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Aza-crown Compounds by the Self-condensation of 2-Amino-benzyl alcohol over a Pincer-Ruthenium Catalyst and Applied in Transfer Hydrogenation of Ketones[§]

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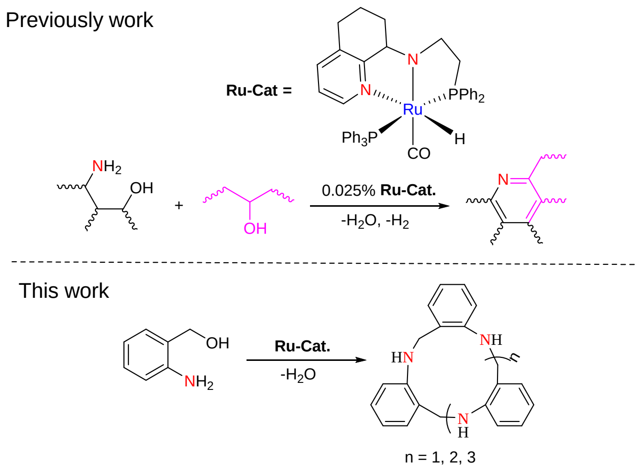
Abstract: A well-defined PNN-Ru catalyst was revisited to self-condense 2-aminobenzyl alcohol in forming a series of novel aza-crown compounds [aza-12-crown-3 (**1**), aza-16-crown-4 (**2**) and aza-20-crown-5 (**3**)]. All aza-crown compounds are separated and determined by NMR, IR, ESI-MS spectra as well as the X-ray crystallography indicating the saddle structure of **1** and twisted 1,3-alternate conformation structure of **3**. These aza-crown compounds have been explored to steady ferric initiation of transfer hydrogenation (TH) of ketones into their corresponding secondary alcohols in the presence of 2-propanol with basic *t*-BuOK solution, achieving a high conversion (up to 95%) by ferric complex with **2** in a low loading (0.05 mol%).

Introduction

The macrocyclic compounds[1] including crown ethers,[2] cryptands,[3] spherands,[4] cyclodextrins[5], and calix[*n*]arenes[1b,1f,6] have been applied in exploring of the non-covalent bond interactions,[7] molecular recognition,[1,2b] and self-assembly[8] and as ligands in catalysis.[9] With respect to catalysis, the transfer hydrogenation (TH) by macrocyclic iron (II) catalysts[10] has been attracted and pioneered by Gao,[9a,11] Mezzetti,[12] and Morris,[13] and developed as both chiral and achiral catalytic platforms.[9a,10,12,13] In the progress of catalysts using macrocyclic molecules[9,10] and supramolecular chemistry,[7,14] the challenge has remained with the issues of convenient syntheses and available numbers of macrocyclic compounds. Moreover, there is a few of aza-crown compounds available.[1b,15] Recently we developed a pincer-ruthenium(II) catalyst for the dehydrogenative coupling-cyclization of γ-amino alcohols with secondary alcohols (Scheme 1),[16] in which substance containing both functional groups of amine and secondary alcohol commonly proceed the coupling-cyclization. Certainly the substance containing both functional groups of amine and primary alcohol, 2-aminobenzyl alcohol, is investigated for the the dehydrogenative coupling-cyclization over the pincer-ruthenium(II) catalyst, interestingly the self-condensation of 2-aminobenzylalcohol is achieved to form a series of aza-crown compounds (aza-12-crown-3 (**1**), aza-16-crown-4 (**2**) and aza-20-crown-5 (**3**), Scheme 1). These aza-crown compounds can be interesting of both novel macrocycles and ligands in coordination chemistry, being similar to the medium-sized multi-anthranilides.[17] Subsequently the aza-crown compounds (**1**, **2** and **3**) have been used in coordinating with ferric chloride and resultant iron complexes are explored for transfer hydrogenation of ketones.[9a,10] The aza-16-crown-4 (**2**) efficiently catalyze transfer hydrogenation of



Scheme 1. Formation of N-heteroaromatics[16] or aza-crown compounds via dehydrogenative coupling of alcohols and amines catalyzed by a pincer-ruthenium catalyst (**Ru-Cat**)

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[§] *Dedicated to Prof. Dr. Shiyong Yang on his 60th birthday.*

