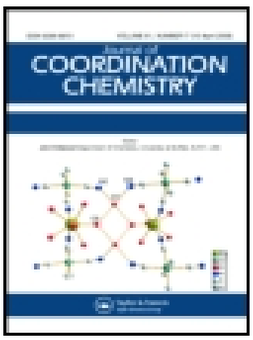

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Application of Ni(II) complexes of air stable Schiff base functionalized N-heterocyclic carbene ligands as catalysts for the transfer hydrogenation of aliphatic ketones

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Abstract

New air stable *N*-heterocyclic carbene functionalized Schiff base ligands (L) of the type 2-[-2-[3-(R)imidazol-1-yl]ethyliminomethyl]phenol [R = methyl (**2**), 2-pyridylmethyl (**3**)] were synthesized and characterized by NMR, IR, MS and CHN analysis. Single crystal X-ray structural analysis of their Ni(II) complexes revealed square planar arrangement of the chelating ligands coordinated in tridentate (**2**, C^N^O) and tetradentate (**3**, N^C^N^O) modes around the metal. The three new isolated and fully characterized complexes were utilized as catalysts for the catalytic transfer hydrogenation of aliphatic ketones in 2-propanol as solvent and source of hydrogen. Based on 0.2 mol% catalyst concentration, the complexes showed activity for aliphatic ketones and 100% conversion (turnover number of 500) for cyclohexanone and all the aromatic ketones tested.

Keywords*:* Catalytic transfer hydrogenation; Aliphatic ketones; N-Heterocyclic carbene; Nickel complexes; Solvent free; Schiff base

1. Introduction

The pioneering work of Wanzlick and Öfele in the late 1960s, followed by ground breaking studies by Arduengo and others, have turned *N*-heterocyclic carbenes (NHCs) into standard ligands of choice that rival other two electron donor ligands [1-5]. Hence, NHCs and their metal complexes have been applied in spheres as varied as catalysis, pharmaceuticals, materials science and as reagents in fine chemicals synthesis [6-8].

Much before the advent of NHCs, the chemistry of Schiff base ligands was well established because of their ease of preparation and immense ability to stabilize metal centers in

both high and low oxidation states. Hence, Schiff base metal complexes of most metals are known [9, 10]. Consequently, their utilization as catalysts for the activation of many reactions including the reduction of ketones, allylic alkylation, Michael addition and a number of coupling reactions has been reported [11-14]. However, despite the variety of compounds based on either NHCs or Schiff bases reported over the decades, reports on NHCs incorporating imines in their structure are quite limited [15].

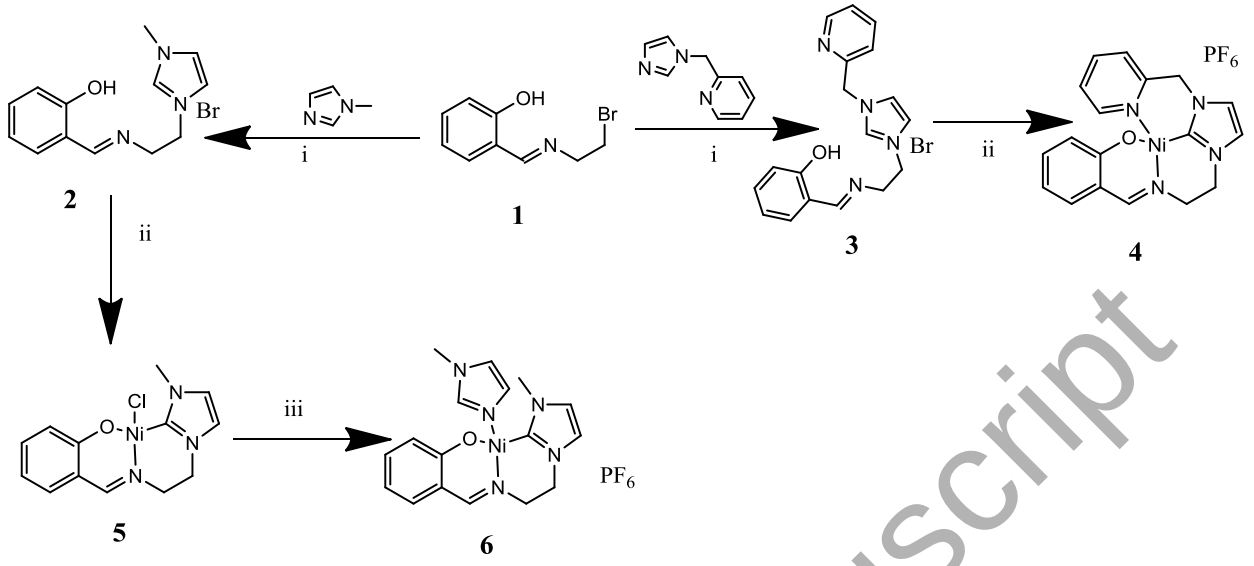
Nickel is a non-toxic, earth-abundant element that is inexpensive, biocompatible and relatively benign to the environment. Therefore, nickel-based catalysts could serve as alternatives to more expensive heavy metal (Pd, Ru and Pt) catalysts that dominate current literature [16-18]. Increasing numbers of catalytic processes that include reduction of ketones, olefin polymerization and several coupling reactions have been initiated by NHC-nickel complexes [19, 20].

