Ferrocenium lons as Catalysts: Decomposition Studies and Counteranion Influence on Catalytic Activity

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Abstract Catalyst decomposition has a negative effect on catalytic activity, and knowledge of decomposition pathways can assist with catalyst development. Ferrocenium cations have been employed as catalysts in a number of organic transformations, and we investigated the stability of a number of ferrocenium salts in solution. The observed rate decomposition constants for [Fc]Cl, [Fc]PF₆, [Fc]BF₄, [Fc]CSA [Fc = ferrocenium, CSA = camphor-10-sulfonate (β)], [AcFc]SbF₆, (AcFc = acetylated ferrocene), and [FcB(OH)₂]SbF₆ [FcB(OH)₂ = ferrocenylboronic acid] were determined in CH₂Cl₂ solution by time-resolved UV-vis spectroscopy. The rate decomposition constants depended on the nature of the counterion, with [Fc]Cl being the most stable complex in solution. The decomposition rate constants dropped by roughly an order of magnitude in most cases when the experiments were performed in nitrogenated solvent, demonstrating that the decomposition is mainly an oxidative process. The cosolvent HFIP (1,1,1,3,3,3-hexafluoropropan-2-ol) slowed the decomposition of the ferrocenium cations as well. Many catalytic or stoichiometric reactions of ferrocenium cations are performed with alcohols; we determined that hexan-1-ol is decomposed over the course of 16 hours, but not oxidized in the presence of a ferrocenium cation. Finally, the different ferrocenium cations were employed in a test reaction to determine catalytic activity. The nucleophilic substitution of hydroxyl groups in a tertiary propargylic alcohol by an alcohol is catalyzed by all complexes, and, again, a counterion dependency of the catalytic activity was observed. Also, HFIP increases the catalytic activity of the ferrocenium cations. The research has importance in the development of ferrocenium-based catalyst systems, because changes in the counterion as well as the architecture of the ferrocenium cation have an influence on stability and catalytic activity.

Key words ferrocenium, homogeneous catalysis, transition metal Lewis acids, catalyst decomposition

Iron catalysis is a vibrant field of current research. Iron is abundant, inexpensive, relatively nontoxic, and environmentally benign, making it an attractive alternative to other transition metals typically employed in catalysis.¹ Ironbased catalysts can be as simple as iron salts such as FeCl₃ Paper

or Fe(OTf)₂.² The number of iron-containing catalyst systems is vast and increasing. More highly sophisticated iron complexes find applications as catalysts in polymerization,^{1c} oxidation,^{1e,3} and cross-coupling reactions,^{1d} among others. Nitrogen-based multidentate ligands perform especially well in the aforementioned examples. These ligands add stability to the iron complex. Still, catalyst decomposition is a general problem in the field.⁴ It is in the nature of catalysts to exhibit a level of reactivity, and decomposition of the catalyst can often accompany catalytic reactions. These unwanted catalyst decay reactions potentially deactivate the catalyst, resulting in lower yields and enantiomeric excesses in cases where a chiral iron catalyst system is involved. As such, knowledge of catalyst decomposition pathways and how to block them is particularly relevant.

Among other iron-based catalyst systems, ferrocenium cations and their derivatives have recently emerged as catalysts in a number of organic reactions.⁵ Some ferrocenium cations are commercially available and are known as oneelectron oxidants. As such, they have been employed as stoichiometric oxidants in the past.⁶ Ferrocenium cations also play a role in electrochemistry, where ferrocenes serve as standards.⁷ Ferrocenium cations or their derivatives have been employed as catalysts in Friedel-Crafts alkylation reactions,⁸ asymmetric alkylation reactions,^{8b} catalytic oxidation reactions,⁹ cyanosilylations,¹⁰ aldol reactions,¹¹ ringopening of epoxides,¹² aromatic iodinations,¹³ the Strecker reaction,¹⁴ the Mannich reaction,¹⁵ or in ring expansions.¹⁶ Ferrocenium cations also have been used as photoinitiators.¹⁷ Still, the catalytic application of ferrocenium cations constitutes an underdeveloped research area. However, due to their simplicity, tunability and availability, ferroceniumbased catalyst systems are attractive targets for research. Accordingly, the number of catalytic applications of these fascinating complexes is rising.8-17

