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# Understanding the factors governing the ammonia oxidation reaction by a mononuclear ruthenium complex†

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Precise regulation of the active site of molecular catalysts is appealing because it could provide insights into the catalytic mechanism and possibly provide a new strategy for catalyst design. A ruthenium complex, [Ru(dpp<sup>Me</sup>, COMe)(bipy)(Cl)] (CSU-3), containing –Me and –COMe substituted dipyrldipyrrole as a pincer ligand, was designed and synthesized. The CSU-3 complex featured a Cl<sup>–</sup> ligand at the axial position as the active site for ammonia oxidation (AO), and is structurally analogous to AO catalyst [Ru(trpy)(dmabpy)(NH<sub>3</sub>)] [PF<sub>6</sub>]<sub>2</sub> (**1**) bearing a terpyridine ligand, but different from AO catalyst [Ru(dpp)(bipy)(NH<sub>3</sub>)] (CSU-2) containing unsubstituted dipyrldipyrrole as a hemilabile ligand with the active site at an equatorial position. To gain insight into the role of active-site and ligand regulation in the AO reaction, the structure and electrochemical properties of CSU-3 and its catalytic performance and mechanism for the AO reaction were comparably studied. Complex CSU-3 has good selective catalytic performance for the oxidation of ammonia to hydrazine with a turnover frequency (TOF) of 258.8 h<sup>–1</sup> and N<sub>2</sub>H<sub>4</sub> formation selectivity of 84.7% at *E*<sub>app</sub> of 1.0 V. The DFT calculations reveal that N<sub>2</sub>H<sub>4</sub> as a dominant product is generated *via* an ammonia nucleophilic attack of ruthenium(IV)-imide to form N<sub>2</sub>H<sub>4</sub>-by-NH<sub>3</sub> substitution.

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## Introduction

Ammonia (NH<sub>3</sub>) as a carbon-free alternative fuel is considered as one of the most important hydrogen carriers;<sup>1–3</sup> however, the classical heterogeneous catalytic cracking reaction for NH<sub>3</sub>-to-H<sub>2</sub> conversion requires a precious metal catalyst and high temperature, and is therefore relatively high cost. Molecular catalytic ammonia splitting is one of the appealing alternative methodologies to produce H<sub>2</sub>.<sup>4,5</sup> Ammonia oxidation (AO) is a critical half-reaction in NH<sub>3</sub>-to-H<sub>2</sub> conversion, and due to the involvement of multiple electron and proton transfers it is kinetically demanding. Molecular catalysts based on transition metals for the oxidation of ammonia might offer many attractive attributes, and a myriad of spectroscopic, kinetic,

thermodynamic, and electrochemical techniques have been used to gain detailed insights into the bond-breaking and bond-forming processes.<sup>6,7</sup>

Numerous transition-metal complexes based on Ru,<sup>8–15</sup> Fe,<sup>16–18</sup> Cu,<sup>19</sup> Ni,<sup>20</sup> and Mn,<sup>21</sup> with various ligands for catalytic AO have been developed,<sup>22–24</sup> since the pioneering work using a [Ru(trpy)(dmabpy)(NH<sub>3</sub>)] [PF<sub>6</sub>]<sub>2</sub> (**1**, Scheme 1, trpy = 2,2':6',2''-terpyridine, dmabpy = 4,4-bis(dimethylamino)-2,2'-bipyridine) catalyst<sup>8</sup> for AO was reported by Smith III, Hamann and co-workers. The electron rich –NMe<sub>2</sub> group in **1** makes the catalyst decrease the onset potential of AO and triggers electrocatalytic oxidation of NH<sub>3</sub> to generate N<sub>2</sub> *via* an ammonia nucleophilic attack (ANA) mechanism, with a TOF<sub>N<sub>2</sub></sub> of 0.7 h<sup>–1</sup>. The N<sub>2</sub>H<sub>4</sub>-ligated intermediates were determined through NMR spectra. As shown in Scheme 1, we recently reported a distinct example of a Ru-based catalyst,<sup>25a</sup> [Ru(K<sup>3</sup>-N,N',N''-dpp)(bipy)(dmsO)] [PF<sub>6</sub>]<sub>2</sub> (CSU-1, bipy = 2,2'-bipyridine, Hdpp = 2,5-di(pyridin-2-yl)-1*H*-pyrrole) and [Ru(K<sup>2</sup>-N,N'-dpp)(bipy)(dmsO)(NH<sub>3</sub>)] [PF<sub>6</sub>]<sub>2</sub> (CSU-2), which exhibits excellent electrocatalysis activity for the AO reaction to generate N<sub>2</sub>H<sub>4</sub> with high selectivity (>99%) and high efficiency (TOF<sub>N<sub>2</sub>H<sub>4</sub></sub> > 100 h<sup>–1</sup>). The mechanism studies show that it benefits from the lower barrier in N<sub>2</sub>H<sub>4</sub> formation involving a bimolecular coupling of Ru<sup>II</sup>-aminyl or Ru<sup>III</sup>-iminyll intermediates, but is unfavorable for N<sub>2</sub> formation *via* the ANA mechanism like in complex **1**.

