Triplet Energy Transfer from Ruthenium Complexes to Chiral Eniminium Ions: Enantioselective Synthesis of Cyclobutanecarbaldehydes by [2+2] Photocycloaddition

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Abstract: *Chiral eniminium salts, prepared from α,β-unsaturated aldehydes and a chiral proline derived secondary amine, underwent, upon irradiation with visible light, a ruthenium-catalyzed (2.5 mol%) intermolecular [2+2] photocycloaddition to olefins, which after hydrolysis led to chiral cyclobutanecarbaldehydes (17 examples, 49–74% yield), with high diastereo- and enantioselectivities. $Ru(bpz)_3(PF_6)_2$ was utilized as the ruthenium catalyst and laser flash photolysis studies show that the catalyst operates exclusively by triplet-energy transfer (sensitization). A catalytic system was devised with a chiral secondary amine co-catalyst. In the catalytic reactions, $Ru(bpy)_3(PF_6)_2$ was employed, and laser flash photolysis experiments suggest it undergoes both electron and energy transfer. However, experimental evidence supports the hypothesis that energy transfer is the only productive quenching mechanism. Control experiments using $Ir(ppy)_3$ showed no catalysis for the intermolecular [2+2] photocycloaddition of an eniminium ion.*

Introduction

The electronic properties of olefins that are conjugated with a carbonyl group are altered by modifications at the carbonyl group. In this context, the formation of eniminium ions from α,β-unsaturated aldehydes has had a major impact on the development of organocatalytic reactions.[1] Kindled by the pioneering studies of MacMillan and co-workers on enantioselective Diels–Alder reactions,[2] a plethora of con-

jugate addition reactions to α,β-unsaturated aldehydes has been shown to proceed enantioselectively via the intermediate formation of eniminium ions **I** (Figure 1).[3,4] Chiral pyrrolidines[5] derived from proline[6] were found to provide a high enantioface differentiation in many of these transformations.[7] In more recent work, the group of Melchiorre has demonstrated that chiral eniminium ions can be favorably used in organocatalytic photochemical transformations.[8] They exploited the known bathochromic absorption shift of eniminium ions relative to their aldehyde congeners[9] to selectively excite the former compounds and demonstrated that eniminium ions of type **I** are strong oxidants in the first excited singlet state (S_1). It was thus possible to induce radical addition reactions at the β-position of eniminium ions by oxidizing suitable radical precursors. Addition reactions of benzyl, alkyl, and acyl radicals were successively performed in an enantioselective fashion employing chiral pyrrolidines as organocatalysts.[10]
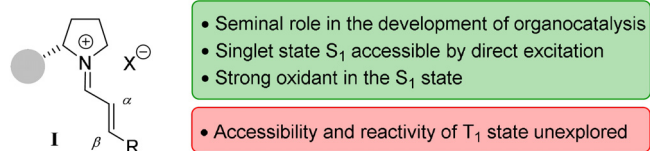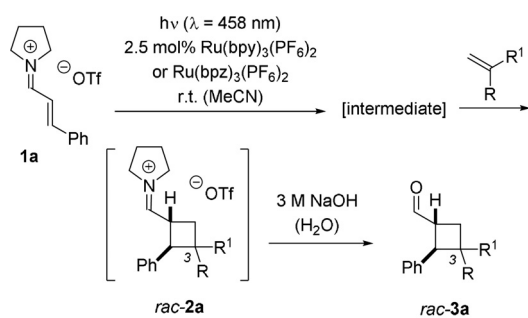
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Figure 1. Generic structure of chiral eniminium ions **I** and their important features.

Prior to the Melchiorre studies, the group of Mariano had performed extensive work on the photochemistry of iminium and eniminium ions.[11] Despite the impressive number of important results that they disclosed, the reactivity of the triplet state T_1 of eniminium ions has remained unexplored.[12] Indeed, there was no indication that intersystem crossing (ISC) from the S_1 state would be feasible, and the [2+2] photocycloaddition chemistry of eniminium ions was found to proceed at the singlet hypersurface.[13] In recent experiments, we have made a few observations that hinted at the possibility to reach the triplet state of eniminium ions by sensitization. It was discovered that the eniminium ion **1a**, derived from cinnamic aldehyde, underwent an intermolecular [2+2] photocycloaddition with olefins to an intermediate product, *rac*-**2a**, which upon hydrolysis generated the cyclobutanecarbaldehydes *rac*-**3a** (Scheme 1).[14] The eniminium triflates of aliphatic α,β-unsaturated aldehydes were not accessible and were not investigated.

Scheme 1. Ru-catalyzed intermolecular [2+2] photocycloaddition of the eniminium salt **1a** to give the racemic cyclobutanes *rac*-**3a**. Tf = trifluoromethanesulfonyl.

The reaction was catalyzed with similar efficiency by the ruthenium complexes tris(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bpy)$_3$(PF$_6$)$_2$] and tris(2,2′-bipyrazine)ruthenium(II) bis(hexafluorophosphate) [Ru-(bpz)$_3$(PF$_6$)$_2$]. In addition, a single experiment was performed with a chiral eniminium ion that suggested that enantioselective reactions[15,16] might be possible.

In the current study we carefully investigated the interaction of the photoexcited ruthenium catalyst Ru(bpz)$_3$(PF$_6$)$_2$ with eniminium ions such as **1a** employing laser flash photolysis. We had previously hypothesized[14] that the eniminium ion quenches the photoexcited state by energy transfer,[17] but had not been able to experimentally exclude an electron-transfer pathway. In a second set of experiments, we explored the scope of the enantioselective [2+2] photocycloaddition reactions of chiral eniminium ions catalyzed by Ru(bpz)$_3$(PF$_6$)$_2$ and we searched for reaction conditions that would allow catalytic enantioselective reactions starting with prochiral α,β-unsaturated aldehydes. Finally, we compared the photocatalysts Ru(bpy)$_3$(PF$_6$)$_2$ and Ir(ppy)$_3$ with Ru-(bpz)$_3$(PF$_6$)$_2$ regarding their quenching by eniminium ions. The results of our work are comprehensively discussed in this account.

