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A Diverse Array of Catalytic Photoredox Reactions Based on Aluminum(III)-Salen Complexes: Understanding the Enhancement of Catalytic Activity via Amine Association

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Since aluminum is an earth-abundant and environmentally benign main-group metal, the development of aluminum-complex-based photoredox catalysts remains a significant issue. Herein, we report aluminum(III)-salen complexes (Al-salens) as versatile photoredox catalysts. The combination of an Al-salen catalyst with an amine under visible-light irradiation allowed the hydrodechlorinative transformations of aryl chlorides, the reductive coupling of carbonyl compounds, and the defluoroallylation of perfluoroalkylarenes. Mechanistic studies using transient absorption spectroscopy suggested that the Al-salen complex associates with the amine via its vacant site to improve the reducing ability of its excited state. After electron transfer between the excited state of the Al-salen/amine complex and an appropriate oxidant, the generated aminium radical cation is leveraged to achieve the oxidative transformations of amines, such as α-arylation and α-cyanation. The diversity of the catalytic photoredox reactions based on Al-salen complexes is comparable to that of heavy-precious-metal-based catalysts.

1. Introduction

Over the past decade, the importance of photoredox catalysis in organic chemistry has drastically increased. Metal complexes have played a vital role as photocatalysts, and heavy-precious-metal-based catalysts, such as Ru, Os, Ir, and Pt complexes, have been adopted in a variety of photoredox reactions.[1–5] Recently, nonprecious first-row-transition-metal-based photocatalysts, such as those based on Ti, Cr, Mn, Fe, Co, and Cu have attracted much attention due to their use in sustainable chemical processes.[6–14] In comparison, photocatalysts based on main-group-metal complexes remain underdeveloped.[15] Aluminum is a main-group metal that is earth-abundant and environmentally benign, and represents a key element with regard to sustainable chemistry. However, few Al-complex-based photoredox catalysts in organic synthesis are reported.[16–18] Our group has previously reported a photocatalytic system that utilizes Phebox-aluminum(III) complexes for the hydrodebromination of aryl bromides with amines.[19] The group of Cozzi has reported the use of the photoredox properties of aluminum(III)-salen complexes (Al-salens) for the initiation step in the radical-chain mechanism of the alkylation of aldehydes with α-bromo esters.[20] The group of Gilmour has developed an exceptional light-enabled deracemization of cyclopropyl ketones[21] and enantioselective energy transfer-enabled cyclization of *N*-aryl α,β-unsaturated amides[22] using a chiral Al-salen complex as the photocatalyst, in which the Lewis-acidic Al-salen complex forms an asymmetric reaction field. These reports suggest that Al-salen have the potential to work as photoredox catalysts with Lewis-acidic properties (Figure 1A). The salen ligand has a planar π-conjugated framework and is an efficient visible-light-absorbing organic dye (Figure 1A,a).[23] The vacant site of the Al center can change its own photoredox properties by interacting with an external ligand (L) (Figure 1A,b).[24,25] Thus, the synergy between the photoredox and Lewis-acidic properties of Al-salens can be expected to deliver diverse catalytic photoredox reactions.[26–31] However, little progress has been made on the application of this synergistic effect and on the understanding of its mechanism. Here, we have developed different catalytic photoredox reactions mediated by the interaction between Al-salens and

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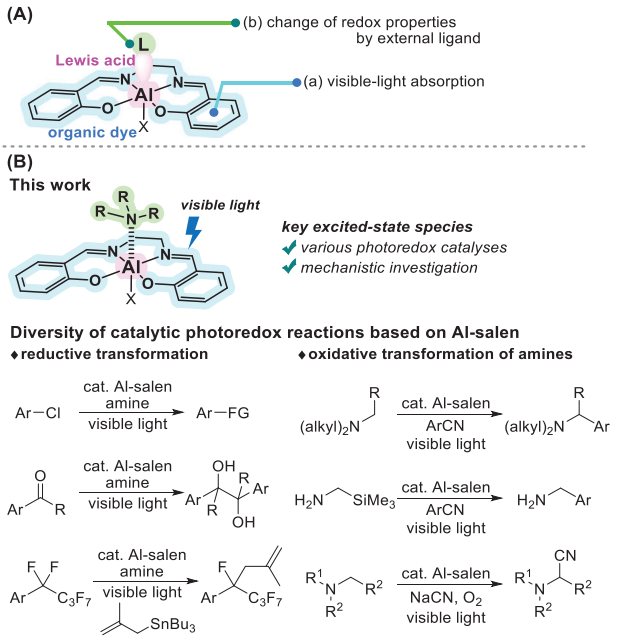


