A Versatile Iridium(III) Metallacycle Catalyst for the Effective Hydrosilylation of Carbonyl and Carboxylic Acid Derivatives

Yann Corre, Vincent Rysak, Xavier Trivelli, Francine Agbossou-Niedercorn, Christophe Michon

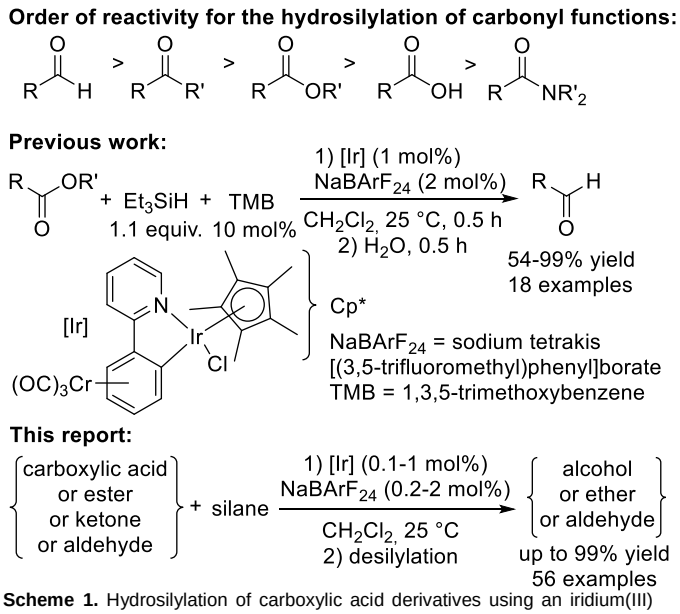
A versatile iridium(III) metallacycle catalyst for the effective hydrosilylation of carbonyl and carboxylic acid derivatives.

Yann Corre,[a,b] Vincent Rysak,[a,b] Xavier Trivelli,[c] Francine Agbossou-Niedercorn*[a,b] and Christophe Michon*[a,b]

Abstract: A versatile iridium(III) metallacycle catalyses rapidly and selectively the reduction of a large array of challenging esters and carboxylic acids as well as various ketones and aldehydes. Reactions proceed with high yields at room temperature through hydrosilylation followed by desilylation. Whether the reaction of various aldehydes and ketones results exclusively in alcohols, the hydrosilylation of esters leads to alcohols or ethers depending on the type of substrate. Regarding the carboxylic acids, the nature of the reagent controls also the outcome of the hydrosilylation reaction, either alcohols or aldehydes being formed.

Introduction

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.[1,2] Indeed, hydrosilylation, which operates without any high pressure equipment and high temperature, can be an interesting alternative to hydrogenation, provided that inexpensive and abundant hydrosilanes are used. Because the reactivity of such reagents and related reaction intermediates is modular and depends on the substituents of the silicon atoms, the hydrosilylation reaction can become a highly chemo- and regioselective reduction method which tolerates various other reducible functional groups.[2] However, whereas several organometallic or organic catalysts were shown to hydrosilylate aldehydes and ketones,[2-5] the hydrosilylation of less reactive substrates like hindered ketones,[6] carboxylic acids[7] and esters[8,9] remains challenging (Scheme 1). Whether several iridium catalysts were effective for the hydrosilylation of carbonyl compounds (e.g. aldehydes and ketones)[3] and carbon-carbon multiple bonds,[10] their applications in the reduction of carboxylic acid derivatives[11] and CO_2[12] remain almost unexplored. Moreover, to the best of our knowledge, only iridium(III) POCOP (i.e. 2,6-bis(di-tert-butylphosphinito)phenyl) catalyst has proved to be versatile for the effective hydrosilylation of a large array of carbonyl and carboxylic acid substrates.[3c,11b] Following our previous studies on hydrosilylation reactions of unsaturated carbon-carbon and carbon–heteroatom compounds using iridium(III) metallacycle catalysts,[13] we have recently reported on the challenging hydrosilylation of amides[13e] and esters.[13d] In the latter case, the combination of a cationic iridium(III) metallacycle and 1,3,5-trimethoxybenzene allows the rapid and selective reduction of esters to aldehydes at room temperature with high yields through hydrosilylation followed by hydrolysis (Scheme 1). 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. Herein, we report the same accessible iridium(III) metallacycle catalyses rapidly and selectively the reduction of a large array of carboxylic acids, esters, ketones and aldehydes with high yields at room temperature through hydrosilylation followed by desilylation (Scheme 1).