Catalytic reduction of ketones to alcohols is a simple but fundamental transformation of immense importance to both academia and industry [21]. However, the selective reduction of aliphatic ketones in particular remains a challenging goal because unlike the aromatic types, only a few substrates have been efficiently converted in good product yields. Thus, the need to develop new catalysts for efficient and selective reduction of a wide range of aliphatic ketones remains a challenge. We herein report new nickel complexes of chelating bi-functional ligands bearing Schiff base and NHC components as cost effective and environmentally benign catalysts for transfer hydrogenation.

2. Results and discussion

2.1. *Synthesis*

Detailed route to the synthesis of all the compounds is presented in scheme 1. Although the identity of ligand **2** is known [22], the high yielding solvent-free approach we adopted as part of the synthesis strategy for **2** and **3** adds green chemistry credentials to this report [15, 23]. For complexation to nickel, the prepared ligands were utilized in situ yielding complexes **4**, **5** and **6**, which are insoluble in alcoholic solvents, partially soluble in chlorinated ones and soluble in acetone, acetonitrile, and DMSO. They also showed good air stability; **4** and **6** might be freely handled and stored in air without decomposition. Complex **5**, however, needs to be handled with more caution as it gradually decomposed on exposure to air and moisture.



i- 60 ^{o}C/ Solvent free
ii- MeOH/KPF_6/Et_3N/NiDME/rt
iii- MeOH/KPF_6/Et_3N/NiDME/Methylimidazole/rt

Scheme 1. Synthetic route to **4**-**6**.

2.2. ***Spectroscopic analysis***

NMR data of **4**, **5** and **6** indicated complexation of the ligands to Ni(II) evidenced by the disappearance (binding) of resonance peaks of key ligand functional groups. These include the peak associated with the Schiff base OH proton that resonates downfield at circa 12.5 ppm and that of the carbene NCHN proton, at circa 10.5 ppm. Disappearance of these peaks from the ^{1}H-NMR spectra of all the complexes is diagnostic of ligand coordination [24]. In comparison to the spectra of **2** and **3**, the spectra of **4**, **5** and **6** showed a general upfield shift in resonance frequencies as further evidence of ligand coordination. For instance, the imine proton that generally resonates at circa 8.5 ppm in the ligands shifted to around 7.8 ppm upon coordination, except for **4** where a slight downfield shift was observed and this could be attributed to the deshielding influence of the *trans* bound pyridyl donor [25-27]. Meanwhile, the two sets of bridging methylene (CH_2) protons α and β to the imine that were observed at circa 4.25 and 4.81 ppm, respectively, in the ligands showed upfield shifts to 3.77 and 3.85 ppm, respectively, upon ligand coordination to nickel. This is an unequivocal confirmation of imine -C^N- coordination to the nickel center through the N- lone pair of electrons that usually shielded the

neighboring methylene protons. All the aromatic protons also shifted upfield, further confirming ligand coordination to nickel. The ^{13}C-NMR data of all the complexes were also indicative of ligand complexation. For instance, a downfield shift was observed for the carbene (NCN) signal which resonated at 137 ppm in **2**, but due to the d_{π}-p_{π} interaction between the carbene and the Ni(II) center in **4** was observed at 152 ppm [28, 29].

