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28 April 2024

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This is the final peer reviewed accepted manuscript of:

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Eur. J. Org. Chem., **2020**, 1486-1490.

The final published version is available online at:

https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/ejoc.201901086

Aluminum(III) Salen Complexes as Active Photoredox Catalysts

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Abstract: Metallosalen are privileged complexes that have found important application in catalysis. In addition, their luminescent properties have also been studied and used for sensing and biological applications. Salen metal complexes can be efficient photosensitizers, but they can also participate to electron transfer processes. Indeed, we have found that commercially available [Al(Salen)Cl] is an efficient photoredox catalyst for the synergistic stereoselective reaction of alkyl aldehydes with different bromo ketones and malonates to give the corresponding enantioenriched α-alkylated derivatives. The reaction was performed in the presence of a MacMillan catalyst. [Al(Salen)Cl] is able to replace ruthenium complexes, showing that also aluminum complexes can be used in promoting photoredox catalytic reactions.

Introduction

Application of new and effective green catalysts for the preparation of high-value molecules is a modern goal in catalysis and synthesis.[1] In this perspective, the development of photoredox mediated methodologies have found an impressive acceleration in the past few years.[2] Photoredox catalysis based on photoinduced electron transfer (PET) or energy transfer processes were described.[3] Transition metal complexes such as ruthenium,[4] iridium,[5] and copper[6] have been used as photocatalysts to promote organic reactions, alone, or in synergistic combination with nickel,[7] palladium,[8] and cobalt.[9] Organic dyes,[10] quantum dots,[11] and semiconductors[12] were also exploited in many reactions and were found able to replace transition metal-based photocatalysts in many applications. Lastly, abundant metals such as iron, chromium, cerium have been also applied in photoredox catalysis.[13]

With the aim to develop economically and environmentally sustainable synthetic methodologies, our group was involved in developing catalytic processes using abundant metal Salen complexes.[14] As Salen is an effective ligand, easily prepared from available precursor, able to bind many metals, we wondered if metal Salen complexes could represent a new class of effective photoredox catalysts. Some years ago, we have reported the photophysical properties of Salen compounds,[15] discovering that when ligand (1*R*,2*R*)-(-)-[1,2-cyclohexanediamino-N,N'-bis(3,5-di-*tert*-butylsalicylidene)] **1** (Figure 1) is bound to Al(III), Zn(II), Sn(II), Si(IV), and Mg(II) an unstructured fluorescence band appears in the 400–700 nm region with a lifetime in the nanosecond range.[15] The (1*R*,2*R*)-[Al(Salen)Cl] complex **2**[16] also exhibits electrogenerated chemiluminescence in acetonitrile solutions, although less efficiently than [Ru(bpy)₃]²⁺ in the same conditions.[17] Furthermore, Garcia has reported an interesting photochemical investigation of [Al(Salen)Cl] complex **2**,[18] in conventional and nonconventional solvents. Given these premises, we decided to investigate the efficiency of Al(III) Schiff bases complexes as photoredox catalysts[19] in a benchmark reaction, reported by MacMillan in 2008 using [Ru(bpy)₃]²⁺ photocatalyst.[20] This paper practically restarted the field of photoredox catalysis in organic synthesis, merging organocatalysis and a photoredox process mediated by [Ru(bpy)₃]²⁺.[20] The proposed photochemical mechanism was a reductive photoinduced electron transfer of the Ru(II) complex with the chiral enamine, formed in situ by the reaction of an imidazolidinone catalyst and an aldehyde.

From this seminal paper, many efficient processes based on Ru(II) or Ir(III) complexes were described.[21] Recently, other experimental evidences obtained by Yoon[22] has shown that the reaction proceeds through a radical chain mechanism. This reaction was successfully performed also with different photocatalysts as organic dyes,[23] semiconductors,[24] iron complexes,[25] under visible light irradiation. Even chiral enamines can behave as organic photocatalysts: upon photoexcitation, they become strong reductants able to reduce the electron poor bromo derivatives, thus initiating the catalytic process.[26]
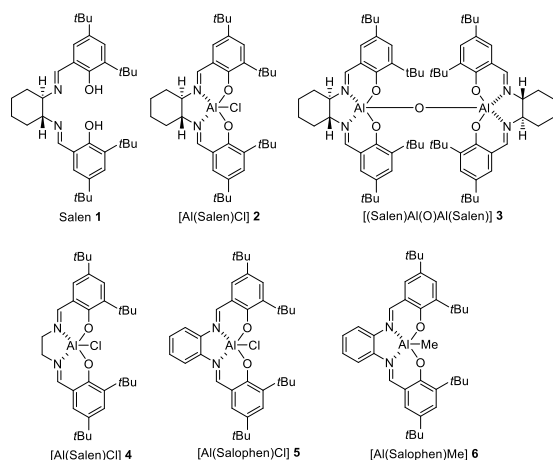

