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## COMMUNICATION

***Sn,P*-coordinated Ru cation: A robust catalyst for aerobic oxidations of benzylamine and benzyl alcohol †**Received 00th January 20xx,  
Accepted 00th January 20xxMichal Aman,<sup>a</sup> Libor Dostál,<sup>a</sup> Aleš Růžička,<sup>a</sup> Jiří Tydlitát,<sup>a</sup> Jens Beckmann,<sup>b</sup> Jan Turek<sup>\*c</sup> and Roman Jambor<sup>\*a</sup>

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**A stable ionic  $\kappa^2Sn,P$ -coordinated Ru complex shows excellent catalytic activity in aerobic oxidations of benzylamine and benzyl alcohol. This complex is stabilized by a stannylene-phosphine *peri*-substituted naphthalene ligand, which can act as either a reducing agent for a Ru(III) complex or as a  $\kappa^2Sn,P$ -chelating ligand for Ru(II) compounds.**

Aerobic oxidations of amines using air as the sole oxidant have attracted increased attention in recent years due to their potential in the production of crucial N-building blocks in a more sustainable chemical industry.<sup>1</sup> In the last decade, metal-catalysed aerobic oxidations of amines have been dominated by gold- and ruthenium-based systems.<sup>2</sup> The main difference between the two metals was found for the aerobic oxidation of primary amines. While the gold-catalysed reactions yield self-coupled imine products, oxidations utilizing ruthenium result in a formation of nitriles due to the problems with overoxidation of imines.<sup>2</sup> For this reason, Ru complexes are frequently studied as homogenous catalysts under inert atmosphere.<sup>3</sup> Furthermore, the selectivity can be significantly altered by the nature of the Ru-catalytic system. The combination of oxygen and Ru-catalyst has been reported by Bäckval (Shvo's catalyst)<sup>4</sup> or Maiti and Lahiri ([Ru(phen)(PPh<sub>3</sub>)<sub>2</sub>(CO)(H)]ClO<sub>4</sub>, phen = 1,10-phenanthroline).<sup>5</sup> In this case, efficient aerobic oxidation of amines was developed by involving additional substrates (*e.g.* 2,6-dimethoxy-1,4-benzoquinone, [Co(salen)]-type complex or TEMPO) acting as cocatalysts.<sup>4,5</sup> A full conversion of primary amines to the corresponding imines was also achieved with the Ru(II) complexes [Et<sub>3</sub>NH]<sub>2</sub>[RuCl<sub>3</sub>(dipic)]<sup>6</sup> and [RuCl<sub>2</sub>( $\eta^6$ -cymene)(L<sup>C,N</sup>SnCl)].<sup>7</sup> These results clearly show the superior catalytic activity and selectivity in comparison to the traditional homogenous Ru(II) complexes such as [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],

[[RuCl<sub>2</sub>( $\eta^6$ -cymene)]<sub>2</sub>] or [RuCl<sub>2</sub>(bpy)<sub>2</sub>] (bpy=2,2'-bipyridyl).<sup>8</sup> Similarly to amines, the oxidation of primary and secondary alcohols plays an important role in the production of fine chemicals.<sup>9</sup> Even though the selective aerobic oxidations of alcohols to aldehydes are more widely studied,<sup>10</sup> a majority of the recently developed low-valent Ru(II) catalytic complexes is frequently used in combination with a variety of stoichiometric oxidants such as TEMPO, H<sub>2</sub>O<sub>2</sub> or *t*BuOOH.<sup>11</sup> These reactions also suffer from the overoxidation of the substrate resulting in a very strong inhibition of the catalyst.<sup>12</sup> Despite the significant progress in the Ru-catalysed aerobic oxidations of amines and alcohols, the search for a versatile catalyst with a good selectivity for a wide range of substrates remains a major challenge. Recently, the field of heterobimetallic catalysis has gained increasing attention since the synergistic effect of two metal centres in the catalytic cycle may surpass the properties of classical metal catalysts.<sup>13</sup> Consequently, a variety of Ru(II) complexes containing ligands based on N-heterocyclic silylenes (NHSi) and germynes (NHGe) were prepared but not yet studied in the aerobic oxidations.<sup>14</sup>

