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Selective hydrogenation of nitriles to secondary amines catalyzed by a pyridyl-functionalized and alkenyl-tethered NHC–Ru(II) complex

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ABSTRACT

A set of Co(III) and Ru(II) compounds are synthesized bearing pyridyl-functionalized and alkenyl-tethered N-heterocyclic carbene (NHC) ligand (L^1). $[Co^{III}(L^1)_3](PF_6)_3$ (**1**) was synthesized by the reaction of $[L^1H]PF_6$, $Co(OAc)_2.4H_2O$, K_2CO_3 in tetrahydrofuran (THF) under refluxing condition. $[Ru^{II}L^1(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (**2**) was synthesized via transmetallation method. For both compounds, the NHC ligand chelates the metal through carbene carbon and pyridyl nitrogen whereas the butenyl unit remains free. Compound **2** hydrogenates organic nitriles efficiently providing selectively secondary amines. In the presence of external amines, unsymmetrical secondary amines are also obtained.

1. Introduction

Amines are an important class of compounds which are present in an extensive range of natural products, drugs, polymers and dyes and agro chemicals as well [1]. Direct base-promoted N-alkylation of amines with alkyl halides or alcohols [2], reductive amination of carbonyl compounds [3], alkylative amination [4], hydroamination of unsaturated hydrocarbons with amines [5] are the traditional methodologies employed to access amines. However, expensive starting materials, generation of wasteful salts and over alkylation cripple the usefulness of the above methods [6]. To overcome these difficulties, metal catalysed direct hydrogenation of carbon–nitrogen triple bonds (nitriles) has come into limelight as efficient and environmentally benign alternative [7]. Homogeneous nitrile hydrogenation using precious metals such as Ir, Rh, Re and Ru are reported [8]. A Fe based catalyst with pincer ligand selectively hydrogenates nitriles to primary amines with high efficiency [9]. Heterogeneous catalysts containing transition metals Co, Ni, Au, Cu, Rh, Pd and Pt have been used on different supports C, TiO_2, SiO_2, Al_2O_3 etc. [10] The product selectivity and functional group tolerance depend on the nature of the catalysts, reaction temperature, hydrogen pressure and the structure of the nitriles [11]. Controlling these parameters, selective formation of primary [12], secondary [13], tertiary amines [14] and imines [15] is achieved.

Metal complexes containing NHC ligands are highly active catalysts for a wide range of important organic transformation reactions [16]. Metal-NHC compounds are stable under oxidative conditions and therefore suitable for oxidation reactions [17]. On the other hand, the use of NHC ligands in direct hydrogenation chemistry has been restricted [18]. The underlying reason is the susceptibility of the (NHC)metal-hydride intermediate toward elimination under reductive conditions causing the breakdown of the metal-NHC catalysts [19]. In spite of these limitations, metal-NHC catalytic systems are developed for the hydrogenation reactions [18] including nitrile hydrogenation [[20],13g]. An effective strategy to suppress ligand dissociation via reductive elimination is to employ chelate ligands. Donor group functionalized NHC ligands are reported to chelate a wide variety of metal ions [21]. Albrecht group has shown that chelation prevents NHC extrusion from the metal during hydrogenation reactions [22].

Introduction of a hemilabile ligand on a NHC ligand improves the stability and enhances the catalytic activity of metal-NHC complex. An array of metal-complexes containing olefin-tethered NHCs, having different linker length between azole ring and terminal alkenyl group, have been synthesized [23]. Depending on the identity of the metal ion and the ancillary ligands around it, the alkenyl donor is found either metal-coordinated and in free form. Many of these are shown to catalytically transfer

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hydrogenate and direct hydrogenate olefins and ketones [17i,j]. A Ru(II) complex with allyl-NHC (Scheme 1a) is shown to be a better catalyst for transfer hydrogenation of unfunctionalised alkenes compared to the corresponding complex bearing NHC ligand with saturated arm (Scheme 1b) [17i]. Peris offered an intriguing possibility that hydrogenation of the alkenyl arm would *in situ* generate a vacant site and thus activate the catalyst [24]. Willans and co-workers introduced pyridyl group as a side arm with allyl-bearing NHC ligand [24a,24d]. A square planar palladium–NHC complex is reported where the C(sp^2)–H of the allyl group is activated and attached to the metal with full retention of the allyl double bond [24g].