Scheme 1. Hydrosilylation of carboxylic acid derivatives using an iridium(III) metallacycle.

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http://uccs.univ-lille1.fr/index.php/annuaire/15-fiches-personnels/81-agbossou-niedercorn-francine
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Supporting information for this article is available on the web.

Results and Discussion

Hydrosilylation of aldehydes

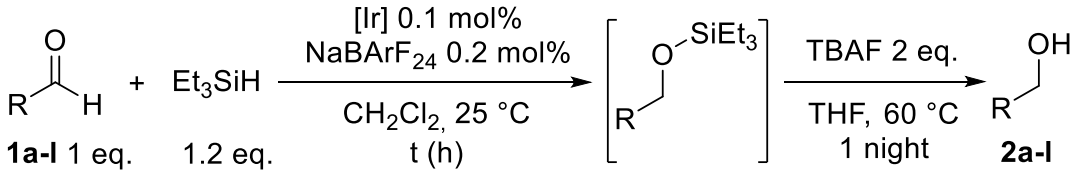
Iridium(III) metallacycle pre-catalyst [Ir], sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBArF_{24}$) additive and reaction conditions (e.g. silane, solvent, temperature) initially used for the reduction of esters into aldehydes (Scheme 1) were applied for the hydrosilylation of a series of aldehydes (Table 1). The corresponding alcohols were recovered in excellent isolated yields from the silylether products through desilylation with tetrabutylammonium fluoride (TBAF). Catalyst and $NaBArF_{24}$ loadings were decreased to respectively 0.1 and

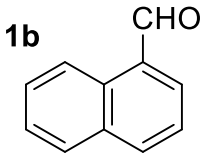
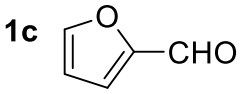
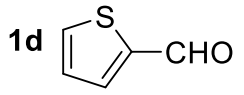
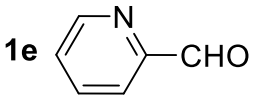
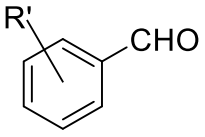
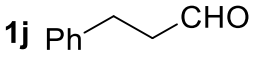
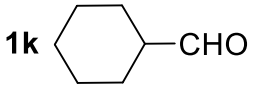
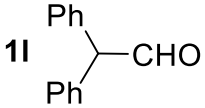
0.2 mol% as the reactions were still performing well without any decrease of activity. The hydrosilylation of aromatic substrates **1a-b** was completed with 5 minutes (entries 1, 2). Whether furan 2-carbaldehyde **1c** reacted readily (entry 3), the hydrosilylation of thiophene 2-carbaldehyde **1d** required 2 hours to go to completion (entry 4). By comparison, the more coordinating pyridine analogue **1e** reacted barely in 24 h (entry 5). Hydrosilylation of ortho- and para- substituted benzaldehydes **1f-i** was straightforward independently of the substitution pattern of the substrate (entries 6-9). Finally, alkyl aldehydes **1j-l** were also readily reduced in 5 to 60 minutes (entries 10-12).

Hydrosilylation of ketones

The same catalytic system was subsequently used for the hydrosilylation of ketones **3a-l** (Table 2). The resulting alcohols **4a-l** were retrieved in average to excellent isolated yields after hydrolysis or desilylation with TBAF. At 2 exceptions, catalyst and additive loadings of 0.5 and 1 mol% allowed all reactions to proceed in few hours. Benzophenone **3a**, acetophenone **3b** and acetonaphtone **3c** were readily reduced in 2 hours (entries 1-3). However, the hydrosilylation of 2-acetylpyridine **3d** proved to be harder most likely because of a possible catalyst inhibition through substrate chelation (entry 4). Reactions of other aromatic and alkyl ketones **3e-h** proceeded also well in 2 to 4 hours (entries 5-8). Moreover, the hydrosilylation of more challenging substrates like sterically hindered ketones[6] was not a limitation. Indeed, the reductions of pivalophenone **3i**, 2-acetylmesitylene **3j** and dicyclohexylmethanone **3k** were straightforward and proceeded in few hours (entries 9-11). However, the hydrosilylation of diisopropylmethanone **3l** proved to be harder requiring a reaction temperature of 40°C and a longer reaction time to go to completion (entry 12).