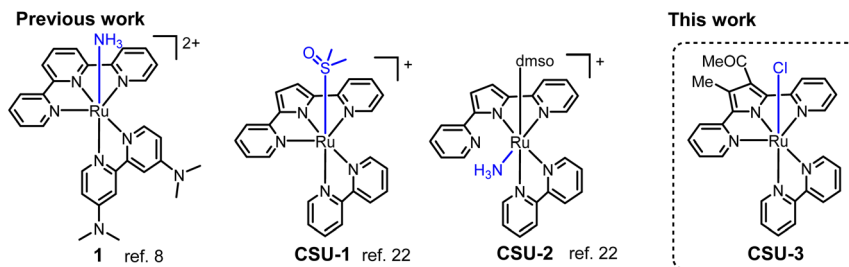
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† Electronic supplementary information (ESI) available: Complex synthesis and structure characterization, electrochemical property measurement methods, ammonia, hydrazine, hydrogen and nitrogen detection methods, and supplementary figures and tables. CCDC 2330568 and 2329730. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4sc02360a>

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Scheme 1 Molecular AO catalysts relevant to this work.

The anionic dipyridylpyrrole  $\text{dpp}^-$  ligand in **CSU-1** and **CSU-2** is structurally analogous with the neutral trpy ligand in **1**; however, their ligated ruthenium complexes exhibit significant differences in their spatial configurations, selectivity, catalytic efficiency and even mechanism for AO. The factors governing ammonia oxidation seem very complicated and deserve further in-depth research. To gain an insight into the role of the active-site in catalysis for the oxidation of ammonia, herein we design a mononuclear ruthenium(II) complex  $[\text{Ru}(\text{dpp}_{\text{Me, COMe}})(\text{bipy})(\text{Cl})]$  (**CSU-3**,  $\text{Hdpp}_{\text{Me, COMe}} = 1-(4\text{-methyl-2,5-di(pyridin-2-yl)-1H-pyrrol-3-yl)ethan-1-one}$ , Scheme 1) and comparably study its electrocatalysis of the AO reaction in  $\text{CH}_3\text{CN}$  media.

To avoid the hemilability of the  $\text{dpp}^-$  ligand to form bidentate  $\text{K}^2\text{-N,N'}$ -coordination modes like in **CSU-2**, we chose the  $\text{dpp}_{\text{Me, COMe}}^-$  ligand in **CSU-3**. The steric effect of the substituted  $-\text{Me}$  and  $-\text{COMe}$  groups causes a smaller interior bond angle (av.  $116.3^\circ$ ) between the pyrrole and pyridine in the free  $\text{dpp}_{\text{Me, COMe}}^-$  ligand (Fig. S1–S4,† crystallographic data in Tables S1 and S2†) compared to the  $121.4^\circ$  in the free  $\text{dpp}^-$  ligand.<sup>23</sup> This leads to an increase in the binding strength of the Ru–N bond between the Ru and N of  $\text{dpp}_{\text{Me, COMe}}^-$  in **CSU-3**, and causes  $\text{dpp}_{\text{Me, COMe}}^-$  binding to the Ru center with a  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$  coordination mode, like trpy in **1**. Thus, the active site in **CSU-3** was regulated to the axial position for a comparative study.

## Results and discussion

### Synthesis and characterization

Treatment of  $[\text{Ru}(\text{dmsO})_4(\text{Cl})_2]$ ,  $\text{Hdpp}_{\text{Me, COMe}}$  and bipy in the presence of  $\text{Et}_3\text{N}$  under refluxing toluene gives a red solid, which is redissolved in MeOH and refluxed for 5 d to afford **CSU-3** in 23% yield. Complex **CSU-3** was fully characterized using NMR, elemental analysis, and infrared spectroscopy (Fig. S5–S8†). The ESI-MS results display a parent peak at  $m/z$  569.0282 assigned to  $[\text{M}]^+$ . Compared to the  $^1\text{H}$  NMR of **CSU-1**, the resonance signal of ligated dmso is absent in **CSU-3**. This result is consistent with what was observed in single crystal X-ray diffraction analysis. As shown in Fig. 1, **CSU-3** displays a slightly distorted octahedral geometry around the ruthenium center. The  $\text{Cl}^-$  ligand in **CSU-3** coordinates with the ruthenium center at the axial position, unlike in **CSU-1** with a dmso ligand at the axial position. Due to the steric effect of the substituted  $-\text{Me}$  and  $-\text{COMe}$  groups on the pyrrole unit, as mentioned in the introduction section, the  $\text{dpp}_{\text{Me, COMe}}^-$  ligand in **CSU-3** as an  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$  pincer ligand strongly coordinates to the ruthenium

center at the equatorial position. This is mirrored by the shorter bond distance of the ruthenium center and the terminal pyridine of the  $\text{dpp}_{\text{Me, COMe}}^-$  ligand in **CSU-3** with Ru1–N1 of 2.107(5) Å and Ru1–N3 of 2.101(4) Å compared to that in **CSU-1** (2.136(2) Å and 2.137(2) Å). Unlike in **CSU-1**, in complex **CSU-3**, the outer donor group is not readily decoordinates to supply a vacant site for coordination of the incoming  $\text{NH}_3$ . The NMR and UV-vis monitoring experiments also confirm that **CSU-3** is very stable in the presence of a coordinating solvent and even  $\text{NH}_3$  (Fig. S9†) due to the negative charge of the  $\text{Cl}^-$  ligand, which makes it a poor leaving group. Thus, the corresponding  $\text{NH}_3$ -ligated complex could not be obtained by direct  $\text{Cl}^-$ -by- $\text{NH}_3$  substitution of **CSU-3**.