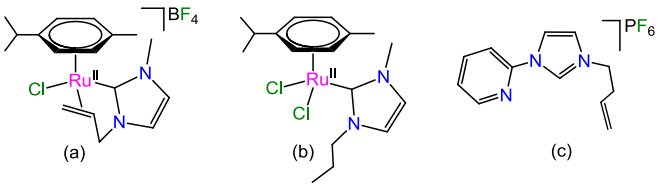
Toward our goal to develop nitrile hydrogenation catalysts, we have synthesized a pyridyl-functionalized chelate NHC ligand ($[L^1H]PF_6$) with tethered butenyl group (Scheme 1c). Arm length of the alkenyl group is purposefully increased to facilitate its coordination to the metal. Chelate complexes $[Co^{III}(L^1)_3](PF_6)_3$ (**1**) and $[Ru^{II}L^1(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (**2**) are synthesized. Compound **1** was found to be catalytically inactive as all metal-sites are occupied by ligands. Catalytic utility of **2** is examined for nitrile hydrogenation. Symmetrical and unsymmetrical secondary amines are obtained in good yields in the presence or absence of external amines, respectively.

2. Results and discussion

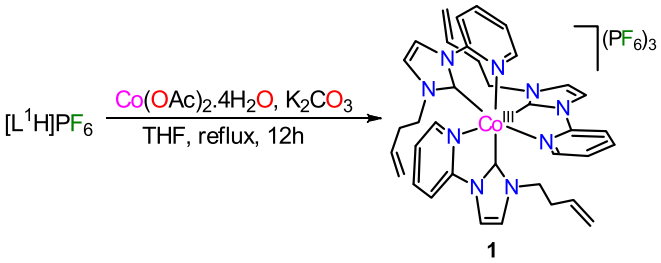
2.1. $[Co^{III}(L^1)_3](PF_6)_3.KPF_6$ (1.KPF_6)

Refluxing a suspension of $[L^1H]PF_6$ with $Co(OAc)_2.4H_2O$ in 4:1 ratio and K_2CO_3 in THF for 12 h, followed by crystallization layering hexane onto a mixed dichloromethane/acetonitrile (5/1) solution, afforded yellow crystals of $[Co^{III}(L^1)_3](PF_6)_3.KPF_6$ (**1**.KPF_6) in moderate yield (60%) (Scheme 2). Employing different ligand to metal ratios (3:1 and 2:1) afforded the crystals of **1**.KPF_6 but in lower yields. Compound **1** could be obtained in highest yield and purity at 4:1 ligand to metal ratio.

A well-resolved ^{1}H NMR spectrum in acetonitrile-d_3 (Fig. 1) suggests a diamagnetic Co^{III} complex **1**. It exhibits six multiplates at δ 2.12, 2.21, 2.72, 3.63, 4.89 and 5.32 ppm for the butenyl wingtip group. The aromatic protons (pyridyl and imidazolium) appear in the range from δ 6.99 to δ 8.43 ppm. The ^{13}C NMR signal corresponding to the carbene carbon resonates at δ 185.1 ppm (Fig. S1). X-ray analysis initially revealed a '$[Co(L^1)_3]$' unit with four well-behaved PF_6 anions. A high residual peak in the different Fourier map was also observed which was identified as potassium. Accordingly, the compound is characterized as $[Co^{III}(L^1)_3](PF_6)_3.KPF_6$ (**1**.KPF_6). The asymmetric unit of **1** contains one third of the molecule related to the remaining part by a C_3 axis passing through the Co center. Three chelate bound NHC ligands occupy six sites of the octahedral geometry around the cobalt centre through carbene carbon (C6) and pyridyl nitrogen (N3) (Fig. 2). The Co1–C6 and Co1–N3 bond distances are 1.902(2) and 1.9892(19) Å respectively. The butenyl group remains uncoordinated. The ESI–MS of **1** shows sequential loss of PF_6 anions to give signals at *m/z* 946.41 ($z = 1$), 400.69 ($z = 2$), 218.78 ($z = 3$) attributed to $[\mathbf{1} - PF_6]^+$, $[\mathbf{1} - 2PF_6]^{2+}$, $[\mathbf{1} - 3PF_6]^{3+}$ respectively (Fig. S2–S3).