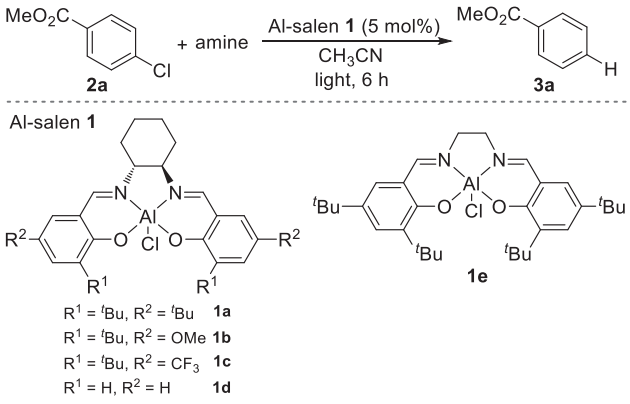
Figure 1. A) The synergy between photoredox and Lewis-acidic properties of Al-salen complexes. B) The diversity of the catalytic photoredox reactions possible using Al-salen complexes.

amines (Figure 1B). In contrast to general cases in which an amine acts as a terminal reductant, the complexization between an Al-salen and an amine to enhance the reducing power of the Al complex in the excited state allows the reduction of various substrates via single-electron transfer (SET). This unprecedented function of amines was elucidated by the mechanistic studies using transient absorption spectroscopy, which revealed that the amines not only act as a terminal reductant, but also via the complexation of Al-salen. Using this SET process, hydrodechlorinative transformations of aryl chlorides, the reductive coupling of carbonyl compounds, and the defluoroallylation of perfluoroalkylarenes were accomplished. An aminium radical cation, generated by the association of Al-salen with an amine in redox process, was leveraged to achieve the oxidative transformations of amines, such as α-arylation and α-cyanation.

2. Results and Discussion

First, the catalytic effects of Al(III)-salen complex **1** in the hydrodechlorination[32–34] of aryl chloride **2a** with various amines under LED irradiation (λ_{max} = 405 nm) were examined (Table 1). Photocatalyst **1a** afforded **3a** in 30% yield (entry 1). A series of terminal reductant trialkylamines was examined (entries 2–6), and 1,2,2,6,6-pentamethylpiperidine (PMP) and *N*-methylpiperidine (NMP) gave satisfying results (entries 5 and 6). Dialkylamines such as piperidine and Et_2NH also afforded high yields of **3a** (entries 7 and 8). On the other hand, the use of a monoalkylamine resulted in a low yield of **3a** (entry 9). The aromatic amine Me_2PhN was found to be ineffective (entry 10). We also compared several Al-salen complexes (**1a**–**1e**) under these reaction conditions in the presence of PMP. The introduction of

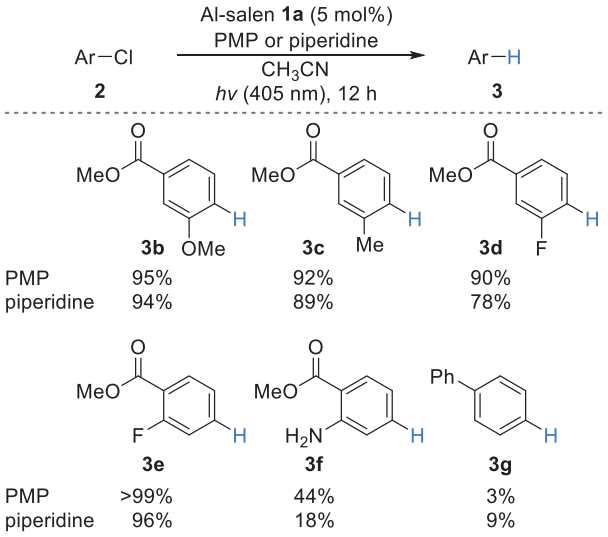
Table 1. Optimization of the reaction conditions for the hydrodechlorination of **2a**.[a]



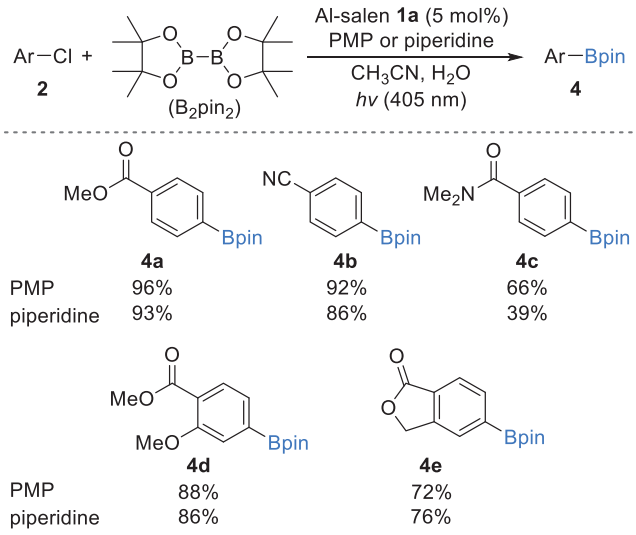
Entry	1	Amine[d]	Light	Yield
1	**1a**	$^{i}Pr_2EtN$	405 nm	30%
2	**1a**	Cy_2MeN	405 nm	74%
3	**1a**	Bu_3N	405 nm	77%
4	**1a**	Et_3N	405 nm	35%
5	**1a**	PMP	405 nm	89%
6	**1a**	NMP	405 nm	86%
7	**1a**	piperidine	405 nm	97%
8	**1a**	Et_2NH	405 nm	82%
9	**1a**	$BuNH_2$	405 nm	39%
10	**1a**	Me_2PhN	405 nm	0%
11	**1b**	PMP	405 nm	0%
12	**1c**	PMP	405 nm	60%
13	**1d**	PMP	405 nm	76%
14	**1e**	PMP	405 nm	60%
15	none	PMP	405 nm	0%
16	**1a**	PMP	none	0%
17	**1a**	PMP	370 nm	68%
18	**1a**	PMP	390 nm	75%
19	**1a**	PMP	427 nm	25%
20[b]	**1a**	PMP	405 nm	89%
21[c]	**1a**	PMP	405 nm	99%