Electronic Supplementary Information (ESI) available: Figures, tables, and giving NMR spectra of the new compounds; CCDC 2008494 for **1**, CCDC 2008495 for **3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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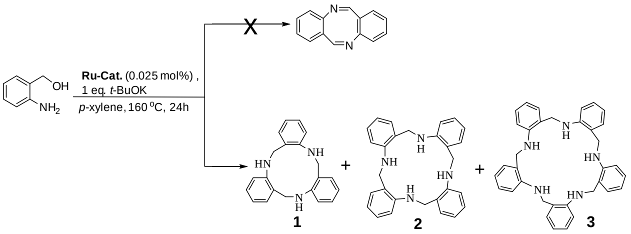
various alkyl- and aryl-containing ketones to the corresponding secondary alcohols.

Results and discussion

Synthesis of flexible CH_2*N*H-bridged aza-crown compounds (1, 2 and 3)



Scheme 2. One-pot synthetic routes to new aza-crown compounds (**1**, **2** and **3**) by 2-aminobenzyl alcohol via **Ru-Cat**

The self-coupling cyclization of 1-(2-aminophenyl)ethanol over the pincer-ruthenium catalyst (**Ru-Cat**) was observed to form 2-(4-methylquinolin-2-yl)benzenamine.[16] Instead of secondary alcohol, the primary alcohol analog 2-aminobenzyl alcohol is explored to form azacyclo compounds (**1**, **2** and **3**, Scheme 2) without observing the expected product (5Z,11Z)-dibenzo[b,f][1,5] diazocine. The mechanism of aza-crown compounds formation is essentially the formation of a series of C-N bond involved borrowing hydrogen (BH) strategy.[18] The catalytic cycle includes dehydrogenation of alcohols, followed by formation of imines with the release of water molecules and finally in-situ hydrogenation of the imines produced the desired N-alkylated amines. In this work, one of 2-aminobenzyl alcohol is first dehydrogenation by a ruthenium catalyst to the corresponding aldehyde, similar to our work on the dehydrogenation of secondary alcohols to ketones.[19] It undergoes condensation reaction with another molecule 2-aminobenzyl alcohol forming imine, then followed by a reduction step with the hydrogen equivalents from dehydrogention of the following 2-aminobenzyl alcohol stepwisely. Finally, the aza-12-crown-3 (**1**), aza-16-crown-4 (**2**) and aza-20-crown-5 (**3**) were obtained. In the presence of *t*-BuOK and **Ru-Cat** as catalyst, 2-aminobenzyl alcohol is refluxed in *p*-xylene at 160 ^{o}C for 24h to produce aza crown compounds **1**, **2** and **3** in isolated 10%, 19%, and 17% yields, respectively.

All the aza-crown compounds, **1** – **3** are characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S1 – S6, SI), high performance liquid chromatography (HPLC) (Figures S7 – S9, SI), MS-ESI (Figure S10) and IR spectra (Figures S13 – S15, SI). It is noticeable the solely individual signal of the ^{1}H and ^{13}C NMR spectra for all the aza-crown compounds (Figures S1 – S6), and also a strong absorption around 3250 cm^{-1} consistent with the bond of NH of their IR spectra (Figures S13 – S15).[12] The data of their elemental analyses are theoretically same with the fact of obtained data within acceptable errors, their retention times in HPLC significantly indicate at around 7.17, 24.88 and 26.28 mins for **1**, **2**, and **3**, respectively. Furthermore, the HPLC-MS spectra show compounds **1**, **2**, and **3** with the [m+1]$^{+}$ peak signals at 316.3, 421.2 and 526.3, respectively. Therefore it could be rationalised as aza crown compounds with the presence of the CH_2*N*H-bridges (n = 3, 4 and 5). Fortunately, the single crystals of aza-crown compounds **1** and **3** are isolated and subjected for the X-ray diffraction to obtain their absolute structures as aza-12-crown-3 (**1**) and aza-20-crown-5 (**3**). With regard to the molecular weights of three aza crown compounds, the second compound is aza-16-crown-4 (**2**).[20]