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Syn thesis

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As part of our long-standing research interest in the catalytic activation of propargylic alcohols,^{18,19} we recently disclosed that ferrocenium hexafluorophosphate (subsequently abbreviated as [Fc]PF₆) and derivatives thereof can serve as catalysts in the conversion of propargylic alcohols 1 to the corresponding propargylic ether 2, by utilizing an alcohol nucleophile (Scheme 1). Their striking advantage is that they can perform the reaction at lower temperatures compared to systems based on ruthenium.^{18f} These results prompted us to investigate the activity of ferrocenium cations in greater details, and for the model reaction in Scheme 1, we discovered that the reaction most likely proceeds through a carbocation intermediate,^{18a} consistent with mechanistic proposals for related ferrocenium-catalyzed processes.^{6b} Still, the exact mode of action of ferrocenium cations in the substitution reaction is not fully understood.



It has been described previously that solutions of ferrocenium cations oxidatively decompose over time in certain oxygen-containing solvents.²⁰ However, little is known concerning details of ferrocenium decomposition chemistry,^{21,22} and the results mainly draw from electrochemistry and cyclic voltammetry experiments,^{20b,23} where irreversible or partially reversible redox processes suggest the decomposition of ferrocenium cations. Counterion influences and substituent effects on the activity have barely been investigated. Herein, we describe a method to systematically quantify the rate of decomposition of a number of ferrocenium cations and their derivatives based on UV-vis spectroscopy. We investigated the dependency of the stability of ferrocenium cations on the counteranion and in the presence of a fluorinated cosolvent. We also investigated the influence of the counterion on the catalytic activity of ferrocenium salts.

Ferrocenium cations are intensely colored compounds, and in past experiments, we occasionally observed decolorization of their solutions during catalytic application, which we attributed to ferrocenium decomposition. Ferrocenium cations exhibit an intense absorption band around 620 nm in their UV-vis spectra, and we decided to utilize time-resolved UV-vis spectroscopy to quantify the decomposition processes. We selected a number of ferrocenium salts to investigate the decomposition rate for the dependency on the ferrocenium architecture and the counterion, as shown in Figure 1.



Figure 1 Ferrocenium salts employed in this study

We selected the known ferrocenium salt $[Fc]Cl^{24}$ and commercial $[Fc]PF_6$ and $[Fc]BF_4$ to investigate the influence of the counterion on the decomposition rate. We generated the complex [Fc]CSA $[CSA = camphor-10-sulfonate (\beta)]$ in solution, which has also been included in this study. The known complexes $[AcFc]SbF_6$ ²⁵ and $[FcB(OH)_2]SbF_6$ ^{8a} were selected to investigate the influence of substituents on the stability and catalytic activity of the ferrocenium cation. Solutions of these substances in both 'ambient', oxygencontaining CH_2Cl_2 and in freshly distilled, nitrogenated CH_2 - Cl_2 were prepared and the intensity of the UV-vis band at 620 nm was observed over time. As illustrated in Figure 2 for $[Fc]PF_6$, the intensity of the band at 620 nm gradually decreased over time and the determination of an observed rate constant is possible.

Plotting of the absorption vs time and fitting the data points either to a first- or a second-order reaction rate law allowed for the determination of rate constants. The plots are given in the supporting information, including R² values; for some measurements, the R² values are a little off, but linear trends could still be established. Induction periods or autocatalysis were not observed. The results are compiled in Table 1.