[a] **2a** (0.2 mmol), amine (0.6 mmol), Al-salen complex **1** (0.01 mmol), CH_3CN (1 mL), room temperature. Yields were determined using gas chromatography.
[b] Solvent (0.5 mL).
[c] Solvent (2 mL).
[d] PMP: 1,2,2,6,6-pentamethylpiperidine; NMP: *N*-methyl piperidine.

MeO groups onto the salen ligand (**1b**) completely suppressed the hydrodechlorination (entry 11). Al-salen complex **1c**, which contains CF_3 groups, exhibited a slightly lower catalytic activity than **1a** (entry 12). Complex **1d** without any ^{t}Bu groups exhibited a comparable catalytic activity to that of **1a** (entry 13). Complex **1e** with an acyclic aliphatic backbone gave a slightly lower yield of **3a** (entry 14). In the absence of either the Al-salen complex or light, the reaction did not occur (entries 15 and 16). After investigating the wavelength of light, 405 nm light was found to be the most effective (entries 5, and 17–19). Finally, dilute conditions



Scheme 1. Scope of aryl chlorides **2** in the hydrodechlorination catalyzed by Al-salen **1a**. **2** (0.2 mmol), PMP or piperidine (0.6 mmol), **1a** (5 mol%), CH_3CN (2 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined via ^1H NMR spectroscopy using an internal standard.



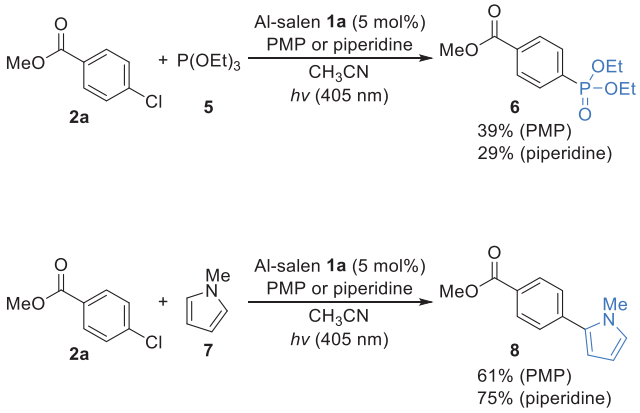
Scheme 2. Borylation of aryl chlorides **2** catalyzed by Al-salen **1a** **2** (0.2 mmol), B_2pin_2 (0.6 mmol), PMP or piperidine (0.4 mmol), **1a** (5 mol%), CH_3CN (1.8 mL), H_2O (0.2 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined via ^1H NMR spectroscopy using an internal standard.

furnished **3a** quantitatively, probably due to the prevention of the self-quenching of photocatalyst **1a** (entries 1, 20, and 21).

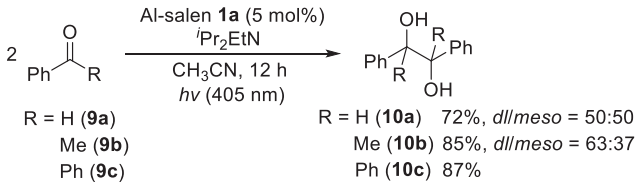
The scope of the aryl chlorides **2** in the hydrodechlorination reaction catalyzed by Al-salen **1a** with PMP or piperidine is illustrated in Scheme 1. Methoxycarbonyl-substituted aryl chlorides with either electron-donating groups or -withdrawing groups furnished high yields of **3b**–**3e**. In addition, the present method is compatible with unprotected amino groups, that is, **3f** was obtained in acceptable yield. Unfortunately, an aryl chloride without a methoxycarbonyl group was not suitable due to its low reduction potential (**3g**). In most cases, the use of PMP gave similar results to that of piperidine.