Results and Discussion

Mechanistic Studies

As alluded to in the introduction, ISC of eniminium ions from the S$_1$ state to the first excited triplet state T$_1$ is slow due to the fact that the states are of identical character (ππ*).[18] In line with our expectation, **1a** did not show any delayed luminescence, neither in solution nor in a matrix at 77 K. However, it was possible to facilitate ISC by an internal heavy atom effect[19] and the eniminium ions derived from bromo-substituted cinnamic aldehydes were phosphorescent (Figure 2). We prepared the achiral eniminium ions **1b**—**d**, all of which showed nearly identical phosphorescence emissions (see the Supporting Information for further details). The energy of the lowest lying triplet state (E_T) was calculated
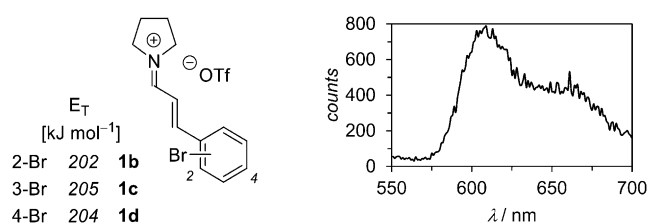

Figure 2. Triplet energies (E_T) of various eniminium ions **1b**–**d** determined from phosphorescence spectra recorded at 77 K in an acetonitrile (MeCN) matrix. The phosphorescence spectrum of **1d** is depicted as an example (excitation wavelength $\lambda = 380$ nm).

from the shortest wavelength onset of phosphorescence as 202–205 kJ mol^{-1}.

To provide further confidence on the phosphorescence measurements, DFT calculations[15a,20] revealed the triplet energy for **1d** to be 195 kJ mol^{-1} (see Section 7 in the Supporting Information), which is in reasonable agreement with the low-temperature data from Figure 2. The same structure without the bromo substituent (**1a**) gave a slightly higher calculated triplet energy of $E_T = 200$ kJ mol^{-1}.

To investigate the photochemical activation step, laser flash photolysis experiments (a description of the setup can be found in the Supporting Information) were performed with Ru(bpz)$_3$(PF$_6$)$_2$ in deoxygenated acetonitrile solution employing either **1a** or **1d** as a potential quencher (Figure 3). Prior to our quenching studies, we reinvestigated the excited-state properties of Ru(bpz)$_3$(PF$_6$)$_2$ upon green-light excitation (532 nm) with laser pulses of about 10 ns duration. The results are displayed in Figure S7 (see the Supporting Information), and they are in good agreement with previous reports.[21] Based on the observed transient absorption and emission signatures, which both decay with an unquenched lifetime of 810 ns, we selected 440 nm ([Ru(bpz)$_3$]$^{2+}$ ground state bleach) and 600 nm (^{3}[Ru(bpz)$_3$]$^{2+}$ luminescence) as the main detection wavelengths for our mechanistic studies.

In the presence of millimolar concentrations of the eniminium ions, the lifetime of ^{3}[Ru(bpz)$_3$]$^{2+}$ was significantly reduced, whereas the initial signal intensity right after the laser pulse remained unchanged. The analyses of the first-order kinetics for both ground-state bleach recovery (blue) and emission decay (red) yielded the very same lifetime at a given quencher concentration (insets of Figure 3). Both lifetime-based Stern–Volmer plots show an upward curvature, which is most likely the result of a kinetic salt effect[22] (the reaction is faster at higher salt/quencher concentrations, in line with Coulombic repulsion between sensitizer and eniminium ions). Therefore, we regard the rate constants at the lowest eniminium ion concentrations (i.e., the lowest ionic strength) as most reliable: These rate constants for the quenching of ^{3}[Ru(bpz)$_3$]$^{2+}$ by **1a** and **1d** were determined as 2.1×10^7 M^{-1}s^{-1} and 3.3×10^7 M^{-1}s^{-1}, respectively. The observed kinetic salt effects, together with the relatively slow (more than two orders of magnitude lower than the diffusion limit) quenching rate constants, provide evidence that Coulombic interactions between ^{3}[Ru(bpz)$_3$]$^{2+}$ and eniminium ions might adversely affect the energy-transfer kinetics. Similar observations were made for the dynamic quenching

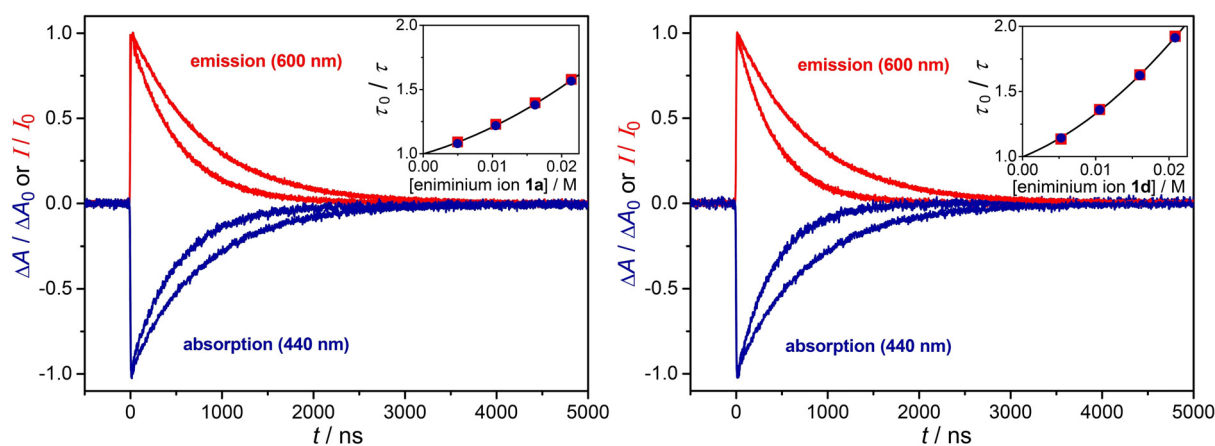**Figure 3.** Quenching of excited Ru(bpz)$_3$(PF$_6$)$_2$ by eniminium ions (left, **1a**; right, **1d**) in Ar-saturated acetonitrile. [Ru(bpz)$_3$]$^{2+}$ (30 μM) was excited at 532 nm (pulse energy, 30 mJ). Main plots, bleach recovery (blue), and emission (red) kinetics in the absence of quenchers and at the highest eniminium ion concentrations (ca. 20 mM) employed. For clarity, the experiments at lower quencher concentrations have been omitted in the main plots. Insets correspond to lifetime-based Stern–Volmer plots. The fit curves are shown to guide the eye and have no kinetic significance. For further details, see the narrative.

of a dianionic sensitizer with a monoanionic quencher[23] as well as for the ^{3}[Ru(bpy)$_3$]$^{2+}$ oxidation by positively charged methyl viologen.[24] At the typical eniminium concentrations during our photochemical reactions (20 mM), however, the quenching efficiencies with the model substrates are high (see Figure 3), enabling acceptable utilization of the photons absorbed by the sensitizer.