Scheme 1. Ru(II) complex with allyl-tethered NHC (a) and the saturated analogue (b); Ligand $[L^1H]PF_6$ employed in this work (c).



Scheme 2. Synthesis of **1**.

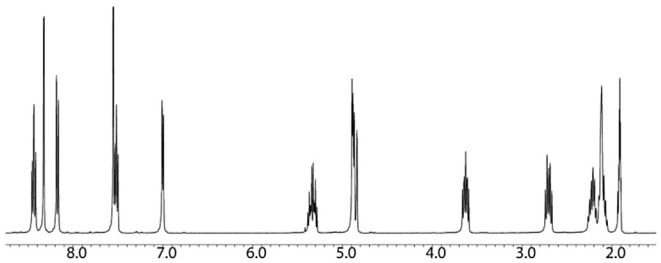


Fig. 1. ^{1}H NMR of compound **1** in CD_3CN.

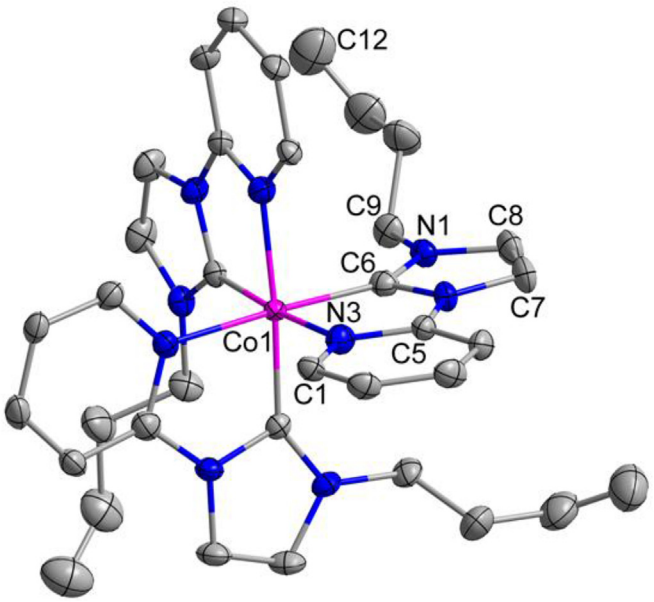
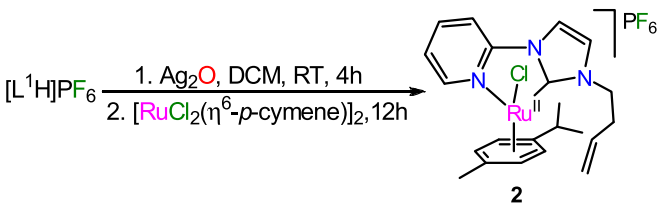


Fig. 2. The cationic unit of **1** with selective atoms labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°):Co1–C6 1.902(2), Co1–N3 1.9892(19), N2–C5 1.406(3), C11–C12 1.303(5), C6–Co1–N3 82.33(9), C1–N3–Co1 128.00(16), N1–C6–N2 104.97(19), N1–C6–Co1 142.57 (18).

2.2. $[Ru^{II}L^1(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (2)

Room temperature reaction of $[L^1H]PF_6$ with Ag_2O in dichloromethane (CH_2Cl_2) followed by transmetallation with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ afforded $[RuL^1(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (**2**) in high yield (85%) (Scheme 3). The ^{1}H NMR (Fig. S4) spectrum of **2** in dichloromethane-d_2 confirms the composition of the complex



Scheme 3. Synthesis of **2**.