Next, we investigated the utility of the photocatalytic method based on Al-salen **1a** in other types of transformations of aryl chlorides.[32–34] After optimizing the reaction conditions of the borylation of aryl chlorides **2** with bis(pinacolato)diborane (B_2pin_2) in the presence of PMP or piperidine,[35,36] electron-deficient aryl chlorides, such as benzoic ester, benzonitrile, and benzamide derivatives, afforded the corresponding boronic esters (**4a–d**) in good yield (Scheme 2). A lactone moiety was also tolerated under the applied borylation conditions (**4e**). Moreover, triethyl phosphite **5** and 1-methylpyrrole **7** also acted as radical coupling partners in reactions with aryl chloride **2a** to give moderate yields of **6** and **8**, respectively (Scheme 3).[37–39]

The photoredox-catalyzed reductive coupling of carbonyl compounds using organic reductants is milder and more environmentally friendly than typical methods that use stoichiometric amounts of low-valent metals.[40–43] Al-salen **1a** mediates the photocatalytic reductive coupling of carbonyl compounds (Scheme 4).[36] Under the conditions using **1a**, $^iPr_2EtN$, and visible-light irradiation, benzaldehyde (**9a**), acetophenone (**9b**), and benzophenone (**9c**) gave the corresponding diols (**10a**–**c**) in 72%, 85%, and 87% yield, respectively, albeit with poor diastereoselectivity. We also demonstrated the photocatalytic ability



Scheme 3. Radical coupling of aryl chloride **2a** with triethyl phosphite **5** or 1-methylpyrrole **7**. **2** (0.2 mmol), **5** or **7** (4 mmol), PMP or piperidine (0.4 mmol), **1a** (5 mol%), CH_3CN (1 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined via ^1H NMR spectroscopy using an internal standard.



Scheme 4. Reductive coupling of benzaldehyde and ketones. **9** (0.4 mmol), $^iPr_2EtN$ (0.8 mmol), **1a** (5 mol%), CH_3CN (2 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined via ^1H NMR spectroscopy using an internal standard.

of Al-salen **1a** in our previously reported $Ir(ppy)_3$-catalyzed defluoroallylation (Scheme 5).[44] The C—F-bond allylation of perfluoroalkylarene **11** with allylic stannane **12** was catalyzed by **1a** to furnish **13** in 91% yield. As shown in Schemes 1–5, Al-salen **1a** exhibits a diverse array of photocatalytic properties in reductive transformations that are comparable to the

Scheme 5. Defluoroallylation of perfluoroalkylarene **11** with allylic stannane **12**. **11** (0.2 mmol), **12** (0.6 mmol), PMP (0.2 mmol), **1a** (5 mol%), DME (1 mL), irradiation (LED; λ_{max} = 405 nm), 24 hours, room temperature. Yields were determined via ^{1}H NMR spectroscopy using an internal standard.

performance of precious-metal-based photocatalysts used in similar reactions.

To gain insight into the photoredox reaction catalyzed by Al-salen **1a**, the observation of excited states of **1a** and the quenching experiments of these excited states were conducted using transient absorption spectroscopy (for the details of the absorption-decay curves, see the Supporting Information).[45] Laser-flash-photolysis (LFP) experiments on the singlet excited state ^{1}[**1a**]* were conducted on the ns timescale (Figure 2A–2C). The absorption spectrum of ^{1}[**1a**]* showed a peak around 550 nm (Figure 2A). Fitting of the time profile monitored at 550 nm with a mono-exponential equation provided a lifetime ($^1\tau$) of 6.91 ns for ^{1}[**1a**]* (Figure S6). As the absorption peak of ^{1}[**1a**]* decreased, a peak corresponding to the absorption band of the triplet excited state ^{3}[**1a**]* appeared around 490 nm (Figure 2A).[46] Next, the effect of the different reaction additives on the singlet excited state ^{1}[**1a**]* was examined. Figure 2B shows the transient absorption spectra of **1a** and its lifetimes in the presence of **2a**, PMP, or piperidine after 0.3–0.5 ns. The addition of aryl chloride **2a** hardly influenced the lifetime or absorption wavelength of ^{1}[**1a**]* (Figure 2B, orange line), which suggests that quenching of ^{1}[**1a**]* by **2a** does not occur. On the other hand, the addition of PMP or piperidine resulted in a bathochromic shift of the peaks to around 570–590 nm (Figure 2B, green and yellow lines) and in a lengthening of the lifetimes ($^1\tau$ = 7.45 ns or 10.5 ns, respectively). These spectra are different from those of the radical anion and radical cation of **1a** (Figures S2, S3).[47] We analyzed a CH_3CN solution of a mixture of **1a** with PMP or piperidine using ESI-MS spectrometry and found peaks for **1a**•PMP and **1a**•piperidine complexes (Figures S28, S29). The formation of these complexes was further corroborated by the results of a ^{27}Al NMR spectroscopic analysis and density-functional-theory (DFT) calculations (Figures S30–S32). The red-shifted peaks in Figure 2B were accordingly attributed to the singlet excited states of the **1a**•amine complexes, that is, ^{1}[**1a**•PMP]* and ^{1}[**1a**•piperidine]*. Next, we examined the quenching of ^{1}[**1a**•amine]* with aryl chloride **2a**. The singlet excited state of ^{1}[**1a**•PMP]* was effectively quenched by aryl chloride **2a** (Figure 2C), which stands in contrast to the lack of quenching observed for ^{1}[**1a**]*. Using Stern-Volmer plots of different concentrations of **2a** (Figures 2C, 2D), the quenching of ^{1}[**1a**•PMP]* was found to be a dynamic process (k_q = 2.60 × 10^9 M^{-1}s^{-1}). Unexpectedly, quenching of ^{1}[**1a**•piperidine]* by **2a** was not observed (Figure S16), and this intriguing result turned our attention to the examination of the triplet species via LFP experiments on the μs timescale. The time profile of ^{3}[**1a**]* monitored at 490 nm,[18] which is the absorption maximum of the transient UV-vis spectrum (Figure 2E), was fitted using a mono-exponential equation (Figure S19) to determine the lifetime of ^{3}[**1a**]* ($^3\tau$ = 53.1 μs). The presence of **2a** did not cause quenching of ^{3}[**1a**]* (Figure 2F, orange line, $^3\tau$ = 53.6 μs). In the presence of piperidine, a red-shifted absorption band of ^{3}[**1a**•piperidine]* was observed at around 510 nm (Figure 2F, yellow line, $^3\tau$ = 52.5 μs). ^{3}[**1a**•piperidine]* was effectively quenched by **2a** (Figure 2G), and Stern-Volmer plots of different concentrations of **2a** demonstrated this to be a dynamic quenching process (k_q = 1.42 × 10^5 M^{-1}s^{-1}) (Figures 2G, 2H). In their entirety, the transient-absorption studies suggest that ^{1}[**1a**•PMP]* and ^{3}[**1a**•piperidine]* are reductants that reduce aryl chlorides **2** via SET.

