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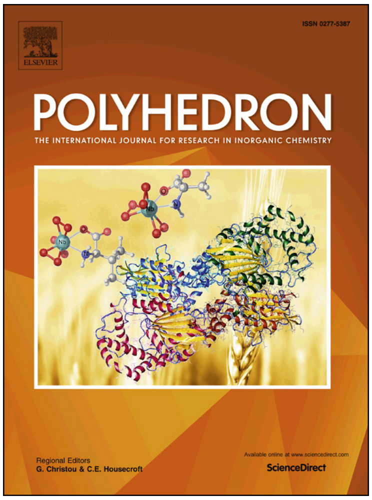

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Symmetric triazolylidene Ni(II) complexes applied as oxidation catalysts

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Abstract

A set of related Ni(II) complexes of *N*-heterocyclic carbene ligands (NHC) [*trans*-$X_2Ni(NHC)_2$] (X= Cl, I) bearing linear straight chain alkyl wingtip substituents have been synthesized and fully characterized. Single crystal XRD data revealed symmetrically aligned Ni(II) centres within square planar coordination of trans halide, trans NHC ligands. The complexes were used for the catalytic oxidation of alkanes under mild conditions in conjunction with tert-butyl hydroperoxide as an oxidant. Under optimized reaction conditions, the catalytic results pointed to good activities of circa 15 and 19% for cyclohexane and *n*-octane respectively. Furthermore, the catalytic systems are shown to be very efficient for the oxidation of linear alcohols to corresponding ketones.

Keywords: NHC ligand; Ni complexes; Oxidation catalysis, n-Octane; Cyclohexane.

Introduction

The direct, catalytic oxidation of alkanes into value-added products under mild reaction conditions is a topic of great interest to academia and industry. This is due to the immense potentials of the functionalised products as building blocks for the pharmaceutical, petrochemical and fine chemicals industries.[1-8] However, the direct, selective catalytic activation and oxidative functionalisation of alkanes to alcohols has to date remained a challenge to researchers worldwide. Recently, considerable effort is directed towards the catalytic oxidation of alkanes in homogeneous solutions using earth-abundant first-row transition metals that include Ti[9], [10], V[11], Mn[5], Fe[12-14], Co[15], Ni[16, 17] and Cu[7, 18]. These have become much more attractive in comparison to late and noble transition metals which until recently have dominated this sphere.

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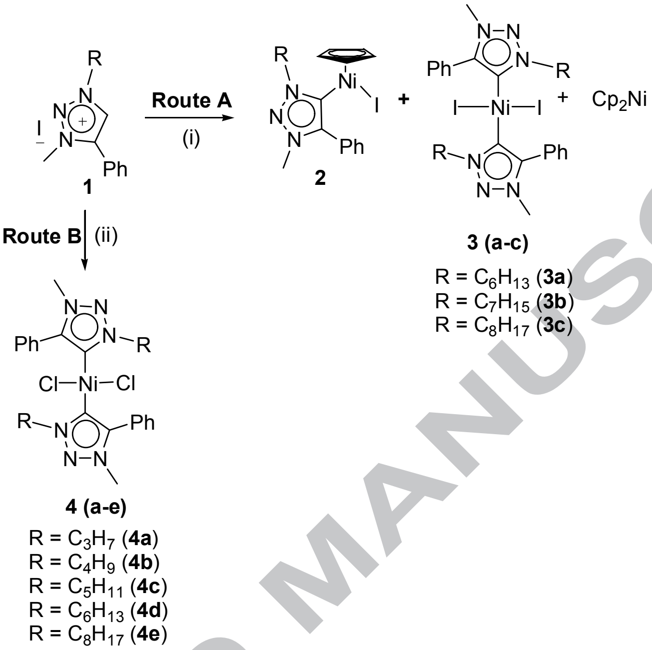
Increased interest in first-row transition metals in catalysis is due to obvious advantages, which include high abundance, low price, low or no toxicity and unique or unusual catalytic characteristics. This work is part of an ongoing study on the use of cheap, bio-compatible metals such as Fe, Co and Ni for the catalytic oxidation of alkanes as a biomimetic strategy aligned to simulate the high efficiencies of monooxygenase enzymes such as cytochrome P450 [12, 13, 15, 27, 28].

Since the first isolation of a stable, free *N*-heterocyclic carbene (NHC) [19], metal complexes with NHC ligands have increasingly found application in homogeneous catalysis.[20-23] The strong σ-donating effects of the NHC ligands toward metal centres make them good candidates for the stabilization of metal ions during catalysis. In this regards, non-toxic and easy to prepare Ni-NHC complexes are now widely used instead of the well-established but more expensive d^8 homologues Pt and Pd.[24-26]. In many instances, the steric and electronic properties of the NHC ligands exert profound effects on the reaction outcome.[13, 27] Hence, herein we present one of the first use of Ni-NHC pre-catalysts for the oxidative functionalisation of a variety of saturated substrates under mild reaction conditions. We envisage that the introduction of hydrophobic alkyl chain groups as wingtip *N*-substituents in the catalyst structure will positively influence its interaction with hydrocarbon substrates for the preferential and selective functionalisation of the latter.