X-ray crystallographic study

The single crystals of the new aza-crown compounds **1** and **3** suitable for the single crystal X-ray diffraction were obtained by the slow diffusion of *n*-hexane into a dichloromethane solution of **1** and **3**, respectively. As shown in Figure 1, a saddle structure of **1** was clearly demonstrated, as in the case of triaza-[1.1.1]cyclophane.[21] Three hydrogens on amino group lay inside of the internal 12-membered ring, and the closest interatomic distance is observed between H_{N1}(1) and H_{N3}(3) as ca. 2.331 Å. In connection with the distorted structure of **1** due to the strong NH⋯N hydrogen bond (2.593 and 2.722 Å, See Figure 2) formed between the intra molecule.[1a,1f,21b] In the same reason, it is noteworthy that the presence of CH_2*N*H group as linker, **1** showed a much more flexible cavity, and the nitrogen atoms in **1** as donor atoms can be coordinated with metal ion to form complexes, which could be applied for ion and molecular recognition and the non-covalent bond interactions. In contrast to the crystal structures of silacalix[3]arenes.[21b] It can be concluded that the bridging CH_2*N*H group effectively reduces the internal 12-membered ring strain.

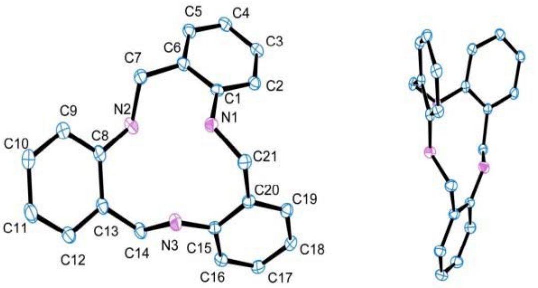


Figure 1 ORTEP representations of **1**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1–C1 1.407(2), N1–C21 1.457(2), N3–C15 1.391(3), N3–C14 1.463(3), N2–C8 1.401(3), N2–C7 1.463(3); C21–N1–C1 121.33(17), C2–C1–N1 123.35(18), C6–C1–N1 117.38(17), C14–N3–C15 121.76(16), C7–N2–C8 119.57(17), C20–C21–N1 112.51(15), C13–C14–N3 110.19(16), C13–C8–N2 120.68(19), C9–C8–N2 120.68(19), C6–C7–N2 109.12(17).

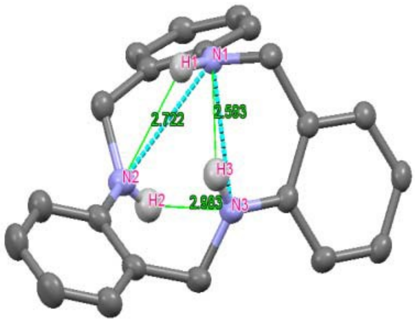


Figure 2 NH⋯N hydrogen-bonding interactions in molecules of 1. Hydrogen bond lengths [Å] and angles [deg]: N(1)⋯H(3) 2.593, N(2)⋯H(1) 2.722; N(1)⋯H(3)–N(3) 102.40, N(2)⋯H(1)–N(1) 104.50.

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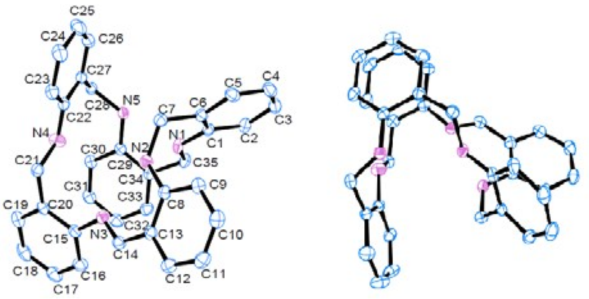


Figure 3. ORTEP representations of **3**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: N2–C7 1.453(3), N2–C8 1.366(3), N5–C29 1.396(3), N5–C28 1.461(3), N1–C35 1.457(3), N1–C1 1.396(3), N3–C14 1.279(3), N3–C15 1.423(3), N4–C21 1.456(3); C8–N2–C7 124.63(19), C28–N5–C29 123 45(18), C34–C29–N5 118.5(2), C30–C29–N5 123.0(2), C1–N1–C35120.93(19), C6–C7–N12 114.17(18), C15–N3–C14 119.3(2), N1–C35–C34 111.24(18), C13–C14–N3 124.6(2), C13–C8–N2 120.1(2), C9–C8–N2 122.1(2), C27–C22–N4 120.1(2), C23–C22–N4 120.8(2), C21–N4–C2 123.3(2), C20–C21–N4 109.44(19), C6–C1–N1 119.4(2), C2–C1–N1 121.8(2), C20–C15–N3 117.3(2), C16–C15–N3 122.4(2), C27–C28–N5 113.47(18).