Recently, we have prepared a *peri*-substituted naphthalene 1-PPh<sub>2</sub>-8-SnL-C<sub>10</sub>H<sub>6</sub> (**1**) (L = 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub><sup>-</sup>) with two different donor atoms (Scheme 1).<sup>15</sup> In this study, we set out to test the coordination ability of **1** towards Ru complexes [[RuX<sub>2</sub>( $\eta^6$ -cymene)]<sub>2</sub>] (X = Cl, I) and [[RuCl<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)]<sub>n</sub>] (Scheme 1) offering potential catalysts for the aerobic oxidations. The reaction of 2 eq. of **1** with [[RuCl<sub>2</sub>( $\eta^6$ -cymene)]<sub>2</sub>] yielded air stable  $\kappa^2Sn,P$  coordinated complex [( $\kappa^2$ -**1**)Ru( $\eta^6$ -cymene)Cl]<sup>+</sup> Cl<sup>-</sup> (**2**). However, the reaction of **1** with [[RuI<sub>2</sub>( $\eta^6$ -cymene)]<sub>2</sub>] provided  $\kappa^1Sn$  coordinated complex [( $\kappa^1$ -**1**)RuI<sub>2</sub>( $\eta^6$ -cymene)] (**3**). When **1** was treated with the Ru(III) complex [[RuCl<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)]<sub>n</sub>], the redox reaction took place to give Sn(IV) complex 1-PPh<sub>2</sub>-8-SnCl<sub>2</sub>L-C<sub>10</sub>H<sub>6</sub> (**5**) together with  $\kappa^2Sn,P$  coordinated Ru(II) complex [( $\kappa^2$ -**1**)Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl] (**4**). Conversely, no insertion of **1** into a Ru-X bond was observed, contrasting strongly with similar reactions of stannylenes Sn(NCH<sub>2</sub>P<sup>*i*</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> or 1-SnAr-2-PR<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (Ar = Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub> or Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = Ph, *i*Pr or Cy, Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).<sup>16</sup> These stannylenes inserted into a M-X bond (M = Ru, Rh, Ir, Au, Ge, Sn) to give a  $\kappa^2Sn,P$  coordination of the

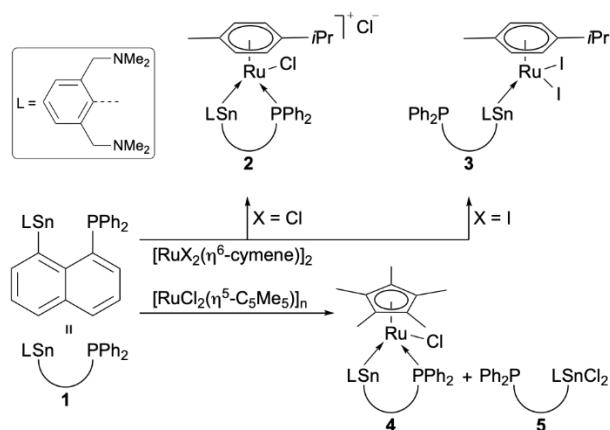
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† Electronic Supplementary Information (ESI) available: CCDC numbers 2041511 (**3**), 2041512 (**2**), 2041513 (**4**). Discussion for an alternative catalytic cycle, experimental details, NMR spectra of **2** - **5**, DFT calculations, catalytic tests together with NMR and GC MS analysis. See DOI: 10.1039/x0xx00000x

resulting chloridostannyl ligands without any sign of the reduction of the metal centres.<sup>16,17</sup>



Scheme 1. Reactivity of **1** towards selected Ru complexes.

Ru(II) complexes **2** – **4** were characterized by NMR spectroscopy and X-ray diffraction analysis (see ESI). Molecular structures of **2** – **4** confirmed substantial differences in the chelating behaviour of **1**. While the complex **2** consists of  $\kappa^2Sn,P$ -coordinated  $[(\kappa^2-1)Ru(\eta^6\text{-cymene})Cl]^+$  cation ( $2^+$ ) that is compensated by  $Cl^-$  (Figure 1), compound **4** is a neutral  $\kappa^2Sn,P$ -coordinated complex  $[(\kappa^2-1)Ru(\eta^5\text{-C}_5\text{Me}_5)Cl]$  (see ESI). In contrast, compound **3** is a neutral  $\kappa^1Sn$ -coordinated complex  $[(\kappa^1-1)Ru]_2(\eta^6\text{-cymene})$ .