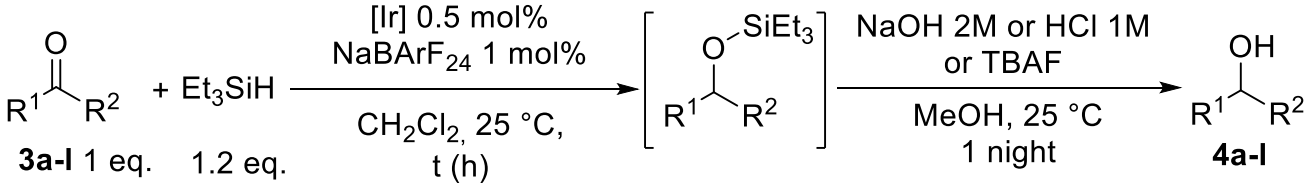
Table 1. Hydrosilylation of aldehydes **1a-l**.

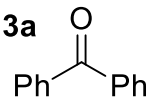
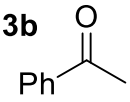
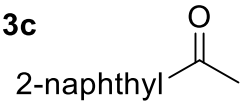
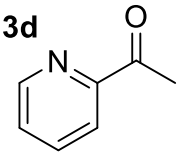
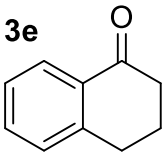
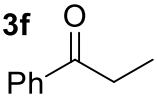
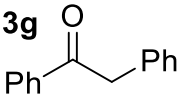
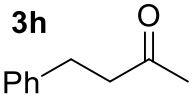
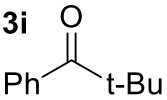
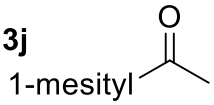
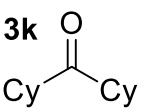
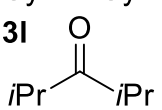


Entry	Aldehyde	Time (min)	Yield [%][a] (isolated yield [%])[b]
1	**1a** Ph−CHO	5	**2a** 100 (99)
2	**1b** 	5	**2b** 99 (85)
3	**1c** 	15	**2c** 100 (71)
4	**1d** 	120	**2d** 100 (50)
5	**1e** 	24 h[c]	**2e** 15 (-)
6	 **1f** R' = *p*-Cl	5	**2f** 100 (83)
7	**1g** R' = *o*-Cl	5	**2g** 100 (98)
8	**1h** R' = *p*-OMe	5	**2h** 100 (92)
9	**1i** R' = *o*-OMe	5	**2i** 100 (99)
10	**1j** 	15	**2j** 99 (83)
11	**1k** 	60	**2k** 100 (75)
12	**1l** 	5	**2l** 100 (94)

[a] Yield in silyl ether determined by ^{1}H NMR. [b] Isolated yield in alcohols **2a-l** after desilylation with TBAF and purification. [c] Temperature = 40 °C.

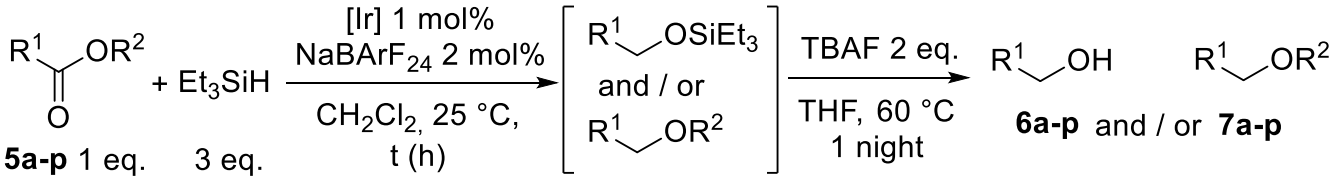
Table 2. Hydrosilylation of ketones **3a-l** into alcohols **4a-l**.



Entry	Ketone	Time (h)	Yield [%][a] (isolated yield [%][b])
1	**3a** 	2	**4a** 100 (54)
2	**3b** 	2	**4b** 100 (55)
3	**3c** 	2	**4c** 100 (86)
4[c]	**3d** 	10	**4d** 33 (-)
5	**3e** 	3	**4e** 100 (99)
6	**3f** 	2	**4f** 100 (78)
7	**3g** 	2	**4g** 100 (89)
8	**3h** 	4	**4h** 89 (53)
9	**3i** 	2	**4i** 97 (87)
10	**3j** 	2	**4j** 77 (51)
11	**3k** 	3	**4k** 100 (64)
12	**3l** 	15	**4l** 100 (-)[d]

[a] Yield in silylether determined by ^{1}H NMR. [b] Isolated yield in alcohols **4a-l**, after hydrolysis or desilylation with TBAF and purification.
[c] Catalyst loading = 1 mol% and temperature = 40 °C. [d] at 40°C because no reaction in 3 hours at 25°C.