Complex **CSU-3** is treated with  $\text{AgOTf}$  ( $\text{OTf}^- = \text{trifluoromethylsulfonate}$ ) in  $\text{CH}_3\text{CN}$  to remove the  $\text{Cl}^-$  ligand, and then ammonia gas is bubbled into the filtrate solution to give  $\text{NH}_3$ -ligated complex  $[\text{Ru}(\text{dpp}_{\text{Me, COMe}})(\text{bipy})(\text{NH}_3)]\text{OTf}$  (**CSU-3-NH<sub>3</sub>**OTf) (Fig. S10–S13†). Its  $^1\text{H}$  NMR spectrum shows a newly added single broad peak at 2.47 ppm due to the incoming  $\text{NH}_3$  (Fig. S10†), which is consistent with what was observed in its ESI-MS spectrum with a parent peak at  $m/z$  551.1135 for  $[\text{CSU-3-NH}_3]^+$  (Fig. S12†) and elemental analysis.

### Electrochemical and electrocatalytic performances

The electrochemical behavior of **CSU-3** was studied using 0.1 M  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$  as the electrolyte, glassy carbon as the

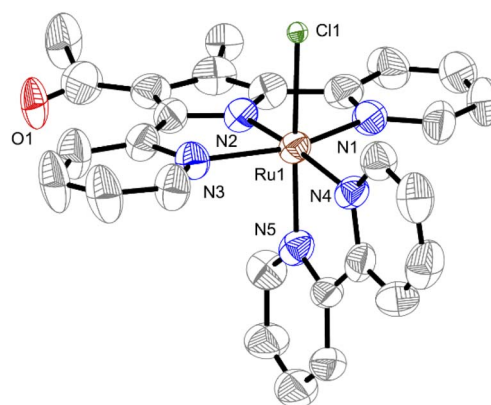


Fig. 1 Solid-state structure of **CSU-3**. The hydrogen atoms are omitted for clarity. Bond distances (Å): Ru1–N1, 2.107(5); Ru1–N2, 1.907(4); Ru1–N3, 2.101(4); Ru1–N4, 2.033(5); Ru1–N5, 2.065(4); Ru1–Cl, 2.4297(14).



working electrode, Pt wire as the counter electrode and Ag/AgCl in saturated KCl aqueous solution as the reference electrode. Unless otherwise specified, all potentials are converted into  $E_{1/2}$  versus  $\text{Cp}_2\text{Fe}^{+/0}$  in  $\text{CH}_3\text{CN}$  by adding  $-0.43$  V to the measured potential.

As shown in Fig. 2a, the cyclic voltammogram (CV) of **CSU-3** displays a reversible wave at  $-0.14$  V followed by two irreversible waves at  $0.98$  and  $1.21$  V, which are assigned to  $\text{Ru}^{\text{III/II}}$ ,  $\text{Ru}^{\text{IV/III}}$  and the ligand oxidation, respectively. The redox potential of  $\text{Ru}^{\text{III/II}}$  is significantly lower than that of **1** ( $\text{Ru}^{\text{III/II}}$   $0.055$  V vs.  $\text{Cp}_2\text{Fe}^{+/0}$  in THF), **CSU-1** ( $0.47$  V vs.  $\text{Cp}_2\text{Fe}^{+/0}$  in  $\text{CH}_3\text{CN}$ ) and **CSU-2** ( $0.43$  V vs.  $\text{Cp}_2\text{Fe}^{+/0}$  in  $\text{CH}_3\text{CN}$ ). Obviously, the redox behavior of the metal center in **CSU-3** is sensitive to the electron donor nature of the  $\text{dpp}_{\text{Me}}, \text{COMe}^-$  ligand with a methyl substituent. Compared to **CSU-1** and **CSU-2** with a  $\pi$ -accepting dmsol ligand at the axial position, the  $\pi$ -electron donating  $\text{Cl}^-$  ligand at the axial position is also a possible reason for the significant negative-shift of redox potential in **CSU-3**.