Despite the notable ^{3}[Ru(bpz)$_3$]$^{2+}$ quenching under the conditions of Figure 3 (main plot), we could not observe any absorption signals in the transient absorption spectra recorded after complete ^{3}[Ru(bpz)$_3$]$^{2+}$ decay, as already indicated by the complete bleach recovery at 440 nm. In line with the previously reported redox potentials of eniminium ions[14] and the fact that ^{3}[Ru(bpz)$_3$]$^{2+}$ is a poor photoreductant,[25] the absence of any quenching-derived signals in the transient absorption spectrum and the complete bleach recovery[26] rule out a photoreduction of both **1a** and **1d**. The observed decay and the absence of detectable quenching products derived from ^{3}[Ru(bpz)$_3$]$^{2+}$ ($E_T = 208$ kJ mol^{-1})[25] are fully compatible with a triplet–triplet energy transfer mechanism.[27] Owing to the moderate ^{3}[Ru(bpz)$_3$]$^{2+}$ quenching rate constants (ca. 10^7 M^{-1}s^{-1}, vide supra) and the assumed fast decay of the eniminium ion triplets, the latter do not accumulate to detectable concentrations, and we estimate an upper limit for the lifetimes of the eniminium ion triplets of about 50 ns under our conditions (deoxygenated acetonitrile, 20°C). We hypothesize that excited-state geometrical reorganization and internal conversion are rapid deactivation pathways for the eniminium ion triplets. For the related methyl cinnamate a triplet lifetime of 10.6 ns has been reported.[28]

Direct excitation of an argon-saturated solution of **1d** (12 mM in deoxygenated acetonitrile) did not yield any detectable transient absorption signals, although a substantial fraction of 410 nm laser light was absorbed by **1d** at the high concentration employed. The result is not in conflict with the observed low-temperature phosphorescence (Figure 2), since emission-based detection is more sensitive than absorption-based detection by orders of magnitude, and, more impor-

tantly, rapid quenching by geometrical reorganization is impossible in a rigid matrix. The ^{3}[Ru(bpz)$_3$]$^{2+}$ quenching by the bromo derivative **1d** was faster by about 50% compared to the unsubstituted eniminium ion **1a** (see Figure 3 and related text). The rate increase is in line with a higher driving force for the triplet–triplet energy transfer with **1d**, which results from the aforementioned triplet energy differences (ca. 5 kJ mol^{-1}).

Typical concentrations of the olefins/dienes used to trap the eniminium triplets are on the order of 0.4 M during the preparative irradiation experiments of this study. These concentrations are clearly high enough for noticeable quenching of even very short-lived eniminium triplets. A preparative-scale photolysis experiment with [Ru(bpz)$_3$]$^{2+}$, **1a**, and 2,3-dimethylbutadiene was performed to assess the overall quantum yield of the transformation (Scheme 2). Concen-
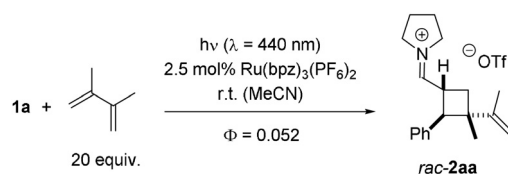
Scheme 2. Ru-catalyzed intermolecular [2+2] photocycloaddition of **1a** ($c = 45$ mM) to deliver *rac*-**2aa** and its quantum yield Φ.

trations were selected to ensure full absorption of the light by the ruthenium catalyst $\{c[\text{Ru(bpz)}_3(\text{PF}_6)_2] = 1.125$ mM; $c(\textbf{1a}) = 45$ mM; $c(\text{diene}) = 0.9$ M$\}$ and UV/Vis spectrometric rate analysis (see Supporting Information) showed the expected zero-order decay of c(**1a**) over time. The quantum yield of the reaction was determined as 0.052 ± 0.003.

The quantum yield of the reaction suggests that the ^{3}[Ru(bpz)$_3$]$^{2+}$ quenching does not proceed with the same efficiency in the preparative-scale experiment as in the spectroscopic studies mentioned above (cf. Figure 3). A further cause for the deviation of the quantum yield from

unity is the rate with which the eniminium triplet is intercepted by the diene. The intrinsic lifetime of the eniminium triplet is short ($\tau < 50$ ns, vide supra), which in turn would require the olefin at the given concentration (0.9 M) to react with a rate constant $k > 2 \times 10^7 \, M^{-1} s^{-1}$ to ensure a high degree ($> 50\%$) of triplet quenching. As seen in many examples,[29,30] the inefficient trapping of a short-lived triplet by an olefin significantly contributes to low quantum yields.

Enantioselective [2+2] Photocycloaddition

In a single preliminary reaction we had previously[14] employed a chiral eniminium ion, **4a**, derived from the tetrafluoroborate salt **5** of a thexyldimethylsilyl (TDS) protected prolinol. Apart from the high enantioface differentiation achieved in the photochemical reaction (enantiomeric ratio $er = 94/6$), a major benefit of the eniminium ions **4** is their facile stoichiometric preparation from **5** by a condensation protocol. In catalytic studies this issue is not relevant and a variety of other chiral secondary amines was tested (vide infra) in the latter context. However, a reliable synthetic protocol was mandatory for an enantioselective [2+2] photocycloaddition in which the amine was used as an auxiliary to have access to clean reaction substrates. This access was guaranteed by condensation of **5** with the respective α,β-unsaturated aldehydes **6** and molecular sieves (MS; 4 Å) in dichloromethane (Scheme 3), which provided
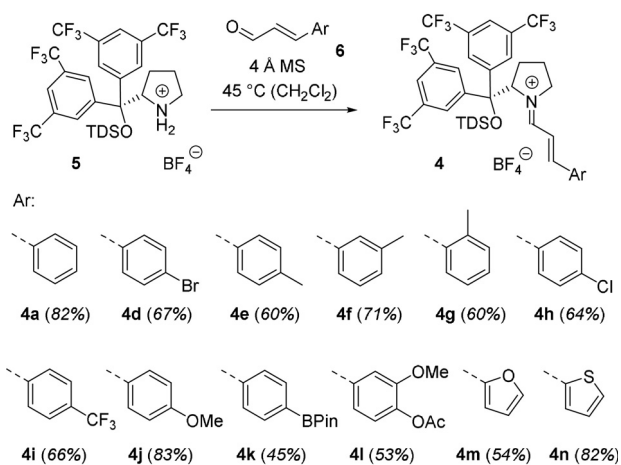
Scheme 3. Preparation of the chiral eniminium ions **4** from the ammonium salt **5**.