Table 3. Hydrosilylation of esters **5a-p** into alcohols **6a-p** and ethers **7a-p**.



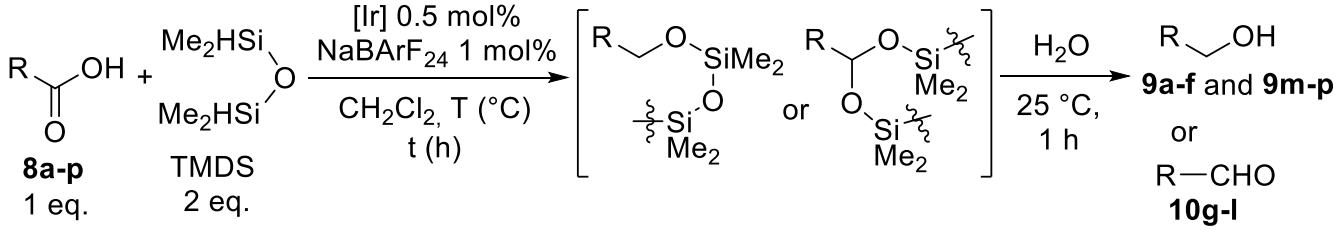
Entry	Ester	Time (h)	Yield [%][a]	Selectivity [%][a] (isolated yield [%])[b]	
1	**5a** R^2 = Me	1	100	**6a** 100 (78)	**7a** 0 (-)
2		1	100	**6b** 92	**7b** 8
3	Ph—CO_2R^2 **5b** R^2 = Et	1	100	**6b** 73[c]	**7b** 19[c]
4	**5c** R^2 = Bn	1	100	**6c** 100	**7c** 0
5		3	100	**6d** 100 (69)	**7d** 0 (-)
6	**5d** R^3 = *o*-Me	1	100	**6d** 85 (-)	**7d** 15 (-)
7	**5e** R^3 = *p*-Me	1	100	**6e** 89 (68)	**7e** 11 (-)
8	**5f** R^3 = *p*-OEt	24	92	**6f** 100 (68)	**7f** 0 (-)
9	**5g** R^3 = *o*-Cl	3	100	**6g** 79 (54) [d]	**7g** 21 (-)[d]
10	**5h** R^3 = *p*-Cl	1	100	**6h** 99 (94)	**7h** 1 (-)
11	**5i**	15	57[e]	**6i** 100 (38)	**7i** 0 (-)
12	**5j**	1	100	**6j** 100 (81)	**7j** 0 (-)
13	**5k**	1	100	**6k** 93 (82)	**7k** 7 (-)
14	**5l**	1	100	**6l** 82 (79)	**7l** 18 (14)
15	**5m**	8	100	**6m** 25(18)	**7m** 75 (53)
16	**5n**	1	100	**6n** 12 (6)	**7n** 88 (46)
17	**5o**	1	100	**6o** 4 (-)	**7o** 96 (92)
18	**5p**	1	100	**6p** 60 (33)	**7p** 40 (22)

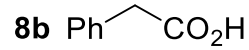
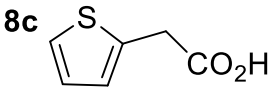
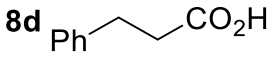
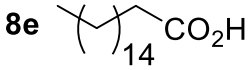
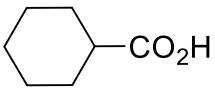
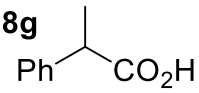
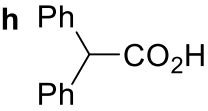
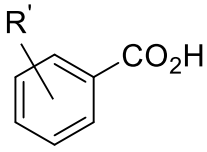
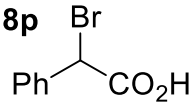
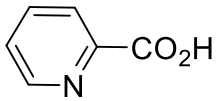
[a] Yield determined by ^{1}H NMR. [b] Isolated yields in alcohols **6a-p** or ethers **7a-p** after desilylation with TBAF and purification. [c] for 2 eq. Et_3SiH with benzaldehyde (8%) as a side product. [d] Same ratio alcohol / ether at t = 6 hours. [e] Temperature = 60 °C and solvent = TCE.