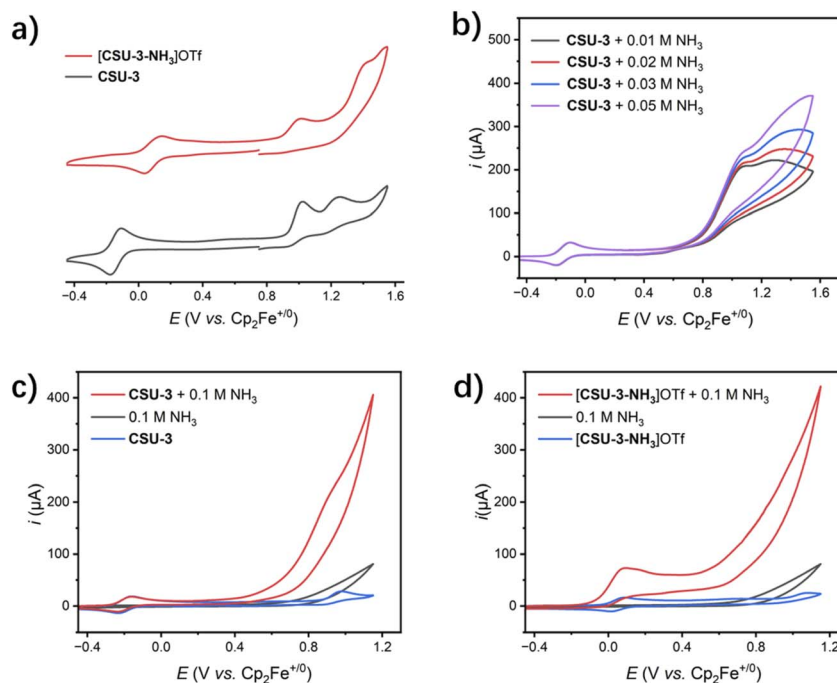
For complex  $[\text{CSU-3-NH}_3]\text{OTf}$ , the first reversible wave ( $0.09$  V) and the second irreversible wave ( $0.97$  V) were attributed to continued oxidation of the ruthenium center ( $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{IV}}$ ). The third irreversible wave at  $1.34$  V is due to ligand oxidation. Compared to **CSU-3**, the redox potential of the first reversible  $\text{Ru}^{\text{III/II}}$  wave in  $[\text{CSU-3-NH}_3]\text{OTf}$  is positively shifted. This suggests that the electron donating ability of  $\text{NH}_3$  is weaker than that of the negatively charged  $\text{Cl}^-$  ligand. The latter acts as a  $\pi$  donor increasing the electron density of the ruthenium center.

The CV plot of **CSU-3** in the presence of  $\text{NH}_3$  with various concentrations ( $0.01$ – $0.05$  M), as shown in Fig. 2b, illustrates

that the  $\text{Ru}^{\text{III/II}}$  couple remains unchanged, and a new oxidation wave ( $\sim 1.06$  V) appears for the  $\text{Ru}^{\text{IV}}$  species. Subsequently, a strong catalytic current ( $i_{\text{cat}}$ ) is observed (Fig. 2c), suggesting that the  $\text{Ru}^{\text{IV}}$  species triggers the oxidation of ammonia. Obviously, when the ruthenium center of **CSU-3** is oxidized to the  $\text{Ru}^{\text{IV}}$  oxidation state, an EC process occurs to generate  $\text{Ru}^{\text{IV}}\text{-NH}_3$  via Cl-by- $\text{NH}_3$  substitution of the  $\text{Ru}^{\text{IV}}$  species from  $2e^-$  oxidation of **CSU-3**, which is also supported by the DFT calculations. According to the CV plot of  $[\text{CSU-3-NH}_3]\text{OTf}$  (Fig. 2d), in addition to the  $\text{Ru}^{\text{IV}}$  species, the  $\text{Ru}^{\text{III}}$  species from  $[\text{CSU-3-NH}_3]\text{OTf}$  also triggers the oxidation of ammonia, which is very similar to what is observed in the **CSU-1**, **CSU-2** and  $[\text{Ru}(\text{K}^3\text{-N,N',N''-dpp})(\text{bpy})(\text{L})] \cdot \text{PF}_6$  ( $\text{L} = \text{pyridine}$ ; 4-methylpyridine; pyrimidine; isoquinoline) catalyst systems and  $\text{Ru}(\text{K}^3\text{-N,N''-dpp})(\text{trpy})(\text{NH}_3) \cdot \text{PF}_6$ .<sup>25b,c</sup>

As shown in Fig. S14 and S15,<sup>†</sup> complexes **CSU-3** and  $[\text{CSU-3-NH}_3]\text{OTf}$  exhibit satisfactory stability, corroborated by 100 consecutive cyclic voltammetry cycles, in which no new redox wave appears and the attenuation of the catalytic current is not significant. A post-catalysis and thoroughly rinsed carbon cloth working electrode displayed no catalytic activity (Fig. S16<sup>†</sup>). This indicates that the catalytic process of **CSU-3** and  $[\text{CSU-3-NH}_3]\text{OTf}$  is homogenous.