The IR spectra of all the complexes distinctly showed disappearance of the ligand hydroxyl (-OH) absorption (circa 3300 cm^{-1}) and slight shifts in wavenumbers toward lower frequencies for the imine (C=N) resonance that points to bidentate -O^N- coordination of the Schiff base moiety to nickel. In addition, positive electrospray mass spectrometric data of **2** and **3** revealed the loss of bromide counter ions from the ligand moieties with base peaks at m/z = 230.1284 and 307.1563, respectively. While for the complexes, m/z = 363.0766 (**4**), 286.0479 (**5**), and 366.0883 (**6**) corresponded to base peaks for [M-PF_6, **4**] [M^+-Cl, **5**] and [M-PF_6, **6**] respectively. Furthermore, the data recorded for combustion analysis (CHN) of the complexes were all within acceptable (± 0.3%) ranges of calculated values, a confirmation that the complexes were isolated in high bulk purity.

2.3. *Analysis of the single crystal structures of 4 and 6 by X-ray diffraction*

Single crystals of **4** and **6** suitable for X-ray diffraction were grown by slow evaporation of acetone solutions of the complexes. Crystal and experimental refinement data are shown in table 1, while selected bond lengths and angles are summarized in table 2. ORTEP diagrams showing unit cell contents with hydrogens omitted for clarity for **4** and **6** are presented in figures 1 and 2, respectively.

As observed in figures 1 and 2, polydentate **2** and **3** are bound to the nickel centers via three (C^N^O) and four (N^C^N^O) donors, respectively. Hence, **4** crystallized in the monoclinic crystal system while **6** crystallized in the lower symmetry triclinic *P*-1 space group. More interesting is the terdentate binding mode of **3**, coordinated via the O(1), N(3), N(4) and the carbene C(1) donors in a square planar geometry with angles of 84.29 to 95.02° around the Ni(II) center in **4**. The bond lengths (Å) of the Schiff base donors to nickel, *i.e.* Ni-O = [1.856 (**4**); 1.851 (**6**)], Ni-N(3) = [1.889 (**4**); 1.888 (**6**)] and Ni-N(4) = [1.894 (**4**); 1.933 (**6**)] are similar to those reported for salicyl-aldiminato phenyl Ni(II) complexes [30-32]. Furthermore, the

imidazolium Ni-C(1) bond lengths (Å) are [1.882 (**4**) and 1.849 (**6**)], also within distances observed in most Ni-NHC complexes [33].

2.4. *Catalytic transfer hydrogenation*

The three complexes were utilized for catalytic transfer hydrogenation (CTH) of cyclohexanone as a model substrate in 2-propanol as solvent and hydrogen source. From results of preliminary optimization studies, all the reactions were conducted with a 0.2 mol% catalyst concentration in refluxing 2-propanol promoted by KOH. No reactions were observed in the absence of KOH, while higher concentrations of the catalysts yielded no improvement in conversions and poor reactivities were observed at lower temperatures. A time dependent reaction profile (figure 3) indicates that a maximum conversion of 100% with a turnover number of 500 was recorded with **4** after a period of 6 h while **5** and **6**, respectively, gave 78% and 95% conversion after 8 h.

The higher turnover number recorded with **4** and **6**, as presented in table 3, are the highest results obtained in nickel catalyzed transfer hydrogenation of ketones and are comparable to some Ru and Pt catalyzed reactions [34-36]. Following the optimization study, **4** and **6** were utilized to study the scope of the CTH on aliphatic ketones; both catalysts gave comparable results for all the substrates presented in figure 4 for complex **4**. Three major factors were considered in substrate reactivity to products, *i.e.* sterics, electro- and chemo-chemistry around the carbonyl functionality. For instance, lower steric interaction and stronger electronic contribution to the C=O bond explains the fact that a *para* substituted saturated ring substrate (**7a**) is significantly easier to reduce than **7b** bearing a sterically hindering *ortho* methyl substituent. Steric hindrance has also been invoked in the past to explain similar results using iron and nickel based catalyst systems [37]. In general, the aliphatic acyclic ketones are significantly more difficult to reduce to products, with conversions ranging from 2% (**7c**) to 32% (**7j**) [38]. The results clearly show dependence of conversion to the alcohol products on increased steric hindrance to the carbonyl due to lengthening of alkyl chains and stability of associated carbocations which leads to slight improvements in conversions to product when more stable carbocations were involved (**7i -j**) [39]. In terms of chemo-selectivity, it is interesting to note that no products of C=C bond reduction were recorded for **7i** and **7j** implying that under the current conditions, the carbonyl bond was selectively activated and functionalized.