Hydrosilylation of esters

Next, the same catalytic system was applied for the hydrosilylation of esters (Table 3). Though these reductions were known to be more difficult,[8,9] most of the reactions proceeded well with iridium(III) metallacycle pre-catalyst [Ir] and $NaBArF_{24}$ additive loadings respectively of 1 and 2 mol%. Alcohols **6a-p** and/or alkyl ethers **7a-p** were obtained with variable selectivities and moderate to high isolated yields depending on the molecular structure of the substrate. Similarly to aldehydes and some ketones, the alcohol products were obtained through desilylation of the related silylethers with tetrabutylammonium fluoride (TBAF). We noticed the use of 3 equivalents of triethylsilane (entries 2, 3) or of a longer reaction time (entries 5, 6) could enhance the reaction selectivity for alcohols by reducing significantly the amount of formed alkyl ethers. Brookhart et al. previously reported iridium(III) POCOP catalyst could cleave alkyl ethers into silylated alcohols and alkanes using triethylsilane.[14]

Table 4. Hydrosilylation of carboxylic acids **8a-p** into alcohols **9a-f,m-p** or aldehydes **10g-l**.



Entry	Carboxylic acid	t (h)	T (°C)	Yield [%][a] (isolated yield [%])[b]
1	**8a** Ph−CO_2H	15	40	**9a** 100 (67)
2	**8b** 	5	25	**9b** 100 (90)
3	**8c** 	15	40	**9c** 100 (68)
4	**8d** 	5	25	**9d** 100 (83)
5[c]		5	25	**9d** 16 (-)
6	**8e** 	15	25	**9e** 100 (84)
7	**8f** 	15	25	**9f** 100 (77)
8	**8g** 	5	25	**10g** 100 (83)
9	**8h** 	15	40	**10h** 100 (88)
10	 **8i** R' = *o*-F	15	40	**10i** 100 (83)
11	**8j** R' = *p*-F	15	40	**10j** 100 (79)
12	**8k** R' = *o*-Cl	15	40	**10k** 100 (79)
13	**8l** R' = *p*-Br	15	40	**10l** 100 (81)
14	**8m** R' = *p*-NO_2	15	40	**9m** 36 (26)
15	**8n** R' = *p*-OMe	15	40	**9n** 100 (93)
16	**8o** R' = *o*-OMe	40	40	**9o** 100 (74)
17	**8p** 	15	40	**9p** 100 (60)
18	**8q** 	24	40	0[d]