Controlled potential coulometry (CPC) experiments were conducted in a sealed Schlenk electrolytic cell with a  $0.01$  mM ruthenium catalyst solution containing  $0.2$  M (or  $2.0$  M)  $\text{NH}_3$  and  $0.1$  M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  supporting electrolyte in anhydrous MeCN. The detection method for the possible products ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{H}_4$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) and blank experiments is described in



**Fig. 2** (a) CV of **CSU-3** and  $[\text{CSU-3-NH}_3]\text{OTf}$  in MeCN solution; (b) CV of **CSU-3** in MeCN in the presence of  $\text{NH}_3$  with various concentrations ( $0.01$ – $0.05$  mM); (c) CV of **CSU-3** in MeCN in the presence of  $0.10$  M  $\text{NH}_3$ ; (d) CV of  $[\text{CSU-3-NH}_3]\text{OTf}$  in MeCN in the presence of  $0.10$  M  $\text{NH}_3$ . Conditions:  $[\text{Ru}] = 1$  mM, rate  $0.1$  V  $\text{s}^{-1}$ ,  $0.1$  M  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte, platinum wire as the working electrode, potential referenced to the  $\text{Cp}_2\text{Fe}^{+/0}$  redox couple.



the ESI (Fig. S17–S21 and Table S5).† The data of catalytic performance are listed in Table 1 and Fig. S22.†

For complex **CSU-3**, the applied potential ( $E_{\text{app}}$ ) is fixed at 0.2 V (entry 1, 2) to only generate  $\text{Ru}^{\text{III}}$  species, and as expected, in CV studies, no oxidation products of ammonia are detected. When holding the  $E_{\text{app}}$  at 1.0 V for a low concentration ammonia solution (0.2 M) for 1 h, the gas products of  $\text{H}_2$  (113.1  $\mu\text{mol}$ , 141.4 equiv. based on Ru) and  $\text{N}_2$  (0.8  $\mu\text{mol}$ , 1 equiv. based on Ru) in the headspace and  $\text{N}_2\text{H}_4$  (112.2  $\mu\text{mol}$ , 140.3 equiv. based on Ru) in the electrolyte solution are determined (entry 3). When the concentration of ammonia is increased to 2.0 M, the catalytic efficiency of **CSU-3** is approximately doubled. In addition, the selectivity of  $\text{N}_2\text{H}_4$  formation and Faraday efficiency (FE) is almost unchanged with changes in ammonia concentration, maintaining a level of 85.6 and 84.7%, respectively. This indicates that  $\text{NH}_3$  is possibly involved in the  $\text{N}_2\text{H}_4$  formation step *via* an ammonia nucleophilic attack mechanism and/or  $\text{N}_2\text{H}_4$  release *via*  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution.

In the  $[\text{CSU-3-NH}_3]\text{OTf}$  catalyst system, only  $\text{N}_2\text{H}_4$  as an anodic product is generated at low electrolytic potential (0.2 V) to only generate  $\text{Ru}^{\text{III}}$  species as the intermediate (entry 5, 6), which is very similar to the results for **CSU-1**, **CSU-2** and  $[\text{Ru}(\text{K}^3\text{-N,N',N''-dpp})(\text{bpy})(\text{L})]\cdot\text{PF}_6$ .<sup>25</sup> This suggests that a bimolecular coupling mechanism of ruthenium amide is possibly involved. Holding the  $E_{\text{app}}$  at 1.0 V ( $\text{Ru}^{\text{IV}}$  species generated at this potential), the catalytic efficiency is greatly enhanced (entry 7, 8).  $\text{TOF}_{\text{N}_2\text{H}_4}$ ,  $\text{FE}_{\text{N}_2\text{H}_4}$ , and  $S_{\text{N}_2\text{H}_4}$  reach  $350.5\text{ s}^{-1}$ , 87.9% and 98.9%, respectively.

## Mechanism

The full mechanism of the AO reaction catalysed by **CSU-3** is proposed by theoretical calculations. As shown in Fig. 3a, **CSU-3** is firstly oxidized to  $[\text{Ru}^{\text{III}}\text{-Cl}]^+$  ( $\Delta G = -8.3\text{ kcal mol}^{-1}$ ). The corresponding calculated  $\text{Ru}^{\text{III/II}}$  redox potential is  $-0.36\text{ V}$ . Direct Cl-by- $\text{NH}_3$  substitution of  $[\text{Ru}^{\text{III}}\text{-Cl}]^+$  and **CSU-3** to generate  $[\text{Ru}^{\text{III}}\text{-NH}_3]^+$