Results and discussion

All the triazolium iodide ligand precursor salts (Scheme 1) were synthesised via the standard "click" 2+3 cycloaddition reactions of organic azides and phenylacetylene followed by subsequent methylation with MeI. Their full characterisation and synthesis details are available in the literature.[13, 29-30] At the beginning of this project, we adopted the method of Nolan and co-workers for the synthesis of NHC-Ni(II) complexes from labile nickelocene (Cp_2Ni).[31] But, we soon realised that the direct reaction of triazolium salts with Cp_2Ni at high temperatures (Route A, Scheme 1) yielded a mixture of products, i.e. the monoNHC products (**2**), the intended products (**3**) and recoverable quantities of unreacted Cp_2Ni. Whilst such attempts proved to be successful, however only low yields (ca. 10%) of some (**3a-c)** of the targeted products were isolated after difficult workup procedures. Therefore, this route is synthetically inadequate for the preparation of pre-catalysts required in relatively good quantities for full analysis and further studies. We then explored the alternative metalation method (Scheme 1, Route B) that was recently reported by Astakhov *et al.*,[32] whereby reaction of an *in situ* generated triazolylidene ligand with anhydrous $NiCl_2$-DME in dry acetonitrile resulted in the exclusive formation of the bis(NHC) complexes **4a-e**.



Scheme 1: Synthesis of Ni-NHC complexes. (i) Cp_2Ni,THF, 80 °C (ii) $NiCl_2$-DME, MeCN TEA, 80 °C.

All the complexes were fully characterized by ^1H-, ^{13}C-NMR, HRMS and EA. NMR spectral data of the compounds synthesised via Route B indicate that the complexes were exclusively obtained as the *bis*NHC versions with no contamination of any side products as observed via Route A (Scheme 1). Isolated yields were much improved from very poor to moderate and high (50-72%). In general, ^1H-NMR resonances for the *N*-alkyl substituents for all the complexes were observed as expected resonating as upfield multiplet signals (0.5 to 4 ppm), whilst resonances integrating to 10H between 6.35 and 8.92 ppm accounted for the aromatic C4-substituents of the ligands, thus signifying a symmetric coordination of the NHC ligand platform. In the ^{13}C-NMR spectra of all the complexes (both series **3** and **4**), resonances at δ 146-149 ppm represents the characteristic metal-carbene (Ni-$C_{carbene}$) bond which is a clear indication of NHC coordination to the metal centre via the carbene C5 atom.

Further confirmation of the structural integrity of the complexes was obtained from X-ray diffraction analysis of single crystals of compounds **3a-c** (Figs. 1-3). Only single crystals suitable for XRD of the diiodido versions of the complexes were isolated. All the structural data showed that each complex contains a symmetric Ni(II) center within a square planar coordination of trans halide, trans NHC ligands. This is consistent with the fact that **3a-c** crystallised in the centrosymmetric *P*-1 space group of the triclinic crystal system. The key structural highlight for these compounds is the centre of inversion at each Ni that is located at the corners and face edges of their unit cells. All the *N*-alkyl chains are linearly oriented away from each other to minimise steric interactions. All the key crystallographic parameters are standard and no major deviations were noted, for example, the Ni–I distances [2.50406(15) , 2.49400 and 2.4914(2) Å for **3a-c** respectively] and the $\mathrm{C_{carbene}}$-Ni(1)-$\mathrm{C_{carbene}}$ angles [180.00] are consistent with those reported for similar compounds.[32] For complex **3b**, the heptyl *N*-substituent of the NHC ligand showed strong anisotropic atomic displacements during refinement, suggesting a statistical positional disorder that was taken into account for the final model (Fig. 2).

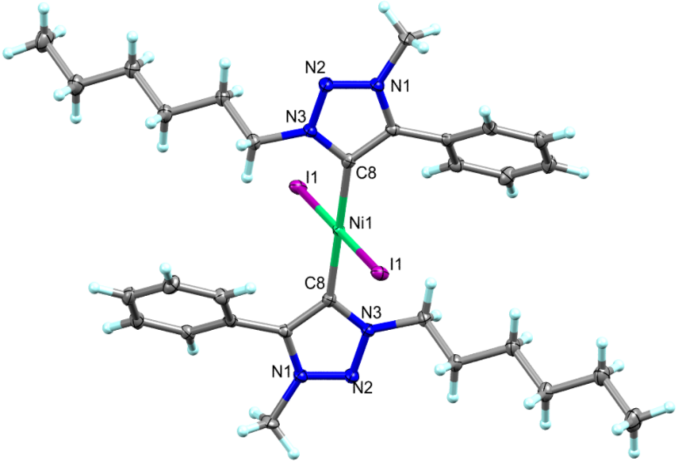


Fig. 1: Molecular structure of complex **3a** with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni(1)–C(8) 1.909(2), Ni(1)–I(1) 2.504(6), C(8)-Ni1-C(8) 180.00, I(1)-Ni(1)-I(1) 180.00, C(8)–Ni(1)–I(1) 88.65(5).