Finally, in an effort to put these results into context, we included a selection of aromatic ketones to this study and all were efficiently and fully converted to respective alcohols (**7k–n**). It is thus clear that the complexes are very effective for the CTH of a wide range of carbonyl containing compounds.

3. Conclusion

Three air stable nickel complexes of Schiff base functionalized *N*-heterocyclic carbene ligands have been synthesized and characterized including structural elucidation by X-ray diffraction analysis. All the complexes were successfully utilized as catalysts in the transfer hydrogenation of a variety of ketones.

4. Experimental

4.1. *Synthesis of 2 and 3*

Into a clean Schlenck tube charged with a stir bar and nitrogen gas was placed 1.0 mmol of the Schiff base and the corresponding substituted imidazole. The mixture was heated for 30 min in the absence of solvent, leading to isolation of the products in excellent yields. Progress of the reactions was monitored by TLC over time.

4.1.1. 2-[2-(3-Methylimidazol-1-yl)ethyliminomethyl]phenol (**2**)**.** The product was isolated as a pale yellow viscous liquid, yield 0.305 g, 98%, ^{1}H-NMR ($CDCl_3$, 400 MHz) 3.97 (s, 3H), 4.15 (t, 2H), 4.73 (t, 2H), 6.82 (m, 2H), 6.97 (m, 1H), 7.23 (m, 2H), 7.34 (dd, 1H), 8.44 (s, 1H), 10.28 (s, 1H), 12.56 (s, 1H, -OH). ^{13}C-NMR ($CDCl_3$, 400 MHz) 37.26, 51.05, 58.59, 116.90, 118.34, 119.23, 122.92, 132.23, 133.15, 133.76, 137.92, 160.68, 169.08. IR (ATR, cm^{-1}): 3394(OH), 3092(CH, sp^2), 1628(C=N), 1575(C=C), 1277(N-C-N). HRMS (ESI) [M^+ - Br] calculated for $C_{13}H_{16}N_3O$: 230.1288, found: 230.1285.

4.1.2. 2-[-2-[3-(2-Pyridylmethyl) imidazol-1-yl]ethyliminomethyl]phenol (**3**)**.** The product was isolated as a reddish brown moisture sensitive viscous liquid, yield 0.38 g, 98%, ^{1}H-NMR (DMSO-d_6, 400 MHz) 4.09 (t, 2H), 4.71 (t, 2H), 5.65 (s, 2H), 5.80 (dd, 1H), 6.97 (dd, 2H), 7.45 (m, 3H), 7.91 (m, 3H), 8.20 (m, 1H), 8.58 (s, 1H), 9.41 (s, 1H), 12.69 (s, 1H). ^{13}C-NMR (DMSO-d_6, 400 MHz) 48.46, 49.54, 57.72, 116.31, 118.57, 118.80, 122.15, 122.53, 122.75,

123.53, 131.82, 132.68, 137.07, 137.54, 149.48, 153.57, 160.03, 167.79. IR (ATR, cm^{-1}): 3395(OH), 3050(CH, sp^2), 1628(C=N), 1575(C=C), 1277(N-C-N). HRMS (ESI) [M^+ - Br] calculated for $C_{18}H_{19}N_4O$: 307.1553, found: 307.1563.