Not necessarily surprising, the complexes [Fc]Cl, [Fc]PF₆, [Fc]BF₄, [FcB(OH)₂]SbF₆, and [AcFc]SbF₆ exhibited instability in oxygen-containing CH₂Cl₂ solutions, as previously reported for [Fc]PF₆.^{21,23b} The complexes [Fc]Cl and [Fc]PF₆ decomposed with rate constants of 6.0×10^{-6} s⁻¹ and 6.5×10^{-5} s⁻¹, respectively (Table 1, entries 1 and 2). The complex [Fc]BF₄ decomposed one to two orders of magnitude faster in oxygen-containing CH₂Cl₂ solution, with a rate constant of 2.5×10^{-4} s⁻¹ (entry 3). Complex [Fc]CSA could not be synthesized in CH₂Cl₂ as a solvent due to the insolubility of the silver camphorsulfonic acid [Ag]CSA required for its synthesis. It could only be generated in solution with a fluorinated cosolvent (*vide infra*).

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As can be seen clearly, the decomposition of the complexes depends on the counterion. The complexes $[FcB(OH)_2]SbF_6$ and $[AcFc]SbF_6$ decomposed in oxygen-containing solvent with observed rate constants of $3.5 \times 10^{-3} \text{ s}^{-1}$. M⁻¹ and $4.5 \times 10^{-5} \text{ s}^{-1}$, respectively. These two complexes contain the same counterion; thus, the architecture of the ferrocenium cations also had an influence on the decomposition rates.

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When the decomposition rates were determined in freshly distilled, nitrogenated CH_2Cl_2 , the decomposition rate constants for $[Fc]PF_6$, $[Fc]BF_4$ and $[FcB(OH)_2]SbF_6$ dropped significantly, by one or two orders of magnitude. The nitrogenated CH_2Cl_2 was presumably not completely oxygen-free. As such, the decomposition of the ferrocenium cations may mainly be an oxidative process, as described previously, which is in line with previous reports for

 $[Fc]PF_6$.^{21,23} However, bimolecular decomposition pathways between cation and anion may also be a possibility. The ferrocenium complexes [Fc]Cl and $[AcFc]SbF_6$ decomposed in nitrogen-saturated CH_2Cl_2 , but not at all or not much slower than in ambient CH_2Cl_2 , and, at least for [Fc]Cl, the reason for that may be that it is the most stable ferrocenium cation in the series.

The decomposition is counterion dependent. Interestingly, the decomposition process is the slowest for the most nucleophilic and 'simplest' counterion Cl⁻. As such, the decomposition is not merely an attack of the counterion on the ferrocenium cation, in which case [Fc]Cl would decompose the fastest, because chloride is the most nucleophilic counterion. Due to the high dilution of the solutions (0.001 M for the UV-vis measurements), bimolecular decomposition pathways seem unlikely, albeit some complexes exhibit

Table 1 Decomposition Rate Constants ^{a,b}							
Entry	Catalyst	Decomposition rate constant in ambient, oxygen-containing CH ₂ Cl ₂	Decomposition rate constant in nitrogenated CH_2Cl_2	Rate law			
1	[Fc]Cl	$6.0 \times 10^{-6} \text{ s}^{-1}$ (±0 × 10 ⁻⁶)	$6.0 \times 10^{-6} \text{ s}^{-1}$ (±1 × 10 ⁻⁶)	1st order			
2	[Fc]PF ₆	$6.5 \times 10^{-5} \text{ s}^{-1}$ (±0.5 × 10 ⁻⁵)	$3 \times 10^{-6} \text{ s}^{-1}$ (±1 × 10 ⁻⁶)	1st order			
3	[Fc]BF ₄	$2.5 \times 10^{-4} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0.5 × 10 ⁻⁴)	$6.5 \times 10^{-6} \text{s}^{-1} \cdot \text{M}^{-1}$ (±0.5 × 10 ⁻⁶)	2nd order			
4	[Fc]CSA	-	-				
5	[FcB(OH) ₂]SbF ₆	$3.5 \times 10^{-3} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0.5 × 10 ⁻³)	$2.7 \times 10^{-4} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0.3 × 10 ⁻⁴)	2nd order			
6	[AcFc]SbF ₆	$\begin{array}{l} 4.5 \times 10^{-5} \text{ s}^{-1} \\ (\pm 0.5 \times 10^{-5}) \end{array}$	2.0 × 10 ⁻⁵ s ⁻¹ (±0)	1st order			

 $^{\rm a}$ Reaction conditions: 0.001 M catalyst in $\rm CH_2\rm Cl_2$ solvent at room temperature.

