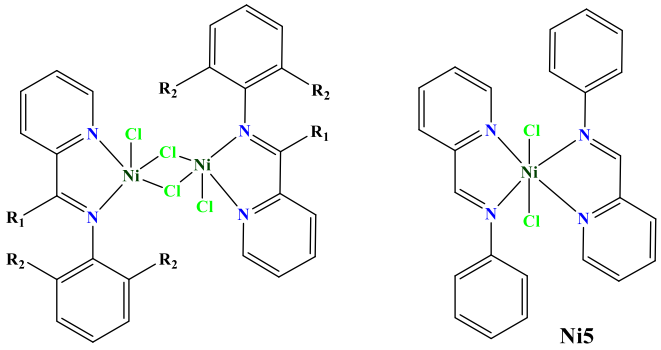
Table 1
Preliminary data of complexes Ni1-Ni5 in the TH of acetophenone[a]



Entry	Complex	Time (h)	[b]Conversion [%]	[c]TOF/h^{-1}
1	Ni1	32	66	2.06
2	Ni2	32	72	2.25
3	Ni3	32	75	2.34
4	Ni4	32	76	2.38
5	Ni5	32	82	2.56

[a] Conditions: acetophenone, (0.23 mL, 2.00 mmol); catalyst, (0.02 mmol, 1.0 mol%); KOH, (5.00 mL of 0.40 M, 2.00 mmol) in 2-propanol); time = 32 h; temperature, 82°C.
[b] Determined by ^{1}H NMR spectroscopy.
[c] TOF =Turn Over Frequency (mmol. of substrate consumed)/(mmol of catalyst x time in h). Percentage conversion is comparable to the yield of 1-phenylethanol.



R_1=H, **R_2**=iPr; **Ni1, R_1**=CH_3, **R_2**=iPr; **Ni2;**
R_1=H, **R_2** = CH_3; **Ni3; R_1**=CH_3, **R_2**=CH_3; **Ni4**

Fig. 1. Structure of Ni(II) complexes Ni1-Ni5 used as catalysts in this study.

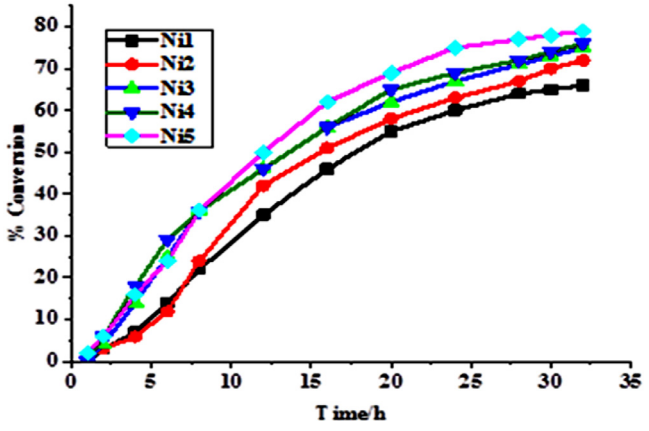
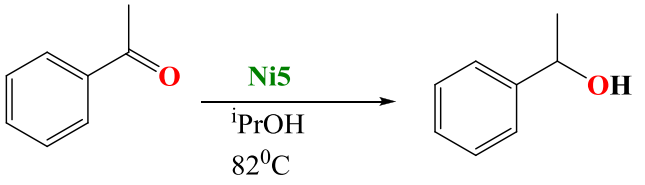


Fig. 2. Conversion vs time graph showing reaction profile of Ni-Ni5 in transfer hydrogenation of acetophenone.