4.2. *Synthesis of nickel complexes*

4.2.1. 2-[-2-[3-(2-Pyridylmethyl)imidazol-1-yl]ethyliminomethyl]phenol nickel(II) (4). Into a Schlenck tube containing **3**, (0.387 g, 1 mmol) was added methanol (10 ml) followed by KPF_6 (0.22 g, 1.2 mmol), and the mixture was allowed to stir for 3 h at room temperature before triethylamine (0.6 ml, 4 mmol) was slowly added to the mixture; upon stirring for 3 minutes, nickel(II) chloride diglyme (NiDME) was added to the mixture and allowed to stir overnight. The precipitated nickel complex was separated by filtration on a filter paper as an orange powder, yield; 0.48 g, 95%. MP = 272–273 °C; ^{1}H-NMR (DMSO-d_6, 400 MHz) 3.66 (t, 2H), 4.33 (t, 2H), 5.70 (s, 2H), 6.73 (dd, 2H), 7.42 (m, 3H, Ar), 7.62 (m, 3H, Ar), 8.11 (dd, 1H, Ar), 8.31 (dd, 1H, Ar), 8.88 (s, 1H, H-C=N). ^{13}C-NMR (DMSO-d_6, 400 MHz) 47.32, 51.65, 60.06, 115.48, 118.90, 119.99, 122.24, 122.63, 124.38, 124.65, 133.70, 135.06, 140.15, 152.77, 153.32, 162.91, 167.07. IR (ATR, cm^{-1}): 3159(CH, sp^2) 1607(C=N), 1534(C=C), 835(N-C-N). HRMS (ESI) [M^+ - Cl] calculated for $C_{18}H_{18}N_4NiO$: 363.0739, found: 363.0766; CHN analysis calculated for $[C_{18}H_{17}NiON_4].PF_6.H_2O$: C, 41.02; H, 3.63; N, 10.63; found: C, 41.35; H, 3.42; N, 10.56.

4.2.2. 2-[2-(3-Methylimidazol-1-yl)ethyliminomethyl]phenol nickel(II) (5). Into a Schlenck tube containing **2**, (0.311 g, 1 mmol) was added methanol (10 ml) followed by KPF_6 (0.22 g, 1.2 mmol) and the mixture was allowed to stir for 3 h at room temperature before triethylamine (0.6 ml, 4 mmol) was slowly added to the mixture; upon stirring for 3 minutes, nickel(II) chloride diglyme (NiDME) was added to the mixture and allowed to stir overnight. The precipitated nickel complex was separated by filtration on filter paper as an orange solid, yield; 0.4 g, 95%. MP = 250 °C (dec.); ^{1}H-NMR (DMSO-d_6, 400 MHz) 3.70 (t, 2H), 4.57 (m, 5H), 6.58 (d, 1H), 6.82 (d, 1H), 7.31 (m, 4H), 7.90 (s, 1H). IR (ATR, cm^{-1}): 1612(C=N), 1537(C=C), 829(N-C-N). HRMS (ESI) [M^+ - Cl] calculated for $C_{13}H_{14}N_3NiO$: 286.0479, found: 286.0479. CHN Anal. calculated for $[C_{13}H_{14}NiClN_3O]\cdot KPF_6$: C, 30.77; H, 2.98; N, 8.28; found: C, 30.32; H, 3.20; N, 7.97.

4.2.3. 2-[2-(3-Methylimidazol-1-yl)ethyliminomethyl]phenol nickel(II) (6). Into a Schlenck tube containing **2**, (0.311 g, 1 mmol) was added methanol (10 ml) followed by KPF_6 (0.22 g, 1.2 mmol) and the mixture was allowed to stir for 3 h at room temperature before triethylamine (0.6 ml, 4 mmol) was slowly added to the mixture; upon stirring for 3 minutes, nickel(II) chloride diglyme (NiDME) and one equivalent of methylimidazole were slowly added to the mixture and allowed to stir overnight. The precipitated nickel complex was separated by filtration using a filter paper as an orange solid, yield; 0.5 g, 90%. MP = 195 °C (melt). ^{1}H-NMR (DMSO-d_6, 400 MHz) 3.13 (s, 3H), 3.73 (m, 5H), 4.59 (t, 2H), 6.64 (dd, 2H), 6.83 (dd, 1H), 7.33 (m, 5H), 7.96 (s, 1H). IR(ATR, cm^{-1}): 1613(C=N), 1539(C=C), 841(N-C-N). LRMS (ESI) [M^+ - PF_6] calculated for $C_{17}H_{20}N_5NiO$: 368.1005, found: 366.088. CHN Anal. calculated for $[C_{20}H_{26}F_6N_5NiO_2]\cdot PF_6$: C, 41.99; H, 4.58; N, 12.24; found: C, 41.67; H, 4.51; N, 12.43.