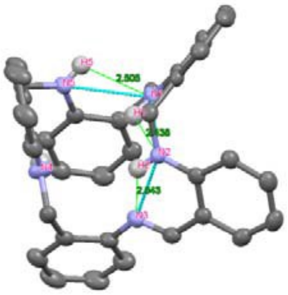


Figure 4 NH···N hydrogen-bonding interactions in molecules of **3**. Hydrogen bond lengths [Å] and angles [deg]: N(1)···H(5) 2.505, N(2)···H(1) 2.438, N(3)···H(2) 2.043; N(1)···H(5)–N(5) 111.21, N(2)···H(1)–N(1) 115.54, N(3)···H(2)–N(2) 133.70.

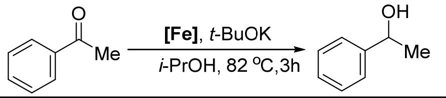
As shown in Figure 3, similar to **1**, a saddle structure of **3** was clearly demonstrated, as in the case of aza-20-crown-5, **3** adopted a excessively twisted 1,3-alternate conformation. Due to the presence of CH_2*N*H group as linker and the strong NH···N intramolecular hydrogen bond (2.043, 2.438 and 2.505 Å, See Figure 4) formed among them. There is a remakable different from the nearly regular pentagonal cavities of corona[5]arenes adopted 1,2,4-alternate conformational structures,[22] **3** exhibited a heavily twisted cavity of the 20-membered ring due to affect of the strong intra molecular NH···N hydrogen bond, and Five bridging nitrogen atoms lay on the 20-membered ring, and the closest interatomic distance is observed between N(2) and N(3) as 2.727 Å and furthest interatomic distance is observed between N (3) and N(5) as 4.990 Å. Similar to **1**, **3** could be a N_5-type ligand to form complexes with metal ions. Moreover, The two planes were made of the N3-C15-C20-C21 and N5-C29-C34-C35 in the structure are almost face-to-face parallel but with a dihedral angle of 14.13°. There are no inter molecular contacts of note in either structure. Also it can be a good model for study of the non-covalent bond interactions, ion and molecular recognition.

Subsequently we tried to use the aza-crown compounds (**1**, **2** and **3**) as macrocyclic ligands coordinated with ferric salt as homogeneous transfer hydrogenation catalysts. The three aza-crown compounds (**1**, **2**, and **3**) reacted with an equivalent of $FeCl_3{\bullet}6H_2O$ in a mixture of dichloromethane and ethanol at room temperature for 24h, respectively, on work-up, obtained **Fe1**, **Fe2** and **Fe3**. The IR spectra (Figure S16 – S18) of **Fe1** – **Fe3** displayed strong absorption bands around 1035 cm^{-1} consistent with the coordination of the Fe-N bond[11] and telescopic vibration of the O-H bond around 3430 cm^{-1}.

Catalytic evaluation in transfer hydrogenation of ketones to alcohols

Based on reported for iron complexes,[11-13] the current investigation explored the potential of **Fe1**, **Fe2** and **Fe3** to serve as catalysts for the transfer hydrogenation of ketones. Using 2-propano (*i*-PrOH) as solvent, acetophenone as the template substrate, the loading of catalyst as well as the type of bases were screened, and identification of robust conditions for the transfer hydrogenation of acetophenone to 1-phenylethanol were listed in Tables 1 and 2.

