Homogeneous Catalysis

Selective Hydrosilylation of Esters to Aldehydes Catalysed by Iridium(III) Metallacycles through Trapping of Transient Silyl Cations

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Abstract: The combination of an iridium(III) metallacycle and 1,3,5-trimethoxybenzene catalyses rapidly and selectively the reduction of esters to aldehydes at room temperature with high yields through hydrosilylation followed by hydrolysis. The ester reduction involves the trapping of transient silyl cations by the 1,3,5-trimethoxybenzene co-catalyst, supposedly by formation of an arenium intermediate whose role was addressed by DFT calculations.

tion of 2-pyridinyl esters.^[8b] The strong organoborane Lewis acid $B(C_6F_5)_3$ catalyses efficiently the hydrosilylation of esters with triphenylsilane to afford silyl acetals along with the over-

reduction products (silyl ethers and alkanes).^[8c] More recently,

Introduction

Aldehydes are important compounds in organic chemistry. Three main synthetic pathways can achieve their preparation starting from widely available chemicals: the hydroformylation of olefins,^[1] the oxidation of primary alcohols^[2] and the reduction of carboxylic acid derivatives.^[3] However, because of the reactivity of aldehydes, problems with chemoselectivity may be encountered. Although the reduction of esters to aldehydes is possible by using diisobutylaluminium hydride or lithium tritert-butoxyaluminium hydride, these reagents are not used regularly on a large scale because of their sensitivity and capricious reputation.^[4] Alternatively, the use of hydrosilanes as reductants is an area of growing interest for the mild and selective reduction of carboxylic acid derivatives by using transition metal or Lewis acid catalysts.^[5] Indeed, this strategy enables the formation of silyl acetals, which can be converted to aldehydes upon hydrolysis. Although the hydrosilylation reaction has been successful for the selective reduction of esters to alcohols or ethers,^[6,7] examples of hydrosilylation of esters to aldehydes are scarce.^[8] A first example using a ruthenium carbonyl catalyst at high temperature showed a rather narrow substrate scope.^[8a] A second method applied a catalyst based on Pd(OAc)₂ and triphenylphosphine for the exclusive reduc-

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the synthesis of aldehydes by ester hydrosilylation and hydrolysis of the resulting silyl acetals was performed independently by Brookhart et al. and Darcel et al.^[8d-e] The former used a combination of 0.1–0.5 mol% of [{Ir(cyclooctene)₂Cl}₂] catalyst and an excess of diethylsilane to reduce a broad scope of substrates in high yields at temperatures from ambient to 50 °C.^[8d] The latter developed N-heterocyclic carbene iron carbonyl catalysts for the hydrosilylation of aromatic and aliphatic esters at 1 mol% catalyst loading in the presence of a slight excess of diethylsilane or diphenylsilane and under UV irradiation at room temperature.^[8e] Besides these significant achievements, our attention was drawn by the seminal work of Nagashima et al. who, after a study on ruthenium-catalysed selective reduction of esters to alcohols and ethers,^[9a] reported on primary alkylation of electron-enriched aromatic compounds with esters using a ruthenium catalyst and a silane reagent (Scheme 1).^[9b,c] During our studies on hydrosilylation reactions of unsaturated carbon-heteroatom compounds,^[10] we observed a novel and original reactivity by using 1,3,5-trimethoxybenzene (TMB) in combination with other catalysts and silane reagents. Herein, we report on the selective hydrosilylation of esters to aldehydes catalysed by an Ir^{III} metallacycle and TMB at room temperature. **Results and Discussion**

Following our previous investigations on Ir^{III} metallacycles as catalysts for the hydrosilylation of imines,^[10] we started our study by focusing on the hydrosilylation of ethyl ester 3a using triethylsilane without any further hydrolysis (Table 1). Interestingly, a catalyst loading of 1 mol% of iridacycle 1 and 2 mol% of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate

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Scheme 1. Esters in alkylation and hydrosilylation reactions.