the desired **4** as their tetrafluoroborate salts.[10a] The salts were isolated by precipitation and were purified by repeated precipitation cycles from dichloromethane/n-heptane. Yields were variable but the method proved applicable to several functionalized compounds (**4d**, **4h–l**) and to the hetaryl-substituted eniminium ions **4m** and **4n**.

Optimization of the reaction conditions for the [2+2] photocycloaddition commenced with a variation of the temperature in the Ru-catalyzed reaction of **4a** and 2,3-

dimethylbutadiene (Table 1). In all experiments, Ru(bpz)$_3$-(PF$_6$)$_2$ was used as the sensitizer and the reaction was terminated after an irradiation time of three hours. The intermediate product iminium ion was hydrolyzed and the reported yield is based on isolated aldehyde **3aa**. The product

Table 1: Reaction optimization of the enantioselective [2+2] photo-cycloaddition of **4a** and 2,3-dimethylbutadiene to give **3aa**.
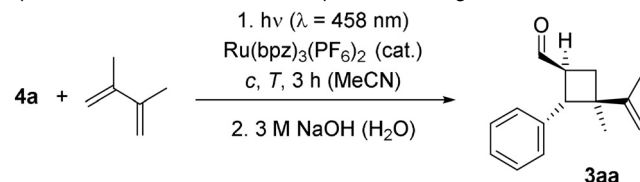
Entry[a]	c [mM]	Diene (equiv)	Cat. [mol%]	T [°C]	Yield [%][b]	er[c]
1	20	20	2.5	−20	44	92:8
2	20	20	2.5	−40	70	94:6
3	20	20	2.5	−60[d]	56	94:6
4	20	20	2.5	−80[d]	51	94:6
5	20	20	1	−40	48	93:7
6	20	50	2.5	−40	62	93:7
7	20	5	2.5	−40	64	93:7
8	10	20	2.5	−40	60	93:7
9	50	20	2.5	−40	60	93:7
10	20	20	–	−40	–	–
11[e]	20	20	2.5	−40	–	–
12[f]	20	20	2.5	−40	67	93:7

[a] Reactions were carried out in acetonitrile solution upon irradiation at $\lambda = 458$ nm for three hours at the indicated concentration (c) and temperature (T) with an excess of diene. [b] Yield of isolated **3aa**. The diastereoselectivity remained identical in all runs with a diastereomeric ratio (dr) of 95:5. [c] The enantiomeric ratio (**3aa**/ent-**3aa**) was determined by chiral-phase GLC analysis. [d] The reaction was performed in propionitrile as the solvent. [e] The reaction was performed without irradiation. [f] The reaction was performed for four hours on a scale of 0.1 mmol and the chiral amine was recovered (89% recovery yield).

exhibits the shown relative configuration in which the bulky substituents (formyl, phenyl, 2-propenyl) are all arranged trans at the cyclobutane core. A minor diastereoisomer (diastereomeric ratio, dr) was detectable, which exhibits a cis orientation between the phenyl and the 2-propenyl group. The ratio of the two product enantiomers (er) was determined by chiral-phase GLC analysis. The propensity of dienes to undergo Diels–Alder reactions with eniminium ions[2a] forced us to start the optimization at low temperature (−20°C, entry 1) to avoid competing thermal reactions. The enantioselectivity improved when lowering the reaction to −40°C (entry 2), while there was no improvement when the temperature was further decreased (entries 3 and 4). A lower catalyst loading (entry 5) had a negative influence both on yield and enantioselectivity. The influence of the diene concentration was marginal (entries 6 and 7) and offered no improvement. Similar observations were made when the concentration of the substrate was varied (entries 8 and 9). Omission of the sensitizer expectedly did not lead to a reaction (entry 10), neither did a control experiment run in the absence of light (entry 11). Since the optimization

reactions were run on small scale, a final experiment was performed with the conditions of entry 2 but on larger scale (entry 12). To our delight, the result was confirmed albeit with a minimal drop in yield (67 vs. 70 %) and *er* (93:7 vs. 94:6).

The absolute configuration of **3aa** was elucidated by its conversion into a compound, the absolute configuration of which had previously been established by X-ray crystallography[15c] (see the Supporting Information for further details). When applying the optimized reaction conditions of Table 1 to other eniminium ions (**4**) the reaction proved to be robust with regard to a modification of the aryl group of the eniminium ion (Scheme 4). The *para*-tolyl product **3ea**, for
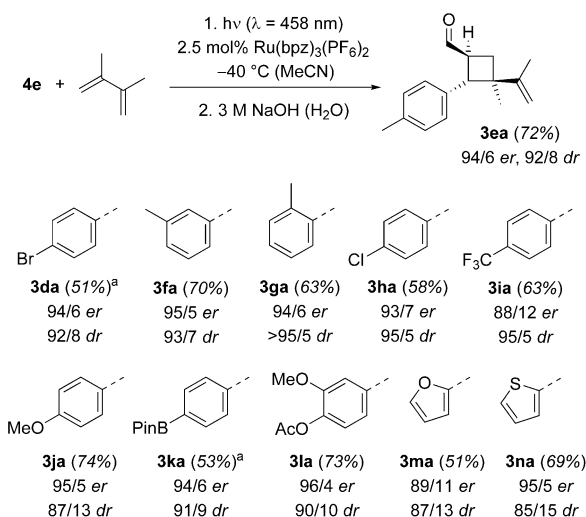
Scheme 4. Enantioselective formation of chiral cyclobutanes by [2+2] photocycloaddition of **4**. [a] 2.5 mol % Ru(bpy)$_3$(PF$_6$)$_2$ was employed as the sensitizer.