4.3. *Catalytic transfer hydrogenation*

All the samples were prepared as follows: into a Schlenck tube fitted with a condenser and stirrer bar was added the substrate ketone (2.1 mmol), nickel catalyst (0.2 mol%), KOH (2 mmol) and 10 ml 2-propanol. The mixture was heated at 82 °C. Conversion of the ketones to corresponding alcohols was monitored using gas chromatography. Aliquots were taken at given time intervals, filtered through a pad of cotton wool and then injected (0.5 µl) into a GC equipped with a DB1 Wax polyethylene column. The product was identified by comparison with standards purchased from Sigma Aldrich. The conversion was calculated from the respective peak area of each product.

4.4. *X-ray data collection and analysis*

X-ray quality crystals of **4** and **6** were selected, attached onto a Mitagen loop, and centered in the X-ray beam by the aid of a video camera. Intensity data were collected on a Bruker APEX2 diffractometer with Mo Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryostream low-temperature apparatus operating at 100(1) K. The initial cell matrix was determined from three series of scans consisting of twelve frames collected at intervals of 0.5° in a 6° range with the exposure time of ten seconds per frame. Each of the three series of scans was collected at different starting angles and the APEXII [40] program suite used to index the reflections and

refined using SAINT [41]. Data reduction was performed using SAINT software, and the scaling and absorption corrections were applied using SADABS [42] multiscan technique. The structures were solved by direct methods using SHELXS [43]. Non-hydrogen atoms were first refined isotropically and then by anisotropic refinement with full-matrix least squares based on F^2 using SHELXL [43]. All hydrogens were positioned geometrically, allowed to ride on their parent atoms and refined isotropically.

Supplementary data

Characterization data (NMR, IR, TOF MS and elemental analysis) for all new compounds accompany this paper as electronic supplementary information. Crystallographic data in .cif format has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 1572704 and CCDC 1572683 for **4** and **6**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk or visit http://www.ccdc.cam.ac.uk.

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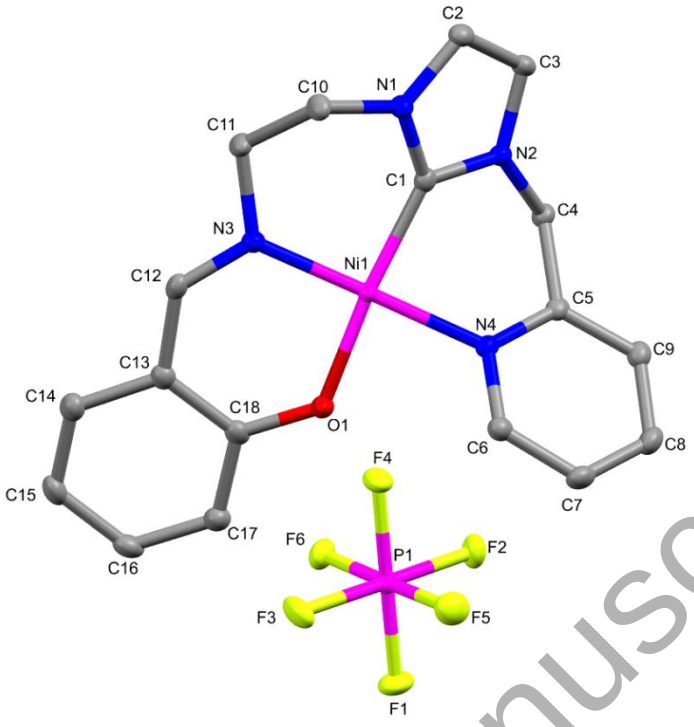


Figure 1. Thermal ellipsoid plot of the asymmetric unit of **4** shown at the 30% probability level with hydrogens omitted for clarity.