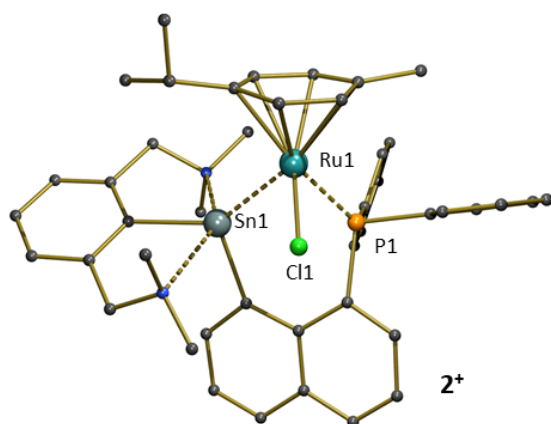
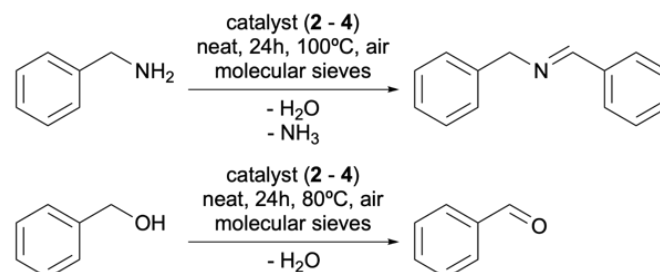


Figure 1. PovRay presentation of the molecular structure of  $2^+$  (hydrogen atoms and  $Cl^-$  anion of **2** are omitted for clarity).

The  $^{31}P\{^1H\}$  NMR spectra of  $\kappa^2Sn,P$ -coordinated complexes showed signals at  $\delta$ 36.2 ppm (for **2**) and 52.6 ppm (for **4**), shifted downfield in comparison with the starting **1** ( $\delta$ -20.0 ppm). In contrast, the signal resonating at  $\delta$  -19.4 ppm was observed in the  $^{31}P\{^1H\}$  NMR spectrum of **3**. This small shift, as compared to **1**, suggests the absence of the  $P \rightarrow Ru$  coordination and confirms the  $\kappa^1Sn$ -coordination of **1** in solution.

A whole set of **2** – **4** was tested in the aerobic self-coupling oxidation of benzylamine. The catalytic tests were performed in neat

benzylamine in the presence of 4Å molecular sieves using air as an oxidant (Scheme 2). Complexes **2** – **4** are all highly active with a catalyst loading of only 0.01 mol % necessary for the complete oxidation. For comparison, 1 mol % loading of the starting Ru complexes was not sufficient for the full conversion (Neither was any other component used for the synthesis of **2** – **4**; for more details see Table S6 in ESI).



Catalyst	Catalyst loading (mol%)	Substrate	Yield (%) <sup>a</sup>
<b>2</b>	0.01	Benzylamine	>99
<b>3</b>	0.01	Benzylamine	>99
<b>4</b>	0.01	Benzylamine	>99
<b>2</b>	0.001	Benzylamine	17
<b>3</b>	0.001	Benzylamine	15
<b>4</b>	0.001	Benzylamine	6
<b>2</b>	0.005	Benzylamine	>99
<b>2</b>	1	Benzyl alcohol	>97
<b>2</b>	0.1	Benzyl alcohol	69
<b>3</b>	0.1	Benzyl alcohol	63
<b>4</b>	0.1	Benzyl alcohol	56

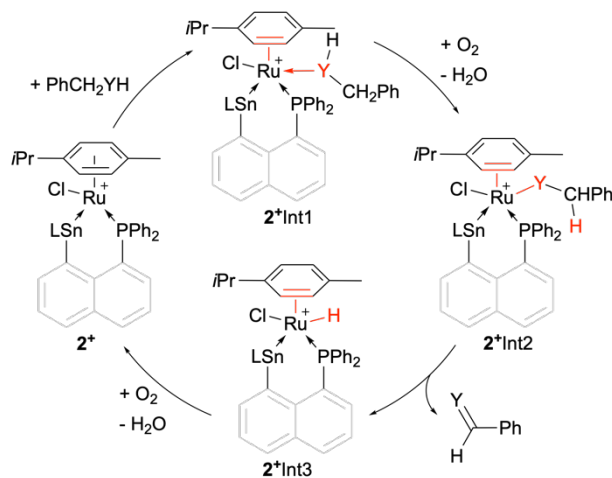
<sup>a</sup> determined by  $^1H$  NMR and GC-MS analysis

Scheme 2. Aerobic oxidations of benzylamine and benzyl alcohol catalysed by **2** – **4**.