as supplementary materials (Figs. S1 – S24). All the complexes (Ni1 - Ni5) were preliminarily evaluated as catalysts using molar ratio of 100/100/1 for ketone/KOH/catalyst and acetophenone as the model substrate (Table 1). The percentage conversions of the ketone substrate to their respective alcohol products were monitored using ^{1}H NMR spectroscopy (Figures. S29-S33). All the complexes (Ni1-Ni5) showed moderate catalytic activities in the transfer hydrogenation of acetophenone to 1-phenylethanol, giving conversions between 66% - 82% (Table 1 and Fig. 2). In terms of kinetics of the reactions, catalysts Ni1-Ni5 complexes demonstrated significant conversions within the first 5 h, after which the kinetic profiles slowed down (Fig. 2). For instance, complex Ni5 furnished a conversion of 25% corresponding to TOF of 5.00 h^{-1} within 4 h, after the rate of the reaction declined. These kinetic profiles may be due to the original homogeneous nature of the complexes at the onset of the reactions and subsequent transformation of homogeneous active species to Ni(0) nanoparticles [26]. From Table 1 and Fig. 2, it was apparent that the ligand backbone of the complexes conferred a significant impact on the performance of the resultant catalysts. In general, complexes bearing less bulky substituents displayed greater catalytic activities as compared to those with bulkier substituents. For instance, complex Ni3, containing the methyl substituent on the phenyl ring (L3), achieved 75% conversions, while complex Ni1, containing the isopropyl substituents, gave conversions of 66% respectively (Table 1 entry 1and 4). This could be ascribed to the high steric effects exhibited by the alkyl substituents around the coordination sphere of the metal, which ultimately limits coordination of the substrate to the metal centre [27]. Indeed, complex Ni5, supported on the unsubstituted ligand L5 was the most active displaying conversions of 82% (Table 1, entry 5). From an electronic perspective, no discernable contribution from the ligand was observed. For instance, the aldimine complex Ni3 and the ketamine analogue complex Ni4 displayed comparable percentage conversions of 75% and 76% respectively. While complexes Ni1- Ni5 compare poorly with some of the most active systems as in trinuclear Ni(II) complexes, as in the case of reports of Bala and co-workers (TOF up to 2000 h^{-1}) [24], they showed comparable catalytic activities to other systems reported in literature [6,23,28–30].

Upon establishing that complexes Ni1-Ni5 show promising catalytic activities in TH of acetophenone, we then investigated the optimum reaction conditions. To achieve this, the effects of catalyst loading, and the role of the nature of base were considered using the most active complex Ni5, was studied (Table 2). From the data, we noted that increasing catalyst loading from 0.5 mol% to 1.0 mol%, increased the percentage conversions from 63% to 82% respectively (Fig. S30). Although an increase in percentage conversion was observed, the TON decreased drastically from 126 and 82 respectively. More significantly, a further increase of the catalyst loading from 1.0 mol% to 1.5 mol%, was marked by a drastic reduction in percentage conversions from 82% (TOF = 2.56 h^{-1}) to 40% (TOF = 0.84 h^{-1}) respectively (Table 2, entries 4 vs 5). Considering the dinuclear nature of complexes Ni1-Ni5, it is expected that the active intermediate is likely to be a mononuclear species (dissociation of the dinuclear pre-catalysts) [20,29]. Thus in this case, the lower catalytic activities reported with the increase in catalyst loading, could be ascribed to a shift in equilibrium

Table 2
Optimization of reaction conditions for effective TH of acetophenone using catalysts Ni5.[a]



Entry	Base	Catalyst loading/mol%	[b]Conversion [%]	[c]TON	[d]TOF/h^{-1}
1	KOH	0.25	39	156	4.88
2	KOH	0.50	63	126	3.94
3	KOH	1.00	82	82	2.56
4	KOH	1.50	40	27	0.84
5	Li_2CO_3	1	55	55	1.71
6	K_2CO_3	1	63	63	1.97
7	Cs_2CO_3	1	49	49	1.53

[a] Conditions: acetophenone, (0.23 mL, 2.00 mmol); KOH, (5.00 mL of 0.4 M, 72 mg, 2.00 mmol) in 2-propanol); temperature = 82 °C, time = 32 h.
[b] Determined by ^{1}H NMR spectroscopy.
[c] TON = Turn over number (mmol. of substrate consumed/mmol. of catalyst) and
[d] TOF = Turn over number (mol. of product/mol. of catalyst x time/h). Percentage conversion equals comparable to the yield of 1-phenylethanol obtained.