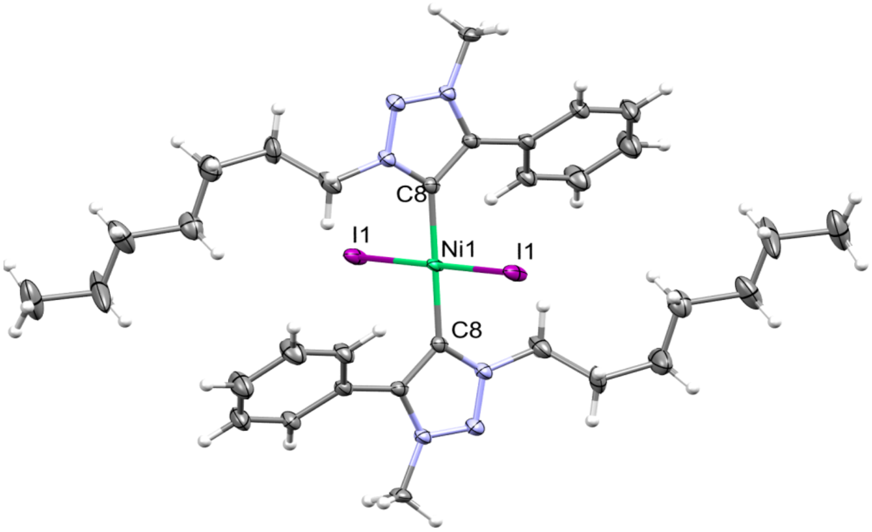


Fig. 2: Molecular structure of complex **3b** with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni(1)–C(8) 1.907(2), Ni(1)–I(1) 2.494 (7), C(8)-Ni1-C(8) 180.00, I(1)-Ni1-I(1) 180.00, C(8)–Ni(1)–I(1) 88.76(7).

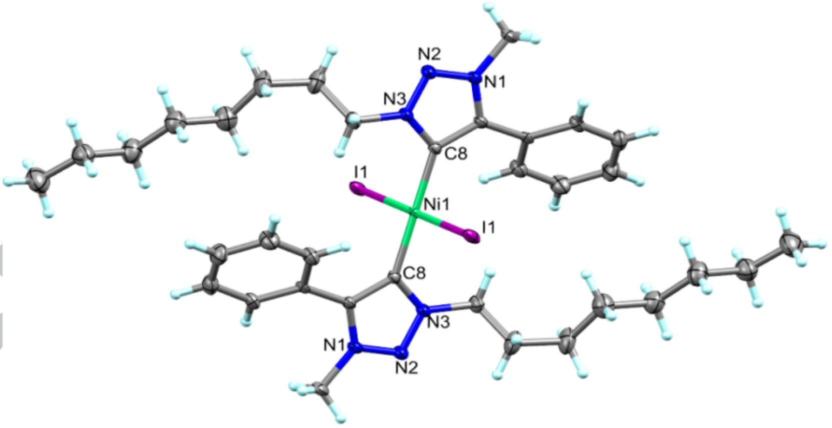


Fig. 3: Molecular structure of complex **3c** with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni(1)–C(8) 1.907(3), Ni(1)–I(1) 2.491(2), C(8)-Ni1-C(8) 180.00, I(1)-Ni1-I(1) 180.00, C(8)–Ni(1)–I(1) 88.65(5).

Electrochemistry

The continued success of NHCs as ancillary ligands in organometallic chemistry and homogeneous catalysis is largely due to the seemingly endless possibility for researchers to fine-tune the steric and electronic properties of complexes via azolium ring and wingtip variations, which routinely alter the topography around metal centers. In many regards, variations in electronic properties of organometallic catalysts usually have the greater influence on their catalytic activity, which could be probed using cyclic voltammograms (CV). Hence, we have determined the CV of compounds **4a-e** as a very convenient technique to observe the impact of changes in electronic properties around the Ni(II) metal centres with subtle changes in ligand architecture. The result presented in Fig. 4 and summarised in Table 1 shows the relative electrochemical responses recorded in DCM/MeCN.

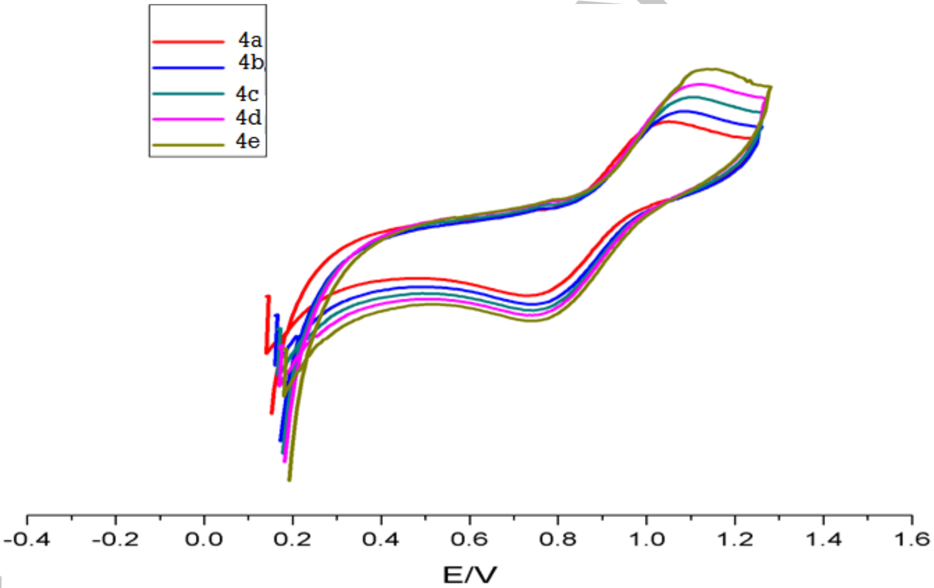


Fig. 4: Comparison of the electrochemical response of **4a-e** probed by CV.

Table 1: Electrochemical data[a] of Ni-NHC complexes in DCM/MeCN solution at 25 °C.

