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A ruthenium-carbamato-complex derived from a siloxylated amine and carbon dioxide for the oxidative α-cyanation of aromatic and cyclic tertiary amines†

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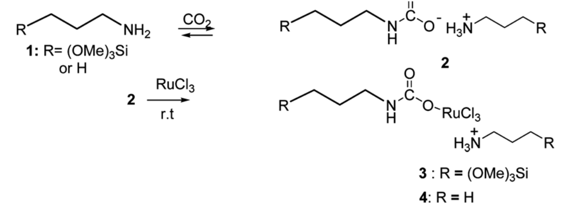
The ruthenium carbamate complex derived from 3-trimethoxysilyl-1-propyl amine and carbon dioxide was found to be a novel catalyst for the oxidative cyanation of aromatic and cyclic tertiary amines to corresponding α-amino nitriles in high to excellent yields by using hydrogen peroxide and molecular oxygen as enviro-economic oxidants. The developed protocol suggested an efficient alternative for recycling carbon dioxide.

Climate change resulting from emissions of CO_2 has been one of the greatest environmental challenges in recent decades.[1] In order to contribute, many research groups have investigated the capturing of carbon dioxide by reaction with amine groups[2] and its recycling as the starting material for the synthesis of fine chemicals. Conversion of CO_2 to useful chemicals is inevitably based on the use of transition metal catalysts.[3] Thus, the organometallic chemistry of carbon dioxide has become a subject of intensive research for many decades. Transition metal carbamates are one of the promising intermediates in the catalytic syntheses of ureas, carbamic acids and their derivatives *via* reaction of free amines with carbon dioxide to give corresponding carbamates followed by complexation with metal.[4]

Oxidative cyanation of tertiary amines is an important synthetic transformation as α-aminonitriles are highly potential precursors for the construction of natural products, bio-active substances, and functional materials.[5] So far oxidative cyanation of tertiary amines at α-position with an appropriate cyano source, such as sodium cyanide or trimethylsilyl cyanide (TMSCN) using oxidants such as O_2, H_2O_2 and TBHP in presence of transition metal catalysts such as Ru, V, Fe, Mo, Co and gold has been established to be a promising approach.[6] However, most of these catalysts are homogeneous in nature which suffer from the drawbacks of difficult recovery and non-recycling ability of the catalyst. In our recent reports, we have developed polymer supported Fe(II)–phthalocyanine[7] and starch-supported $RuCl_3$ (ref. 8) as efficiently reusable catalytic systems for this reaction. Further in recent years, several groups reported that either a visible-light photoredox system, or some promoters such as a tropylium ion and an iodine molecule have been used to mediate the α-cyanation of tertiary amines.[9] However, these methods require longer reaction time (20–30 h) in completion of the reaction.

In the present paper we describe the use of ruthenium carbamate complex synthesized from the siloxy-group containing amine and carbon dioxide followed by its complexation with ruthenium trichloride for the oxidative cyanation of the tertiary amines by using hydrogen peroxide/molecular oxygen as oxidants with NaCN in acetic acid. Importantly the presence of silicon into the ruthenium-carbamate structure facilitates the reaction and decreases the reaction time significantly.

Trimethoxysilylpropyl amine **1** is known to react with carbon dioxide (CO_2) at room temperature and atmospheric pressure to form the corresponding ionic liquid: 3-(trimethoxysilyl) propylammonium-3-(trimethoxysilyl)-propyl carbamate (TMSAC)[10] **2** as shown in Scheme 1. The formation of ionic liquid **2** was confirmed by FTIR, ^{1}H NMR and elemental analysis as given in the literature.[10] The obtained viscous ionic liquid **2** was treated with anhydrous ruthenium trichloride and stirred for 24 h at room temperature to obtain the ruthenium carbamates



Scheme 1 Synthesis of ruthenium carbamato complex **3** and **4**.

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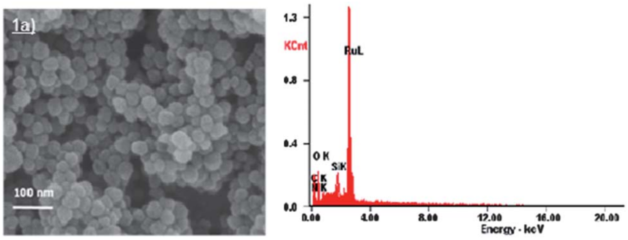


Fig. 1 (a) SEM image; (b) EDX spectrum of ruthenium complex **3**.

complex **3**. The precipitated black-brown solid was separated by centrifugation and washed with ethanol, dried in vacuum.