towards the inactive dinuclear compounds, in good agreements with the reports of Kalman and co-workers [31]. In addition, the influence of the bases was investigated using K_2CO_3, Li_2CO_3, and Cs_2CO_3 as given in Table 2, entries 5-7. From this study, KOH was found to be the most active, while Cs_2CO_3 displayed the lowest catalytic activity (Table 2, entries 3 and 7). This trend is consistent with the order of stability and strengths of the bases and agrees with the findings reported by van Putten et al. [32].

We then shifted our focus to probe the substrate scope using substituted aromatic and aliphatic ketones under the optimised conditions (Table 3). From the results in Table 3, the introduction of electron-withdrawing substituents at the ortho- or para-positions of the acetophenone derivatives resulted in higher percentage conversions. For example, para-chloroacetophenone attained percentage conversions of 97%, while acetophenone showed percentage conversions of 82% under similar reaction conditions (Table 3, entries 1 and 2). On the other hand, the introduction of electron-donating substituents at either the ortho- or para-position witnessed lower conversions, consistent with our previous reports [17]. For instance, 4-methyl acetophenone achieved conversion of 55% compared to 82% attained for acetophenone (Table 3, entries 1 and 5). The position of either electron-donating or withdrawing groups on the phenyl ring of acetophenone derivatives play a significant role in controlling the conversions of the substrates. For example, para-chloroacetophenone showed conversions of 97% while the analogous ortho-chloroacetophenone gave 90%. This observation could be attributed to the inductive effect which ultimately decreases electron density on the carbonyl carbon resulting in greater activity [22]. However, an opposite trend was observed in the case of electron-donating groups. For example, higher conversions of 59% was recorded for 2-methyl acetophenone, compared to conversions of 50% obtained for 4-methyl acetophenone substrate. This observation agreed with the earlier findings of Wang and co-workers, where 4-methylacetophenone gave conversions of 64%, compared to conversions of 67% recorded for 2- methyl acetophenone [29].

Significantly, the complexes also catalysed the transfer hydrogenation of heteroaryl ketones substrates, for instance, 2-acetylpyridine, giving conversions of 66% (Table 3, entry 6). The use of heterocyclic ketones as in 2-acetylpridine, expectedly [17] resulted in lower percentage conversion of 66% (Table 2, entry 6). Similarly, fused aromatic and aliphatic ketone substrates

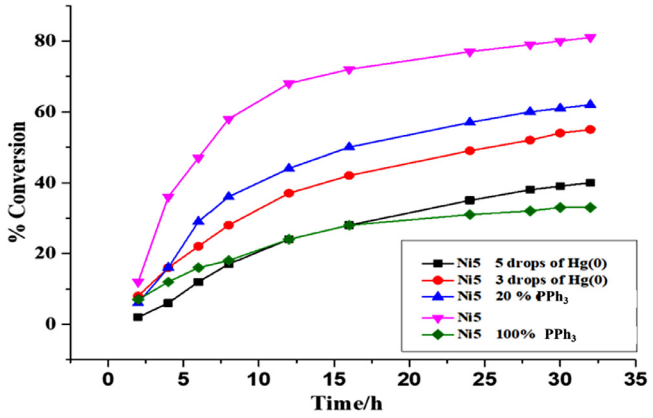


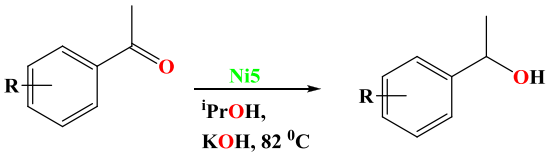
Fig. 3. The plot of conversion vs time in the showing TH of acetophenone using complex Ni5 in the presence of Hg(0) and phosphine poisoning agents.