and  $[\text{Ru}^{\text{II}}\text{-NH}_3]^+$ , respectively, is unfavourable due to the high energy barrier (Fig. S25†). For example, two possible substitution pathways, namely the concerted associative pathway ( $I_a$ ) and dissociative pathway ( $D$ ), are considered. The energy barriers of the  $I_a$  pathway ( $\Delta G^\ddagger = 26.2\text{ kcal mol}^{-1}$ ) and  $D$  pathway ( $\Delta G^\ddagger = 24.7\text{ kcal mol}^{-1}$ ) are high enough to hinder direct Cl-by- $\text{NH}_3$  substitution of  $[\text{Ru}^{\text{III}}\text{-Cl}]^+$ , which is in agreement with what is observed in CV studies and synthetic experiments. A subsequent oxidation of  $[\text{Ru}^{\text{III}}\text{-Cl}]^+$  generates  $[\text{Ru}^{\text{IV}}\text{-Cl}]^{2+}$  ( $\Delta G = 22.5\text{ kcal mol}^{-1}$ ,  $E_{\text{cal.}} = 0.98\text{ V}$ ). The subsequent Cl-by- $\text{NH}_3$  substitution of  $[\text{Ru}^{\text{IV}}\text{-Cl}]^{2+}$  to produce  $[\text{Ru}^{\text{IV}}\text{-NH}_3]^{3+}$  is an endergonic step with  $\Delta G$  of  $= 12.3\text{ kcal mol}^{-1}$ . Subsequently, deprotonation of  $[\text{Ru}^{\text{IV}}\text{-NH}_3]^{3+}$  affords ruthenium(IV)-imido complex  $[\text{Ru}^{\text{IV}}\text{-NH}_2]^{2+}$ , which is a key intermediate for  $\text{N}_2\text{H}_4$  formation.

Complex  $[\text{Ru}^{\text{IV}}\text{-NH}_2]^{2+}$  is nucleophilically attacked by  $\text{NH}_3$  to produce terminal hydrazinium-ligated  $[\text{Ru}^{\text{II}}\text{-NH}_2\text{NH}_3]^{2+}$ , only overcoming an energy barrier of  $1.7\text{ kcal mol}^{-1}$ , followed by an energetically favourable deprotonation process to generate terminal hydrazine-ligated  $\text{Ru}^{\text{II}}$ -intermediate  $[\text{Ru}^{\text{II}}\text{-NH}_2\text{NH}_2]^+$  ( $\Delta G = -17.4\text{ kcal mol}^{-1}$ ). Obviously, an N–N bond is readily formed *via* ammonia nucleophilic attack of  $[\text{Ru}^{\text{IV}}\text{-NH}_2]^{2+}$  of **CSU-3** ( $\Delta G^\ddagger = 1.7\text{ kcal mol}^{-1}$ ), unlike **1** and **CSU-2** *via* ammonia nucleophilic attack of  $\text{Ru}^{\text{IV}}$ -imide with higher barriers ( $\Delta G^\ddagger = 24.1$  and  $7.7\text{ kcal mol}^{-1}$ , respectively). The single-site molecular catalytic pathway of **CSU-3** is confirmed by the linear relationship between the catalytic current and concentration of ammonia and catalyst (Fig. S23 and S24†). Furthermore, the pathway of generating hydrazine-bridged bimetallic  $[\text{Ru}^{\text{III}}\text{-}\mu\text{-N}_2\text{H}_4\text{-Ru}^{\text{III}}]^{4+}$  *via* bimolecular N–N coupling  $[\text{Ru}^{\text{IV}}\text{-NH}_2]^{2+}$  (grey line in Fig. 3b) is excluded due to the high energetic barrier ( $\Delta G^\ddagger = 10.8\text{ kcal mol}^{-1}$ ).

$\text{N}_2\text{H}_4/\text{N}_2$  selectivity is usually based on the hydrazine-ligated  $\text{Ru}^{\text{II}}$ -intermediate, which could oxidize the ruthenium centre leading to hydrazine oxidation to generate  $\text{N}_2$ ,<sup>8,17,19a,20a</sup> but also could cause  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution to produce  $\text{N}_2\text{H}_4$ . As shown in Fig. 3c,  $\text{N}_2\text{H}_4$  release through  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution to generate  $[\text{Ru}^{\text{II}}\text{-NH}_3]^+$  *via* the  $I_a$  and  $D$  pathways was

Table 1 The electrocatalytic performances of **CSU-3** and  $[\text{CSU-3-NH}_3]\text{OTf}^a$

Entry	Cat.	$c_{\text{NH}_3}$ (mol L <sup>-1</sup> )	$E_{\text{app}}$ (V)	$\text{TOF}_{\text{H}_2}$ (h <sup>-1</sup> ) $n_{\text{H}_2}$ ( $\mu\text{mol}$ )	$\text{TOF}_{\text{N}_2\text{H}_4}$ (h <sup>-1</sup> ) $n_{\text{N}_2\text{H}_4}$ ( $\mu\text{mol}$ )	$\text{TOF}_{\text{N}_2}$ (h <sup>-1</sup> ) $n_{\text{N}_2}$ ( $\mu\text{mol}$ )	$Q^b$ (C)	$\text{FE}_{\text{N}_2\text{H}_4}$ $^c$ (%)	$S_{\text{N}_2\text{H}_4}$ $^d$ (%)
1	<b>CSU-3</b>	0.2	0.2	Trace	Trace	Trace	—	—	—
2	<b>CSU-3</b>	2.0	0.2	Trace	Trace	Trace	—	—	—
3	<b>CSU-3</b>	0.2	1.0	141.4 <b>113.1</b>	140.3 <b>112.2</b>	1.0 <b>0.8</b>	25.3	85.6	99.3
4	<b>CSU-3</b>	2.0	1.0	276.0 <b>220.8</b>	258.5 <b>206.8</b>	2.9 <b>2.3</b>	47.1	84.7	98.9
5	$[\text{CSU-3-NH}_3]\text{OTf}$	0.2	0.2	5.0 <b>4.0</b>	4.8 <b>3.8</b>	Trace	0.8	87.9	100
6	$[\text{CSU-3-NH}_3]\text{OTf}$	2.0	0.2	19.5 <b>15.6</b>	19.1 <b>15.3</b>	Trace	3.3	89.5	100
7	$[\text{CSU-3-NH}_3]\text{OTf}$	0.2	1.0	169.3 <b>135.4</b>	165.3 <b>132.2</b>	1.8 <b>1.4</b>	28.5	89.5	98.9
8	$[\text{CSU-3-NH}_3]\text{OTf}$	2.0	1.0	366.9 <b>293.5</b>	350.5 <b>280.4</b>	3.8 <b>3.0</b>	60.7	89.1	98.9