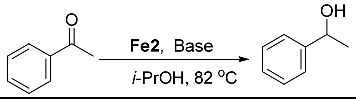
Table 1. Catalyst screening and identification of robust conditions for the transfer hydrogenation of acetophenone.[a]



Entry	[Fe]	µmol of [Fe]	Conv. (%)[b]
1	**Fe1**	2.5	5
2	**Fe2**	2.5	60
3	**Fe3**	2.5	41
4[c]	none	--	34
5[d]	**Fe2**	2.5	2
6	$FeCl_3$	2.5	35
7	**Fe2**	1	38
8	**Fe2**	2	54
9	**Fe2**	5	61
10	**Fe2**	10	62

[a]Conditions: 5 mmol acetophenone, 5 mmol *t*-BuOK, 10 mL *i*-PrOH, 82°C, 3h; [b]Determined by GC: based on acetophenone consumption with dodecane as the internal standard; [c] In the absence of iron complexes; [d] In the absence of *t*-BuOK.

Table 2. The effect of base on the transfer hydrogenation [a]



Entry	Time (h)	Base (5 mmol)	Conv. (%)[b]
1	3	*t*-BuOK	60
2	3	*t*-BuONa	49
3	3	NaOH	45
4	3	KOH	43
5	3	$Ca(OH)_2$	11
6	3	LiOH	8
7	6	*t*-BuOK	74
8	12	*t*-BuOK	96
9	24	*t*-BuOK	97

[a]Conditions: 5 mmol acetophenone, 2.5 µmol **Fe2**, 5 mmol base (1 eq.), 10 mL *i*-PrOH, 82 °C 3 ~ 24 h; [b]Determined by GC: based on acetophenone consumption with dodecane as the internal standard.

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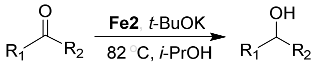
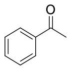
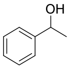
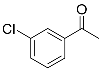
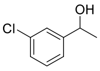
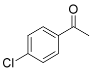
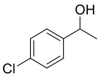
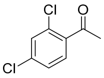
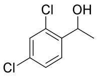
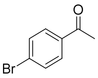
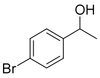
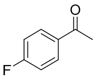
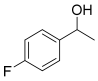
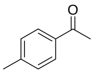
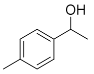
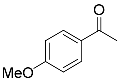
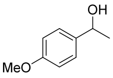
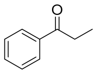
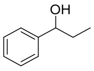
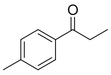
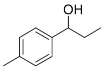
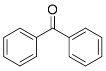
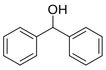
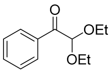
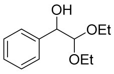
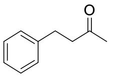
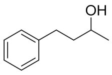
The reactions were typically performed with freshly distilled and degassed 2-propanol at 82 °C over 3 hours under an atmosphere of nitrogen. Firstly, a selection of iron catalysts (2.5 μmol), **Fe1**, **Fe2** and **Fe3**, was investigated with the loading of base set at an equimolar ratio of *t*-BuOK to the acetophenone as a template substrate (5 mmol), respectively (entries 1-3, Table 1). It was found that only the **Fe2** catalyst has activity with the 60% conversion to 1-phenylethanol (entry 2, Table 1), **Fe1** has only 5% conversion less than blank control 34% (entries 1 and 4, Table 1), and 41% for **Fe3** is similar to blank control (entries 3 and 4, Table 1). Meanwhile without *t*-BuOK (entry 5, Table 1), **Fe2** showed only 2% conversion to 1-phenylethanol. Moreover, it was also found that the $FeCl_3{\bullet}6H_2O$ has no catalytic activity (35%, entry 6, Table 1) exhibited similar conversion to blank control (34%, entry 4, Table 1). With the amount of *t*-BuOK now fixed at 5 mmol, and the amount of **Fe2** catalyst was changed between 1μmol and 10 μmol resulting in conversions of 38% (1μmol), 54% (2 μmol), 60% (2.5 μmol), 61% (5 μmol) and 62% (10 μmol) (entries 2 and 7-10, Table 1), respectively.

Secondly, in order to investigate the effect of base on the transfer hydrogenation of acetophenone, six different bases, *t*-BuOK, *t*-BuONa, NaOH, KOH, $Ca(OH)_2$, LiOH, were screened with the

Table 3. Exploring substrate scope in the transfer hydrogenation of ketones by **Fe2** under the optimal condition [a]



Entry	Substrates	Products	t(h)	Conv.(%)[b]
1			12	96
2			24	97
3			24	93
4			6	97
5			24	84
6			24	79
7			24	94
8			48	60
9			24	95
10			24	56
11			24	69
12			3	99
13			24	95

[a]Conditions: 5 mmol subustrate, 5 mmol *t*-BuOK, 2.5 umol **Fe2**, 10 mL *i*-PrOH, 82℃; [b] Determined by GC: based on ketones consumption with dodecane as the internal standard.