When the catalytic loading of **2** – **4** was lowered to 0.001 mol %, different conversions were observed showing complex **2** as the most effective (Scheme 2 and Figures S26 – S28, ESI). A full conversion of benzylamine was detected with the loading 0.005 mol % of **2** (Figures S23 – S25, ESI). Since the number of ruthenium-based catalysts for the selective alcohol oxidations by air as the sole oxidant is still rather limited,<sup>18</sup> complex **2** was also tested in the additive and solvent-free synthesis of benzaldehyde (Scheme 2). Almost full conversion was achieved for **2** with a loading of 1 mol % (Figures S29 – 30, ESI). Thus, the complex **2** represents a rare example of a versatile Ru-catalyst for aerobic oxidations of amines and alcohols. Although the Shvo's catalyst  $RuH_2(CO)(PPh_3)_3$ <sup>19a</sup> or Szymczak's amide-derived NNN-Ru(II) hydride<sup>19b</sup> are one of the most efficient Ru-catalysts (0.01 mol % loading) for oxidation of alcohols and amines (conversions up to 96%), the dehydrogenation reactions need to be performed under inert argon atmosphere.<sup>19</sup> Oxygen was used as an oxidant using the Shvo's catalyst (2 mol %) in combination with 2,6-dimethoxy-1,4-benzoquinone and  $[Co(salen)]$ -type complex<sup>4</sup> or with  $[Ru(phen)(PPh_3)_2(CO)(H)]ClO_4/TEMPO$  system (2 mol %).<sup>5</sup> In general, the dehydrogenation of amines or alcohols using air as an oxidant is

more typical for gold (1 mol % loading),<sup>2e,f</sup> iron (2.5 mol %),<sup>20</sup> palladium (1 mol %),<sup>21</sup> and copper (5 mol %)<sup>22</sup> complexes, but, higher catalytic loadings are necessary.

Given the promising results of the catalytic activity of **2**, we have performed a preliminary computational study focusing on the thermodynamic aspects of the catalytic cycle and identification of the key intermediates in the aerobic oxidations catalysed by **2**<sup>+</sup>. We have proposed two plausible pathways involving either the Ru or Sn atom as a catalytic centre. Based on the thermodynamic data (Tables S2 and S4, ESI), the interaction of both substrates with the Ru centre seems to be more likely (Scheme 3; please see ESI for the discussion of the alternative pathway). The activation of the benzylamine resulting in the formation of the intermediate **2**<sup>+</sup>Int1A is slightly exergonic with a  $\Delta G$  value of  $-1.2$  kcal mol<sup>-1</sup>. The formed N→Ru interaction is considerably strong with a bond length of 2.110 Å, which is well below the sum of the van der Waals radii of 4.12 Å. The major geometrical change was observed for the coordination of the cymene ligand, which changes from  $\eta^6$  to  $\eta^2$  (Figure S5, ESI). The lability of the cymene ligand is well known and a similar decrease in hapticity was also observed in Ru-catalysed *ortho*-arylation reactions.<sup>23</sup> As a consequence, both Ru-Sn and Ru-P interactions become stronger than in **2**, which is reflected in shorter bonding distances and higher values of the Wiberg bond index<sup>24</sup> (WBI<sub>Ru-Sn/P</sub>; Table S3, ESI). In the following step ( $\Delta G = -9.2$  kcal mol<sup>-1</sup>), Ru(III) complex **2**<sup>+</sup>Int2A is obtained from the reaction of **2**<sup>+</sup>Int1A with molecular oxygen. The bonding pattern in **2**<sup>+</sup>Int2A is very similar to **2**<sup>+</sup>Int1A with an expected elongation of the Ru-Sn and Ru-P bonds due to the newly formed Ru-N covalent bond. The third step involves elimination of the benzylimine yielding Ru(III) hydride **2**<sup>+</sup>Int3A ( $\Delta G = -0.1$  kcal mol<sup>-1</sup>). Analogous to **2**<sup>+</sup>Int1A and **2**<sup>+</sup>Int2A, the Ru centre in **2**<sup>+</sup>Int3A is stabilized by the Ru-Sn and Ru-P interactions, which confirms the crucial effect of the  $\kappa^2$ Sn,*P*-bidentate ligand. Finally, the regeneration of the catalyst **2**<sup>+</sup> proceeds readily through a highly exergonic H<sub>2</sub> elimination from **2**<sup>+</sup>Int3A followed by a formation of H<sub>2</sub>O upon oxidation by air ( $\Delta G = -79.3$  kcal mol<sup>-1</sup>).



Scheme 3. Proposed mechanism of aerobic oxidations catalysed by **2**<sup>+</sup> (Y = NH or O).