^b The average of two runs is reported.

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second-order decomposition kinetics. The decomposition rate laws are first-order or pseudo-first-order for some of the complexes. It has been described that the first step of the oxidative decomposition of the ferrocenium cation constitutes an attack of oxygen on the iron center system, followed by the formation of oxygen-bridged dimeric ferrocenium species.^{21,23b} The nucleophilic Cl⁻ counteranion may, through the formation of ion pairs with the ferrocenium cation, slow down this pathway. Interestingly, for [Fc]Cl being the most stable ferrocenium cation in solution, there are barely differences in the decomposition rate constants in ambient and nitrogenated CH₂Cl₂.

It is known that PF_6^- and BF_4^- hydrolyze to a variety of products in the presence of water (some of them being Fand HF).²⁶ Ferrocenium cations are known to serve as catalyst for the photodecomposition of chloroform to produce HCl,²⁷ and it may be that CH_2Cl_2 is decomposed in the same way. It has been described that ferrocenium cations decompose rapidly in acidic solutions.²⁸ As such, the hydrolysis products of the counteranions may accelerate the decomposition. It would not be surprising that [Fc]Cl is the most stable one in oxygen-containing solutions, because Cl⁻ does not decompose and thereby increase the acidity of the solution.

The boronic acid-containing complex $[FcB(OH)_2]SbF_6$ is the least stable in solution. It is known that boronic acids are mild Lewis acids, which contain two labile hydroxyl groups; they are catalysts in their own right.²⁹ As such, it may be that the boronic acid group catalyzes the decomposition of the complex, presumably through interaction with molecular oxygen.

The solvent HFIP (1,1,1,3,3,3-hexafluoropropan-2-ol) has recently been discovered to have a beneficial influence on catalytic processes in a variety of chemical reactions.³⁰ It has a high ionizing power, is a good hydrogen bond do-nor,^{31,32} is a poor hydrogen bond acceptor, is very polar, and

is not very nucleophilic.³³ HFIP can aid in dissolving salts that are otherwise insoluble in organic solvents. Furthermore, it stabilizes potential carbocation intermediates.^{8b,34} We performed the same time-resolved UV-vis experiments with HFIP as a co-solvent (CH₂Cl₂/HFIP, 12:1) under otherwise identical conditions. The results of these experiments are compiled in Table 2.

For [Fe]Cl, one of the most stable complexes in solution, the decomposition rate constant remained roughly the same in the presence of HFIP. However, the rate constants decreased significantly for $[Fc]PF_6$ to 8.0 × 10⁻⁷ M⁻¹·s⁻¹, which is roughly two order of magnitudes slower than without that co-solvent (Table 2, entry 2). Under these reaction conditions, [Fc]BF₄ decomposed very fast, and a rate constant could not be determined (entry 3). The stabilizing effect is even more pronounced for $[FcB(OH)_2]SbF_6$, where the rate constant dropped to $2.5 \times 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$, which is roughly three orders of magnitude slower than without HFIP (entry 5). The complex [Fc]CSA could not be generated without the HFIP solvent, because the known³⁵ camphorsulfonic acid silver salt [Ag]CSA is not soluble in CH₂Cl₂, which is required for the synthesis of the complex. Still, in solution the complex has a lifetime in the presence of HFIP with a decomposition rate constant of $7.5 \times 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$ (entry 4).