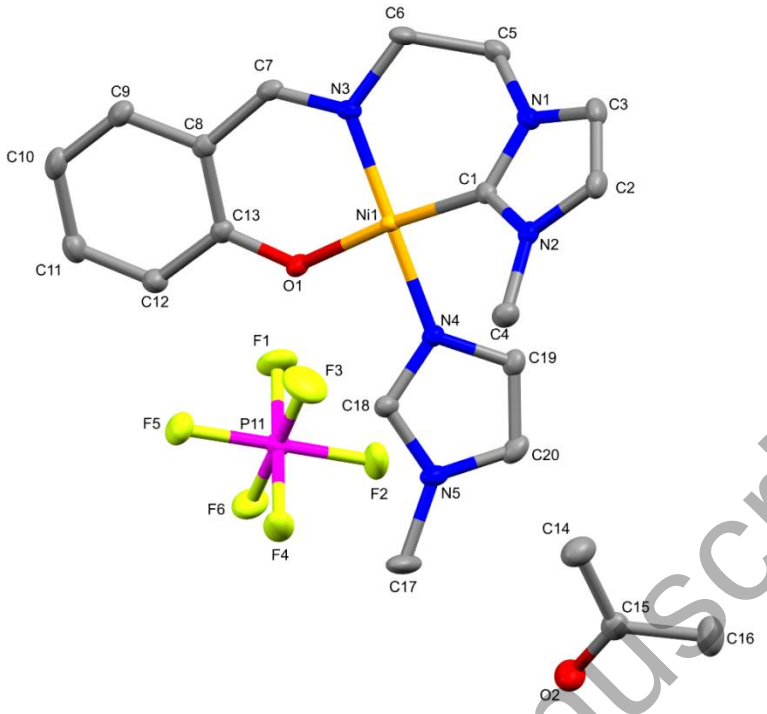


Figure 2. Thermal ellipsoid plot of the asymmetric unit of **6** shown at the 50% probability level with hydrogens omitted for clarity.

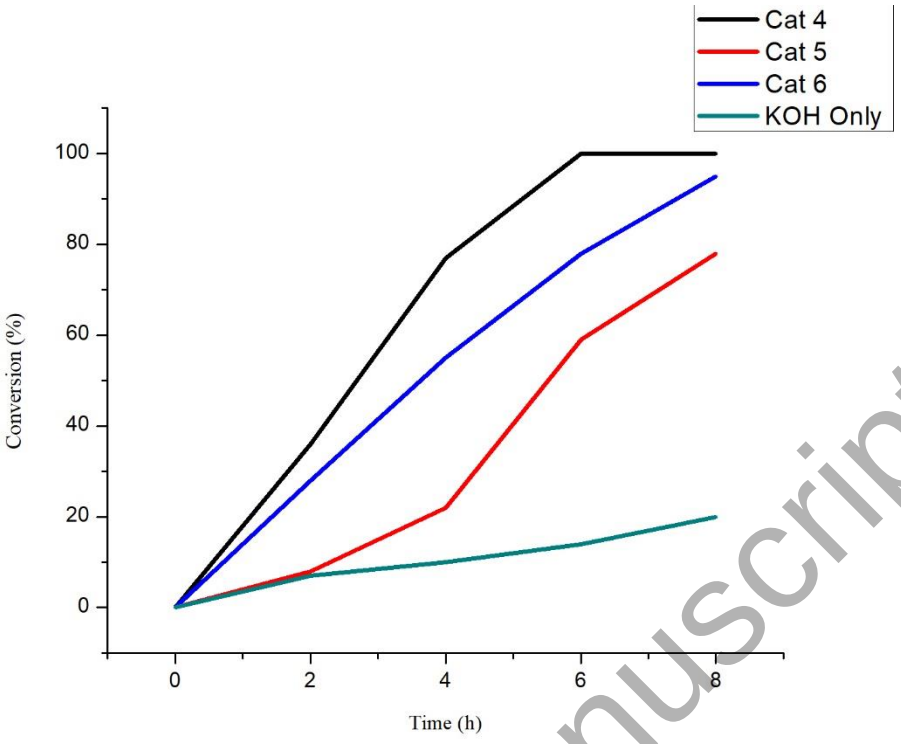


Figure 3. Time dependent CTH of cyclohexanone over a period of 8 h.

