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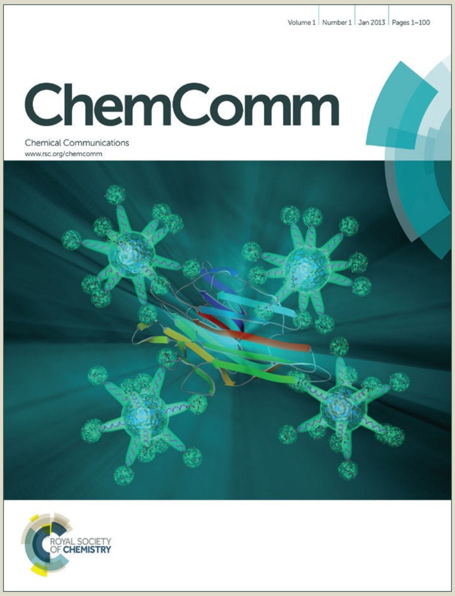

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# Enantioselective rhodium/ruthenium photoredox catalysis en route to chiral 1,2-aminoalcohols

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**A rhodium-based chiral Lewis acid catalyst combined with [Ru(bpy)$_3$](PF$_6$)$_2$ as photoredox sensitizer allows for the visible-light-activated redox coupling of α-silylamines with 2-acyl imidazoles to afford, after desilylation, 1,2-amino-alcohols in yields of 69-88% and with high enantioselectivity (54-99% ee). The reaction is proposed to proceed via an electron exchange between the α-silylamine (electron donor) and the rhodium-chelated 2-acyl imidazole (electron acceptor), followed by a stereocontrolled radical–radical reaction. Substrate scope and control experiments reveal that the trimethylsilyl group plays a crucial role in this reductive umpolung of the carbonyl group.**

Organosilicon compounds are of tremedeous utility in organic synthesis.[1] For example, silyl groups introduced in the α-position of amines serve as convenient precursors for the mild generation of α-aminoalkyl radicals (Figure 1).[2] The silyl group in α-silylamines not only serves as a redox handle to facilitate a single electron oxidation (SET, single electron transfer),[3] but also results in a subsequent rapid cleavage of the C-Si bond under release of α-aminoalkyl radicals, which then may either add to a variety of electron-deficient alkenes or become involved in iminium chemistry after further oxidation. Here we report a less common reactivity of α-silylamines, namely a visible-light-induced redox-coupling with ketones,[4] and demonstrate how to perform this reaction under conditions of enantioselective catalysis.[5]

We recently reported the photoredox coupling of tertiary amines with 2-trifluoroacetyl imidazoles under stereoselective formation of 1,2-aminoalcohols, catalyzed by a chiral iridium complex as dual chiral Lewis acid / photoredox catalyst.[6] However, this method is limited to ketones containing α-CF$_3$ groups, apparently to render the carbonyl compound a better electron-acceptor. In order to expand the substrate scope, we turned our attention to dual catalysis, namely using a chiral Lewis acid in combination with a separate photosensitizer.[7,8] Encouragingly, the chiral-at-metal rhodium-based Lewis acid Λ-**RhO**[9-11] together with the established photosensitizer [Ru(bpy)$_3$](PF$_6$)$_2$ (Rubpy) catalyzed the photoactivated reaction of the benzoyl imidazole **1a** with the α-silylamine **2a** to provide under C-C bond formation the silylether product **3a'** in 68% and with 41% ee (Table 1, entry 1).[12] Removing the trimethylsilyl (TMS) group with TBAF ahead of the workup increased the yield of the corresponding alcohol **3a** to 73% (entry 2). The enantioselectivity of the aminoalcohol coupling product was then stepwise improved by increasing the steric bulk of the substituent at the imidazole nitrogen (R$^1$, entries 3-5), with the best result obtained for a 2-phenylphenyl substituent, reaching 93% ee. Importantly, replacing the rhodium-catalyst with the analogous iridium congener Λ-**IrO**[13-15] abolished product formation, both in the presence or