<sup>a</sup> [Cat.] = 0.01 mM; electrolysis time, 1 h;  $E_{\text{app}}$  vs.  $\text{Cp}_2\text{Fe}^{+/0}$ ; carbon cloth (1 cm<sup>2</sup>) as the working electrode; molar ratio of  $\text{N}_2$ ,  $\text{N}_2\text{H}_4$ , and  $\text{H}_2$  determined by taking the average of two tests for the electrolyte in CPC experiments, and the generation of these compounds in the control CPC experiment (Table S5) is subtracted. The maximum relative errors of 1.5%, 2.2% and 3.5% for production of  $\text{H}_2$ ,  $\text{N}_2\text{H}_4$  and  $\text{N}_2$ . <sup>b</sup> Charge passed in CPC experiments in 1 h. <sup>c</sup>  $\text{FE}_{\text{N}_2\text{H}_4} = n_{\text{N}_2\text{H}_4}/Q \times 100\%$ . <sup>d</sup>  $S_{\text{N}_2\text{H}_4} = n_{\text{N}_2\text{H}_4}/(n_{\text{N}_2\text{H}_4} + n_{\text{N}_2}) \times 100\%$ .





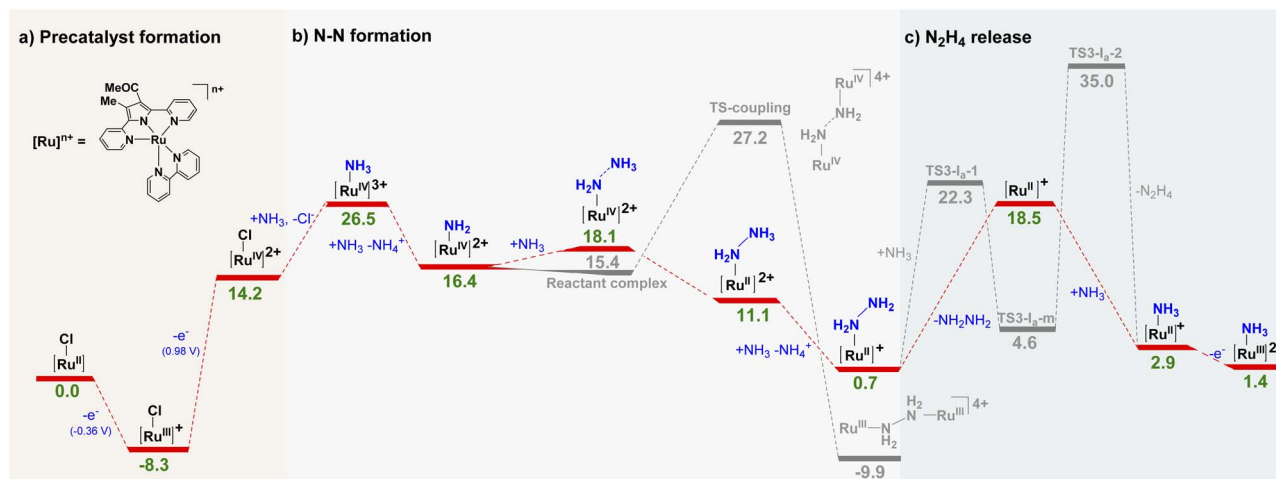


Fig. 3 The possible mechanism of AO catalyzed by CSU-3. (a) Precatalyst formation, (b) N–N formation, and (c)  $\text{N}_2\text{H}_4$  release. The free energy changes ( $\Delta G$ ) are presented in the individual reaction steps in  $\text{kcal mol}^{-1}$ , with the calculated potentials in parentheses versus  $\text{Cp}_2\text{Fe}^{+/0}$  in  $\text{CH}_3\text{CN}$ .

considered. Compared to the  $I_a$  mechanism with two transition states with large energetic barriers ( $\Delta G^\ddagger = 21.6$  and  $30.4 \text{ kcal mol}^{-1}$ ), the release of  $\text{N}_2\text{H}_4$  via the  $D$  pathway is more favourable due to the lower energetic barrier of  $17.8 \text{ kcal mol}^{-1}$ , which is also lower than that in the CSU-2 catalytic AO system ( $\Delta G^\ddagger = 23.4 \text{ kcal mol}^{-1}$ ).