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loading of base set at an equimolar ratio of acetophenone and the loading of **Fe2** fixed at 0.05 mol% (entries 1-6, Table 2). It was found that in the six bases, *t*-BuOK was found to achieve the best conversion of 60%. To explore the effect of reaction time on the transfer hydrogenation of acetophenone, *t*-BuOK as the co-catalyst, the tests were conducted over different reaction times from 3 to 24 hours (entries 1 and 7 – 9, Table 3) with the S/C ratio set at 2000 and the reaction temperature at 82^{o}C, which resulted in conversions of 60% (3h), 74% (6h), 96 % (12h) and 97 % (24h)

Finally, to examine the capability of **Fe2** as a tolerant robust catalyst, a wide of ketone substrates were screened (entries 1-13, Table 3). Typically, the catalytic tests were conducted under the optimal conditions established of 5 mmol ketone, 0.05 mol% **Fe2**, 5mmol *t*-BuOK at 82 °C over 3 - 48 hours with bench 2-propanol. The transfer hydrogenation of polar bonds of thirteen ketones was achieved using **Fe2** with good to high conversions range from 56% to 99% (entries 1-13, Table 5). Aryl ketones contained electron-withdrawing groups such as halides (F, Cl, Br, entries 2-6, Table 3) displayed higher conversions than the electron-donating acetophenones with methyl or methoxy substituents (entries 7-8, Table 3). It is easy to understand that the number of electron-withdrawing groups on the benzene ring has increased the rate of transfer hydrogenation due to the increasing of polarity of carbonyl group. Such as, the dichloro-substitution on acetophenone (entry 4, Table 3) demonstrated higher rate than that monochloro-substitution on acetophenone (entries 2-3, Table 3). On the other hand, 1-phenyl-1-propanone produced 95% of 1-phenyl-1-propanol (entry 9, Table 3). Similarly, the electron-donating group methyl substitution on the aryl ring of 1-phenyl-1-propanone have reduced the transfer rate, only producing 56% of 1-(4-methylphenyl)-1-propanol (entry 10, Table 3). Meanwhile, benzophenone containing the strong electron-donating group phenyl obtained lower conversion, only 66%. In contrast, 2,2-diethoxyacetophenone containing the diethoxy group produced 99% of 2,2-diethoxy-1-phenylethan-1-ol. In addition, 4-phenyl-2-butanone also obtained 95% conversion over 24 hours. So **Fe2** can be a wide adaptable catalyst for transfer hydrogenation.

Conclusions

We have developed a novel route to prepare three novel aza-crown compounds [aza-12-crown-3 (**1**), aza-16-crown-4 (**2**) and aza-20-crown-5 (**3**)] *via* a ruthenium catalyzed the self-condensation of 2-aminobenzyl alcohol. All the azacyclo compounds were separated and identified by NMR, ESI-MS, elemental analysis as well as X-ray crystallography for **1** and **3**. With regard to the presence of CH_2NH group as linker and the strong inter molecular NH--H hydrogen bond formed between them, the titled compounds displayed unique spatial configurations and formed NH---N H-bond macroporous caves which can be suitable for study of ion and molecular recognition and the non-covalent bond interactions. Also, macrocyclic $N_3 \sim N_5$ (**1**, **2** and **3**) as donor ligands for iron complexes (**Fe1**, **Fe2** and **Fe3**) has been independently assessed as a catalyst in the transfer hydrogenation of ketones to secondary alcohols, only **Fe2** could catalyze the transfer hydrogenation of ketone, and more than thirteen of ketones was transformed into their corresponding alcohol in high yields.

Experimental section

General information.