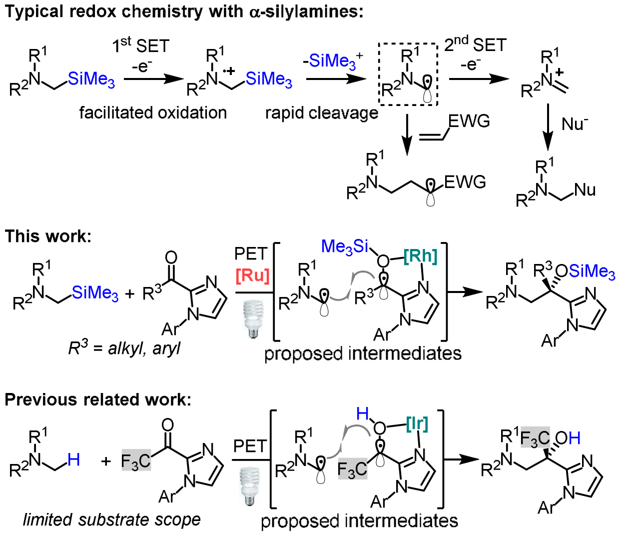

**Fig. 1** α-Aminoalkyl radical generation and follow-up chemistry with α-silylamines serving as convenient radical precursors.

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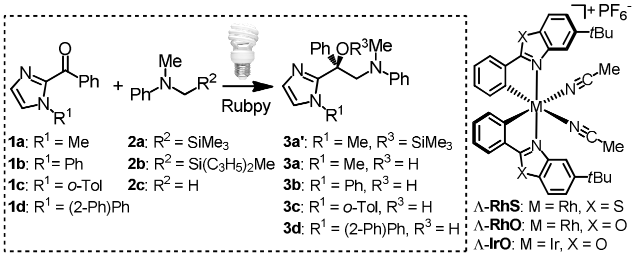
absence of an additional photosensitizer (entries 6 and 7). However, the previously developed second-generation chiral-at-metal rhodium-based Lewis acid Λ-**RhS**,[16] in which the benzoxazole ligands are replaced with benzothiazoles, provided in combination with $[Ru(bpy)_3]^{2+}$ the best results with 76% yield and 95% ee for the reaction **1d** + **2a** → **3d** (entry 8).[17] Control experiments confirm that this reaction requires both visible light and the ruthenium photosensitizer (entries 9 and 10). Furthermore, the TMS group appears crucial for this reaction as a substrate (**2b**) with the more bulky bis(cyclopropyl)methylsilyl group affording only 7% yield of the aminoalcohol (entry 11), whereas a related amine (**2c**) devoid of any silyl group suppressed product formation completely (entry 12).

**Table 1** Initial experiments[a]



| entry | cat | sens[b] | hν[c] | cpd **1** | cpd **2** | *t* (h) | yield (%)[d] | ee (%)[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | Λ-**RhO** | Rubpy | yes | **1a** | **2a** | 14 | 68 (**3a'**) | 41 |
| 2 | Λ-**RhO** | Rubpy | yes | **1a** | **2a** | 14 | 73 (**3a**) | 41 |
| 3 | Λ-**RhO** | Rubpy | yes | **1b** | **2a** | 14 | 74 (**3b**) | 82 |
| 4 | Λ-**RhO** | Rubpy | yes | **1c** | **2a** | 14 | 73 (**3c**) | 88 |
| 5 | Λ-**RhO** | Rubpy | yes | **1d** | **2a** | 14 | 72 (**3d**) | 93 |
| 6 | Λ-**IrO** | Rubpy | yes | **1d** | **2a** | 24 | 50 (**3d**) | 0 |
| 7 | Λ-**IrO** | none | yes | **1d** | **2a** | 24 | 43 (**3d**) | 3 |
| 8 | Λ-**RhS** | Rubpy | yes | **1d** | **2a** | 5 | 76 (**3d**) | 95 |
| 9 | Λ-**RhS** | Rubpy | none | **1d** | **2a** | 20 | n.r. | n.d. |
| 10 | Λ-**RhS** | none | yes | **1d** | **2a** | 20 | n.r. | n.d. |
| 11 | Λ-**RhS** | Rubpy | yes | **1d** | **2b** | 20 | 7 (**3d**) | 79 |
| 12 | Λ-**RhS** | Rubpy | yes | **1d** | **2c** | 20 | n.r. | n.d. |