example, was isolated in 72 % yield with an *er* of 94:6 and a *dr* of 92:8. Likewise, the other eniminium ions **4** reacted smoothly with the respective aldehydes in the two-step protocol (51–74 % yield) with a notable functional-group tolerance. Apart from alkyl groups in *meta* (product **3fa**) and *ortho* positions (product **3ga**), the compatibility with bromo (product **3da**), chloro (product **3ha**), trifluoromethyl (product **3ia**), methoxy (product **3ja**), pinacolatoboryl (product **3ka**), and acetoxy (product **3la**) groups is remarkable. The oxidation-sensitive hetaryl groups furyl (product **3ma**) and thiophenyl (product **3na**) were also tolerated. For products which did not allow direct assessment of the *er* by chiral-phase GLC it was determined, after reduction to the respective alcohols, by chiral-phase HPLC analysis.

Regarding the alkene scope, olefins with a conjugated π-system reacted in a similar fashion as 2,3-dimethylbutadiene (Scheme 5). However, with the exception of 1-(2-propenyl)-cyclopentene (product **3af**), the simple diastereoselectivity regarding the stereogenic center at C3 was only moderate. Two diastereoisomers were obtained and the *er* value was determined for each diastereoisomer separately. The difference for major and minor diastereoisomer was not very large
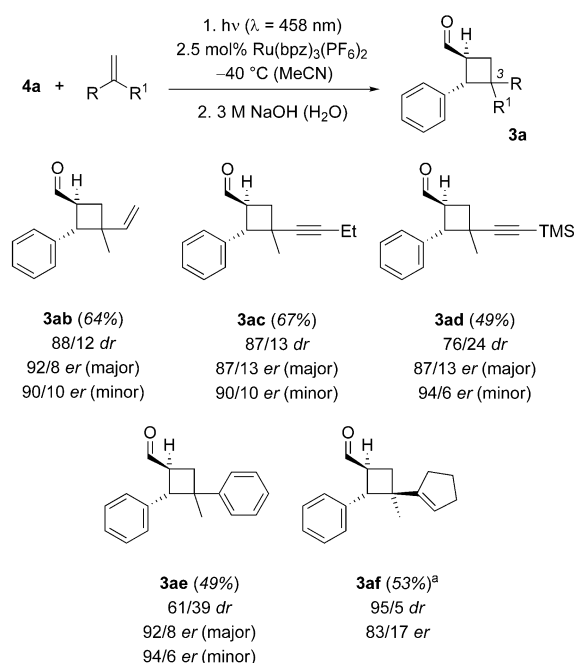
Scheme 5. Enantioselective formation of chiral cyclobutanes by [2+2] photocycloaddition of eniminium ion **4a** with different olefins to products **3a**. [a] 2.5 mol % Ru(bpy)$_3$(PF$_6$)$_2$ was employed as the sensitizer.

in line with a similar mode of attack of the olefin at the triplet eniminium ion.

Simple olefins, which are typically employed in enone [2+2] photocycloadditions[30] such as isobutene or 2,3-dimethyl-2-butene, were not suitable as reaction partners in the reaction of eniminium ions. This reluctance to undergo [2+2] photocycloaddition with non-activated olefins is similar to results with other Ru- or Ir-sensitized reactions that proceed via triplet states of low energy.[15a,c,31]

The attack of an olefin at such a molecule in the triplet state is associated with a loss of its relatively strong π-double bond. If this energy penalty is not compensated by the formation of a stable 1,4-diradical (^{3}D) the reactions appear infeasible. Indeed, the suggested reaction pathway for the eniminium ion [2+2] photocycloaddition involves, after energy transfer, an initial C–C bond formation at the α-carbon atom of the triplet intermediate (T_1) with concomitant formation of the 1,4-diradical **7** (Scheme 6).

It could be questioned whether olefins such as 2,3-dimethylbutadiene trap the photoexcited triplet **4**(T_1) by initial electron transfer.[32] Apart from the fact that a different regioselectivity would be expected if this were the case, electrochemical data disfavor this mechanistic pathway. Based on the measured redox potential of **4d** (En$^+$) in the ground state [$E_{1/2}$(En$^+$/En$^•$) = −0.58 V vs. SCE in MeCN] and on its triplet energy (E_T = 206 kJ mol^{-1} = 2.14 eV), its calculated redox potential in the excited state is $E_{1/2}$(En^{*+}/En$^•$) = +1.56 V. Electron transfer to 2,3-dimethylbutadiene (Db) with a reported[33] E_{ox}(Db$^{•+}$/Db) = +1.96 V (vs. SCE in MeCN) would be strongly endothermic.
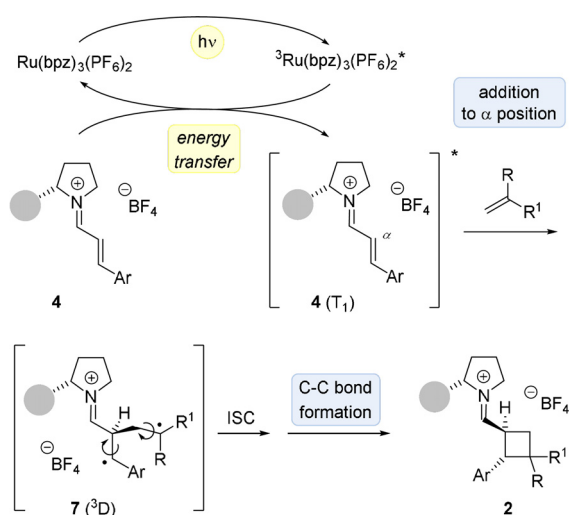
Scheme 6. Suggested reaction pathway for the Ru-catalyzed [2+2] photocycloaddition of **4** with olefins.

Catalytic Enantioselective [2+2] Photocycloaddition.