The synthesized complex **3** was characterized by IR, SEM and elemental analysis. The morphological features of the synthesized complex were determined by FESEM analysis (Fig. 1a). The as-synthesized complex **3** leads to a well-defined spherical nanoparticles in the range of 100–200 nm as illustrated in SEM micrograph. Elemental analysis based on EDX measurement provides detailed chemical information of the ruthenium-carbamate catalyst **3** as shown in Fig. 1b.

Further, energy-dispersive X-ray spectroscopy elemental mapping was performed to understand the distribution of elements in the as synthesized ruthenium-carbamate complex **3**. The thoroughly and uniform distribution of Ru, C, N, O and Si can easily be seen in Fig. 2. In addition, elemental analysis verified the successful synthesis of **3** (found: C, 27.08; H, 5.52; N, 4.85; Cl, 14.24; calcd for $C_{13}H_{34}Cl_3N_2O_8RuSi_2$: C, 27.46; H, 5.94; N, 4.85; Cl, 14.74%).

The thermal stability of the prepared catalyst was determined by thermogravimetric (TG) and differential thermal analysis (DTA) of the synthesized ruthenium complex as shown in Fig. 3. Initial weight loss occurs in the region of 100–120 °C, suggested the removal of absorbed water molecules. Then the synthesized complex is stable up to 250–260 °C and starts losing weight probably due to the evaluation of carbon dioxide and then maximum weight loss is found to occur in the range of 320–400 °C which is probably due to the loss of organic moieties.

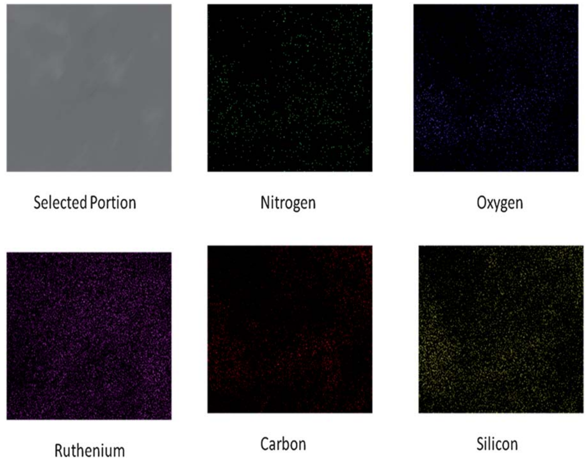

Selected Portion
Nitrogen
Oxygen
Ruthenium
Carbon
Silicon

Fig. 2 Elemental mapping of ruthenium complex **3**.

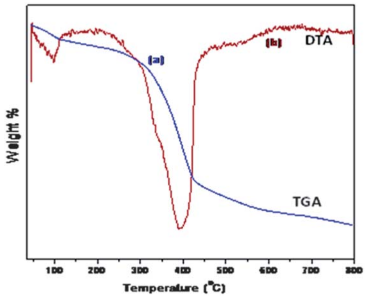
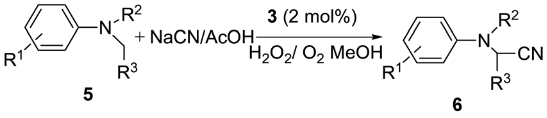


Fig. 3 (a) TGA and; (b) DTA curve of the ruthenium complex **3**.

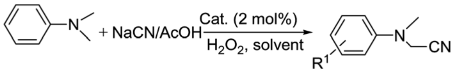


Scheme 2 Ru-catalyzed oxidative cyanation.

The catalytic efficiency of the prepared catalyst **3** was tested for the oxidative cyanation of a variety of tertiary amines **5** to α-aminonitriles **6** with hydrogen peroxide/molecular oxygen in the presence of NaCN and acetic acid by using methanol as solvent (Scheme 2).