Complex	$E_{1/2}$ (CV) [V]
4a	0.829
4b	0.831
4c	0.832
4d	0.833
4e	0.835

[a] Potential measured vs Ag/AgCl (0.004m, 0.1 M NBu_4BF_4) in 2 mM DCM/MeCN solutions at a scan rate of 100 mV s^{-1}.

All the compounds showed reversible oxidation responses circa 0.832 V which correlates well with findings in the literature which according to Crabtree et al. corresponds to the $Ni^{II/III}$ oxidation wave.[33-34] The influence of the wingtip alkyl *N*-substituents (-R, Scheme 1) is conveniently evaluated by comparing half wave potentials ($E_{1/2}$) of **4a-e**. Noteworthy, is the fact that increase in the length of the alkyl substituents had a negligible influence on the values of the oxidation potentials. This perhaps indicates that any differences in catalytic activities of the complexes will largely be due to structural and geometric changes rather than any major deviations in electronic properties.

Oxidation of *n*-octane

The oxidative functionalisation of *n*-octane is arguably the most attempted amongst straight chain alkanes due to the fact that is it a mid-range substrate with properties intermediate between those of light alkanes (gases that are difficult to handle and requiring specialised equipment for handling) and heavy alkanes (waxes that are difficult to oxidise under mild conditions). Hence, activities of the two sets of complexes were explored in the oxidation of *n*-octane with the results presented in Table 2.

Table 2: Ni(II) complexes promoted catalytic oxidation of *n*-octane.[a]

Catalyst	**Conversion (%)**	**Product distribution (%)**[b]			
		octanones (4-;3-;2-)	**octanols (4-;3-;2-;1-)**	**octanal**	**octanoic acid**
$NiCl_2$	6	71 (12;31;28)	27 (8;12;7;0)	2	0
3a	8	43 (5;15;23)	46 (4;15;20;7)	7	4
3b	9	41 (6;14;21)	53 (7;17;21;8)	6	0
3c	11	39 (7:14:18)	57 (5:19:23:10)	4	0
4a	16	59 (8:18:33)	31 (4;10;15;2)	4	6

4b	16	57 (8;17;32)	34 (4;11;15;4)	4	5
4c	17	52 (6;18;28)	40 (3;11;21;5)	4	4
4d	19	48 (7;16;25)	45 (5;12;21;7)	5	2
4e	19	44 (4;16;24)	48 (6;15;22;5)	5	3

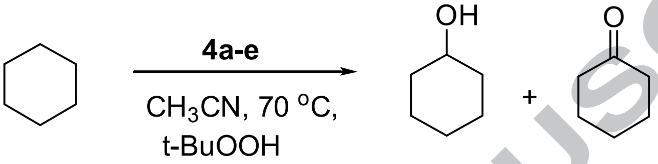
[a]Conditions for all reactions: solvent (MeCN) = total vol. 5 mL; *n*-octane = 1 M; oxidant (tBuOOH) =14 M equivalent; catalyst = 1 mM ; 80 °C; 12 h. [b] Total conversion based on product formed = [products]/[initial conc. of substrate]$_o$ x 100. Selectivity (%) towards ketone formation = molar amount of ketone/total molar amount of products (alcohol and ketone) x 100. Conversion data are averaged over two runs that agree within ±5%.

Optimisation and control studies at lower temperatures showed low substrate conversions and in the absence of a catalyst and/or oxidant, the results showed 0% conversion of the substrate. Control reactions utilising the $NiCl_2$ precursor salt as catalyst resulted in circa 6% conversion of *n*-octane. Screening of the diiodido complexes (**3a-c**) under optimised conditions showed low catalytic activities (8, 9 and 11% respectively) that are generally less than the dichlorido analogues **4a-e**. This is in agreement with the ease of dissociation of the iodide ligand as compared to lighter halogens in the presence of coordinating solvents such as acetonitrile to form cationic complexes that interact poorly with alkanes. Hence, the oxidation of *n*-octane with catalysts **4a-e** produced up to 19% substrate conversion to a mixture of isomeric alcohols and ketones. Also, compared to the $NiCl_2$ control reaction, the improved substrate conversion is indicative of the influence of coordinated NHC ligands on the Ni(II) catalysts. The influence of the wingtip *N*-substituents on the catalytic results is minimal but noticeable with total conversion showing gradual increase (16% for **4a** vs 19% for **4d-e**) as the length of the substituent increased, which tallies with the CV data discussed earlier. In addition, the pattern of product distribution follows this trend with an increase in alcohol production with increase in *N*-alkyl chain length. Furthermore, in all sets of catalysts, C(2) products (mainly 2-one) dominated while the terminal C(1) position is the least reactive and the catalysts are more reactive to internal carbons in general.

Oxidation of cyclohexane

In the application of complexes **4a-e** as catalysts for oxidation catalysis, the oxidation of cyclohexane was tested due to the importance of the product [ketone-alcohol (K-A oil)] as a feedstock to the polymer and allied industry.[35-36] Cyclohexane to oxidant ratio of 1:14 and 12h reaction time was adopted for all the studies reported in Table 3. As expected, K-A oil was the main product with varying compositions of the ketone and alcohol in the mixture depending on the catalyst used.