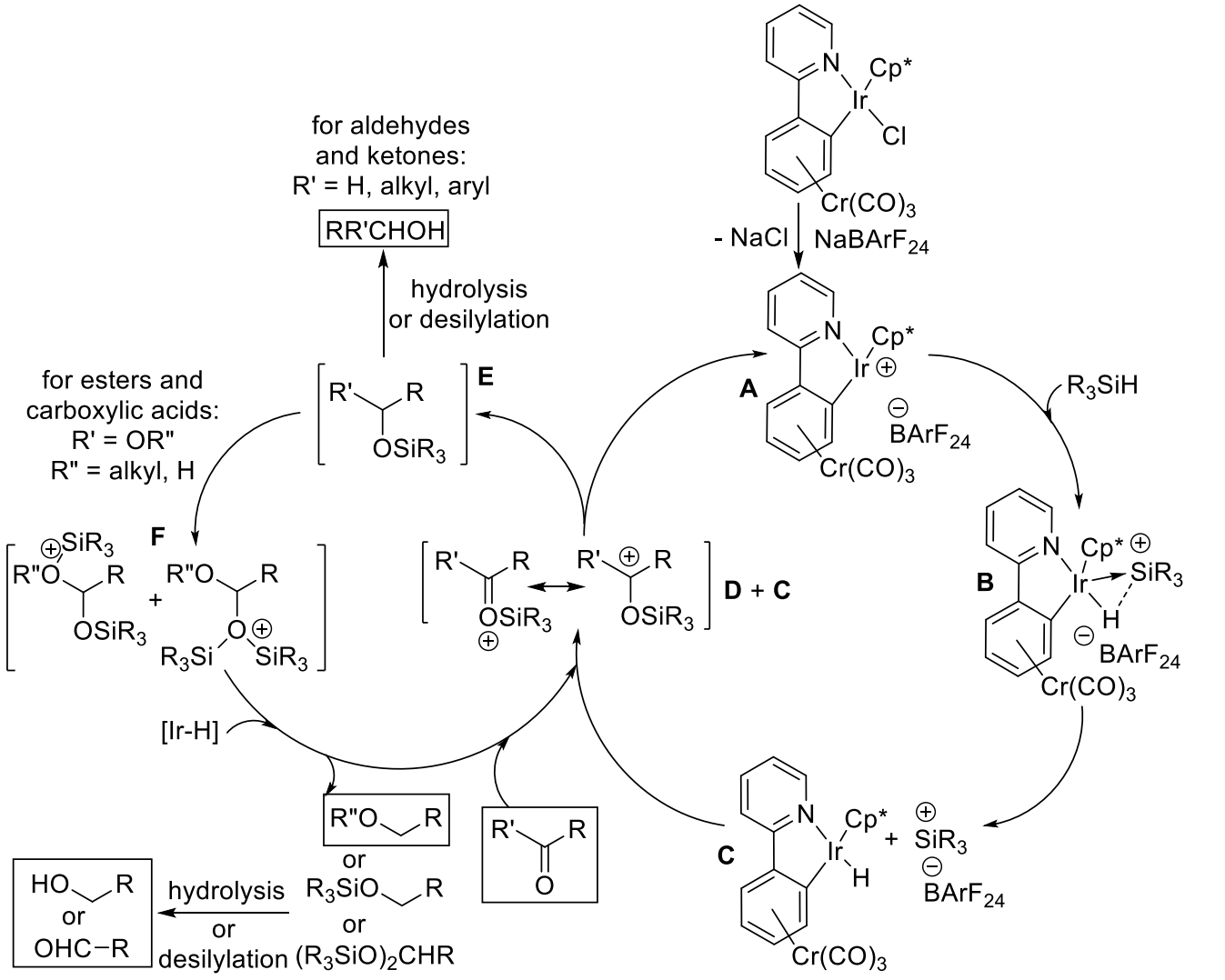
[a] Yield measured by ^{1}H NMR. [b] Isolated yields in alcohols **9a-f** and **9m-p** or aldehydes **10g-l** after hydrolysis and purification. [c] with 4 eq. Et_3SiH. [d] Same result in 24 hours at 80°C in TCE.

According the present results, iridium(III) metallacycles catalysed a similar ether cleavage depending on the substrate basicity. Although aromatic ethers **7b** and **7d** were converted to alcohols **6b** and **6d** (entries 2,3,5,6), alkyl ethers **7m** and **7o** remained unreacted (entries 15,17). The reaction of benzoate derivatives **5a-c** led to benzyl alcohol independently of the nature of the R^2 substituent (entries 1-4). Hydrosilylation of ortho- and para- substituted benzoates **5d-e** and **5g-h** was straightforward to the related alcohols as the main products without any effect of the substitution pattern of the reagent (entries 5-7,9-10). However, the para- substitution by an ethoxy group led to a less reactive substrate **5f** which was fully reduced in 24 hours (entry 8).

Similarly, the hydrosilylation of thiophene derivative **5i** proved to be difficult, a reaction of 15 hours being required to obtain the related alcohol in an average yield (entry 11). Interestingly, the reaction of lactone **5j** led effectively to the related 1,2-phenylenedimethanol (entry 12). Whether the hydrosilylation of cyclohexyl and benzyl ethyl esters **5k-l** afforded alcohols as the major products (entries 13-14), the reaction of other alkyl substrates **5m-o** resulted predominantly in the related ethyl ethers (entries 15-17), probably due to their longer alkyl chains and their less sterically hindered structures. Finally, the hydrosilylation of methyllinoleate **5p** was far less selective resulting in the corresponding alcohol along with significant amount of the methyl ether product (entry 18).