All experiments with metal complexes were carried out under nitrogen. All solvents were reagent grade or better and used after being distilled under nitrogen. Most of the chemicals used in the catalytic reactions were repurified according to standard procedures (vacuum distillation). All ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AVIII–500 NMR spectrometer. GC analyses were carried out on an Agilent 6820 instrument. HPLC analysis were carried out on Waters 600 instrument using a column BDS HYPERSIL C18 (250 x 4.6 mm x 5.0 um), acetonitrile: water (PH = 4, Aqueous KH_2PO_4 (0.05 mol/L) solution) = 70:30, flow rate = 1 mL/min, wave length = 254 nm; ESI-MS analysis were carried out on 3200 QTRAP 1200 infinity series instrument using a column C18, acetonitrile : water = 70:30, flow:1 mL/min, electronic energy = + 40eV, Q1MS scan range = 50 ~ 600

Synthesis of aza-crown compounds

Under an atmosphere of nitrogen, a 100 mL Schlenk tube, equipped with a stir bar under N_2, was loaded with 2-aminobenzyl alcohol (1.2 g, 10 mmol), *t*-BuOK (1.1 g, 10 mmol) and **Ru-Cat.** (1.9 mg, 2.5 umol) in *p*-xylene (15 mL). The mixture was stirred at 160 ^{o}C for 24 hours. On cooling to room temperature, the mixture was diluted with water and extracted with ethyl acetate (10 mL) for three times. The organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuum to afford the yellow liquid product. The residue was purified by silica gel column chromatography to afford three yellow products. Eluent component is petroleum ether/ethyl acetate = 400/1, obtained 0.10 g **1** (10%); Eluent component is petroleum ether/ethyl acetate = 30/1, obtained 0.19 g **2** (19%); Eluent component is petroleum ether/ethyl acetate = 10/1, obtained 0.17 g **3** (17%).

Aza-12-crown-3 (1): Mp: 161-163 ^{o}C, ^{1}H NMR (DMSO-*d*, 500 MHz) δ

7.15-7.14 (d, *J* = 5 Hz, 3H), 7.03-7.00 (m, 3H), 6.69-6.68 (d, *J*= 5 Hz, 3H), 6.53-6.50 (m, 3H), 5.43 (s, 3H, N*H*), 4.28 (s, 6H);^{13}C NMR (DMSO-*d*, 125 MHz) δ 146.76, 131.37, 128.66, 124.34, 116.34, 113.40, 65.38, 46.58. ESI-MS: [M+1]/z = 316.3; FT-IR (KBr, cm^{-1}): 3250 (s, ν_{NH}), 3022 (w), 1623(w), 1506 (w), 1459 (m,ν_{CH2}), 1396 (m), 1076 (w), 755 (s).

Aza-16-crown-4 (2)[20]: Mp: 240-244 ^{o}C, ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.23-7.19 (m, 8H), 6.84-6.82 (d, *J*=10 Hz, 4H), 4.33 (s, 8H); ^{13}CNMR (DMSO-*d*, 125 MHz) δ 146.76, 131.37, 128.66, 124.34, 116.34, 113.40, 65.38, 46.58. ESI-MS: [M+1]/z = 421.2; FT-IR (KBr, cm^{-1}): 3250 (m, ν_{NH}), 3040 (w), 2966 (w), 2849 (w), 1617 (s), 1567 (s, ν_{CH2}), 1508 (s), 1450 (s), 1333 (w), 1299 (w), 905 (w), 880 (w), 805 (w), 739 (m).

Aza-20-crown-5 (3): Mp: 217-219 ^{o}C, ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.13-7.10 (m, 10H), 6.74-6.69 (m, 10H), 4.92 (s, 5H, N*H*), 4.06 (s, 10H); ^{13}CNMR (DMSO-*d*, 125 MHz) δ 146.76, 131.37, 128.66, 124.34, 116.34, 113.40, 65.38, 46.58; ESI-MS: [M+1]/z = 526.3; FT-IR (KBr, cm^{-1}): 3396 (m), 3308 (s, ν_{NH}), 2854 (m), 1608 (m), 1586 (m), 1562 (s, ν_{CH2}), 1506 (w), 1455 (w), 1331 (w), 1309 (w), 1250 (w), 1125 (w), 1044 (w), 743 (s).