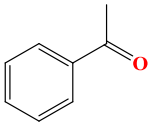
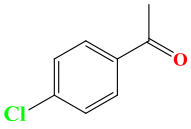
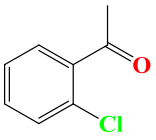
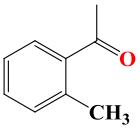
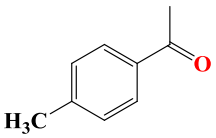
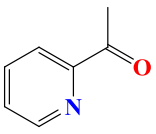
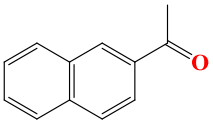
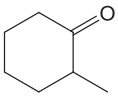
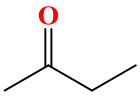
(Table 3, entries 7 - 9) displayed lower conversions, when compared to the acetophenone substrate. This trend is common and has been reported by for example Azouzi et al. [33] and Huo et al. using Fe(II) chiral catalysts [34].

In order to gain insight into the nature of the active species, we attempted to investigate the homogeneity or formation of active heterogeneous Ni(0) nanoparticles using Hg(0) and sub-stoichiometric poisoning tests [34–35]. For mercury poisoning tests, 3 or 5 drops of Hg(0) was added at the onset of the reaction to a solution of the catalyst, Ni5 and KOH in ^{i}PrOH and refluxed at 82 °C in the presence of acetophenone substrate. From Fig. 3, a significant reduction in the percentage conversions of catalyst Ni5 was observed, thus implicating the presence of active Ni(0) nanoparticles in the reaction mixture [35]. It is also important to note that the addition of 5 drops of Hg(0) resulted in a further drop in percentage conversion (Fig. 3) consistent with previous findings [26,35].

To confirm the results from the mercury poisoning experiments, we further conducted sub-stoichiometric poisoning tests by adding 20% and 100% mol. equivalent of PPh_3 (with respect to the amount of catalyst) to the catalyst solution. Indeed, From Fig. 3, we observed a decrease in the percentage conversions in both cases. For example, using 20% PPh_3, conversions of 62% compared to 82%

Table 3
Transfer hydrogenation data of ketone substrate scope study using complex Ni5[a]



Entry	Substrate	[b]Conversion[%]	[d]TOF/h^{-1}
1		82	2.56
2		97	3.09
3		90	2.81
4		59	1.84
5		55	1.72
6		66	2.06
7		60	1.88
8		61	1.90
9		52	1.62

[a] Conditions: acetophenone, (0.23 mL, 2.00 mmol); catalyst, Ni5 (6.12 mg, 0.02 mmol, 1 mol%); KOH, (5.00 mL of 0.4 M, 2.00 mmol) in 2-propanol); temperature, 82°C, time 32 h.
[b] Determined using ^{1}H NMR spectroscopy.
[d] TOF = (mmol. of substrate consumed)/(mmol. of catalyst x time/h).

in the original reaction was reported. At 100% PPh_3 equivalent, a pure heterogeneous catalyst is expected to undergo complete deactivation [36,37]. However, in our case, about 40% conversion was recorded within 32 h (Fig. 3). The incomplete deactivations observed for Hg(0) and PPh_3 poisoning experiments, thus point to the presence of both homogeneous Ni(II) and Ni(0)-nanoparticle as the active species [35].

3. Conclusions

In conclusion, a series of imino-pyridine Ni(II) dinuclear complexes were successfully evaluated as catalysts in the transfer hydrogenation of ketones. The complexes demonstrated moderate catalytic activities, controlled by the nature of the coordinated ligand and reaction conditions. The complexes catalyzed a wide range of ketone substrates including aromatic, aliphatic and hetero-aryl ketones. Deactivation studies pointed to the presence of both homogeneous Ni(II) and Ni(0) nanoparticles as the active species. Thus, in this contribution, we report a relatively facile, easily accessible and cheaper Ni(II) catalyst in the transfer hydrogenation reactions which could form a viable platform to the design of affordable catalysts for the transfer hydrogenation reactions.