Figure 1. Chemical structures of Salen **1** ligand and Al(III) complexes used in this study.

We have chosen this reaction to evaluate the properties of [Al(Salen)Cl] as photocatalysts for multiple reasons. First, aluminum is quite abundant and replacement of low abundant metals such as ruthenium and iridium is actually one of forefront research in photoredox catalysis. Second,

[Al(Salen)Cl] can have a dual role, as a photocatalyst as well as a Lewis acid catalyst.[16] Third, [Al(Salen)Cl] has been widely used as chiral catalyst,[16] and these properties could be combined with its photophysical properties.

Results and Discussion

We tested several M(III) Schiff bases complexes as photocatalysts, using the standard reaction conditions developed by MacMillan (Table 1 and Table S1). Al(III) complexes were found the most effective catalysts. Although Al(III) complexes with Salophen ligand, complexes **5** and **6**, were also conceivable catalysts (Table 1 entry 5 and 6), better conversion and yield were obtained using (*R,R*)-[Al(Salen)Cl] (**2**).
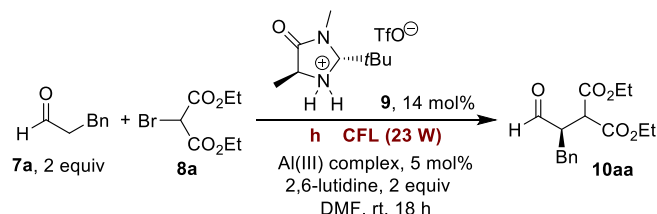

Table 1. Screening of Al(III) complex in photocatalytic stereoselective alkylation of aldehyde **7a** with **8a**.[a]

| Entry	Al(III) complex	Conversion (%)[b]	ee (%)[c]
1	**1**	37	n.d.
2	**2**	99 (83)[d]	89
3	**3**	86	88
4	**4**	50	89
5	**5**	68	89
6	**6**	72	88
7	-	12	n.d.

[a] Reaction was performed on 0.2 mmol of **8a** in DMF (1 mL). [b] Conversion determined by ^{1}H NMR analysis of reaction crude using internal standard method. [c] Determined by HPLC analysis on crude reaction mixture using chiral stationary phase. [d] Yield determined after chromatographic purification. n.d. = not determined.

The best conditions for performing the reaction were: 5 mol% of the photocatalyst **2**, 14 mol% of the imidazolidinone catalyst **9** in DMF with 2,6-lutidine as the organic base and compact fluorescent lamp (CFL, 23W) as light source. Chiral (Salen)-metal complexes catalyze an array of asymmetric nucleophile-electrophile reactions[16] including TMSN₃ and carboxylic acid additions to meso epoxides,[27] hetero Diels-Alder reaction,[28] and TMSCN addition to aldehydes.[29] In addition, **2** was described to promote the enantioselective addition of HCN to imines.[30] Moreover, recent strategies have been developed in which, a chiral metal complex can serve as a sensitizer for photoredox catalysis and at the same time provide very effective asymmetric induction for the enantioselective alkylation reactions.[31] Thus, taking into account the fact that chiral Salen metal complexes constitute an established class of catalysts for asymmetric transformations, we have performed the model reaction using 20 mol% of morpholine as the organic catalyst (see SI, Table S2). Also in this case the desired product was isolated in good yield, but in a racemic form. Moreover, the use of the commercially available (*S,S*)-[Al(Salen)Cl] *ent*-**2** gave practically identical results (see Table S2). Both experiments are ruling out a possible role the role played by the chiral (*R,R*)-Cl[Al(Salen] metal complexes in transmitting chiral information in these reactions. These optimized reaction conditions were explored with a series of aldehydes (**7a-e**, Scheme 1). In general, good yields and enantiomeric excesses were collected for the selected aldehydes. In addition, the reaction proceeded also with bromo ketones (**8c-e**).