Correspondingly, the oxidation of the benzyl alcohol follows a similar catalytic mechanism. Although the structure of the intermediates is very similar (Figure S5, ESI), the thermodynamics of the individual catalytic steps are different. The first step involving the interaction of **2**<sup>+</sup> with benzyl alcohol is now endergonic ( $\Delta G = 12.8$  kcal mol<sup>-1</sup>), while  $\Delta G$  values of  $-31.2$  and  $-3.9$  kcal mol<sup>-1</sup> were found for the formation of **2**<sup>+</sup>Int2B and **2**<sup>+</sup>Int3.<sup>25</sup>

To support this mechanism, we have performed additional mechanistic and kinetic studies. The use of pure oxygen instead of air shortened the reaction time to 12 h supporting thus **2**<sup>+</sup>Int1 → **2**<sup>+</sup>Int2 oxidation step involving O<sub>2</sub> (Table S7, Figure S51, ESI). The conversion of the benzylamine was monitored by the <sup>1</sup>H NMR spectroscopy and used for the determination of the oxidation rates from the slope of the plot of ln(M<sub>0</sub>/M<sub>t</sub>) versus time (min). The kinetic studies showed a linear dependence of ln(M<sub>0</sub>/M<sub>t</sub>) versus time indicating a pseudo-first order reaction with  $k = 0.379$  h<sup>-1</sup> (Figure S52, ESI). This value suggests fast conversion in comparison to the Pd-based system, where  $k = 0.016$  h<sup>-1</sup> was detected for 1 mol % of the Pd catalyst.<sup>21</sup> Moreover, the rates depend on the concentration of **2** with a  $k = 0.01$  h<sup>-1</sup> for 0.001 mol % of **2** (Table S8, Figure S66, ESI). The oxidation of benzylamine by O<sub>2</sub> also proceeds in the toluene solution and a linear dependence with a rate of  $k = 0.006$  h<sup>-1</sup> was determined for a molar ratio of [**2**]:[benzylamine] = 1:20000 (equivalent of 0.005 mol %), while a rate of  $k = 0.16$  h<sup>-1</sup> was found for a molar ratio of 1:100 (Table S8, Figure S67, ESI). This is in accordance with the proposed **2** → **2**<sup>+</sup>Int1 transformation as the rate determining step. The Hg poisoning test did not provide substantial changes, indicating a homogenous character of the catalysis (Figure S51, ESI). Compound **2** is air stable (even in CD<sub>3</sub>OD) and no reaction was observed in the presence of benzylamine or benzyl alcohol at room temperature (ESI). Finally, the catalytic oxidation (0.05 mol% of **2**) was studied as an NMR tube experiment. The <sup>31</sup>P NMR spectrum revealed four signals at  $\delta$ -14.2, 30.2 (compound **2**), 65.4 and 82.5 ppm after 1 h in accordance with a suggested mechanism (Figure S86, ESI). Importantly, the signal at  $\delta$  31 ppm of **2** was observed after 14 h (Figure S87, ESI). Similar experiment was performed under argon atmosphere to inhibit the oxidation of proposed **2**<sup>+</sup>Int1. The <sup>31</sup>P NMR spectrum revealed two signals at 30.3 (compound **2**) and 81.8 ppm (Figure S88, ESI). This experiment further corroborates the suggested mechanism having **2** → **2**<sup>+</sup>Int1 as the initial step.

In summary, the *peri*-substituted naphthalene 1-PPh<sub>2</sub>-8-SnL-C<sub>10</sub>H<sub>6</sub> (**1**) with a N→Sn coordinated stannylene group demonstrated an interesting reactivity with different Ru compounds. For the Ru(III) complex **1** acts as a mild reducing agent, while it serves as a neutral  $\kappa^1$ Sn- and  $\kappa^2$ Sn,*P*-chelating ligand for Ru(II) compounds. Because of a strong N→Sn coordination, no insertion of **1** into a Ru-X bond was observed. From the studied set of compounds the ionic  $\kappa^2$ Sn,*P* coordinated complex [( $\kappa^2$ -**1**)Ru( $\eta^6$ -cymene)Cl]<sup>+</sup> Cl<sup>-</sup> (**2**) showed the most promising catalytic activity in aerobic oxidation reactions. Finally, the preliminary DFT studies confirmed the crucial effect of the  $\kappa^2$ Sn,*P*-bidentate ligand.

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There are no conflicts to declare.

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