Synthesis of iron(Ⅲ) complexes (Fe1 - Fe3)

Synthesis of Fe1

A small Schlenk tube, equipped with a stir bar, was evacuated and back-filled with nitrogen. Under an atmosphere of nitrogen, the tube was charged with **1** (0.16 g, 0.5 mmol) in dichloromethane (15 mL). Under N_2, $FeCl_3{\bullet}6H_2O$ (0.13 g, 0.5 mmol) and ethanol (10 mL) were introduced to the tube and the reaction mixture stirred at room temperature for 24 h. The resulting precipitate was filtered and washed with ethanol (3 × 10 mL), then washed with dichloromethane (3 × 10 mL). The titled complex **Fe1** was obtained as brown solid (0.12 g, 47%). FT-IR (KBr, cm^{-1}): 3432 (m, ν_{OH}), 1602 (m, ν_{NH}), 1510 (m), 1454 (s, ν_{CH2}), 1301 (w), 1254 (m), 1045 (m, Fe-N), 751 (s), Anal. Calcd for **Fe1** [$C_{21}N_3H_{21}FeCl_3(H_2O)_4$]: N, 7.64, C, 45.88, H, 5.31; Found: N, 7.66, C, 45.98, H, 5.28.

Synthesis of Fe2.

By using the same procedure described for the synthesis of **Fe1**, **Fe2** was obtained as a brown powder (0.12 g, 81%). FT-IR (KBr, cm^{-1}): 3407 (m, ν_{OH}), 1609 (m, ν_{NH}), 1500 (m), 1452 (s, ν_{CH2}),1028 (s, Fe-N), 754 (s); Anal. Calcd for **Fe2** [$C_{28}N_4H_{28}Fe_3Cl_7(OH)_2H_2O$]: N,6.30, C, 37.85, H, 3.63, Found: N, 6.25, C, 38.28, H, 3.58.

Synthesis of Fe3

By using the same procedure as that described for the synthesis of **Fe1**, **Fe3** was obtained as a brown powder (0.15 g, 84 %). FT-IR (KBr, cm^{-1}): 3423 (m,ν_{OH}), 1600 (m, ν_{NH}), 1494 (m), 1456 (s, ν_{CH2}), 1034 (s, Fe-N), 755 (m); Anal. Calcd for **Fe3** [$C_{35}N_5H_{35}Fe_3Cl_8(OH)(H_2O)_2$]: N, 6.80, C, 40.8, H, 3.91; Found: N, 6.57, C, 39.92, H, 4.10.

General procedure for the transfer hydrogenation of ketones under nitrogen

Under a nitrogen atmosphere, the selected ketonic substrate (5.0 mmol) was dissolved in dry and degassed 2-propanol (3 mL) under a nitrogen atmosphere and the solution stirred and heated to 82 °C. On reaching this temperature, a solution of base (5mmol) in 2-propanol (4 mL) was introduced followed by a solution of catalyst (1-10 µmol) in 2-propanol (3 mL), taking the total volume of solvent to 10 mL. At the specified reaction time (3 – 48 h), 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of 2-propanol precooled to room temperature, dodecane introduced, before being analyzed by GC. The composition of the reaction mixture was confirmed by running GC of a mixture of pure ketone, alcohol and dodecane.

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X-ray Structure Determination

A single-crystal X-ray diffraction study of **1** and **3** were conducted on a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections (Table S1, see SI). Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. Using the SHELXL-2015 package, structural solution and refinement were performed.[23]

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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Graphical for Table of Contents

Aza-crown Compounds by the Self-condensation of 2-Aminobenzyl alcohol over a Pincer-Ruthenium Catalyst and Applied in Transfer Hydrogenation of Ketones

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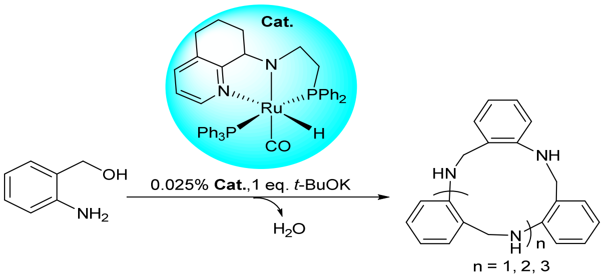

Three aza-crown compounds are easily synthesized through the self-condensation of 2-aminobenzyl alcohol over a pincer-ruthenium catalyst, and applied in the efficient transfer hydrogenation of various ketones into secondary alcohols.