The cyanation of *N*,*N*-dimethylaniline (1 mmol) with NaCN (1.2 mmol) in the presence of **3** (2 mol%) as a catalyst and hydrogen peroxide (H_2O_2) as oxidant is chosen as a representative example. The results of the optimization experiments are summarized in Table 1. In a controlled blank experiment, the reaction did not take place in the absence of catalyst even after prolonged reaction time (6 h) (Table 1, entry 1). Similarly, no reaction was occurred by using ionic liquid **2** (2 mol%) as catalyst under identical experimental conditions (Table 1, entry 2). Whereas, the reaction was completed within 2.5 h in the presence of complex **3** (2 mol%) and afforded 92% yield of the desired product (Table 1, entry 3). When ruthenium trichloride (2 mol%) was used as a catalyst, the reaction was

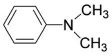
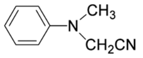
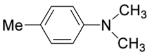
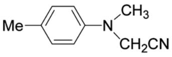
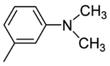
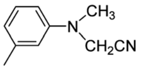
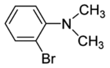
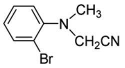
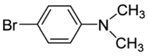
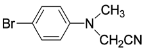
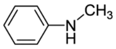
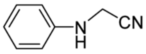
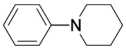
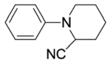
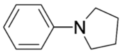
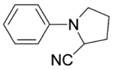
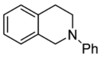
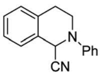
Table 1 Results of the optimization experiments



Entry	Catalyst (2 mol%)	Solvent	Time (h)	Yield[a] (%)
1	—	MeOH	6	—
2	**2**	MeOH	6	—
3	**3**	MeOH	2.5	92
4	$RuCl_3$	MeOH	3.5	90
5	**3**	MeOH	5.0	—[b]
6	**3**	THF	5.0	—
7	**3**	CH_3CN	5.0	Trace
8	**4**	MeOH	3.5	80

[a] Isolated yield. [b] In the absence of acetic acid.

Table 2 Ruthenium complex **3** catalyzed oxidative cyanation of tertiary amines[a]

Entry	Reactant **5**	Oxidant	Product **6**	Time (h)	Yield[b] (%)
1		H_2O_2 O_2		2.5	92 85
2		H_2O_2 O_2		2.0	94 89
3		H_2O_2 O_2		2.0	92 85
4		H_2O_2 O_2		3.5	72 64
5		H_2O_2 O_2		3.0	70 62
6		H_2O_2 O_2		1.5	92 85
7		H_2O_2 O_2		2.0	90 74
8		H_2O_2 O_2		2.0	91 70
9		H_2O_2 O_2		2.5	82 75
10	$(n\text{-Bu})_3N$	H_2O_2 O_2	—	5.0	—

[a] *Reaction conditions*: substrate (1 mmol), NaCN (1.2 eq.), **3** (2 mol%), acetic acid (1 mL), methanol (2 mL) at room temperature. [b] Isolated yields.

completed within 3.5 h and afforded 90% yield of the desired product (Table 1, entry 4). These results showed that the ruthenium is an essential component for the reaction. Furthermore, there was no reaction occurred in the absence of acetic acid (Table 1, entry 5) because it contribute to form HCN reacting with NaCN which in turn used for cynation,[11] indicating that the presence of acetic acid is vital for the reaction. The use of coordinative solvent, such as acetonitrile and tetrahydrofuran, was found to be ineffective for this transformation (Table 1, entry 6 and 7). However, methanol was found to be best reaction media for the reaction. To evaluate the effect of silicon presented in complex **3** on the catalytic efficiency for the oxidative cyanation, we synthesized the ruthenium carbamato complex **4** (Scheme 1) by using *n*-propylamine in place of trimethoxysilylpropyl amine **1**. The synthesized complex was tested for the oxidative cyanation of *N*,*N*-dimethylaniline under described reaction conditions. The reaction was found to be very slow and provided 80% yield of the corresponding α-cyanation product in 3.5 h (Table 1, entry 8).