Table 3: Peroxide promoted catalytic oxidation of cyclohexane based on catalysts **4a-e**.[a]



Entry	Catalyst	Conversion (%)	Ketone (K) (%)	Alcohol (A) (%)	K/A
1	**4a**	15	78	22	3.5
2	**4b**	15	69	31	2.2
3	**4c**	14	71	29	2.4
4	**4d**	14	61	39	1.6
5	**4e**	12	59	41	1.4

[a]Conditions for all reactions: Conditions for all catalytic reactions: same as Table 1. Total conversion based on product formed = [products]/[initial conc. of substrate] x 100. Selectivity (%) towards ketone (or alcohol) formation = molar amount of ketone (or alcohol)/total molar amount of products (alcohol and ketone) x 100.

The results suggest that the catalysis is insensitive to variations in the catalyst structure with total maximum conversion of 15%. This is not entirely surprising considering that the substrate is linearly planar and was unaffected by the subtle variations in the NHC ligands' architecture. Hence, the total conversion of the substrate and the relative ketone/alcohol (K/A) ratio remained essentially the same. In addition, cyclohexanone is the more dominant product in all the systems tested with K/A values decreasing as the wingtip alkyl chain size increased. However, in comparison, catalysts **4a-e** are slightly more active on *n*-octane than cyclohexane.

Oxidation of alcohols

Previous reports [4-7, 13, 18] have affirmed that alcohols are the primary products of alkane oxidation. It was proposed that overoxidation of the primary products led to the domination of ketones as the final products often observed in many homogenous alkane oxidation reactions. In an effort to shed more light on this phenomenon, we tested a number of alcohols (1-, 2-, 3- and 4-

octanol) towards further oxidation under the same conditions utilised for the *n*-octane oxidation reactions (*vide supra*). These new substrates are the primary and only products expected in the direct oxidation of *n*-octane if there is no overoxidation with complex **4a** (the most effective in the production of ketones, Tables 2 & 3). The results presented in Fig. 5 confirm that accumulation of ketones is gradual and time dependent; with a maxima at circa 12 h reaction time. In general, the 2- and 3- octanones accumulated more readily with conversions of 72 and 63% respectively at 12 h. This is in agreement with the product profile in Table 1 for the direct oxidation of *n*-octane and also supports many reports that indicate the C(2) position as the most reactive site in *n*-octane oxidation.[15, 37-41]

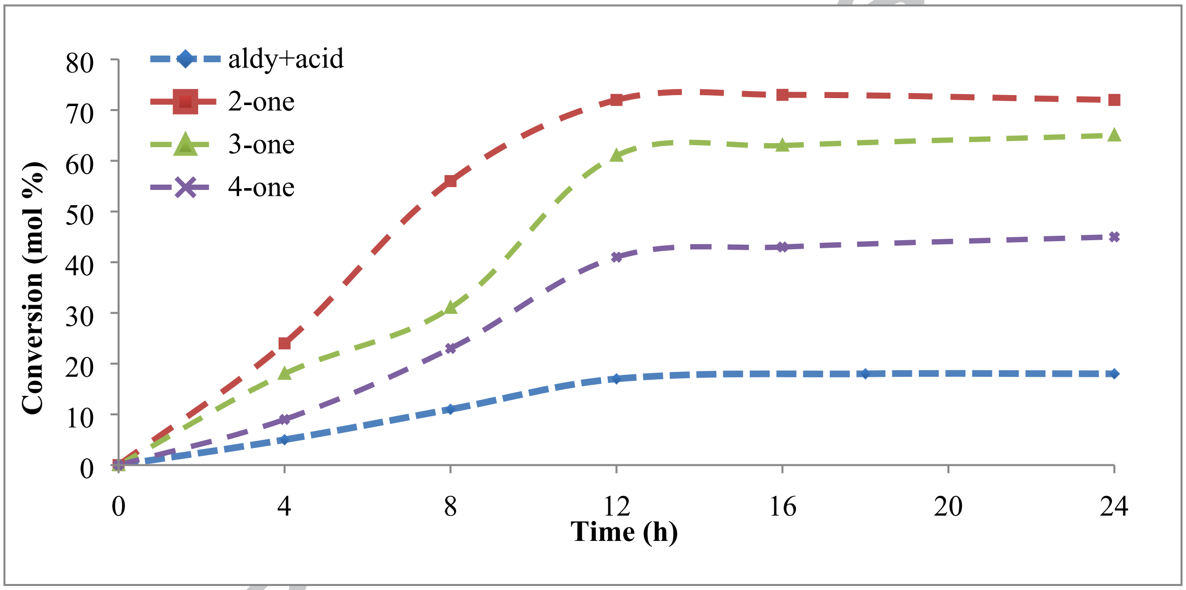


Fig. 5: Peroxide promoted catalytic oxidation of alcohols (1-, 2-, 3- and 4- octanol) utilising complex **4a** as catalyst. Conditions for all catalytic reactions: same as Table 1.

Mechanistic considerations

The addition of a stoichiometric amount of a radical scavenger (diphenylamine, PH_2NH) to the most active alkane oxidation mixture retarded (6% yield) the reaction. [42-43] This is not surprising as it conforms to well-established reports in the literature [44-47] that identified the formation of alkyl(hydro)peroxo radicals as the main pathway to the formation of mainly alcohol and ketone products in the oxidation of paraffin substrates with peroxide oxidants. In the systems reported herein, we propose that the oxidation process proceeded via a Fenton-like mechanism involving reactive Ni(II) species stabilised by the NHC ligands. In particular, Hikichi and coworkers [47] have reported on a Ni(II) alkylperoxo complex [Ni^{II}(OOtBu)Tp^{iPr2}] generated in the presence of tBuOOH for the oxidation of cyclohexane with cyclohexanone as the major product. On the basis of which they proposed involvement of the Ni(II) alkylperoxo radical in the reaction.