(NaBArF₂₄) as additive led selectively to silyl acetal 4a in a 58% yield, but an additional time lapse did not allow the reaction to reach completion (Table 1, entry 1). Surprisingly, under similar reaction conditions, the use of iridacycle 2 in combination with NaBArF₂₄ led to a mixture of three products, among which ethyl and silyl ethers 5a and 6a were the major ones and silyl acetal 4a was the minor one (overall yield: 48%; Table 1, entry 2). The addition of three equivalents of triethylsilane afforded mainly 5a (68%) along with 6a (32%) and 4a (14%) in an overall quantitative yield (Table 1, entry 3). When three equivalents of triethylsilane were used with iridacycle 1, we obtained 4a as the major product (75%) with some ethers 5a (19%) and 6a (6%), and the overall yield was quantitative (Table 1, entry 4). With 2 mol% of tritylBArF₂₀, ethyl ether 5a was formed as the main product in 44-53% overall yield (Table 1, entries 5 and 6). This trend can be explained by the propensity of the trityl cation to interact with the silyl ether group and allow its elimination.

In an attempt to adjust the silane reactivity, several ether additives were tested (see Table S1 in the Supporting Information). The use of one equivalent of TMB led to the quantitative synthesis of silyl acetal 4a (Table 1, entry 7). Whereas 1 or 5 mol% of TMB led to the formation of product 4a with some ethyl ether 5a in lower overall yields (Table 1, entries 8 and 9), a TMB loading of 10 mol% again afforded selectively silyl acetal 4a in quantitative yield (Table 1, entry 10). Under these reaction conditions, iridacycle 1 led to a less efficient catalyst (Table 1, entry 11), and a 0.1 mol % loading of complex 2 resulted in low yields, independently of the reaction time (Table 1, entry 12). The presence of an Ir^{III} metallacycle proved to be critical to allow the hydrosilylation of ester 3a (Table 1, entry 13). Furthermore, the use of 1.2 equivalents of triethylsilane proved to be essential to reach full conversion (Table 1, entries 14, 15). In the presence of TMB, the addition of three equivalents of triethylsilane allowed the formation of 4a with some ethers 5a and 6a in a 60:35:5 ratio (Table 1, entry 15). Replacement of triethylsilane by 1,1,3,3-tetramethyldisiloxane (TMDS) resulted in lower yield and selectivity (Table 1, entry 16). Finally, we noticed that the hydrosilylation reaction was sensitive to the nature of the ester group. Indeed, methyl ester 3b, a weaker electron-donating group, led mainly to methyl ether **5b** along with some silyl acetal 4b (7:3 ratio) in a modest yield (Table 1, entry 17). By comparison, ester 3c bearing an electron-rich iso-

| Table 1. Catalytic study. | | | | | | | | | |
|--|-----|----------------------|----------------|-----------------------------|-----------|-------------------------|--------------------------|--|--|
| $\begin{array}{c} \begin{array}{c} & & & \\ & & $ | | | | | | | | | |
| Entry | 3 | lr complex [mol%] | TMB [mol %] | Yield [%] ^[a] | S 4 a- | electivity -c/5 a–c/ | / ^[а] ба–с | | |
| 1 ^[b] | 3 a | 1 (1) | 0 | 58 | 100 | 0 | 0 | | |
| 2 | 3 a | 2 (1) | 0 | 48 | 17 | 54 | 29 | | |
| 3 ^[c] | 3 a | 2 (1) | 0 | 100 | 14 | 68 | 32 | | |
| 4 ^[c] | 3 a | 1 (1) | 0 | 100 | 75 | 19 | 6 | | |
| 5 ^[d] | 3 a | 1 (1) | 0 | 53 | 0 | 84 | 16 | | |
| 6 ^[d] | 3 a | 2 (1) | 0 | 44 | 0 | 85 | 15 | | |
| 7 | 3 a | 2 (1) | 100 | 100 | 100 | 0 | 0 | | |
| 8 ^[e] | 3 a | 2 (1) | 1 | 63 | 83 | 17 | tr. | | |
| 9 ^[e] | 3 a | 2 (1) | 5 | 71 | 68 | 32 | tr. | | |
| 10 | 3 a | 2 (1) | 10 | 100 | 100 | 0 | 0 | | |
| 11 | 3 a | 1 (1) | 10 | 89 | 100 | 0 | 0 | | |
| 12 ^{tt]} | 3 a | 2 (0.1) | 10 | 17 | 100 | 0 | 0 | | |
| 13 | 3 a | - | 10 | 0 | - | - | - | | |
| 14 ^[g] | 3 a | 2 (1) | 10 | 62 | 100 | 0 | 0 | | |
| 15 ^(c) | 3 a | 2 (1) | 10 | 100 | 60 | 35 | 5 | | |
| 16 ^[n] | 3 a | 2 (1) | 10 | 65 | 18 | 23 | 59 | | |
| 17 ^(e) | 3 b | 2 (1) | 10 | 53 | 30 | 70 | tr. | | |
| 18 | 3 c | 2 (1) | 10 | 100 | 100 | 0 | 0 | | |
| [a] Determined by ¹ H NMR spectroscopy. [b] 68% yield in 24 h. [c] Reaction with 3 equiv triethylsilane. [d] 2 mol% CPh ₃ BArF ₂₀ . [e] tr.=trace. [f] 22% in 2 h. [g] 1 equiv Et ₃ SiH. [h] 1.2 equiv of TMDS. | | | | | | | | | |