In all the tested reactions, the use of [Al(Salen)Cl] photocatalyst yielded conversion values comparable to those obtained in the case of [Ru(bpy)₃]²⁺,[20] although the photocatalyst loading was 10 times higher in the present case compared to the original paper.

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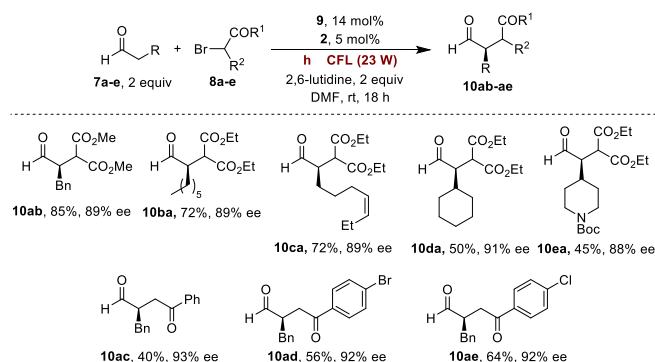
Scheme 1. Enantioselective [Al(Salen)Cl] promoted α-alkylation of different aldehydes with bromoderivatives **8a-e**.

The reaction is completely inhibited when carried out in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or oxygen, confirming the radical nature of the process (Scheme 2).
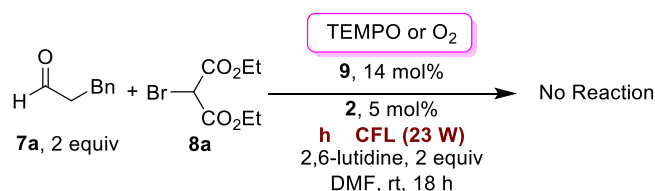
Scheme 2. Control test to support a radical reaction pathway.

A photophysical analysis of photocatalyst **2** and of the reaction mechanism was carried out.

Compound **2** absorbs mainly in the UV region with a tail in the visible up to 420 nm and emits with a maximum at 475 nm and a lifetime of 1.08 ns in DMF (Figure 2). [Al(Salen)Cl] (**2**) is stable under the tested reaction conditions, as confirmed by the absorption spectrum of the reaction mixture after 6 hours of irradiation (Figure S3). A further proof of the stability is the fact that the lifetime of the fluorescent excited state of **2** in the reaction mixture does not change at the end of the reaction.
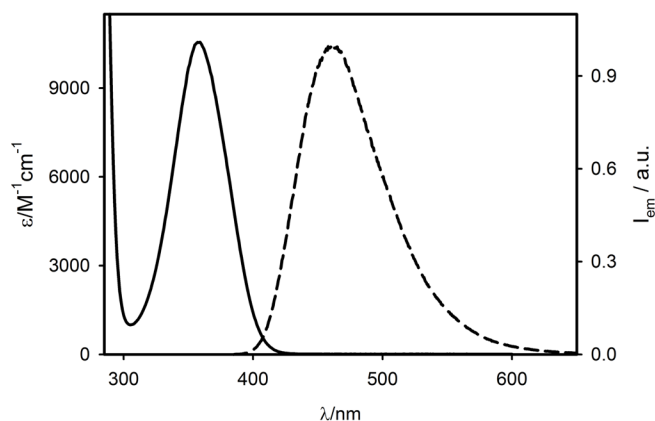

Figure 2. Absorption (solid line) and emission spectra (dashed line) of [Al(Salen)Cl] **2** in DMF. λ_{ex} = 340 nm