Perspectives on nickel based alkane oxidation catalysis

There are very few reported examples of Ni-catalysed oxidation of especially straight chain alkanes under mild reaction conditions. Catalytic oxidation of cyclohexane is the most reported subject in this field; hence, Table 4 summarises comparable catalytic systems based on cyclohexane. Due to variability in the reporting of productivity data, some of the results presented in Table 4 were normalised to the catalyst concentration and expressed in units of turnover numbers (TON) or conversion (%) for ease of comparison.

Table 4: A comparison of the catalytic activities of Ni catalysts for the oxidation of cyclohexane.

Entry	Catalyst[a]	Reaction conditions Solvent/Temp/Oxidant	Conv.[b]	TON[c]
1	Complex **4a**	ACN/ 80°C/ *t*BuOOH	15	150
2[d]	$[Ni(TPA)(CH_3CN)_2](BPh_4)_2$	DCM:ACN/ RT/ *m*-CPBA	14.9	149
3[e]	$[Ni_2(TPA)_2(\mu\text{-}NO_3)_2](BPh_4)_2$	DCM:ACN/ RT/ *m*-CPBA	8.6	656
4[f]	Ni(Tp)	DCM/ 40°C/ *m*-CPBA	0.72	234
5[g]	$[Ni(L)(CH_3CN)_2](BPh_4)_2$	DCM:ACN/ RT/ *m*-CPBA	8.8	622
6[h]	$[Ni(L)(CH_3CN)](BPh_4)_2$	DCM:ACN/ RT/ *m*-CPBA	7.6	533

[a] The most active catalyst from each publication is quoted.

[b] Conv. (total conversion) = moles of products/ moles of cyclohexane x100.

[c] TON = moles of products/ moles of catalyst.

[d] TPA = tris(2-pyridylmethyl)amine.[48]

[e] TPA = tris(2-pyridylmethyl)amine. NO_3 = nitrate, co-ligand.[49]

[f] Tp = hydrotris(pyrazolyl)borate.[51]

[g] L = *N*,*N*-diethyl-*N'*-*N'*-bis(pyrid-2-ylmethyl)ethane-1,2-diamine.[52]

[h] L = N-benzyl-*N'N'*,*N'*-tris(pyrid-2-yl-methyl)-ethylenediamine.[53]

In this work, the most active catalyst proceeded very effectively with total conversion of *circa* 15% with high selectivity to ketone products (78%). A close result was reported by Nagataki *et al.* [48] reported with *m*-chloroperbenzoic acid (*m*-CPBA) promoted by a simple Ni^{II}(TPA) complex at room temperature (entry 2). The catalytic reaction proceeded very effectively with total conversion of *circa* 15% giving higher selectivity to alcohol products (89%) possibly suggesting a different reaction pathway. The same group also reported [49] that introducing NO_3^- as a co-ligand (entry 3) decreased the oxidation reaction (giving total conversion of 8.6%). Similar phenomenon was observed by Hitomi *et al.*[50] using Fe^{II}(TPA) as a catalyst. Hikichi *et al.* [51] have reported catalytic cyclohexane oxidation with *m*-CPBA catalyzed by Ni(II) complexes with hydrotris(pyrazolyl)borate ligands. The catalytic reactions proceeded ineffectively with total conversion of 0.72% mainly aimed at achieving high alcohol selectivity (A/K =32) and TON (234). In a similar vein, Palaniandavar and coworkers [52] used *m*-CPBA catalyzed by Ni(II) complexes with tripodal N4 ligands for which they reported circa 9% conversion of cyclohexane with TON of 622 and an impressive 90% cyclohexanol selectivity. The same group reported even higher selectivity to cyclohexanol (92%) with pentadentate N5 ligands, although the conversion and TON values are lower for these systems (entry 6). [53]

Conclusion

In the present study, highly symmetric square planar Ni(II) NHC complexes were successfully synthesised and fully characterised. Application of the metal complexes as catalysts in alkane oxidation resulted in a mixture of isomeric oxidised products, mainly ketones and alcohols. Based on the results, we conclude that the trends in catalytic activities of the metal complexes are attributable to subtle changes around each Ni(II) centre as a result of NHC ligand structural variations. Thus, for the oxidation of cyclohexane, the observed trend is due to a decline in substrate accessibility to the Ni centres as the size of the geometrically unconstrained alkyl substituents increased from **4a** to **4e**. Whilst for the oxidation of the straight chain substrate *n*-octane, it is most likely due to increased lipophilicity of **4a-e** as the size of the alkyl substituents increased, thereby improving their compatibility with the non-polar substrate. Finally, **4a** was found to be an effective catalyst for the oxidation of alcohols to ketone products, which serves to shed more light on the sequence of the catalytic oxidation of alkanes to the major (ketone and alcohol) products.

Experimental

All solvents were freshly distilled before used. All triazolium salts **1** were prepared as described in published literature. [13, 22-24] All NMR experiments were done using a 400 MHz Bruker ultrashield spectrometer with samples dissolved in deuterated solvents. Chemical shifts (δ) in ppm are reported with respect to tetramethylsilane (TMS) as internal standard.