In the hydrodechlorination of **2a** under an O_2 atmosphere, the use of piperidine resulted in no reaction, and the use of PMP furnished **3a** in 61% yield (Scheme 6). These results are consistent with the involvement of different spin multiplicities in the reaction mechanism, the singlet excited state ^{1}[**1a**•PMP]* and triplet excited state ^{3}[**1a**•piperidine]*, as suggested by the transient-absorption-spectroscopy studies.

Based on the mechanistic studies, a plausible mechanism for the Al-salen **1a**-catalyzed hydrodechlorination of aryl chlorides **2** with amines is proposed in Scheme 7. An amine coordinates to the Lewis-acidic Al center in **1a** in the ground state.[48] The absorption of visible light by the **1a**·amine complex creates the singlet excited state (^{1}[**1a**•amine]*). An SET from the singlet state ^{1}[**1a**•PMP]* to **2** then furnishes radical cation [**1a**•PMP]$^{•+}$ and radical anion **2**$^{•-}$. In the case of piperidine, the triplet excited state ^{3}[**1a**•piperidine]* is generated via intersystem crossing (ISC) and then acts as a reductant. The transient absorption spectroscopic studies in Figure 2 support the reduction of aryl chlorides **2** by excited state [**1a**•amine]*. At present, it is not yet entirely clear why the active state for the reduction of **2** differs between **1a**•PMP and **1a**•piperidine. The [**1a**•amine]$^{•+}$ species dissociates into **1a** and aminium radical cation **A**. The mesolysis of the C—Cl bond in **2**$^{•-}$ generates an aryl radical and Cl$^-$. Finally, the aryl radical abstracts a hydrogen atom from **A**, to afford **3** and iminium ion **B**.[32] The reducing power of the excited state **1a*** is not enough to reduce aryl chlorides (E(**1a**$^{•+}$/**1a***) = -1.76 V vs. SCE[49] and E(**2a**/**2a**$^{•-}$) = -2.01 V vs. SCE[49]). On the other hand, the redox potential of ^{1}[**1a**•PMP]* (E([**1a**•PMP]$^{•+}$/^{1}[**1a**•PMP]* = −2.32 V vs. SCE[49]) is sufficient. Therefore, the coordination of amines to the aluminum center creates a species with sufficient reducing power to realize the effective reduction of aryl chlorides **2**.