consisting of one NHC ligand and one *p*-cymene. The ^{13}C NMR signal corresponding to the carbene carbon appears at δ 184.1 ppm (Fig. S5). X-ray structure of **2** revealed a distorted octahedral geometry around Ru center (Fig. 3). The NHC ligand chelates the metal though carbene carbon (C1) and nitrogen atom (N3) of the pyridine ring. The Ru1–C1 and Ru1–N3 bond distances are 2.033(2) and 2.100(2) Å respectively. One chloro ligand and the *p*-cymene ring complete the coordination sphere around the metal center. The butenyl unit does not take part in chelation with the metal center. ESI–MS reveals a signal at *m/z* ($z = 1$) 470.09 which is assigned for $[\mathbf{2}–PF_6]^+$ unit (Fig. S6–S7).

2.3. Catalysis

The catalytic utility of both compounds towards nitrile hydrogenation reactions was evaluated. Catalyst **1** (2 mol% loading) with H_2 (60 bar) at 80 °C in dry isopropanol (^{i}PrOH) for 12 h was found ineffective for the hydrogenation of benzonitrile. However, under identical conditions, catalyst **2** resulted in 90% conversion (entry 1, Table 1), yielding dibenzylamine as the sole product. No benzylamine, tribenzylamine or dibenzylimine was detected in the GC–MS. Lowering of the temperature, H_2 pressure, time, and switching the solvent from isopropanol to toluene, 1,4-dioxane, THF reduced the product formation significantly. Under the optimized

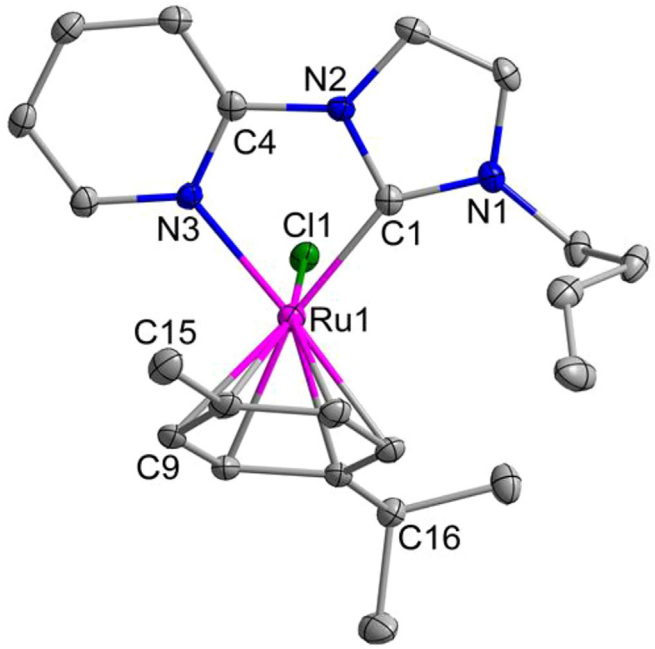


Fig. 3. The cationic unit of **2** with selective atoms labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–C1 2.033(2), Ru1–N3 2.100(2), Ru1–Cl1 2.246(2), Ru1–C9 2.246(2), Ru1–C12 2.222(2), N2–C4 1.398(3), C21–C22 1.321(4), N3–Ru1–C1 76.88(9), N3–Ru1–Cl1 87.33(5), C1–Ru1–Cl1 84.15(7), N3–Ru1–C9 93.80(8), C12–Ru1–C9 77.93(9).

reaction conditions, the substrate scope was explored using different nitriles and the results are summarised in Table 1. Aromatic nitriles with electron withdrawing groups afforded relatively high yields than the same bearing electron donating groups resulting in corresponding symmetrical secondary amine products. Due to greater electron withdrawing effect of chlorine in comparison bromine, 4-chlorobenzonitrile gave higher conversion (98%) (entry 2, Table 1) than 4-bromobenzonitrile (92%) (entry 3, Table 1). For 4-methylbenzonitrile, 89% conversion was observed similar to benzonitrile (entry 4, Table 1). Due to the presence of electron donating group, comparatively lower conversions were observed for 4-methoxybenzonitrile (75%) (entry 5, Table 1) and 4-(dimethylamino)benzonitrile (60%) (entry 6, Table 1). The reaction was extended to nitriles containing heterocyclic rings. High conversions were observed for isonicotinonitrile (entry 7, Table 1; 82%) and furan-2-carbonitrile (entry 8, Table 1; 85%). Aliphatic nitrile cyclohexanecarbonitrile (entry 9, Table 1) is less reactive and takes more time to reach completion – only 48% conversion was obtained in 12 h. Low conversion (<10%) was obtained for anthracene-9-carbonitrile (entry 10, Table 1) due to bulkiness of the substrate.