The α,β-unsaturated aldehydes **6**, which serve as precursors for **4**, exhibit a higher triplet energy than the respective salts. The triplet energy of cinnamic aldehyde (**6a**) for example has been determined as $E_T = 300 \text{ kJ mol}^{-1}$.[34] As a consequence, a negligible sensitized conversion is to be expected if **6a** is irradiated in the presence of 2,3-dimethylbutadiene under the reaction conditions shown in Scheme 4. Indeed, only minimal quantities of *rac*-**3aa** (<10%) were detected in this reaction, which in turn suggests that an in situ formation of the eniminium salt and the use of catalytic quantities of a chiral amine might lead to a catalytic enantioselective [2+2] photocycloaddition reaction (Scheme 7). Formation of **I** would occur from **6** with a given chiral secondary amine, and after successful photocycloaddition **3** would be generated from **II**, liberating the amine.

The choice of the amine was guided by the search for secondary amines that would be stable in the presence of photoexcited ruthenium complexes. Melchiorre and co-workers had earlier found fluorinated proline derivatives to be more resistant towards oxidation.[10a] In addition, we considered some imidazolidinone derivatives[2b] as suitable catalysts.
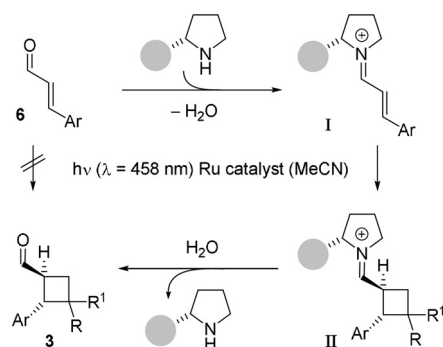

Scheme 7. Potential catalytic cycle for the formation of the cyclobutanes **3** from aldehydes **6** by iminium ion catalysis.

As a test reaction for the suggested catalytic [2+2] photocycloaddition we studied the transformation of **6a** with 2,3-dimethylbutadiene. Details of our optimization attempts are provided in the Supporting Information. The major findings can be summarized as follows:

a) The reaction required a proton source to establish the equilibrium between aldehyde and eniminium ion. Ru-(bpz)$_3$(PF$_6$)$_2$ suffered protonation under these conditions and could not be used. To our delight, Ru(bpy)$_3$X$_2$ turned out to be a competent catalyst and was employed either as hexafluorophosphate (X = PF$_6$) or as tetrakis[3,5-bis(tri-fluoromethyl)phenyl]borate (X = BArF)[35] salt. Like Ru-(bpz)$_3$(PF$_6$)$_2$, Ru(bpy)$_3$(PF$_6$)$_2$ did not show any significant background reaction, that is, it did not catalyze the direct conversion **6a** → *rac*-**3aa** at $\lambda = 458$ nm. Ru(bpy)$_3$(PF$_6$)$_2$ was preferentially used in acetonitrile as the solvent while Ru(bpy)$_3$(BArF)$_2$ was used in nonpolar media, for example, in trifluorotoluene.

b) The experimental window for the variation of reaction conditions was narrow. Regarding the reaction temperature, the Diels–Alder reaction of the diene with the eniminium ion turned out to be a competitive thermal pathway at $T \geq 0\,°C$. All reactions were therefore performed at a temperature of $-10\,°C$ or lower. Despite the beneficial influence of a lower reaction temperature on the enantioselectivity, the conversion suffered most likely due to slow formation of the eniminium ion and/or slow hydrolysis of **II**. Addition of water did not improve the performance of the catalytic reaction. Among the acids we tested, only trifluoroacetic acid (TFA) and trichloroacetic acid allowed a significant turnover, while several other acids either failed or gave poor results.

c) The stability of **3aa** and the amine catalyst were limited under the reaction conditions. Recovery of the amine catalyst was found to be low, indicating its partial decomposition. When **3aa** was subjected to either the reaction conditions or to conditions in which one of the reaction parameters was altered it could never be fully recovered (see the Supporting Information for further details).

Despite the challenge posed by the above-mentioned limitations, we successfully managed to elaborate reaction conditions which enabled catalytic enantioselective access to **3aa**. Reaction conditions *A* (Scheme 8) require a relatively low amine catalyst loading (20 mol%) and delivered the desired product in a yield of 55% and with an *er* of 82:18. The preferred catalysts under these reaction conditions were the amine **8a** and Ru(bpy)$_3$(BArF)$_2$ (2.5 mol%) in combination with 40 mol% TFA in trifluorotoluene as the solvent. The enantioselectivity of the catalytic reaction was significantly improved when employing the amine catalyst **8b** (50 mol%) and Ru(bpy)$_3$(PF$_6$)$_2$ (2.5 mol%) as the sensitizer under reaction conditions *B*. With an *er* of 96:4 it even exceeded the selectivity which had been obtained under stoichiometric conditions (Table 1). Although the latter result does not provide evidence for a catalytic turnover it demonstrates the potential of the method for enantioselective reactions by an in situ formation of a stoichiometric chiral eniminium ion. We
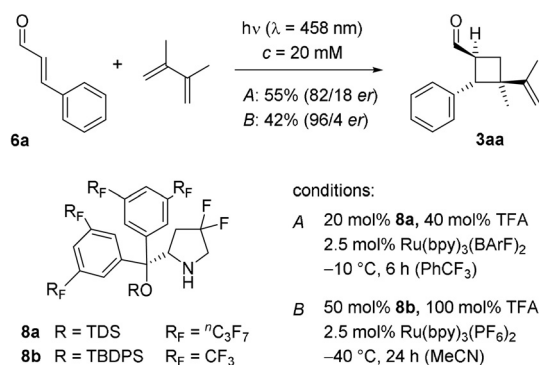
Scheme 8. Formation of enantioenriched compound **3aa** from cinnamic aldehyde (**6a**) under catalytic conditions.