Hydrosilylation of carboxylic acids

Since the catalytic system was found to be effective in the hydrosilylation of esters, we subsequently studied the more challenging reduction of carboxylic acids (Table 4).[7] Whether iridium(III) metallacycle pre-catalyst and $NaBArF_{24}$ additive loadings were reduced to respectively 0.5 and 1 mol%, the change of triethysilane for 1,1,3,3-tetramethyldisiloxane (TMDS) proved to be critical to allow the hydrosilylation to proceed (entries 4,5). We noticed also an increase of the reaction temperature to 40°C was often required to recover products in high yields. Hydrolysis of the resulting silyl ethers or acetals to the corresponding alcohols or aldehydes could be performed by simple addition of water to the reaction mixture. Indeed, hydration of the remaining 0.5 mol% of $NaBArF_{24}$ resulted in a catalysis producing a Brønsted acid, which could cleave chemoselectively the generated silyl acetals.[13d,15] On the whole, we obtained selectively alcohols **9a-f,m-p** or aldehydes **10g-l** in good to high isolated yields depending on the molecular structure of the substrate. The hydrosilylation of benzoic acid **8a** and 2-thiophene acetic acid **8c** required 15 hours of reaction at 40°C to afford the related alcohols (entries 1, 3). By comparison, the reaction of phenylacetic acid **8b** and 3-phenylpropionic acid **8d** were faster, alcohols **9b** and **9d** being obtained in only 5 hours at 25°C (entries 2, 4). However, alkyl substrates **8e** and **8f** needed 15 hours to lead to the corresponding alcohols (entries 6, 7). To our surprise, the hydrosilylation of 2-phenylpropanoic acid **8g** and diphenylacetic acid **8h** afforded aldehydes **10g-h** (entries 8, 9). Whether a similar trend was observed for halogenated benzoic acids **8i-l** (entries 10-13),



Scheme 2. Reaction mechanism proposal.

the reaction of other electron poor substrates like para-nitrobenzoic acid **8m** and 2-bromo-2-phenylacetic acid **8p** led to alcohols **9m** and **9p** (entries 14, 17). If the hydrosilylation of para-methoxybenzoic acid **8n** was rather straightforward to the alcohol **9n** (entry 15), ortho-methoxybenzoic acid **8o** was far less reactive probably due to its chelation to the catalyst (entry 16). Such inhibition effect was confirmed by the unreactivity of pyridine-2-carboxylic acid **8q**, a stronger chelate which prevented any reaction to occur (entry 18).

Reaction mechanism

Regarding the reaction mechanism, an ionic hydrosilylation[14,16] pathway could be presumed. Djukic et al. have already shown through a combination of organometallic syntheses and DFT calculations a cohesive hydridoiridium(III)→silylium donor−acceptor complex could exist.[17] Hence, we assumed our reaction pathway could differentiate from the others involving iridium catalysts[2,16] by the activation mode of the silane. At first, precatalyst is dehalogenated by $NaBArF_{24}$ to give a transient cationic complex **A** (Scheme 2) which was observed by ESI-MS during the analysis of a reaction crude mixture (Figure S1 in the Supporting Information).[13a,e] The iridium catalyst activates the silane reagent through the formation of a silane–iridium adduct **B**.[16,17] Such an activation process would produce an iridium hydride complex **C**[18] and a silyl cation.[19] The latter may activate the carbonyl group of the substrate and generate a silyloxy carbonium species **D**, which can be stabilised by an electron-donating group R'. Reaction with a first equivalent of the iridium hydride complex **C** affords silyl intermediate **E** along with the cationic iridium catalytic species **A**. At that stage, several pathways are possible depending on the nature of the substrate. In the case of aldehydes and ketones, a further hydrolysis or desilylation of silyl ether **E** offers the alcohol product. Concerning the hydrosilylation of carboxylic acids **8a-p** or esters **5a-p**, the silyl intermediate **E** can react further through activation of its ether or hydroxy groups by silyl cation and formation of intermediates **F**. After reaction with a second equivalent of iridium hydride complex **C**, alkylether, silylether or acetal products are either formed along with the release of the catalytic cationic iridium species **A** and a final hydrolysis or desilylation step affords the organic product as an alcohol, ether or aldehyde.

Concerning the hydrosilylation of esters **5a-p**, alcohols **6a-p** and/or ethers **7a-p** are obtained depending on the nature of the substrates and their steric hindrance. Although aromatic and sterically hindered esters are mainly reduced to alcohols, linear alkyl esters are converted to ethers. Moreover, iridium(III) metallacycle catalyst can cleave alkyl ether[14] into silylated alcohols and alkanes depending on the substrate basicity. Although aromatic ethers **7b** and **7d** were converted to alcohol **6b** and **6d**, alkyl ethers **7m** and **7o** remained unreacted.