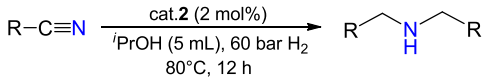
The scope of the catalyst was expanded for unsymmetrical secondary amines using an external amine. Reaction of benzonitrile with hexylamine in 1:1 ratio under optimized condition resulted in the formation of a mixture of N-benzylhexan-1-amine and dibenzylamine in 48:52. The selectivity was raised with increase in amount of external amine. N-benzylhexan-1-amine and dibenzylamine were obtained in 80:20 and 98:2 ratios when benzonitrile with hexylamine were used in 1:2 and 1:3 ratios respectively in 12 h. Further substrate scope was examined and results are summarised in Table 2. In all cases conversion is 100%. Benzonitrile was subjected to react with cyclohexylamine, cyclopropanamine, isopropylamine, and pentylamine and the corresponding cross products were obtained in 98%, 85%, 50% and 68% selectivity respectively (entries 1–4, Table 2). Reactions of 4-methylbenzonitrile with cyclohexylamine and aniline afforded 98% and 65% of unsymmetrical products respectively (entries 5–6, Table 2). The cross coupled products were observed in 72%, 80%, and 94% selectivity in the reaction of 4-chlorobenzonitrile with cyclohexylamine, aniline and cyclopropanamine respectively (entries 7–9, Table 2). Furan-2-carbonitrile afforded the unsymmetrical amine in 90% selectivity with reaction of cyclohexylamine (entry 10, Table 2).

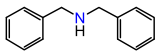
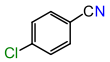
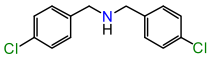
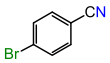
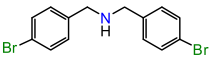
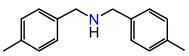
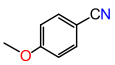
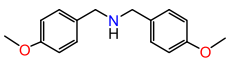
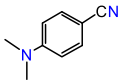
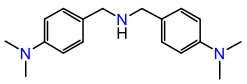
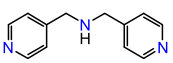
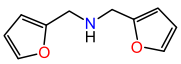
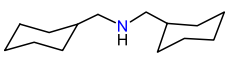
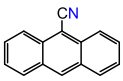
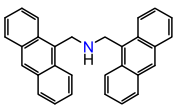
Nitrile hydrogenation, in principle, may gives rise to different amines (Scheme 4). Reduction of nitriles provides primary amines (B) and the intermediate imines (A). The B then attacks A, and subsequent elimination of ammonia followed by hydrogenation leads to the formation of secondary amines (E). Use of external amine in the reaction affords the unsymmetrical secondary amine (F). The ability of the catalyst to initially give a mixture of primary amine and imine is vital for the formation of secondary amine. To the best of our knowledge, compound **2** is the only catalyst that gives selectively secondary amine under homogeneous conditions and the efficiency matches with the heterogeneous systems Pd/C, Rh/C, Pt/C [13].

The role of the tethered butenyl unit for the catalytic activity of **2** was examined. An analogous pyridyl-functionalized NHC ligand $[L^2H]PF_6$ (Scheme S1) where butenyl unit is replaced by ^{n}butyl group was made. Following a synthetic procedure similar to **2**, complex $[RuL^2(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (**3**) is synthesised (Scheme S1) and characterised by ESI–MS, ^1H, and ^{13}C NMR (Fig. S8–S11). The catalytic efficiency of **3** was compared with **2** for the conversion of benzonitrile to dibenzyl amine and N-benzylcyclohexanamine in presence of external cyclohexyl amine. Complexes **2** and **3** showed similar activity discrediting any significant effect of the butenyl group. This is consistent with the observation that the butenyl