General procedure for the synthesis of the diiodido Ni(II) complexes (3a-c)

The reported method [31] was modified: To a solution of triazolium salts **1** in THF (15 mL) nickelocene (0.5 equiv) was added. The mixture was stirred at 90 °C for 24 h. All volatiles were removed under vacuum and the residue was extracted with hot toluene (20 mL). The extract was then filtered through a plug of Celite. Combined extracts were concentrated under vacuum and passed through a chromatography column that was eluted with EtOAc/pentane (1:1). Coloured fractions were collected and the second fraction was evaporated to dryness to give analytically pure **3(a-c)**.

Characterisation data:

(**3a**). Yield: 0.081 g (**10** %) of brown-red crystals. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.95 (t, J_{HH} = 7.5 Hz, 6H, 2CH$_3$), 1.40 (m, 4H, 2CH$_2$), 1.91-2.00 (m, 8H, 4CH$_2$), 2.61 (m, 4H, 2CH$_2$), 4.26 (s, 6H, 2CH$_3$), 4.54 (t, J_{HH} = 7.6 Hz, 4H, 2CH$_2$), 7.39-7.79 (m, 10H, 2Ar). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz): δ 15.61, 25.92, 29.60, 35.52, 41.76, 43.43, 54.23, 119.54, 125.69, 126.94, 127.94, 128.06, 128.16, 128.54, 128.69, 128.80, 128.81, 128.98, 129.53, 129.53, 131.88, 148.14. . Anal. Calcd for $C_{30}H_{42}I_2N_6Ni$ (799.19): C, 45.09; H, 5.30; N, 10.52. Found: C, 45.11; H, 5.41; N, 10.53.

(3b) Yield: 0.081 g (**10** %) of red crystals. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.77 (t, J_{HH} =7.5 Hz, 6H, 2CH$_3$), 0.11-1.39 (m, 8H, 4CH$_2$), 2.01 (m, 4H, 2CH$_2$), 3.79 (s, 6H, 2CH$_3$), 4.26 (t, J_{HH} = 7.6 Hz, 4H, 2CH$_2$), 7.48-7.68 (m, 10H, 2Ar). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz): δ 14.08, 22.62, 26.20, 28.89, 29.14, 29.26, 29.44, 31.77, 39.32, 54.63, 121.78, 129.71, 131.98, 142.95, 149.09. Anal. Calcd for $C_{32}H_{46}I_2N_6Ni$ (826.12): C, 46.46; H, 5.60; N, 10.16. Found: C, 46.47; H, 5.66; N, 10.16.

(**3c**). Yield: 0.065 g (**9** %) of red crystals. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.97-1.03 (t, J_{HH} =7.4 Hz, 6H, 2CH$_3$), 1.40-1.56 (m, 10H, 5CH$_2$), 193 (m, 4H, 2CH$_2$), 4.07 (s, 6H, 2CH$_3$), 4.36 (t, J_{HH} =

7.6 Hz, 4H, 2CH$_2$), 7.42-7.83 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.6 MHz): δ 11.09, 11.18, 22.91, 23.76, 39.84, 52.03, 56.62, 119.81, 121.44, 152.27, 125.66, 158.52, 125.84, 128.89, 129.09, 129.13, 129.92, 13061, 143.57, 147.57. Anal. Calcd for $C_{34}H_{50}I_2N_6Ni$ (855.30): C, 47.75; H, 5.89; N, 9.83. Found: C, 47.75; H, 5.90; N, 9.85.

General procedure for the synthesis of the dichlorido Ni(II) complexes (4a-e)

The reported method [32] was modified: To a solution of triazolium salts **1** in THF (15 mL) was added anhydrous NiCl$_2$ (0.5 eq), and Et$_3$N (4 eq) in dry acetonitrile (20 mL) and heated under reflux for 6 h. All volatiles were removed under reduced pressure, and the residue obtained was chromatographed on a silica gel column, with neat CHCl$_3$ as eluent to give **4**.

Characterisation data:

(**4a**). Yield: 0.451 g (56 %) of brown crystals. ^1H NMR (CDCl$_3$, 400 MHz): δ 0.94 (t, J_{HH} = 7.4 Hz, 6H, 2CH$_3$), 2.01-2.03 (m, 4H, 2CH$_2$), 4.13 (s, 6H, 2CH$_3$), 4.38 (t, J_{HH} = 7.6 Hz, 4H, 2CH$_2$), 7.46-7.56 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.6 MHz): δ 1.67, 14.86, 25.39, 43.85, 5.95, 121.97, 131.27, 132.75, 142.60, 148.41. Anal. calculated for $C_{24}H_{30}Cl_2N_6Ni$ (532.13): C, 54.17; H, 5.68; N, 15.81; found: C, 54.18; H, 5.67; N, 15.81. TOF MS$^+$ (ESI) m/z calculated for $C_{24}H_{30}N_6Ni^+$ [M+Na]$^+$: 484.218; found 484.299.