With the optimal reaction conditions, the scope of this oxidation was examined with a variety of tertiary amines by using hydrogen peroxide/and molecular oxygen as oxidants,‡ the results of these experiments are summarized in Table 2. In general hydrogen peroxide was found to be better oxidant than molecular oxygen (Table 2). The substrates bearing an electron-donating group, such as a methyl or methoxy group, were found to be more reactive and afforded better yields of the corresponding α-aminonitriles (Table 2, entry 2 and 3). Whereas, the substrates having a relatively weak electron-withdrawing group, such as bromine, oxidative cyanation proceeded cleanly, producing the desired aminonitrile in moderate yields (Table 2, entry 4 and 5). Cyclic amines such as *N*-phenyl piperidine, *N*-phenylpyrrolidine and *N*-phenyltetrahydro-isoquinoline yielded corresponding α-aminonitriles in good yields (Table 2, entries 7–9). Tertiary alkylamines such as tributylamine (Table 2, entry 10) did not produce any product under described reaction conditions. The conversion and selectivity of the product was confirmed by GCMS and identity was confirmed by comparing the physical and spectral data with those of authentic samples.

After completion of the reaction, the ruthenium containing ionic liquid was recovered easily and quantitatively from the reaction mixture by precipitation with diethyl ether followed by filtration. The recovered catalyst was reused for six subsequent experiments by using *N*,*N*-dimethylaniline as substrate and hydrogen peroxide as oxidant under the optimized experimental conditions. The yield and reaction time of these recycling experiments remained same, established the recycling ability of the synthesized catalyst (Fig. 4).

Although, the mechanism of reaction is not clear at this stage, we presume the same mechanistic pathway as proposed by Murahashi *et al.*[11] The reaction might be involving the formation of reactive oxo-ruthenium species from the reaction

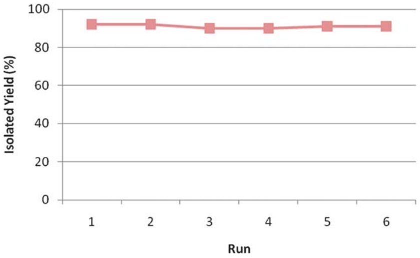
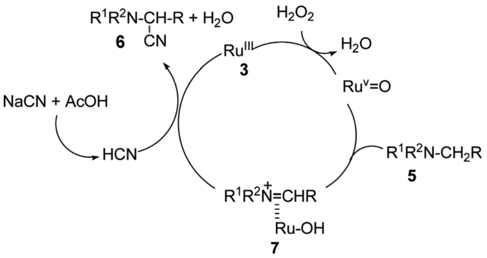


Fig. 4 Recycling of the catalyst **3**.



Scheme 3 Probable mechanistic pathway.

of ruthenium and H_2O_2. This species subsequently reacts with tertiary amines to give intermediate **7**. The *in situ* generation of HCN and its subsequent attack to the intermediate iminium ion **7** yields the corresponding α-aminonitrile **6** as shown in Scheme 3.

In conclusion, we have developed a novel ruthenium catalyst derived from carbon dioxide and an amine. The developed catalyst showed higher catalytic activity for the oxidative cyanation of tertiary amines to valuable compounds α-aminonitriles in high yields with hydrogen peroxide, molecular oxygen in the presence of NaCN in acetic acid. To the best of our knowledge, this is the first report on the utilization of carbon dioxide for the synthesis of ruthenium carbamate complex for the oxidative cyanation of tertiary amines.

We are thankful to the Director of CSIR-IIP for his kind permission to publish these results. S.K. and P.K. acknowledge the CSIR, New Delhi, for their Research fellowships. DST is kindly acknowledged for funding under an Indo-Korean joint research project.

Notes and references

‡ General experimental procedure: A 25 mL round bottomed flask equipped with a magnetic stirrer bar was charged with tertiary amine (1 mmol), NaCN (1.2 mmol), MeOH (2 mL), catalyst 3 (2 mol%) and AcOH (1 mL). To the resulting stirred reaction mixture aqueous hydrogen peroxide (1.5 mmol, 35 wt%) was added drop wise over a period of 30 min and the stirring was continued at room temperature. The progress of the reaction was monitored by TLC (SiO_2). After completion of the reaction, the catalyst was recovered by precipitation with diethyl ether followed by filtration. The obtained organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under vacuum to give crude product, which was purified by flash chromatography to afford pure α-aminonitrile. The conversion of tertiary amines into corresponding α-aminonitriles and their selectivity was determined by GC-MS (EI quadrupole mass analyzer, EM detector) and the identity of the selected products was established by comparing their spectral data with authentic samples.

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