[a] Reaction conditions: To a mixture of **1a**-**d** (0.1 mmol), $[Ru(bpy)_3](PF_6)_2$ (1.0 mol% or none), and catalyst (4 mol% or none) in MeCN/DMAC (4:1) (1ml) was added the amine **2a**-**c** (0.15 mmol). The reaction mixture was degassed and stirred at r.t. under nitrogen and, except for entry 9, irradiated with a 23 W CFL. Afterwards, the solvent was evaporated to dryness and the residue was redissolved in THF, then treated with TBAF (0.5 mmol). The TBAF addition was omitted for entry 1. The product was isolated by flash chromatography.

[b] Rubpy = $[Ru(bpy)_3](PF_6)_2$.

[c] 23 W compact fluorescent lamp (CFL) at a distance of approx. 5 cm from Schlenk tube.

[d] Isolated yields. n.r. = no reaction.

[e] Determined by HPLC on chiral stationary phase. n.d. = not determined.

Having discovered this reaction, we next investigated the substrate scope with respect to α-trimethylsilyalkylamines (Fig. 2). Accordingly, both *para*- and *meta*-methylated *N*-phenyl moieties within the α-silylamines afforded the individual products (**3e** and **3f**) in very good yields (80-81%) and with excellent enantioselectivities (97-98% ee). An *N*-benzyl group was well tolerated, providing the C-C-coupling product **3g** in 78% yield and with a slightly reduced 93% ee. A reaction with *N*-(trimethylsilylmethyl)-1,2,3,4-tetrahydroquinoline provided the 1,2-amino alcohol **3h** with 70% yield and 95% ee. *N*,*N*-Diaryl-*N*-(trimethylsilylmethyl)amines also gave satisfactory results (products **3i** and **3j**).