propyl substituent afforded selectively silyl acetal **4c** in quantitative yield (Table 1, entry 18).

The scope of the hydrosilylation reaction was studied for a series of aromatic and aliphatic esters under the optimised conditions determined above (Scheme 2). Hydrolysis of the resulting silyl acetals to the corresponding aldehydes could be performed in most cases by simple addition of water to the reaction mixture. Indeed, hydration of the remaining NaBArF₂₄ resulted in a catalysis producing a Brønsted acid, which could cleave chemoselectively the generated silyl acetals.[11] Methyl 2-phenylacetate (3b) led to the corresponding aldehyde in moderate yield, and the hydrosilylation of phenyl acetates 3a and 3c could be performed readily. Reagent 3d with 2-phenylpropanoate skeleton was also reduced selectively without any effect of the steric hindrance of the substrate. Though the hydrosilylation of ester 3e based on a furan heterocycle was straightforward, the reduction of thiophene-based ester 3f proved to be more challenging and led only to the corresponding acetal.^[12] Hydrosilylation of benzyl benzoate (3 m) and related ortho- and para-substituted esters 3g-k, 3n proceeded selectively to the desired aldehydes in high yields independently of the substitution pattern of the reagent. However, ortho substitution by a methoxy group led to unreactive substrate 31, which probably strongly chelates the catalyst. Finally, linear and cyclic aliphatic esters **3o-s** were reduced selectively to the corresponding aldehydes in high yields, with the excep-

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Scheme 2. Reaction scope. [a] Yields measured by ¹H NMR spectroscopy, isolated yields in brackets. [b] Isolated as the 2,4-dinitrophenylhydrazone adduct. [c] 2.2 equiv Et₃SiH was used and the product was hydrolysed with 4 equiv H₂O. [d] Isolated as the resulting acetal; no hydrolysis observed with HCl (2 μ) or NaOH (2 μ) in THF.

tion of ester $\mathbf{3q}$, whose resulting acetal could not be hydrolysed.^[12]

Regarding the reaction mechanism, precatalyst 2 is first dehalogenated by NaBArF₂₄ to give transient cationic complex ${\bf 8}$ (Scheme 3).^[10b] The iridium catalyst activates triethylsilane through the formation of silane-iridium adduct **9**.^[13,14] Such an activation process would produce iridium hydride complex 10^[10a, 15] and a triethylsilyl cation.^[16] The latter may activate the carbonyl group of ester substrate 3 and generate a silyloxy carbonium species, which is stabilised by the electron-donating group R'. Reaction with a first equivalent of the iridium hydride complex 10 affords silyl acetal 4 along with the cationic iridium catalytic species 8. At this stage, the generation of iridium hydride complex 10 and the triethylsilyl cation seems to be faster than the formation of silyl acetal 4 and release of species 8. Indeed, we observed that alkyl ether 5 and silvl ether 6 were the major reaction products with respect to 4 when no TMB was used as co-catalyst (Table 1, entry 2). Hence, TMB would trap the remaining triethylsilyl cation, probably through an aromatic electrophilic substitution generating an Si-C arenium (Wheland-type) intermediate.^[16] Final hydrolysis of silyl acetal 4 is catalysed after hydration of the remaining NaBArF₂₄ additive^[11] and affords the desired aldehyde product, whereas the Si-C Wheland intermediate would probably be involved in the reduction of another molecule of ester 3. Without TMB, silyl acetal 4 reacts further through activation of its ether groups by the triethylsilyl cation. This affords, after reaction with a second equivalent of iridium hydride complex 10, alkyl ether 5 and silyl ether 6 as well as the catalytic cationic iridium species 8. This second pathway was confirmed by some experimental results. First, when a large excess of triethylsilane was used (3 equiv), the synthesis of ethers 5a and 6a was almost quantitative (Table 1, entry 3). In addition, the combined use of iridium precursor, [trityl][B(C₆F₅)₄] additive and triethylsilane led mainly to ethyl ether 5a in 44-53% yield (Table 1, entries 5, 6). This confirmed the propensity of strong electrophiles such as triethylsilyl and trityl cations to eliminate ether groups and form products **5** and **6** (Scheme 3). In such a case, it is likely that average yields could only be obtained when 1.2 equivalents of triethylsilane were used as two equivalents of iridium hydride complex **10** are required for that pathway.