Figure 4. LFP experiments (excitation with 30 mJ pulses at 532 nm) on an Ar-saturated [Ru(bpy)$_3$](PF$_6$)$_2$ solution (28 μM in acetonitrile) containing 12 mM of **1a**. Main plot, transient absorption spectrum recorded by time integration over 200 ns with a 3.5 μs time delay (black), along with the isolated spectrum of the radical **1a·** (green). Left inset, kinetic absorption traces at 395 nm (green, photoproduct formation) and 455 nm (black, incomplete bleach recovery). Right inset, normalized kinetic emission monitored at 610 nm. For further details, see the narrative and the Supporting Information.

verified this notion by performing the previously described reaction sequence **6a→4a→3aa** (Scheme 3, Table 1) as a one-pot reaction without the isolation of **4a**. The intermediate **4a** was generated in the first operation by condensation of **6a** and **5** in dichloromethane. After removal of the molecular sieves by filtration, 2,3-dimethylbutadiene (20 equiv) and 2.5 mol% Ru(bpy)$_3$(PF$_6$)$_2$ were added and the mixture was irradiated as previously described (see the Supporting Information for further details). After typical work-up **3aa** was obtained in a yield that was significantly higher than the overall yield (57%) of the consecutive process. When the precondensation of **6a** and **5** was performed at ambient temperature, the yield of **3aa** was 66% (92:8 *dr*, 94:6 *er*), and when performed at 45°C it increased to 71% (94:6 *dr*, 95:5 *er*). Without compromising the stereoselectivity a significant improvement in synthetic efficiency could thus be achieved.

Ru(bpy)$_3$(PF$_6$)$_2$ and Ir(ppy)$_3$

Since Ru(bpy)$_3$(PF$_6$)$_2$ served as a competent catalyst in the catalytic and in some of the stoichiometric photocycloaddition reactions, its mode of action requires discussion. Its redox potential in the excited state[36] [$E_{1/2}$(Ru^{III}/Ru^{II}*) = −0.81 V vs. SCE in MeCN] is sufficiently negative to reduce, for example, either **4d** or potentially also **1a** with a redox potential[14] of $E_{1/2}$(**1a**$^+$/**1a·**) = −0.83 V. Its triplet energy E_T is tabulated[25] as 205 kJ mol^{-1} which is sufficient to involve eniminium ions in an energy-transfer process. Laser flash photolysis studies were performed with Ru(bpy)$_3$(PF$_6$)$_2$ in acetonitrile solution employing **1a** as a quencher. Under the reaction conditions of Figure 4, ^{3}[Ru(bpy)$_3$]$^{2+}$ emission quenching by **1a** was observed with about 45% efficiency (right inset), corresponding to a quenching rate constant of about 6 × 10^7 M^{-1} s^{-1}, which is more than twice as high as observed with photoexcited [Ru(bpz)$_3$]$^{2+}$ (see Figure 3).

As opposed to the system Ru(bpz)$_3$(PF$_6$)$_2$/**1a**, for which a triplet-energy transfer is the only thermodynamically feasible quenching pathway, incomplete bleach recovery (indicating oxidative quenching)[26] at 455 nm was detected when [Ru(bpy)$_3$]$^{2+}$ was used (left inset of Figure 4), and a new species (monitored at 395 nm) was formed with the same rate
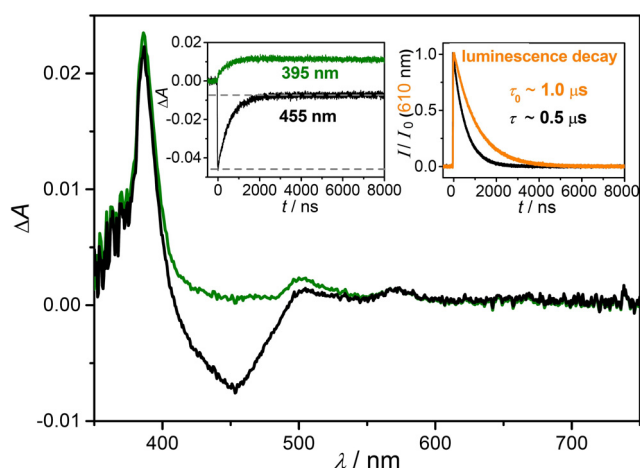
as the ^{3}[Ru(bpy)$_3$]$^{2+}$ decay. The decomposition of the transient absorption spectrum after the sensitizer triplet decay (main plot of Figure 4) indeed revealed the presence of the oxidized Ru^{III} species and the eniminium radical **1a·** (see Section 8 in the Supporting Information). Given that **1a·** is almost transparent at the wavelength used to study the [Ru(bpy)$_3$]$^{2+}$ bleach recovery (455 nm), the efficiency of the photoinduced electron transfer can be estimated.

Photoredox reactions via excited triplet states frequently proceed with high quantum yields of long-lived photoproduct formation ([Ru(bpy)$_3$]$^{3+}$ and **1a·** in the present case) because of a spin-forbidden in-cage recombination.[37] Assuming a cage escape yield of 100% and transparency of **1a·** at 455 nm, the ^{3}[Ru(bpy)$_3$]$^{2+}$ quenching efficiency (as determined from emission kinetics) and the fraction of the offset relative to the initial bleach amplitude at 455 nm (highlighted as horizontal lines in Figure 4) would have to be identical. However, the latter amounts to about 17%, and thus falls short by a factor of 2.5 compared to the overall quenching efficiency (ca. 45%). The spectroscopic results thus indicate that there is a certain degree of energy transfer involved in the quenching of photoexcited Ru(bpy)$_3$(PF$_6$)$_2$ by **1a**, which does not produce any additional transient absorption signals. Although the exact ratio of energy transfer to electron transfer cannot be quantified, given that the exact cage escape yield of electron transfer[38] quenching is unknown, it appears as if the electron transfer is a nonproductive quenching pathway. Not only its mesomeric structure, **1a″**, but also DFT calculations (Figure 5) suggest that **1a·**, obtained by reduction of eniminium ion, exhibits no spin density at the α-carbon atom. Product formation (*rac*-**3aa**) with 2,3-dimethylbutadiene would therefore require an addition of the β-carbon atom to one of the internal carbon atoms, C2 or C3, with concomitant formation of a primary radical center. Given the
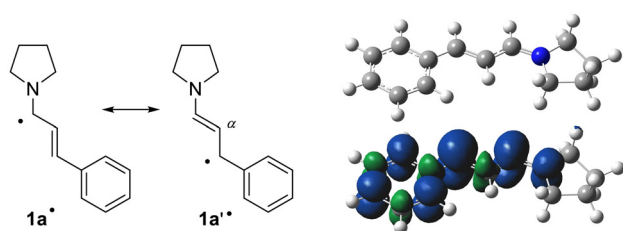
Figure 5. The spin density at **1a·** is located exclusively at the former eniminium carbon atom and at the β-carbon atom: Mesomeric structures (left) and DFT calculation (right). Blue color represents positive spin densities, whereas green represents negative spin densities. See the Supporting Information for further details.