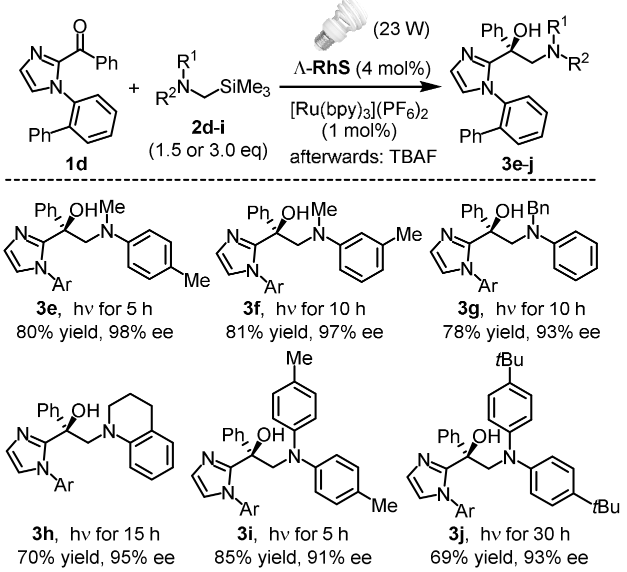


**Fig. 2** Substrate scope with respect to α-silylamines.

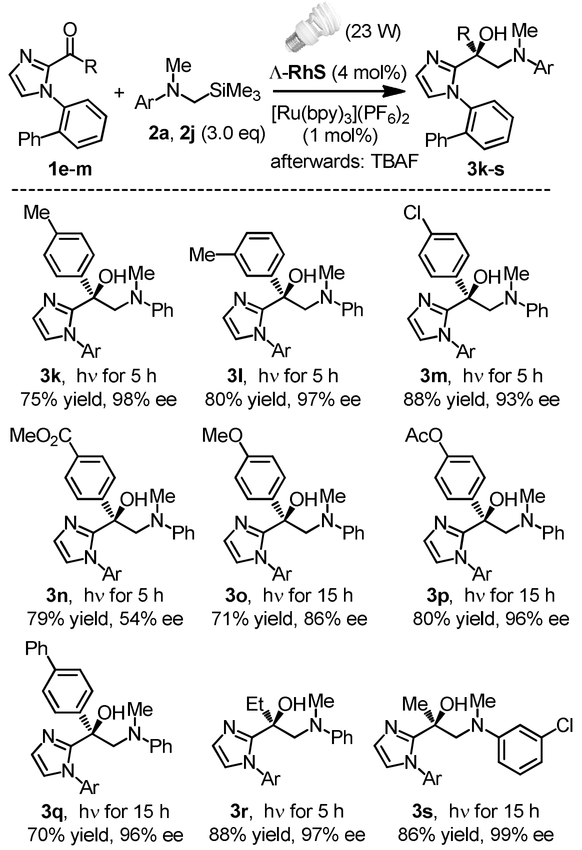


**Fig. 3** Substrate scope with respect to 2-acyl imidazoles.

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Next, the substrate scope with respect to 2-acyl imidazole was evaluated. Fig. 3 reveals that both aromatic as well as aliphatic substituents at the acyl group are tolerated (substituent R in Fig. 3), providing the respective 1,2-amino alcohols **3k-s** in 70-88% yield and with enantioselectivities of 54-99% ee. With respect to substituents in the aromatic moiety, methyl groups (products **3k** and **3l**) and a phenyl group (product **3q**) gave excellent enantioselectivities of 96-98% ee. An acetoxy substituent also afforded the product **3p** with high yield and high enantioselectivity. However, more strongly electron withdrawing or electron accepting substituents led to inferior results. For example, while a chloro substituent still provided the product **3m** with high yield (88%) and satisfactory enantioselectivity (93% ee), a methyl ester or methoxy group in *para*-position afforded the products **3n** and **3o** only with 54% ee and 86% ee, respectively.

A proposed mechanism is illustrated in Fig. 4. Accordingly, visible light activated $[Ru(bpy)_3]^{2+}$ oxidizes in a well-established mechanism the silylmethylamine to the corresponding radical cation, which subsequently undergoes a rapid desilylation to provide an α-aminomethyl radical.[2,3,18] To take into account the observed silyl effect, we propose that the released trimethylsilyl group is captured by the rhodium-coordinated 2-acyl imidazole (intermediate **I**) to afford the very electron deficient silylated intermediate **II**. This is followed by an electron transfer from the the reduced sensitizer to regenerate the photosensitizer in the ground state and provide a rhodium coordinated, silylated ketyl (intermediate **III**), which then undergoes a radical-radical recombination[19,20] with the α-aminomethyl radical to form the rhodium-coordinated C-C coupling product (intermediate **IV**). Replacement of the product (**3**) by a new substrate (**1**) will then initiate a new catalytic cycle. Thus, in this mechanism, Rubpy serves as a light-activated electron shuttle between the α-silylamine (electron donor) and the 2-acyl imidazole (electron acceptor), followed by a radical-radical coupling, whose stereochemistry is controlled by the chiral rhodium Lewis acid. Fig. 5 shows a crystal structure of a derivative of intermediate **I** and the structure of the proposed intermediate **III** which can rationalize the observed *S*-configuration of the products.

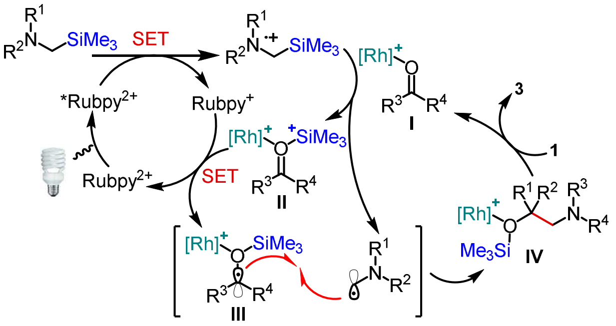

**Fig. 4** Proposed mechanism for the observed silyl effect in the visible-light activated Rh/Ru dual catalysis. SET = single electron transfer.