To further confirm the proposed reaction mechanism, the role of TMB in the trapping of the triethylsilyl cation was studied from a broad viewpoint. In the first instance, we did not consider the actual kinetic aspects of the transfer of the silylium cation Et₃Si⁺, and focused on the thermochemistry of its interaction, particularly with the arene additive as well as with the various organic molecules involved in the catalysis. First, the possible interaction of the silvlium-activated ester cation with TMB was found to be highly unfavourable (Figure 1 a and Figure S2 in the Supporting Information). Conventional COSMO (CH₂Cl₂)/DFT-D computation of the Gibbs enthalpy of the reaction depicted in Figure 1a for a model reaction, with or without the BArF₂₄ anion, produced an endoergonic value of around +23 kcalmol⁻¹, which cleared doubts about a possible interaction of intermediate carbocationic species with the arene additive. Figures 1 b-f depict the possible scenarios of addition of the silvlium cation Et₃Si⁺ to the ester PhCH₂C(O)OEt, the acetal PhCH₂C(OSiEt₃)(OEt), TMB, 1,3-dimethoxybenzene and 1,4-dimethoxybenzene. On thermochemical grounds, the addition of the silylium cation at the carbonyl oxygen atom is greatly favoured over other competing interactions with the arene additive, which are disfavoured by about 16 kcal mol⁻¹ for TMB. It is therefore likely that the first step of the catalysis, which entails reduction of the ester to the acetal, does not necessarily involve explicitly the arene additive. The interaction of the latter with Et_3Si^+ tends to be more critical in the second step, in which the acetal undergoes reduction to an ether. In this case, the silvlium cation has an affinity for TMB of -24 kcal mol⁻¹ for a reaction affording a typical Si-C Whe-

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Scheme 3. Proposed reaction mechanism.



Figure 1. DFT-D (ZORA-PBE-D3(BJ)/all-electron TZP) calculated thermochemistry with COSMO solvation (CH₂Cl₂, T=298.15 K; see the main text for detail.

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land intermediate, and O binding of Et_3Si^+ is disfavoured by about 6 kcalmol⁻¹ (Figure 1d and Figure 2). The fact that the affinities of the silylium cation for the acetal and for TMB are almost equal within 1 kcalmol⁻¹ may explain the minimal conversion of the acetal to ethers in the course of the catalysis. In this case, we hypothesise that TMB moderates the electrophi-

licity of Et_3Si^+ by dragging it into an equally probable interaction with the arene, with possible subsequent formation of silylated TMB and release of H⁺, which would be detrimental to the hydrido iridium catalytic species and would end the catalysis. The affinity of Et_3Si^+ for the other two dimethoxybenzene isomers is characterised by preferential binding to the oxygen

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atoms as formation of the corresponding Wheland intermediates is disfavoured by about 7–10 kcal mol⁻¹. The affinity of the two dimethoxybenzene isomers for Et_3Si^+ is overall 3–5 kcal mol⁻¹ lower than that of TMB, and the diversion of Et_3Si^+ by interaction could be disfavoured.