Orbital interaction and electrostatic force between Ru and hydrazine in  $[\text{Ru}^{\text{II}}-\text{NH}_2\text{NH}_2]^+$  play a key role in the stabilization of the binding of the dative ligand. The energy of the lowest unoccupied molecular orbital of  $[\text{Ru}^{\text{II}}]^+$  from CSU-3 shows a higher value of  $-0.078 \text{ au}$  compared to  $[\text{Ru}(\text{trpy})(\text{dmabpy})]^+$  from **1** ( $-0.093 \text{ au}$ ), indicating the relatively weaker Ru– $\text{N}_2\text{H}_4$  bond in  $[\text{Ru}^{\text{II}}-\text{NH}_2\text{NH}_2]^+$ , which is more labile (Fig. S26†). Meanwhile, natural population analysis shows that the partial charge at the ruthenium centre of  $[\text{Ru}^{\text{II}}-\text{NH}_2\text{NH}_2]^+$  from CSU-3 is more positive than that from **1** (Table S6†), indicating that the influence of the electrostatic interaction is not as large as that of orbital interaction because  $\text{N}_2\text{H}_4$  binds less strongly to the complex, where the partial charge at the ruthenium is larger. After  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution, the formed  $[\text{Ru}^{\text{II}}-\text{NH}_3]^+$  is continuously oxidized to  $[\text{Ru}^{\text{III}}-\text{NH}_3]^{2+}$ , and the catalytic cycle restarts. Obviously, except for the Cl-by- $\text{NH}_3$  substitution in the precatalyst formation step,  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution (or  $\text{N}_2\text{H}_4$  release) is the rate-determining step for the catalytic oxidation of ammonia to hydrazine. According to the literature,<sup>7</sup> one-electron metal-based oxidation of  $[\text{Ru}^{\text{II}}-\text{NH}_2\text{NH}_2]^+$  to  $[\text{Ru}^{\text{III}}-\text{NH}_2\text{NH}_2]^{2+}$  in the complex **1** catalytic system is calculated to be the most endergonic step ( $31.7 \text{ kcal mol}^{-1}$ ) in the AO reaction. This electron transfer step seems to be a key ingredient in  $\text{NH}_3$  conversion into  $\text{N}_2$ . Hence, we believe that this very thermodynamically demanding step is the possible reason that  $\text{N}_2$  generation is unfavourable in the CSU-3 catalytic system.

## Conclusions

In summary, a mononuclear ruthenium complex CSU-3 and its selective catalysis for ammonia oxidation is reported. The  $\text{dppMe}$ ,

$\text{COMe}^-$  as a pincer ligand coordinates to the ruthenium center, and the  $\text{Cl}^-$  ligand occupies the axial position. The redox potential of  $\text{Ru}^{\text{III/II}}$  in CSU-3 is negatively shifted to about  $0.14 \text{ V}$  and  $0.61 \text{ V}$  due to the electron donor nature of the dipyrrolylpyrrole ligand and the  $\text{Cl}^-$  axially coordinated ligand, compared to structurally analogous complex **1** and CSU-1, respectively. Complex CSU-3 could selectively catalyze the oxidation of ammonia to generate  $\text{N}_2\text{H}_4$  as a dominant product via ammonia nucleophilic attack of the ruthenium(IV) imide forming a N–N bond, followed by an  $\text{N}_2\text{H}_4$ -by- $\text{NH}_3$  substitution, which is significantly distinguished from the structurally analogous **1** producing  $\text{N}_2$  via an ANA mechanism and is also different from CSU-1 and CSU-2 bearing similar hemilabile dipyrrolylpyrroline ligands, which more efficiently give the  $\text{N}_2\text{H}_4$  product via a bimolecular coupling mechanism of the ruthenium(III)-iminy radical. DFT calculation indicates that  $\text{N}_2\text{H}_4$  release is the rate-determining step for  $\text{NH}_3$ -to- $\text{N}_2\text{H}_4$  conversion catalysed by CSU-3. The weak orbital interaction between the HOMO of  $\text{N}_2\text{H}_4$  and the LUMO of  $D$  (the LUMO is the orbital that the dissociated  $\text{N}_2\text{H}_4$  binds to) in the CSU-3 catalyst system may be the main reason why  $\text{N}_2\text{H}_4$  is more easily released than in the **1** catalyst system.

## Data availability

All data included in this paper are available upon request by contact with the corresponding author.

## Author contributions

X.-Y. Yi designed research; G. Chen, X.-L. Ding, P. He, and T. Cheng. performed research; G. Chen., X.-L. Ding, Y. Chen, J. Lin, X. Zhang, S. Zhao and N. Qiao analyzed data; G. Chen and X.-Y. Yi wrote the paper.

## Conflicts of interest

There are no conflicts to declare.



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