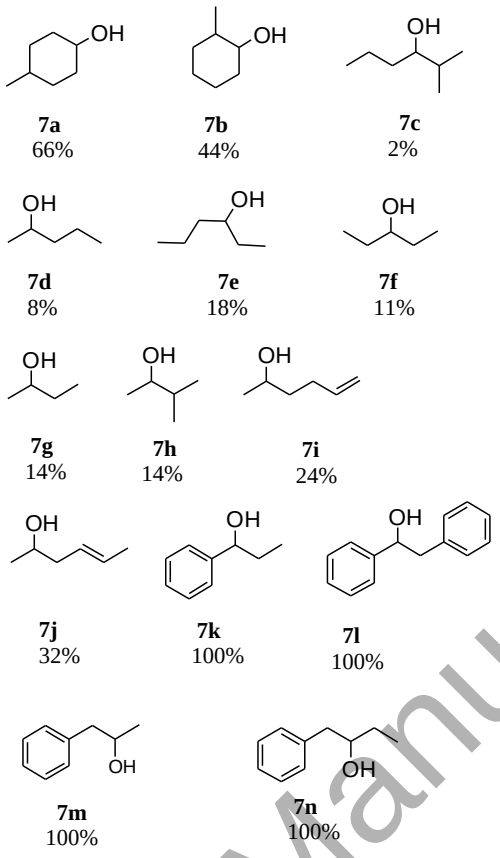


Figure 4. Scope of products in the CTH by **4**. Conversions determined by analysis of GC data. Reaction conditions: (82 °C; 6 h; 0.2 mol% concentration of **4**).

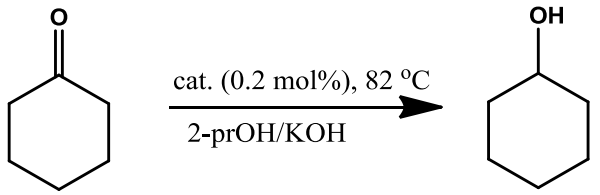
Table 1. Crystal and structure refinement data for **4** and **6**.

Parameters	**4**	**6**
Empirical formula	$C_{18}H_{17}F_6N_4NiOP$	$C_{20}H_{26}F_6N_5NiO_2P$
Formula weight	509.03	572.14
Crystal system	Monoclinic	Triclinic
Space group	*P* $2_1/c$	*P* -1
a, Å	9.4412(2)	9.4647(3)
b, Å	16.0341(3)	11.8703(4)
c, Å	12.5906(2)	12.0481(4)
α, deg	90	108.613(2)
β, deg	95.0740(10)	90.1570(10)
γ, deg	90	112.821(3)
Cell volume, $Å^3$	1898.51(6)	1169.90(7)
Z	4	2
D_{calcd}, Mg/m^3	1.781	1.624
μ, mm^{-1}	1.184	0.974
F(000)	1032	588
Crystal size, mm^3	0.260 × 0.140 × 0.070	0.250 × 0.240 × 0.130
Θ_{min},Θ_{max}, deg	2.062 to 27.460	1.803 to 27.076
Reflections collected	22556	22394
Independent reflections	4310 [R(int) = 0.0335]	5035 [R(int) = 0.0240]
Completeness to theta	100.0%	99.9%
Goodness-of-fit on F^2	1.028	1.054
Final R indices	0.0267, 0.0590	0.0267, 0.0642
R indices (all data)	0.0350, 0.0624	0.0317, 0.0664
Largest diff. peak and hole $e.Å^{-3}$	0.327 and -0.275	0.316 and -0.281

Table 2. Selected bond lengths [Å] and angles [°] for **4** and **6**.

Bond length	**4**	**6**
Ni–O (1)	1.8511(12)	1.8586(11)
Ni–N (3)	1.8880(14)	1.8893(13)
Ni–N (4)	1.9327(14)	1.8938(15)
Ni–C (1)	1.8491(17)	1.8818(15)
Bond angle	**4**	**6**
C–Ni–O	170.22(7)	173.59(6)
C–Ni–N4	88.01(7)	90.27(6)
C–Ni–N3	92.09(7)	91.93(6)
O–Ni–N3	95.02(6)	93.72(5)
O–Ni–N4	85.70(6)	84.29(5)
N4–Ni–N3	173.35(6)	175.68(6)

Table 3. CTH of cyclohexanone catalyzed by **4**, **5** and **6**.



Catalyst	Conversion (%) [a]	Time (h)	TON [b]
4	100	6	500
5	78	8	390
6	95	8	475

[a] Determined by analysis of GC data. Time = 6 h (**4**); 8 h (**5**, **6**)

[b] Turnover number = mol product/mol catalyst.

Graphical abstract