Regarding the hydrosilylation of carboxylic acids, alcohols **9a-f,m-p** or aldehydes **10g-l** are obtained selectively after a subsequent hydrolysis, without any defined influence of the substrates, that is to say with no clear effect of the steric and electronic parameters of the carboxylic acids (Table 4). As opposed to the use of Lewis acid catalysts like tris(pentafluorophenyl)borane[7d] or Gallium trichloride,[7g] the emission of hydrogen gas was not observed along our iridium catalysed reactions. The use of 2 equivalents of 1,1,3,3-tetramethyldisiloxane (TMDS) does not always allow the formation of a single acetal. If the reaction selectivity depends on the molecular structure of the starting substrate, a rationalisation based on electronic or steric effects was not possible (Scheme 2, Schemes S1-S3, Figures S2-S5 in the Supporting Information). At this stage, further investigations on the reaction mechanism proved to be difficult.

Conclusions

To summarise, we have shown a versatile iridium(III) metallacycle catalyses effectively the reduction of various carbonyl and carboxylic acid derivatives with high yields at room temperature through hydrosilylation followed by desilylation or hydrolysis. The reaction of aldehydes and ketones, including sterically hindered substrates, results exclusively in alcohols. The hydrosilylation of more challenging compounds like carboxylic acid derivatives proceeds also well. Esters lead rapidly to either alcohols or ethers depending on the substrate basicity. Similarly, the nature of the carboxylic acid reagents controls also the outcome of the hydrosilylation reaction, either alcohols or aldehydes being formed. According our present and past works, the reactivity of iridium(III) metallacycles is promising in catalytic hydrosilylations of organic compounds.

Experimental Section

General Procedure for the catalysis

In a Schlenk tube, the reagent (0.15 mmol, 1 eq.) and iridium (III) catalyst (0.1-1 mol%) are introduced. $NaBArF_{24}$ salt (0.2-2 mol%) is then added in a glovebox. Under nitrogen, dichloromethane (2 mL, dry) and the silane reagent (0.18 mmol, 1.2-3.0 eq.) are subsequently added by syringe and the reaction mixture is stirred at 25°C for a defined time (the Schlenk tube being closed under N_2). In order to follow the advancement of the reaction, aliquots (0.1 mL) were taken at defined times. They were filtered over Celite and washed with dichloromethane (3 mL) before being analysed by GC. Alternatively, ^{1}H NMR analyses could be performed on the samples after their evaporation under vacuum. At the end of the hydrosilylation reaction, the crude reaction mixture is hydrolysed or desilylated following method A, B, C or D. Afterwards, the resulting solution is extracted with diethylether and washed with brine. Organic phases are then dried over $MgSO_4$ and evaporated under vacuum. The resulting solid or oily residue is then purified by flash chromatography or preparative TLC.

Method A (for ketones 3f, 3k): After filtration of the crude mixture over a pad of silica subsequently washed with dichloromethane, solvents are evaporated under vacuum. The resulting crude mixture is then dissolved in methanol and an aqueous solution of hydrochloric acid (1M, 1.5 mL) is added. The resulting solution is vigorously stirred during 12 hours at room temperature. In some cases, a reaction time of 24 to 48 hours is necessary to recover products in high yields.

Method B (for ketones 3a, 3e, 3h, 3i, 3j): After filtration of the crude mixture over a pad of silica subsequently washed with dichloromethane, solvents are evaporated under vacuum. The resulting crude mixture is then dissolved in methanol and an aqueous solution of sodium hydroxide (3M, 1.3 mL) is added. The resulting solution is vigorously stirred during 12 hours at room temperature. In some

cases, a reaction time of 24 to 48 hours is necessary to recover products in high yields.

Method C (for aldehydes and esters, for ketone 3b, 3c, 3g): After filtration of the crude mixture over a pad of silica subsequently washed with dichloromethane, solvents are evaporated under vacuum. The resulting crude mixture is then dissolved in distilled THF (5 mL) under nitrogen and one equivalent of tetrabutylammonium fluoride (TBAF, THF, 1M) is added at room temperature. The resulting solution is vigorously stirred during 12 hours at room temperature. In some cases, a reaction time of 24 to 48 hours is necessary to recover products in high yields.

Method D (for carboxylic acids): After full-conversion, 100 µL of water (1440 eq.) are added to the crude reaction mixture in dichloromethane and the resulting solution is vigorously stirred during 1 hour at room temperature. In some cases, a reaction time of 4 hours is necessary to recover products in high yields.

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