Table 1

Table 1. Catalytic hydrogenation of various nitriles to symmetrical secondary amines.[a]



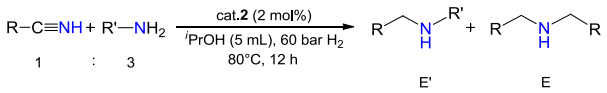
Entry	Substrates	Product	Conv (%)[b]
1			90
2			98
3			92
4			89
5			75
6			60
7			82
8			85
9			48
10			<10

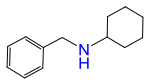
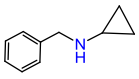
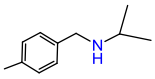
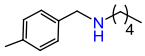
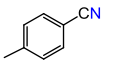
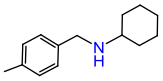
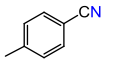
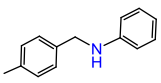
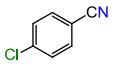
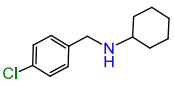
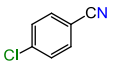
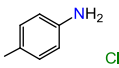
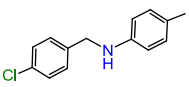
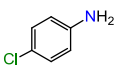
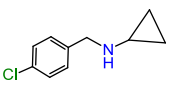
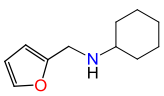
[a]All reactions were carried out using nitrile (1 mmol) and catalyst **2** (0.02 mmol) at 80°C, 60 bar H_2 pressure in 5 mL ^{i}PrOH; [b]Determined by GC-MS analysis using n-dodecane as an internal standard.

group of **2** is readily hydrogenated during the course of the reaction giving **3**, as evidenced by the ^{1}H, ^{13}C and ESI–MS spectra (Fig. S15–S17). Another pyridyl-functionalized NHC ligand [L^{3}H]Br (Scheme S2) with mesityl wingtip and the corresponding complex

Table 2

Table 2. Catalytic hydrogenation of various nitriles to unsymmetrical secondary amines.[a,b,c]



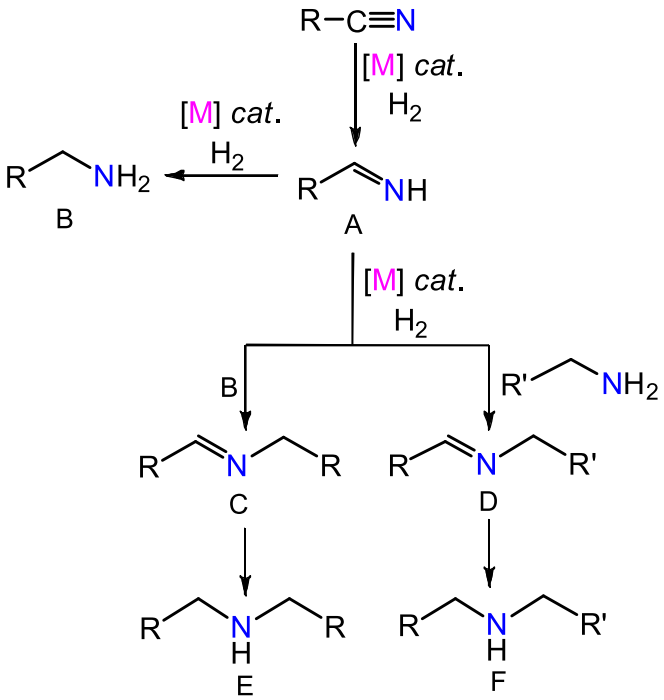
Entry	Nitriles	Amines	Product	Selectivity (E′:E)
1				98:2
2				85:15
3				50:50
4				68:32
5				98:2
6				65:35
7				72:28
8				80:20
9				94:6
10				90:10

[a]All reactions were carried out using nitrile (1 mmol), external amine (3 mmol) and catalyst **2** (0.02 mmol) at 80°C, 60 bar H_2 pressure in 5 mL ^{i}PrOH; [b]100% conversion; [c]Determined by GC-MS analysis using n-dodecane as an internal standard.