We investigated the first step of the photocatalytic cycle by quenching experiments. Upon addition of each of the reaction components (at the same concentration used in the optimized reaction conditions) to a DMF solution of complex **2**, we discovered that diethyl bromomalonate **8a** was the only one able to quench the fluorescence of the photocatalyst. In particular, the Stern-Volmer plot (Figure 3) shows a linear correlation between the ratio τ^0/τ and the quencher concentration, as expected for a dynamic quenching process according to the Stern-Volmer equation:

$$\tau^0/\tau = 1 + K_{SV}[Q] = 1 + k_q \tau^0 [Q] \qquad\qquad (1)$$
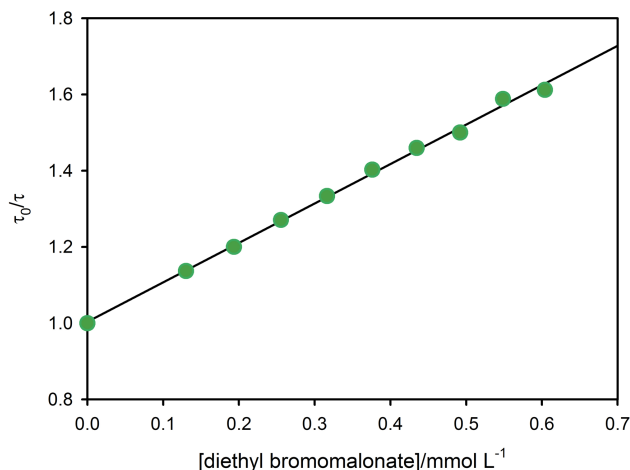
Figure 3. Stern-Volmer plot of [Al(Salen)Cl] **2** in DMF solution in the presence of increasing amounts of diethyl bromomalonate **8a**.

where τ^0 and τ are the lifetimes in the absence and in the presence of the quencher Q (i.e. diethyl bromomalonate **8a**), respectively, K_{SV} is the Stern-Volmer constant and k_q is the quenching constant. The analysis of the plot in Figure 3 yielded the following quenching constant: $k_q = 9.5 \times 10^8$ $M^{-1}s^{-1}$.

The observed quenching process is consistent with a photoinduced oxidative electron transfer in which compound **2** is oxidized and **8a** is reduced. Indeed, the estimated potential for oxidation of the fluorescent excited state *2 is -1.47 V vs SCE, sufficiently negative to drive **8a** reduction (-0.62 vs SCE).[32] The estimation is based on the reported potential for the first oxidation (+1.44 V vs SCE in acetonitrile[33]) and the energy of the fluorescent excited state of **2** ($E_{00} = 2.91$ eV).

On the basis of the photophysical evidences, we propose the reaction mechanism illustrated in Scheme 3. Contrary to [Ru(bpy)₃]²⁺, [Al(Salen)Cl] acts as a reductant for initiating the chain mechanism. The ability of the amidoalkyl radical **IV** to behave as strong reducing agent induces the reduction of bromoderivative, regenerating radical **III**. The addition of radical **III** to enamine **II** is the enantiodiscriminating step. The same photocatalytic mechanism was previously proposed by some of us in the case of [Fe(bpy)₃]²⁺ photocatalyst.[25]