4. Experimental section

4.1. Materials and instrumentation

The synthetic protocols, unless otherwise mentioned, were performed under N_2 gas standard Schlenk or vacuum line techniques. All other chemical reagents including 2-pyridinecarboxaldehyde (99%), 2-acetylpyridine (≥99%), 2,6-diisopropylaniline (97%), 2,6-dimethylaniline (99%), $NiCl_2$ (98%), 2-propanol (≥99.5%), para-toluene sulfonic acid monohydrate (p-TsOH) (≥99.9%), acetophenone (≥99.99%), potassium hydroxide, potassium tert-butoxide, Cs_2CO_3, 1-acetonaphthone (≥ 99.99%), 2-chloroacetophenone (≥ 99.99%), 2-methylacephenone (≥ 99.99%), 4-methyl-2-cycloactephenone (≥ 99.99%),2-hydroxy acetophenone(≥ 99.99%), 4-chloroacetophenone (≥ 99.99%), and 4-methylacetophenone (≥ 99.99%), triphenylphosphine (PPh_3) (≥ 99.99%), mercury (Hg(0)), were all purchased from Sigma-Aldrich. Solvents including deuterated NMR solvents were stored in a desiccator. ^{1}H NMR and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on a 400 MHz Bruker Ultra shield NMR spectrometer in $CDCl_3$ solvent. The infrared spectra were recorded on a Perkin Elmer, Spectrometer 100. LC Premier micro-mass Spectrometer model LC-MS-2002 was used for mass spectral analyses. Micro-analyses were performed on a Thermal Scientific Flash 2000. The magnetic moments were determined using Evans balance (Sherwood MK-1).

4.2. General procedure for transfer hydrogenation of ketones

The catalytic transfer hydrogenation of ketones was performed in two-necked round bottom flasks connected to a reflux condenser. In a typical experiment, acetophenone (0.23 mL, 2.00 mmol), a solution of 0.4 M of 5.00 mL of KOH in iPrOH and the respective Ni(II) complex (0.02 mmol, 1.00 mol %) was refluxed at 82 °C. During the reaction, about 0.1 mL of the reaction mixture was withdrawn at regular time intervals and analyzed for percentage conversion and yield using ^{1}H NMR spectroscopy. The relative signals of the methyl group of acetophenone (2.50-2.60ppm) and methyl signal of 1-phenylethanol (1.49 ppm) of the products were used to calculate the respective percentage conversions.

4.2.1. Mercury poisoning experiment

The mercury poisoning experiment according to the general procedure described in section 3.2. In this experiment, a solution of acetophenone (0.23 mL, 2.0 mmol), complex Ni5 (12 mg, 0.02 mmol, 1.00% mmol), and a solution of 0.4 M of 5.00 mL of KOH in iPrOH and 3 and 5drops of Hg(0) drops were introduced and refluxed for 32 h. During the reaction period, about 0.1 mL of the reacting mixture was sampled at regular time intervals, cooled, and percentage conversion determined using ^{1}H NMR spectroscopy.

4.2.2. Sub-stoichiometric poisoning experiments

Acetophenone (0.23 mL, 2.0 mmol), Ni5 (12.40 mg, 0.01 mmol, 1 mmol%), a solution of 0.4 M of 5.00 mL of KOH in iPrOH, and triphenylphosphine, PPh_3 (20% and 100% equivalent) were refluxed at 82 °C for 32 h. During this period, about an appropriate amount of the sample was withdrawn at regular time intervals and analysed for percentage conversion using ^{1}H NMR spectroscopy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Nokwanda Tsaulwayo: Data curation, Investigation, Methodology. **Robert.T. Kumah:** Data curation, Investigation, Software, Validation, Writing - original draft. **Stephen.O. Ojwach:** Conceptualization, Supervision, Resources, Funding acquisition, Writing - review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.129987.

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