(**4b**). Yield: 0.532 g (**68** %) of yellow-brown powder. ^1H NMR (CDCl$_3$, 400 MHz): δ 0.01-0.06 (t, J_{HH} = 7.4 Hz, 6H, 2CH$_3$), 1.49-1.55 (m, 4H, 2CH$_2$), 2.09-2.12 (m, 4H, 2CH$_2$), 4.33 (s, 6H, 2CH$_3$), 4.70-4.76 (t, J_{HH} = 7.6 Hz, 4H, 2CH$_2$), 7.66-7.80 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.6 MHz): δ 14.05, 28.98, 29.04, 31.70, 50.45, 119.35, 125.69, 128.07, 128.28, 128.48, 128.82, 130.64, 130.75, 147.3. Anal. calculated for $C_{26}H_{34}Cl_2N_6Ni$ (560.18): C, 55.75; H, 6.12; N, 15.00; found: C, 55.81; H, 6.14; N, 15.04. TOF MS$^+$ (ESI) m/z calculated for $C_{26}H_{34}N_6Ni^{+:}$ 488.220; found 488.227.

(**4c**). Yield: 0.602 g (72 %) of brown powder. ^1H NMR (CDCl$_3$, 400 MHz): δ 0.82-0.83 (t, J_{HH} = 7.4 Hz, 6H, 2CH$_3$), 1.26-1.36 (m, 12H, 6CH$_2$), 2.03 (m, 4H, 2CH$_2$), 4.25 (s, 6H, 2CH$_3$), 4.74 (t, J_{HH} = 7.6 Hz, 4H, 2CH$_2$), 7.52-7.69 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.6 MHz): δ 14.08, 22.62, 26.66, 28.81, 29.10, 31.77, 39.12, 44.64, 127.52, 127.71, 128.01, 128.85, 129.06, 148.54. Anal. calculated for $C_{28}H_{38}Cl_2N_6Ni$ (588.24): C, 57.17; H, 6.51; N, 14.29; found: C, 57.18; H, 6.52; N, 14.30. TOF MS$^+$ (ESI) m/z calculated for $C_{28}H_{38}N_6ClNi^+$ [M-Cl]$^+$: 551.220; found 551.221.

(**4d**). Yield: 0.582 g (61 %) of brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95-0.97 (t, J_{HH} =7.5 Hz, 6H, $2CH_3$), 1.42 (m, 12H, $6CH_2$), 2.14 (m, 4H, $2CH_2$), 4.35 (s, 6H, $2CH_3$), 4.70 (t, J_{HH} = 7.6 Hz, 4H, $2CH_2$), 7.66-7.84 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 22.62, 26.66, 28.81, 29.10, 31.77, 39.12, 44.64, 127.52, 127.71, 128.01, 128.85, 129.06, 148.54. Anal. calculated for $C_{30}H_{40}Cl_2N_6Ni$ (588.24): C, 58.47; H, 6.87; N, 13.64; found: C, 58.50; H, 6.88; N, 13.671. TOF MS$^+$ (ESI) m/z calculated for $C_{30}H_{42}N_6Ni^+$ [M+Li]$^+$: 551.298; found 551.308.

(**4e**). Yield: 0.611 g (65 %) of brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.78-0.81 (t, J_{HH} =7.4 Hz, 6H, $2CH_3$), 1.19-1.76 (m, 10H, $5CH_2$), 1.78-1.82 (m, 4H, $2CH_2$), 3.93-3.95 (s, 6H, $2CH_3$), 4.01 (t, J_{HH} = 7.6 Hz, 4H, $2CH_2$), 7.34-7.56 (m, 10H, 2Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 1.87, 13.92, 22.32, 22.44, 25.83, 29.14, 30.96, 38.61, 54.37, 65.83, 127.67, 128.69, 128.84, 129.51, 129.68, 131.81, 143.25, 148.43. Anal. calculated for $C_{34}H_{50}Cl_2N_6Ni$ (670.28): C, 60.73; H, 7.50; N, 12.50; found: C, 60.77; H, 7.53; N, 12.52. TOF MS$^+$ (ESI) m/z calculated for $C_{34}H_{50}N_6Ni$ [M+Li]$^+$: 607.36; found 607.30.

Typical procedure for the oxidation of substrates

Oxidation reaction was carried by mixing 1.0 mL of a 10.0 mM stock solution of catalyst in MeCN, 1.0 mL of a 1.0 M stock solution of the substrate (*n*-octane, cyclohexane or alcohol) and tert-butyl hydroperoxide (1.0 mL of 70% aq., 14 M). The reaction volume was kept constant (5 mL) by adding MeCN. The reaction mixture was stirred for the indicated time and temperature.

All products analyses by GC followed the method developed by Shul'pin [45, 46], using a Fisons Instruments model 8160 gas chromatograph equipped with a DBWAX capillary column (column length: 30 m; internal diameter: 0.32 mm; film: 0.25 mm) with helium as carrier gas and FID detector. Blank experiments confirmed that in the absence of a catalyst, no products (negligible) of alkane or toluene oxidation were observed.

X-ray structure determination

The structures were solved by direct methods using SHELXS.[54] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXS. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams were generated using SHELXTL, PLATON[55] and ORTEP-3[56].

Electrochemistry

Cyclic voltammetry was performed using a standard three-electrode configuration: a platinum disk electrode was used as the working electrode, a platinum wire as the auxiliary electrode, and a silver electrode as reference, separated from the test solution by a fine porosity frit. The electrochemical measurement of respective Ni-NHC complexes (2 mM) in DCM/MeCN and 0.1 M NBu_4BF_4 was used as the supporting electrolyte. Data workup was performed on OriginPro v8.0988.

Appendix A. Supplementary data

CCDC 1566136, 1571157 and 1566137 contains the supplementary crystallographic data for **3a**, **3b** and **3c** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.)

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