To explore the possibility offered by the new photocatalyst **2**, application towards the synthesis of Pregabalin[34] was investigated. Pregabalin is a drug used for the treatment of epilepsy, neuropathic pain or other anxiety disorders. The photoredox access to racemic pregabalin was reported by MacMillan, by a Giese type reaction.[35] For accessing Pregabalin we have considered the retrosynthetic analysis depicted in Scheme 4. Key intermediate of the synthesis is the chiral oxo-malonate derivative accessible by our photocatalytic methodology from aldehyde **7f**.
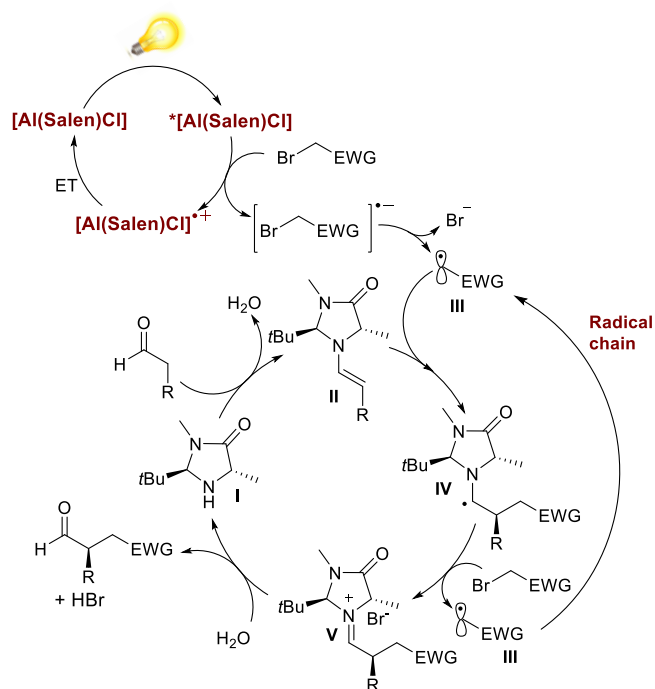
Scheme 3. Proposed mechanism for the Al(salen) mediated alkylation of aldehydes.
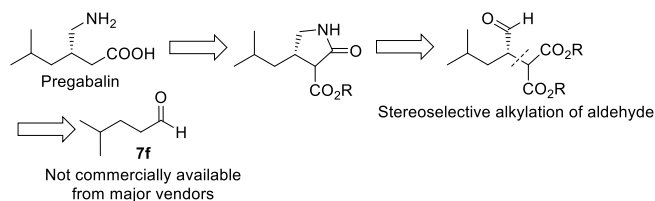
Scheme 4. Retrosynthetic approach to Pregabalin.

4-Methyl-pentanal **7f** is not commercially available and was prepared by oxidation, after a careful study of different methodologies. For all the tested methods the major problem encountered was connected with the extreme volatility of the aldehyde **7f**. In addition, traces of CH_2Cl_2, used as reaction solvent for the synthesis of **7f**, were always present after a careful and difficult fractional distillation and were found to inhibit the photoredox reaction. In order to obtain the aldehyde **7f** avoiding the use of chlorinated solvents, we select the Stahl[36] procedure and **7f** was obtained after distillation in 64% yield as 77% mixture with CH_3CN. The solution was used directly in photocatalytic reaction.

The alkylation reaction was carried out in the conditions reported in Scheme 5 and the desired product was obtained in satisfactory yield and excellent enantiomeric excess.
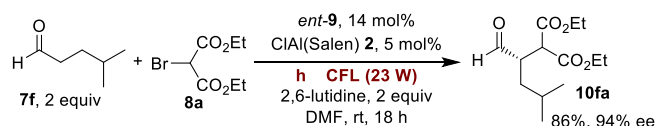
Scheme 5. Enantioselective [Al(Salen)Cl] promoted α-alkylation of **7f**.

Finally, the synthesis of Pregabalin was carried out by the reactions depicted in Scheme 6. The pyrrolidine promoted synthesis of the benzylimine **11**[37] was quantitative. Further reduction with $NaBH_4$ in MeOH gave the intermediate **12** in 71% of yield as mixture of diastereoisomer. After hydrolysis of the ester followed by decarboxylation, the key intermediate **13**[38] for the synthesis of Pregabalin was obtained in 83% yield.
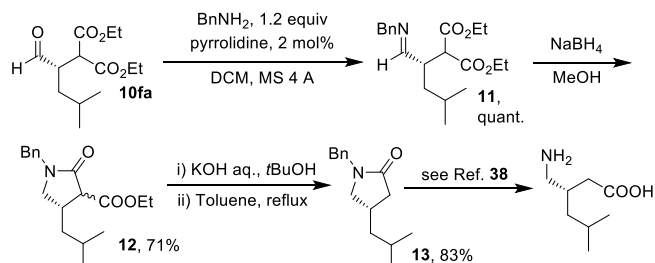
Scheme 6. Formal synthesis for Pregabalin.

Conclusions

We have shown that [Al(Salen)Cl] is an effective photocatalyst based on an earth abundant element. The photophysical investigations suggested that [Al(Salen)Cl] in its fluorescent excited state is able to directly reduce the bromo derivatives, forming the corresponding radical species after debromination. Application of the new photocatalyst towards the synthesis of pregabalin was reported. As the Lewis acidic properties of [Al(Salen)Cl] and its photoredox properties, we are currently exploring the use of [Al(Salen)Cl] in synergistic type of catalysis.

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