The reaction mechanism shown in Scheme 7 involves the oxidation of amines to aminium radical cation **A**. Aminium radical cations are known as key intermediates in the generation of α-amino radicals or iminium ions during the functionalization of amines mediated by photoredox catalysts.[50–55] Therefore, we attempted the transformation of amines using the catalytic Al-salen photoredox system. First, the decyanative cross-coupling of aryl cyanides **14** with trialkylamines was investigated (Scheme 8).[36] There are some reports for aromatic amines for this type of coupling,[56–59] but the use of trialkylamines as coupling partners mediated by photoredox catalysts has not been established.[58] Gratifyingly, Al-salen **1a** mediated the coupling of 1,4-dicyanobenzene with tributylamine in DMA under visible-light irradiation, giving benzylic amine **16a,** although the

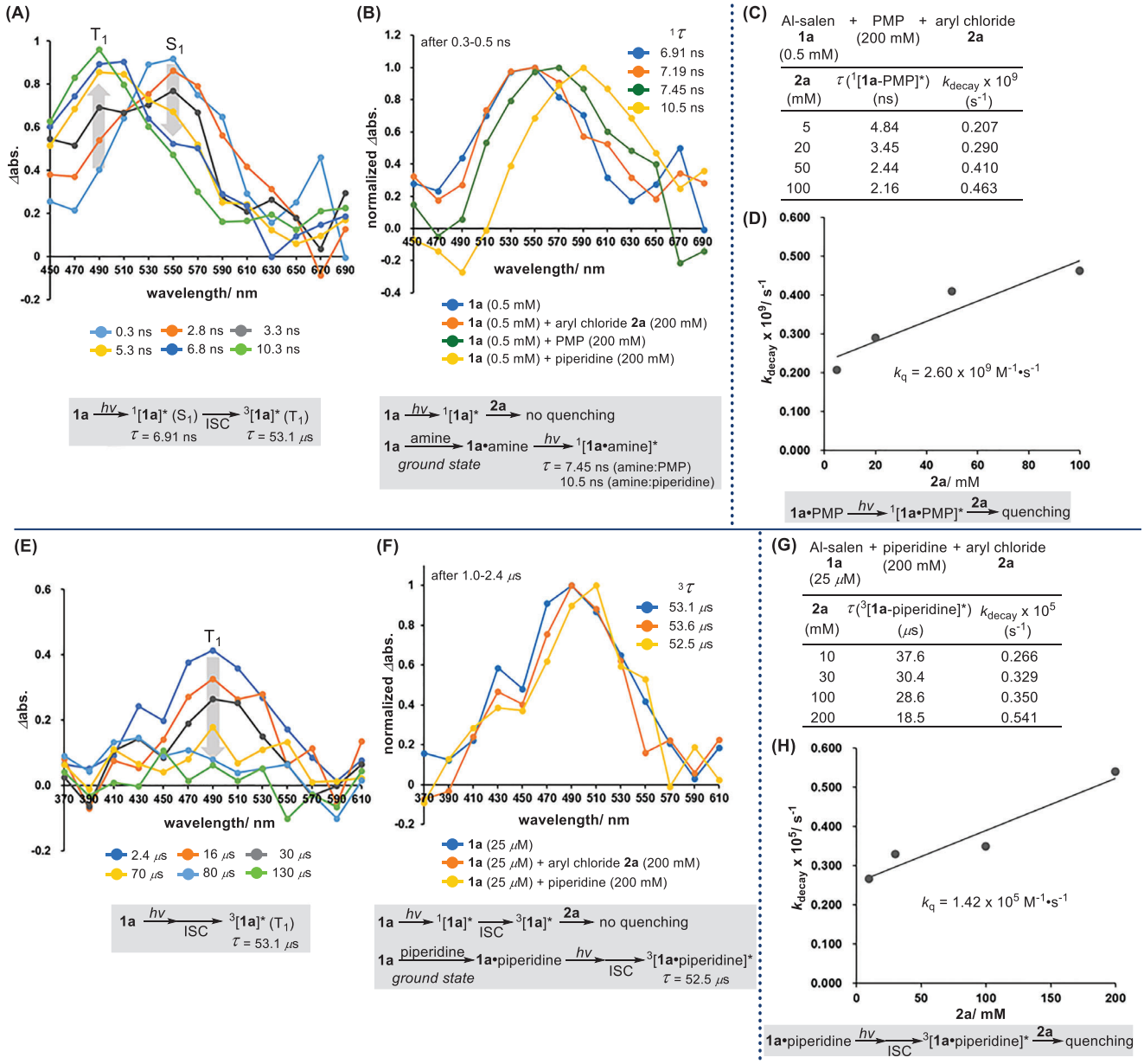
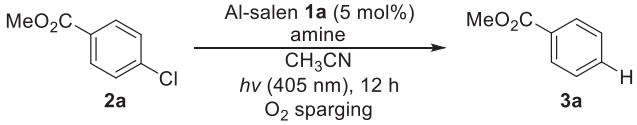