Interestingly, the decomposition rate constants in solutions with HFIP as the cosolvent are roughly the same in ambient and nitrogenated CH_2Cl_2 , with the exception of $[Fc]PF_6$ (where the decomposition rate constant is slowed down in nitrogenated CH_2Cl_2) and $[Fc]BF_4$ (where it was not possible to determine the decomposition rate constant in ambient CH_2Cl_2 due to fast decomposition). This may be an indication that the HFIP solvent mainly blocks the oxidation of the complex. HFIP has been employed in epoxidation reactions and activates hydrogen peroxide through a polar mechanism,³⁶ and it has also been employed as solvent in

Table 2	Decom	position R	ate Cons	tants in C	H ₂ Cl ₂	/HFIP ((12:1)	a,b
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Entry	Catalyst	Decomposition rate constant in ambient, oxygen- containing solvent	Decomposition rate constant in nitrogenated solvent	Rate law
1	[Fc]Cl	5.0 × 10 ⁻⁶ s ⁻¹ (±0)	$2.5 \times 10^{-6} \text{ s}^{-1}$ (±0.5 × 10 ⁻⁶)	1st order
2	[Fc]PF ₆	$8.0 \times 10^{-7} \mathrm{M^{-1} \cdot s^{-1}}$ (±1 × 10 ⁻⁷)	$5.0 \times 10^{-6} \mathrm{M^{-1} \cdot s^{-1}}$ (±1 × 10 ⁻⁶)	2nd order
3	[Fc]BF ₄	-	$7.5 \times 10^{-5} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0.5 × 10 ⁻⁵)	2nd order
4	[Fc]CSA	7.5 × 10 ⁻⁶ M ⁻¹ ·s ⁻¹ (±0.5 × 10 ⁻⁶)	$4 \times 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$ (±0 × 10 ⁻⁶)	2nd order
5	[FcB(OH) ₂]SbF ₆	$2.5 \times 10^{-6} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0.5 × 10 ⁻⁶)	$2 \times 10^{-6} \text{ s}^{-1} \cdot \text{M}^{-1}$ (±0 × 10 ⁻⁶)	2nd order
6	[AcFc]SbF ₆	$1.0 \times 10^{-5} \text{ s}^{-1}$ (±1 × 10 ⁻⁵)	$3.5 \times 10^{-5} \text{ s}^{-1}$ (±0.5 × 10 ⁻⁵)	1st order

^a Reaction conditions: 0.001 M catalyst in CH₂Cl₂/HFIP (12:1) at room temperature.

^b The average of two runs is reported.

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the Brønsted acid-catalyzed Bayer–Villiger oxidation.³⁷ Consequently, it may accelerate the oxidative decomposition of ferrocenium cations. On the other hand, it has been described that HFIP efficiently solvates cations in solution,^{8b,30a} and, as such, the solvent may stabilize the ferrocenium cation. If the first step of oxidative ferrocenium decomposition is the formation of an Fe–O–O–Fe species in solution as mentioned above,^{23b} the HFIP may form a protective solvation shell around the ferrocenium cations,^{31,34} slowing any sort of decomposing attack by oxygen. Also, HFIP has been described to form hydrogen bonds to anions,³⁷ which may prevent decomposition of the counteranions as described above. The stabilization of transition metal catalysts by HFIP is an important concept, and we are not aware of published research in that direction.

We have previously applied ferrocenium salts as catalysts for the etherification of propargylic alcohols with alcohol nucleophiles.¹⁸ Other authors also employed ferrocenium salts either catalytically or stoichiometrically in organic synthesis, where alcohols were either reactants or products.⁵ Ferrocenium cations are oxidants, and in principle should be able to oxidize primary alcohols. This would have an impact on the use of ferrocenium cations as catalysts in the presence of alcohols, as the redox process would destroy the catalyst.