Figure 6. Quenching of excited Ir(ppy)$_3$ by **1a** (3 mM) in Ar-saturated acetonitrile. Ir(ppy)$_3$ (40 µM) was excited at 450 nm (pulse energy, 7 mJ). Main plot, transient absorption spectrum after ^{3}Ir(ppy)$_3$ decay with the detection window highlighted in the inset. Inset, kinetic transient absorption (blue) and emission (red) traces. For further details, see text.

high regioselectivity observed in radical addition reactions to 2,3-dimethylbutadiene in favor of attack at C1[39] this mechanistic option seems highly unlikely. In addition, it appears unreasonable to assume a complete change in mechanism when exchanging Ru(bpz)$_3$(PF$_6$)$_2$ to Ru(bpy)$_3$(PF$_6$)$_2$.

Based on the spectroscopic data we speculated that back-electron transfer from **1a·** to ground-state ruthenium(III) is a more realistic scenario given the high energetic preference for this process [$E_{1/2}$(Ru^{III}/Ru^{II}) = +1.31 V vs. SCE in MeCN]. In other words, only the energy transfer, but not the electron-transfer pathway, is productive for the [2+2] photocycloaddition mediated by Ru(bpy)$_3$(PF$_6$)$_2$. To further substantiate this hypothesis, we briefly studied Ir(ppy)$_3$ as a potential catalyst. This iridium(III) complex is a very strong reductant in the excited state[36] [$E_{1/2}$(Ir^{IV}/Ir^{III}*) = −1.73 V] and its lowest triplet state has an energy of E_T = 236 kJ mol^{-1}.[40] While energy transfer to **1a** is favored only by about 35 kJ mol^{-1} the electron transfer is exothermic by almost 90 kJ mol^{-1} (0.9 eV). Laser flash photolysis experiments with 450 nm excitation of Ir(ppy)$_3$ confirmed the expectation that its triplet state is efficiently quenched. Simultaneously analyzing the ^{3}Ir(ppy)$_3$ emission decay and the photoproduct formation kinetics (Figure 6, inset), we estimated the quenching rate constant to be as high as 1.6×10^{10} M^{-1} s^{-1}, which is at least 250 times faster than with the excited ruthenium complexes. Employing 3 mM of **1a** only, the ^{3}Ir(ppy)$_3$ quenching efficiency amounts to 99%. The observed transient absorption spectrum after the ^{3}Ir(ppy)$_3$ decay (Figure 6, main plot) is in line with electron-transfer quenching, since it corresponds to the superposition of **1a·** (see Figure 4) and the oxidized Ir complex absorption bands.[41] More than 400 laser flashes on the very same deoxygenated solution neither changed the transient absorption spectrum nor its intensities, indicating that unproductive recombination between **1a·** and the oxidized complex is the main deactivation pathway of the radical pair.

In line with the efficient electron transfer to **1a**, Ir(ppy)$_3$ turned out to be a poor catalyst for the reaction **1a**→*rac*-**3aa**. Reactions were attempted both in MeCN and in CH$_2$Cl$_2$ at two different wavelengths (λ = 420 nm and λ = 440 nm). After reaction times which typically led to complete conversion with Ru(bpz)$_3$(PF$_6$)$_2$ and Ru(bpy)$_3$(PF$_6$)$_2$ (t = 2 h), almost no product formation (<10%) was recorded. The result supports the hypothesis that energy transfer is the only productive [2+2] photocycloaddition reaction pathway while an
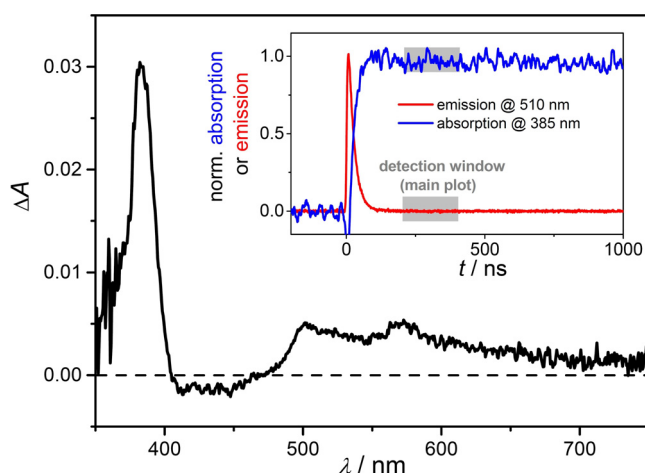
electron transfer from the photoexcited catalyst to the eniminium ion does not promote the photocycloaddition.

Conclusion

In summary, it has been found that photoexcited eniminium ions can not only be generated by direct irradiation but that their first excited triplet-state T$_1$ is accessible by triplet-energy transfer. For eniminium ions derived from cinnamic aldehydes the triplet energy is in a range ($E_T \approx 200$ kJ mol^{-1}) that allows sensitization by the ruthenium catalysts Ru(bpz)$_3$-(PF$_6$)$_2$ and Ru(bpy)$_3$(PF$_6$)$_2$. Subsequent reaction with olefins lead to the formation of cyclobutanes, and this reaction can be performed enantioselectively if guided by a chiral amine. It has thus been possible to access a product class (cyclobutanecarbaldehydes) which has not yet been prepared directly by enantioselective [2+2] photocycloaddition chemistry. Laser flash photolysis has been applied as an analytic tool to study the decay of photoexcited ruthenium and iridium catalysts. A notable observation is the fact that the catalyst that is quenched most rapidly by eniminium ions does not catalyze the [2+2] photocycloaddition. Electron transfer to eniminium ions seems to be a nonproductive pathway under the chosen reaction conditions, but only energy transfer enables rapid product formation. Electron and energy transfer can occur as competing events as seen for Ru(bpy)$_3$(PF$_6$)$_2$ with only the latter reaction channel generating an intermediate which can be intercepted by an olefin. The findings presented herein could significantly contribute to the ongoing and fast development of photochemical reaction sequences via triplet states.[17]

Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · enantioselectivity · homogenous catalysis · photochemistry · ruthenium

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