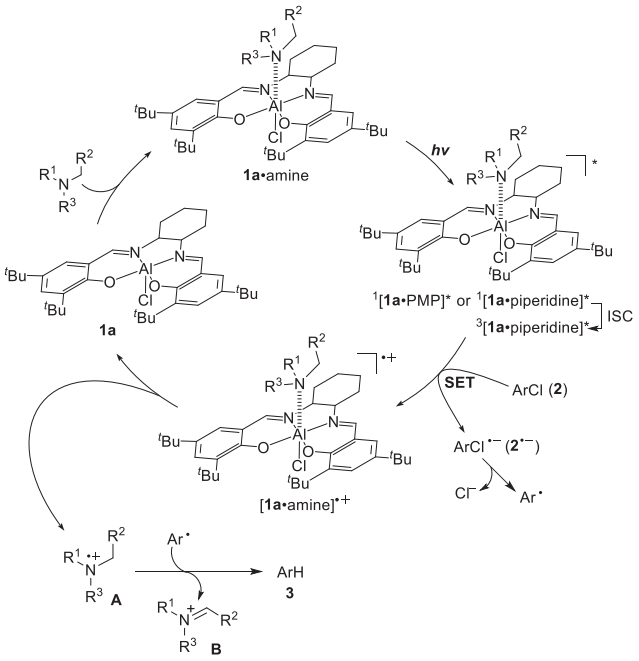
Figure 2. a) Transient absorption spectra of **1a** in CH_3CN on the ns timescale. b) Effect of additives on the transient absorption spectra of ^{1}[**1a**]* in CH_3CN. c) Quenching experiments conducted on ^{1}[**1a**•PMP]* with **2a**. Lifetimes of ^{1}[**1a**•PMP]* monitored at 570 nm in CH_3CN. d) Stern-Volmer plot of the lifetime of ^{1}[**1a**•PMP]* as a function of the concentration of **2a**. e) Transient absorption spectra of **1a** in CH_3CN on the μs timescale. f) Effect of additives on the transient absorption spectra of ^{3}[**1a**]* in CH_3CN. g) Quenching experiments conducted on ^{3}[**1a**•piperidine]* with **2a**. Lifetimes of ^{3}[**1a**•piperidine]* monitored at 510 nm in CH_3CN. h) Stern-Volmer plot of the lifetime of ^{3}[**1a**•piperidine]* as a function of the concentration of **2a**.



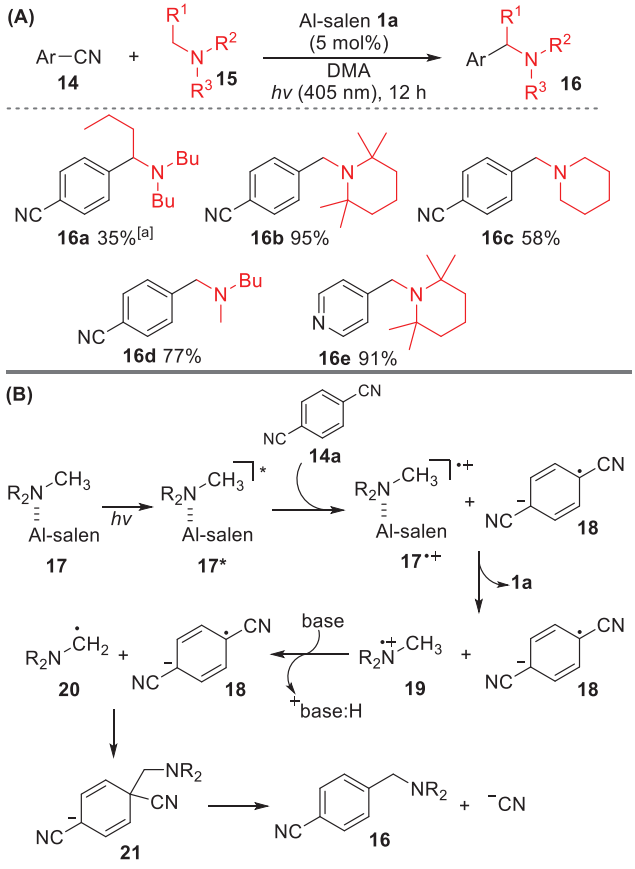
amine	yield of **3a**	recovery of **2a**
piperidine	0%	98%
PMP	61%	36%

Scheme 6. Comparison of PMP and piperidine in the hydrodechlorination reaction under an O_2 atmosphere. **2a** (0.2 mmol), PMP or piperidine (0.6 mmol), **1a** (5 mol%), CH_3CN (1 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined using gas chromatography.

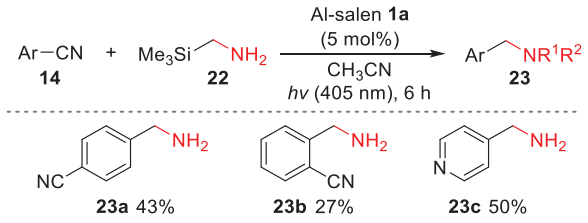
yield was only 35%. The reaction of PMP smoothly gave product **16b** in a high yield. The couplings using 1-methylpiperidine and butyldimethylamine regioselectively occurred at a methyl group (**16c** and **16d**). 4-Cyanopyridine was also applicable to this coupling system (**16e**). A plausible mechanism for the decyanative coupling reaction between 1,4-dicyanobenzene **14a** with dialkylmethylamine is illustrated in Scheme 8B. The excited state **17*** of complex **1a**•amine reduces **14a** to give radical cation **17**$^{\bullet+}$ and radical anion **18**. The dissociation of aminium radical cation **19** followed by the site-selective deprotonation at the Me group[60–64] generates α-amino radical **20**. The coupling between **20** and **18** gives anion **21**. Finally, the rearomatization via elimination of CN^- affords **16a**.