Control experiments shown in Fig. 6 demonstrate that the silyl group, although crucial for observing the C-C-coupling product with an 2-acyl imidazole, is actually not required for the production of intermediate α-aminomethyl radicals,[21] as demonstrated by trapping with an electron deficient alkene. These experiments support the mechanistic picture that the trimethylsilyl group exerts an important role as an additional Lewis acid[22,23] to activate the rhodium-coordinated 2-acyl imidazole and facilitates a reduction by lowering the ligand-centered LUMO, whereas the related di(cyclopropyl)-methlysilyl group is too bulky to interact with the rhodium-coordinated substrate.

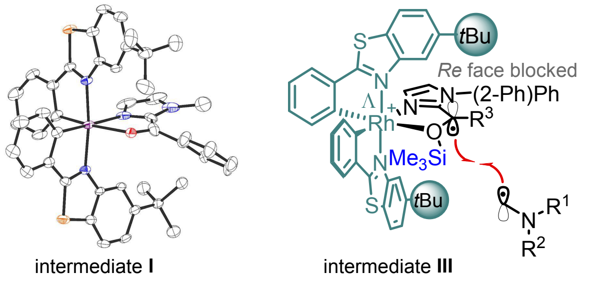

**Fig. 5** Crystal structure of a derivative of intermediate **I** (CCDC no. 1480695) and the proposed structure of intermediate **III** with the indicated stereocontrolled radical-radical recombination.

In conclusion, we have discovered a visible-light-driven enantioselective radical-radical cross-coupling promoted by the cooperativity between a rhodium-based chiral Lewis acid and a ruthenium photosensitizer and in which a trimethylsilyl group appears to play a crucial role as an *in situ* released Lewis acid. In this way synthesized nonracemic 1,2-aminoalcohols represent a reductive umpolung of the carbonyl reactivity triggered by a photoinduced electron transfer.[24,25]

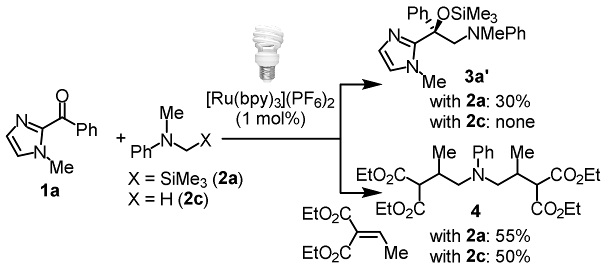

**Fig. 6** Mechanistic experiments.

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## Notes and references

‡**Representative reaction:** A 10 mL Schlenk tube was charged with **Λ-RhS** (5.20 mg, 0.0060 mmol), $[Ru(bpy)_3](PF_6)_2$ (1.30 mg, 0.0015 mmol) and **1m** (39.3 mg, 0.15 mmol). A solution of **2j** (103 mg, 0.45 mmol) in MeCN/DMAC (4:1, 1 mL) was added. After degassing *via* three freeze-pump-thaw cycles, the Schlenk tube was sealed and positioned at a distance of 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at r.t. for 15 h under nitrogen. Afterwards, the mixture was concentrated under reduced pressure, redissolved in THF (2 mL), and TBAF (1.0 mL, 1.0 M in THF, 1.0 mmol) was added. The mixture was stirred at r.t. for 0.5 h and quenched with saturated aqueous solution of $NH_4Cl$. After extraction with EtOAc (3 × 10 mL), the combined organic layers were concentrated and subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:7 to 1:4) to afford the product **3s** as a white solid (53.0 mg, 0.13 mmol, 86% yield). Enantiomeric excess of 99% was determined by HPLC (Chiralpak OD-H

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column, UV-detection at 254 nm, *n*-hexane/isopropanol = 90 : 10, flow rate 1.0 mL/min, $t_r$ (minor) = 8.3 min, $t_r$ (major) = 7.4 min); $[\alpha]_D^{20} = -8.2°$ (*c* 1.0, $CH_2Cl_2$).

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