In case the ferrocenium cations oxidize alcohols, their decomposition rate constant should increase. In order to investigate the stability of ferrocenium cations in the presence of an alcohol, we performed time-resolved UV-vis experiments similar to those in Tables 1 and 2 with some ferrocenium salts, but in the presence of a tenfold excess of butan-1-ol without and in the presence of HFIP. [The results of these experiments are compiled in the Supporting Information (SI), Table S1.] The results are somewhat inconclusive and no clear trend could be established. Obviously, butan-1-ol can accelerate or slow down the decomposition of ferrocenium cations, and a clear stabilizing or destabilizing effect of HFIP could not be established. It may be that the decomposition of the ferrocenium cation is more divergent in the presence of butan-1-ol, which would make it more difficult to establish a trend. In any event, butan-1-ol seems to not dramatically accelerate the decomposition of ferrocenium cations by several order of magnitudes, as the decomposition rate constants still ranged from about 1×10^{-4} to 1 $\times 10^{-6} \text{ s}^{-1} \text{ or s}^{-1} \cdot \text{M}^{-1}$.

We were still interested to see if ferrocenium cations are capable of oxidizing primary alcohols. In a stoichiometric experiment, we tried to determine what the products are of the reaction between hexan-1-ol and [Fc]PF₆ (Scheme 2). We combined an equimolar amount of hexan-1-ol and [Fc]PF₆ in CH₂Cl₂; after 16 hours at 45 °C, we filtered the reaction mixture through a short pad of silica gel, removed the solvent, and recorded ¹H and ¹³C{¹H} NMR and IR spec-

tra (see SI). Indeed, the hexan-1-ol has been almost completely reacted to give an unidentifiable and inseparable mixture of compounds.



However, we did not detect oxidation products of hexan-1-ol. In the IR spectrum of the reaction mixture, the diagnostic band for OH had disappeared, but no carbonyl stretches were observed. Furthermore, in the ¹H NMR spectra, characteristic resonances around 9.5 ppm for aldehydes or 11.5 ppm for carboxylic acids were missing. Likewise, in the ¹³C{¹H} NMR spectrum no peaks around 175 ppm for carboxylic acids or around 200 ppm for aldehydes were detected. The ¹H NMR spectrum indicates some elimination, isomerization, or substitution. As such, it appears that the ferrocenium cations do not oxidize primary alcohols, but alcohols may interfere with the ferrocenium cation in general and accelerate its decomposition.

We next tested the catalytic activity of the ferrocenium salts in Figure 1 in a propargylic substitution test reaction (Table 3). We have previously shown that propargylic alcohol **3** and butan-1-ol can be converted to the corresponding propargylic ether **4**, catalyzed by $[Fc]PF_6$.^{18e} We employed the other ferrocenium catalysts shown in Figure 1 including $[Fc]PF_6$ in the test reaction under strictly identical conditions in non-deoxygenated CH_2Cl_2 at 45 °C. We decided to employ 'regular', non-deoxygenated CH_2Cl_2 , because chemical reactions that can be performed under ambient conditions are of greater interest to synthetic organic chemists. Furthermore, the reaction produces water, which makes the use of thoroughly dried solvents obsolete. Conversion to the products was determined by GC after 2, 6, and 24 hours (Table 3).

As can be seen from Table 3, we observed again a counteranion dependency on the activity of the corresponding ferrocenium salt. Conversions of 84 to 99% were determined after 24 hours. However, most interestingly, after 2 and 6 hours, respectively, conversion rates varied widely. The catalysts [AcFc]SbF₆ and [Fc]Cl converted the starting materials into the product within two hours to roughly 90% of the product, after which the composition of the reaction mixture stayed approximately the same. Catalyst [FcB(OH)₂]SbF₆ performed, within the first 6 hours, more slowly. The catalysts [Fc]PF₆ and [Fc]BF₄ performed very slowly after 2 hours, and it took 24 hours until almost complete conversion was observed.

 Table 3
 Catalytic Activity of Different Ferrocenium Complexes in Propargylic Etherification Reactions^a



^a Reaction conditions: propargylic alcohol **3** (0.68 mmol), butan-1-ol (0.74 mmol), ferrocenium catalyst (0.017 mmol, 2.5 mol%), CH₂Cl₂, 45 °C. Conversions were determined by GC. The average of two runs is reported. ^b Within experimental error, the conversion rates stayed approximately the same after 2 h reaction time.