[RuL[3](η^6-*p*-cymene)Cl]Br (**4**) were also synthesised (Scheme S2) and characterised by ESI–MS, ^{1}H, and ^{13}C NMR (Fig. S12–S14). Compound **4** afforded 75% conversion of benzonitrile to dibenzyl amine under optimized conditions which is significantly lower than that obtained for **2** (90%). In the case of added external amine (cyclohexyl amine), the conversion was same (100%) but the selectivity was less (68:32 vs 98:2). The lower activity and selectivity of **4** is ascribed to the steric crowding imposed by the mesityl group.

3. Conclusion

In conclusion, we have successfully synthesized chelate Co(III) and Ru(II) complexes bearing pyridyl and butenyl functionalized NHC ligands. The Ru(II) complex is an effective homogeneous catalyst for symmetrical and unsymmetrical secondary amines via hydrogenative coupling of nitriles and nitriles/amines, respectively, in excellent yields and selectivity. The butenyl entity does not appear to significantly improve the activity and selectivity of the



Scheme 4. Metal catalysed hydrogenation of nitriles to symmetrical and unsymmetrical secondary amines.

catalyst. Further studies are being carried out in our laboratory for wider applications of this catalytic system.

4. Experimental section

4.1. General Procedures and Materials

Solvents were dried by conventional methods, distilled over nitrogen and deoxygenated prior to use. $RuCl_3.nH_2O$ (39% Ru) was purchased from Arora Matthey, India. $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ [25], $[L^1H]PF_6$, $[L^2H]PF_6$ and $[L^3H]Br$ was synthesized following the literature procedures [26].

4.2. Physical measurements

^1H NMR spectra were obtained on a JEOL JNM-LA 400 MHz spectrometer. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl ether and dried in vacuum for at least 48 h prior to elemental analyses. ESI–MS was recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer using acetonitrile as solvent.

4.3. X-ray data collections and refinement

Single crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo-Kα radiation ($\lambda_\alpha = 0.71073$ Å). The frames were indexed, integrated and scaled using SMART and SAINT software package [27], and the data were corrected for absorption using the SADABS program [28]. The structures were solved and refined using SHELX suite of programs [29] while additional crystallographic calculations were performed by the programs PLATON [30]. The crystallographic figures have been generated using Diamond 3 software [31] (50% probability thermal ellipsoids). The hydrogen atoms were included into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'. Crystallographic data and pertinent refinement parameters for **1,** and **2** are presented in Table S1. CCDC 1403193, 1407915 contain the supplementary crystallographic data for all compounds. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.4. Synthesis of $[Co^{III}(L^1)_3](PF_6)_3.KPF_6$ (1.KPF_6)

A suspension of $[L^1H]PF_6$ (80 mg, 0.23 mmol), $Co(OAc)_2.4H_2O$ (14.3 mg, 0.056 mmol), and K_2CO_3 (26.5 mg, 0.19 mmol) in THF (20 mL) was refluxed for 12 h. The mixture was cooled to room temperature and filtered over a pad of celite. The resultant solution was concentrated under reduced pressure and 10 mL hexane was added while stirring to get a yellow precipitate. The precipitate was washed with hexane (3 × 10 mL) and dried under vacuum. X-ray quality crystals of compound **1.KPF$_6$** were obtained by layering hexane onto a mixed solution of dichloromethane/acetonitrile (5/1) of the yellow precipitate inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 50 mg (60%). ESI–MS, *m/z*: 946.41 $[\mathbf{1} - PF_6]^+$, 400.69 $[\mathbf{1} - 2PF_6]^{2+}$, 218.78 $[\mathbf{1} - 3PF_6]^{3+}$; ^1H NMR (400 MHz, CD_3CN, 294 K): δ 8.43 (t, J = 8 Hz, 1H), 8.33 (d, J = 2 Hz, 1H), 8.17 (d, J = 8 Hz, 1H), 7.55 (m, 2H), 7.00 (d, J = 6 Hz 1H), 5.32 (m, 1H), 4.89 (m, 2H) 3.63 (m, 1H), 2.72 (m, 1H), 2.21 (m, 1H), 2.12 (m, 1H); ^{13}C NMR (125 MHz, CD_3CN, 294 K): 185.1, 150.9, 148.8, 145.1, 131.9, 128.4, 126.9, 121.0, 118.9, 115.2, 50.0, 33.3; IR (KBr, cm^{-1}): ν(PF_6) 841 (s); Anal. Calcd for $C_{36}H_{39}N_9CoKP_3F_{24}$: C, 33.88; H, 3.08; N, 9.88. Found: C, 33.48; H, 2.89; N, 9.08.