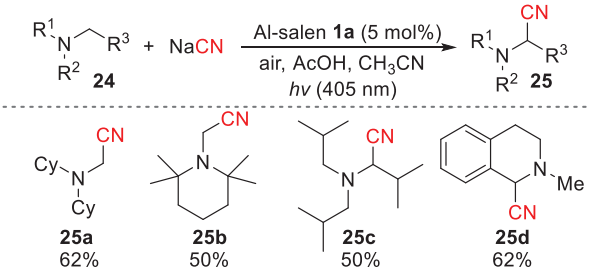
Scheme 7. Plausible reaction mechanism for the hydrodechlorination of **2a** with amines catalyzed by Al-salen **1a**.



Scheme 8. A) Decyanative cross-coupling of aryl cyanides **14** with trialkylamines **15**. **14** (0.2 mmol), **15** (0.6 mmol), **1a** (5 mol%), DMA (2 mL), irradiation (LED; λ_{max} = 405 nm), 12 hours, room temperature. Yields were determined by ^{1}H NMR spectroscopy using an internal standard. [a] **15** (2 mmol) was used. B) Plausible reaction mechanism.



Scheme 9. Decyanative cross-coupling of aryl cyanides **14** with $Me_3SiCH_2NH_2$ **22**. **14** (0.2 mmol), **22** (0.3 mmol), **1a** (5 mol%), CH_3CN (2 mL), irradiation (LED; λ_{max} = 405 nm), 6 hours, room temperature. Yields were determined via ^{1}H NMR spectroscopy using an internal standard.



Scheme 10. α-Cyanation of amines using O_2 and NaCN. [a] **24** (0.2 mmol), NaCN (0.6 mmol), **1a** (10 mol%), AcOH (0.6 mmol), CH_3CN (2 mL), irradiation (LED; λ_{max} = 405 nm), 8 hours, room temperature, in air. Yields were determined via ^{1}H NMR spectroscopy using an internal standard.

C-Silylated methylamine ($Me_3SiCH_2NH_2$) **22** is a liquid, easy-to-handle, commercially available reagent, and is often used as an alternative to gaseous $MeNH_2$ which is difficult to handle.[65–67] However, the use of **22** in the photocatalyzed decyanative coupling has not been reported.[68] It was found that electron-deficient aryl cyanides, 1,4-dicyanobenzene, 1,2-dicyanobenzene, and 4-cyanopiridine, reacted with **22** to afford unprotected benzylic amines **23a**, **23b**, and **23c**, respectively (Scheme 9). A plausible mechanism for the reaction between **14** and **22** is illustrated in Figure S36.

Next, we examined the α-cyanation of amines under the aerobic conditions in conjunction with a CN^- source (Scheme 10).[69–71] Al-salen **1a** was found to mediate the targeted reaction with reference to the reported reaction conditions.[36,71] Cy_2MeN, PMP, and $^iBu_3N$ effectively underwent cyanation to give **25a**, **25b**, and **25c** in 62%, 50%, and 50% yield, respectively. When a tetrahydroisoquinoline substrate was used, benzylic cyanation product **25d** was obtained selectively. The proposed mechanism, with reference to the Ir-catalyzed photoinduced reaction reported by Oderinde and Emmert[71] is shown in Figure S37.

3. Conclusion

We have revealed the outstanding features of Al(III)-salen complexes as photoredox catalysts. The combination of Al-salen **1a** with amines facilitates the hydrodechlorination of aryl chlorides, the borylation of aryl chlorides with B_2pin_2, the reductive coupling of carbonyl compounds, and the defluoroallylation of perfluoroalkylarenes. In addition, Al-salen photocatalysts can mediate the light-driven oxidative transformation of amines to achieve both the decyanative coupling of aryl cyanides with

trialkylamines and the α-cyanation of trialkylamines. Mechanistic studies using transient absorption spectroscopy revealed the prominent role that the complexation of Al-salen with an amine plays in improving the excited-state reducing power, thus achieving the reductive transformation of various substrates. Various photoredox catalytic reactions presented above demonstrate the versatility of Al-based catalysts compared to heavy-precious-metal-based catalysts. We expect that this work will serve as a platform upon which further studies into potential photoredox catalysts of main-group-metal complexes will be based.

Supporting Information

Details of the instruments and methods; synthetic procedures, characterization data, and DFT calculation are available in the Supporting Information. The authors have cited additional references within the Supporting Information.[72–102]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aluminum · amines · mechanistic study · photoredox catalysis · transient absorption spectroscopy

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