⁴ The reaction was performed in CH₂Cl₂/HFIP (12:1).

Some of the experiments in Table 3 were also performed in the presence of HFIP. Again, there is a remarkable influence of HFIP on the catalytic performance. In presence of HFIP, the reactions went to completion pretty much after 2 hours. HFIP itself does not catalyze the reaction. It may be that the HFIP either slows catalyst decomposition, thereby increasing performance. However, as described above, HFIP is known to stabilize carbocation intermediates in solution.^{8b,34} We speculated previously that the reaction proceeds through a carbocation intermediate,^{18a} which may explain the improved catalytic performance in the presence of HFIP. As mentioned above, [Fc]CSA could not be synthesized in CH₂Cl₂ as solvent, but it could be generated in solution with HFIP as the cosolvent. With HFIP as the cosolvent, [Fc]CSA performed comparable to [FcB(OH)₂]SbF₆.

These findings are remarkable regarding several respects. It has previously been reported that the counteranion can have an influence on catalytic activity.³⁸ The catalyst [Fc]Cl with the chloride counteranion is significantly more active than [Fc]PF₆ and [Fc]BF₄. However, [Fc]Cl is also the most stable complex among the three, as demonstrated in Table 1. The decomposition of [Fc]PF₆ and [Fc]BF₄ may produce species in solution that are less catalytically active than [Fc]⁺. The role of the B(OH)₂ unit in [FcB(OH)₂]SbF₆ with respect to catalytic activity is unclear and currently under further investigation. However, although the complex decomposes faster than [Fc]PF₆, it shows higher catalytic activity in the initial two hours of the reaction. Here, opposing trends may be at play: the $B(OH)_2$ unit may be beneficial for catalytic activity, as described before.^{8b,29} It has been described previously that the $B(OH)_2$ unit in the corresponding ferrocenium cation can assist with the formation of carbocations from alcohols by hydroxide abstraction.^{8b} Furthermore, [FcB(OH)₂] has an affinity for alcohols that may increase catalytic activity.³⁹ However, the decomposition of [FcB(OH)₂]SbF₆ is also accelerated compared to [Fc]PF₆.

Finally, [AcFc]SbF₆ showed the highest catalytic activity. It decomposes roughly as fast as [Fc]PF₆ but exhibited much higher activity. The complex [AcFc]PF₆ demonstrates high conversion in the early stage of the reaction, likely due to its high electrophilicity, which outcompetes decomposition pathways. As shown in our recent work, we assume that the ferrocenium cation assists in the formation of a carbocation intermediate, which is subsequently attacked by an alcohol nucleophile.^{18a} Ferrocenium-assisted carbocation formation from alcohols has been described previously.^{8b,29} The acetyl unit in [AcFc]SbF₆ in combination with the non-coordinating SbF₆⁻ counteranion makes the ferrocenium cation more electrophilic, which may facilitate carbocation formation and consequently increase catalytic activity. The electrophilic B(OH)₂ unit in [FcB(OH)₂]SbF₆ also facilitates carbocation formation,^{8b} but the complex is, at the same time, the least stable in CH₂Cl₂ solution. As such, some of the ferrocenium cations suffer from competitive decomposition and thus require HFIP to stabilize either the catalytically active species or relevant cationic intermediates.

The findings in Tables 1–3 are of importance to the field of ferrocenium catalysis research. Catalyst decomposition can be an issue, and the rate of decomposition depends on the counterion and on substituents on the cyclopentadienyl ring. Many catalytic applications of the ferrocenium cation are performed at elevated temperatures, which may accelerate the decomposition. On the other hand, the concentrations we employed for the UV-vis experiments are much lower than under catalysis conditions. Catalyst decomposition may still be slow enough compared to the reaction times to drive a reaction to completion. HFIP slows down catalyst decomposition and increases catalytic performance.