4.5. Synthesis of $[Ru^{II}L^1(\eta^6\text{-}p\text{-cymene})Cl]PF_6$ (2)

A solution of $[L^1H]PF_6$ (60 mg, 0.17 mmol) in dichloromethane (20 mL) was treated with Ag_2O (46 mg, 0.20 mmol), and the suspension was stirred for 4 h at room temperature under the exclusion of light and in N_2 atmosphere. After 4 h, $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (52 mg, 0.085 mmol) was added and the solution was further stirred for 12 h at room temperature. The mixture was subsequently filtered over a pad of celite and the solution was concentrated under reduced pressure and 10 mL hexane was added while stirring to get a greenish–yellow precipitate. The precipitate was washed with hexane (3 × 10 mL) and dried under vacuum. X-ray quality crystals were grown by layering hexane onto a dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 90 mg (85%). ESI–MS, *m/z*: 470.09 $[\mathbf{2}-PF_6]^+$; ^1H NMR (500 MHz, CD_2Cl_2, 294 K)): δ 9.07 (d, J = 5.96 Hz, 1H), 8.06 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 2.32 Hz, 1H), 7.64 (d, J = 8.24 Hz, 1H), 7.42 (t, J = 6.84 Hz 1H), 7.30 (d, J = 1.84 Hz 1H), 6.01 (m, 2H) 5.81 (d, J = 6.88 Hz, 1H), 5.42 (d, J = 6.4 Hz, 1H), 5.29 (m, 2H), 5.16, (d, J = 10.5 Hz, 1H), 4.55 (m, 1H), 4.42 (m, 1H), 2.76 (m, 2H), 2.41 (m, 1H), 2.18 (s, 3H), 0.95 (m, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2, 294 K): 184.1, 155.3, 141.5, 133.1, 124.8, 123.6, 118.9, 116.3, 112.2, 107.7, 106.1, 91.2, 90.5, 86.6, 82.9, 51.2, 34.4, 31.3, 29.8, 22.5, 21.9, 19.1; IR (KBr, cm^{-1}): ν(PF_6) 855 (s); Anal. Calcd for $C_{22}H_{27}N_3RuPF_6Cl$: C, 42.92; H, 4.42; N, 6.83. Found: C, 42.12; H, 4.05; N, 6.21.

4.6. General Procedure for the catalytic hydrogenation of nitriles

All of the hydrogenation reactions were performed at constant pressures using a stainless steel 50 mL Parr hydrogenation reactor. The reactor was flushed three times with hydrogen gas at 2–4 bar

prior to the addition of catalyst and substrate. Catalyst **1** (0.02 mmol), nitrile (1 mmol), and dodecane (1 mmol) in case of symmetrical amine synthesis or, catalyst **1** (0.02 mmol), nitrile (1 mmol), amine (3 mmol) and dodecane (1 mmol) in case of asymmetrical amine synthesis were dissolved in ^{i}PrOH (5 mL) under a nitrogen atmosphere. The solution was then injected into the reactor against a flow of hydrogen gas. The hydrogen gas was adjusted to 60 bar. The temperature of the system was maintained at 80 °C using a thermostat. Small aliquots of the reaction mixture were withdrawn after 12 h with a syringe and diluted with 2 mL of EtOAc and passed through a very short column of silica and subjected to GC–MS analysis. A few selected secondary amines were purified by flash chromatography and characterized by ^{1}H and ^{13}C NMR spectra.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.12.034.

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