Figure 2. Gas-phase singlet ground-state geometries of: a) the cationic Whe-land-type adduct, and b) the O-silylium adduct resulting from the interaction of Et_3Si^+ with TMB.

Several attempts were made to crystallise the adduct of TMB and the triethysilyl cation. Even though such a compound could not be evidenced, other unrelated arenium species did crystallise (see Scheme S1–S4, Figure S1 and Table S1 in the Supporting Information).

Conclusions

The combination of a cyclometallated iridium(III) complex and TMB catalyses efficiently and selectively the hydrosilylation of esters with triethylsilane to give aldehydes at room temperature in high yields. Hydrolysis of the resulting acetals allows, in most cases, straightforward formation of the aldehyde. The selective ester reduction is most probably favoured by trapping of transient silyl cations leading to an arenium intermediate, which inhibits any further reductive transformation of the acetal. In the presence of TMB, no further reduction of the key silyl acetal intermediate ensues, and formation of the aldehyde product is more often than not straightforward upon hydrolysis. However, in the absence of TMB, further dealkoxylation of the silyl acetal occurs and affords alkyl and silyl ether products. Our results highlight that the reactivity of silanes and related intermediates is modular and depends on the substituents of the silicon atoms. We believe that the reactivity of Lewis acids such as carbocations^[17] may be tuned by using such a methodology.

Experimental Section

General procedure for catalysis

In a glovebox, iridium(III) catalyst **2** (1 mol%), TMB (10 mol%), and NaBArF₂₄ (2 mol%) were introduced into a Schlenk tube. Under nitrogen, distilled ester (0.31 mmol, 1 equiv) and dry dichloromethane (2 mL) were added followed by triethylsilane (0.34 mmol, 1.1 equiv). The reaction mixture was then heated at 25 °C with stirring. To monitor the progress of the reaction, aliquots (0.1 mL) were taken at defined times, filtered through Celite with a CH₂Cl₂ wash (3 mL), evaporated under vacuum and analysed by ¹H NMR spectroscopy. After 0.5 h, water (2 equiv) was added and the reaction mixture was filtered through MgSO₄ and the solvent evaporated under vacuum. The crude product was then purified by flash chromatography or preparative TLC.

Volatile compounds were isolated as 2,4-dinitrophenylhydrazone adducts. After reaction, the crude product was filtered through MgSO₄ and diluted with ethanol (1 mL). The resulting solution was treated with 0.5 mL of Brady's reagent [solution of 2,4-dinitrophenylhydrazine (0.3 g), H₂O (1.5 mL), ethanol (5 mL) and H₂SO₄ conc. (1 mL)] for 30 min with vigorous stirring. The resulting orange precipitate was isolated by filtration through filter paper, washed with ethanol (10 mL) and dried under vacuum.

Computational details

Computations were performed by DFT with the PBE^[18] GGA functional implemented in the Amsterdam Density Functional package (ADF2013^[19]) and augmented with Grimme's DFT-D3(BJ)^[20] implementation of dispersion with a Becke–Johnson (BJ) damping function. Scalar relativistic corrections with the Zeroth Order Regular Approximation^[21] were applied with ad hoc all-electron (AE) basis sets consisting of polarised triple- ζ (TZP) Slater-type orbitals. Geometry optimisation by energy gradient minimisation was carried out in all cases with a numerical grid accuracy between 4.5 and 8, an energy gradient convergence criterion of 10^{-3} a.u. and a very tight SCF convergence criterion. Vibrational modes were computed to verify that the optimised geometries were related to energy minima without considering residual modes between 0 and 90*i* cm⁻¹. Representations of molecular structures and isosurfaces were produced with ADFview 2013.

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| hydrosilylation • iridium • synthetic methods | | | | | | | | | |

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FULL PAPER

Winning combination: A combination of an Ir^{III} metallacycle and 1,3,5-trimethoxybenzene provides efficient catalysis of the hydrosilylation of esters to aldehydes (see figure). By using triethylsilane and a further hydrolysis step, the reactions proceed rapidly with high yields and selectivities under mild conditions. The trapping of transient silyl cations was performed for the first time and studied by DFT calculations.



Homogeneous Catalysis

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Selective Hydrosilylation of Esters to Aldehydes Catalysed by Iridium(III) Metallacycles through Trapping of Transient Silyl Cations