In conclusion, we demonstrated through time-resolved UV-vis spectroscopy that a number of ferrocenium cations decompose in CH_2Cl_2 solution, and that the decomposition rate constant is counterion-dependent. The rate of decomposition depends also on the architecture of the ferrocenium cation. The decomposition is slowed down in nitrogenated CH_2Cl_2 in most cases, giving evidence that the decomposition process is mainly an oxidative process. In the presence of the fluorinated cosolvent HFIP, the decomposition process is slowed down. HFIP obviously stabilizes ferrocenium cations in solution. Catalytic applications of ferrocenium cations often involve alcohols, and it appears that ferrocenium hexafluorophosphate decomposes hexan-1-ol

Synthesis

over the course of 16 hours, but not oxidatively. The catalytic activity of the ferrocenium salts was investigated in a propargylic etherification test reaction. Again, the counterion as well as the architecture of the ferrocenium salts had an influence on the catalytic activity, and HFIP improves catalytic performance. The ferrocenium ions presumably assist in the formation of carbocation intermediates in the test reaction, and the most Lewis-acidic ferrocenium salt exhibited the highest activity. The results are of importance for catalysis researchers who employ ferrocenium cations as catalysts, because catalyst decomposition may impair catalytic activity.

CH₂Cl₂ was freshly distilled from CaCl₂. The ferrocenium salts [Fc]Cl,²⁴ [AcFc]SbF₆,²⁵ and [FcB(OH)₂]SbF₆^{8a} and silver camphor-10-sulfonic acid (β)³⁵ were synthesized according to the literature. Commercial [Fc]PF₆, [Fc]BF₄, and HFIP (SigmaAldrich) were used as received. NMR spectra were obtained at room temperature on a Bruker Avance 300 MHz instrument and referenced to a residual solvent signal. IR spectra were recorded on a Thermo Nicolett 670 FTIR. UV-vis spectra were recorded on a Bruker Scion 456 instrument.

Generation of [Fc]CSA

Silver camphor-10-sulfonic acid (β) (0.046 g, 0.136 mmol) was completely dissolved in 1 ml of HFIP using a sonicator. To a solution [Fc]Cl (0.030 g, 0.135 mmol) in CH₂Cl₂ (1 mL), the [Ag]CSA solution was added dropwise with stirring, and a precipitate formed. The mixture was transferred into a test tube and centrifuged. After 5 min, the [Fc]CSA solution was decanted from the silver chloride precipitate and used as is.

Time-Resolved UV-vis Spectrometry; General Procedure

The ferrocenium salt was weighed and added to a volumetric flask filled with CH_2Cl_2 (25 mL) to give a 0.001 M solution. Then some of the solution (13 mL) was added to a vial, quickly placed in the UV-vis spectrophotometer and the spectra were recorded in 15 second time intervals. For the experiments with nitrogenated CH_2Cl_2 , freshly distilled and nitrogenated CH_2Cl_2 was utilized for the formation of the solutions. For the HFIP experiments, the ferrocenium salt was dissolved in HFIP (1 mL) and placed in the volumetric flask, followed by CH_2Cl_2 .

GC Experiments; General Procedure

2-Phenylbut-3-yn-2-ol (**3**, 0.099 g, 0.68 mmol), butan-1-ol (0.055 g, 0.74 mmol), and the ferrocenium catalyst (0.017 mmol, 2.5 mol%) were combined in CH₂Cl₂ (1 mL) and heated at 45 °C. After the time specified, an aliquot of the reaction mixture was filtered through a short pad of silica gel and a GC was recorded.

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Supporting Information

Supporting information for this article is available online at https://dx.doi.org/10.1055/s-0040-1705992. Included are: plots of the absorbance vs time for all entries in Tables 1, 2 and S1; IR and NMR spectra of the reaction in Scheme 2; Table S1 with decomposition rate constants in the presence of butan-1-ol.

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