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Efficient hydrosilylation of imines using catalysts based on iridium(III) metallacycles.

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Ir(III) metallacycles were applied as catalysts for the hydrosilylation of various ketimines and aldimines in combination with sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate, $NaBArF_{24}$, as additive. By using a slight excess of organosilane reagent, reactions proceeded rapidly and efficiently, at low catalyst loadings and at room temperature. Several examples of cationic Ir(III) catalysts could be synthesised, characterized and tested. In-situ generated catalysts proved to be more active as compared to isolated ones and non-coordinative $BArF_{24}$ anion was the most adapted in order to reach high catalytic activities.

Introduction

Amines are ubiquitous in natural products, building blocks or targets for fine chemicals, farming related chemicals and biologically active compounds.[1] Among the several synthetic methods for amine, the transition-metal catalysed reduction of imines is a valuable pathway which can be performed by hydrogenation,[2] hydrogen transfer[3] or hydrosilylation.[4] The latter, which operates in mild reaction conditions without any autoclave pressure, is an interesting alternative to hydrogenation provided inexpensive and abundant hydrosilanes are used. The stereoselective synthesis and reactivity of metallacycles like iridacycle **1** and chromiumtricarbonyl-bound iridacycle **2** have been studied by some of us for several years (Scheme 1).[5] Recently, complexes of type **2** were found to display novel catalytic virtues for the conversion of terminal aromatic alkynes into racemic *N*-phenyl, 1-arylethylamines by tandem hydroamination and hydrosilylation/protodesilation reactions under mild ‘‘one pot’’ conditions.[5a] The peculiar efficiency of such catalyst in promoting hydrosilylation was assigned to the intervention of Ir–hydrido intermediate **3**,[5a,e] a key species for the transfer of the hydritic H atom to the electrophilic imine substrate. In addition, other reports stated on the efficiency of such iridacycles for hydrogenation reactions.[2h-i,3e-h]

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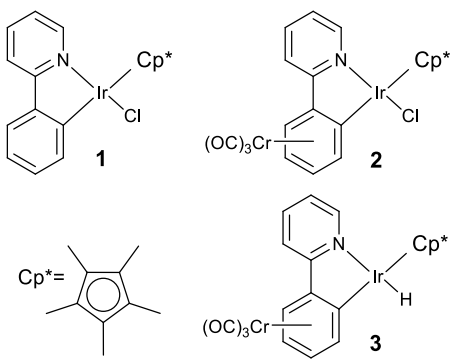
Electronic Supplementary Information (ESI) available: [experimental procedures, analytical data, NMR spectra, HRMS spectra]. See the web (free of charge).

Hence, considering the interest of some of us on the synthesis and reactivity of iridacycles,[5] and the complementary research of others on the synthesis of amines using hydroamination reaction,[6] we investigated Ir(III) metallacycles as catalysts for the hydrosilylation of imines.

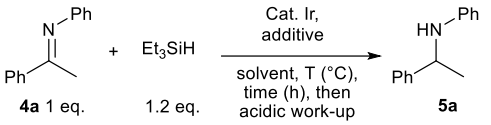


Scheme 1. Studied iridacycles.

Results and discussion

Screening of catalysts, additives and reaction conditions was performed on the hydrosilylation of *N*-phenylethylideneaniline **4a** and we rapidly noticed the use of an additive was critical to displace the iridium chloride ligand and afford an active cationic catalyst (Table 1). Iridacycle **1** proved to be the most active catalyst as compared to chromiumtricarbonyl bound iridacycle **2** (entries 1-4). Dichloromethane and 1,1’,2,2’-tetrachloroethane led to good yields and were the most interesting solvents considering their polarity or high boiling point (entries 3-6). The use of toluene and tetrahydrofuran implied lower yields (entries 7-9). By changing the couteranion of the Ir(III) catalyst, we confirmed the less coordinating the anion was, the higher were the yields (entries 10-15). The activity increased according to the following order:

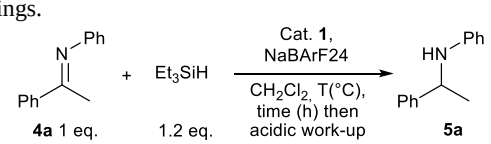
Table 1. Screening of catalysts, additives, solvents, times and temperatures.



Entry	Cat. (mol%)	Additive (mol%)	Solvent	Time (h)	T (°C)	Yield (%)[a]
1	**1** (2.5)	-	CH_2Cl_2	40	40	17
2	**2** (2.5)	-	CH_2Cl_2	40	40	11
3	**1** (2.5)	NH_4BF_4 (10)	CH_2Cl_2	40	40	67
4	**2** (2.5)	NH_4BF_4 (10)	CH_2Cl_2	40	40	34
5	**1** (2.5)	NH_4BF_4 (10)	TCE[b]	40	40	71
6	**1** (2.5)	NH_4BF_4 (10)	TCE	20	100	83
7	**1** (2.5)	NH_4BF_4 (10)	THF[c]	40	40	12
8	**1** (2.5)	NH_4BF_4 (10)	toluene	40	40	11
9	**1** (2.5)	NH_4BF_4 (10)	toluene	20	100	38
10	**1** (2.5)	NH_4PF_6 (10)	CH_2Cl_2	20	25	52
11	**1** (1)	$NaBF_4$ (2)	CH_2Cl_2	20	25	<5[d]
12	**1** (1)	$NaPF_6$ (2)	CH_2Cl_2	20	25	37
13	**1** (1)	$NaSbF_6$ (2)	CH_2Cl_2	20	25	62
14	**1** (1)	$NaBArF_{24}$ (2)[e]	CH_2Cl_2	0.25	25	100
15	**2** (1)	$NaBArF_{24}$ (2)	CH_2Cl_2	0.25	25	69

[a] Measured by ^{1}H NMR after work-up. [b] TCE: 1,1',2,2'-tetrachloroethane. [c] THF: tetrahydrofuran. [d] 8 % yield in 40 h. [e] $NaBArF_{24}$: sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate.

Table 2. Effects of catalyst and additive loadings.



Entry	Cat. **1** (mol%)	$NaBArF_{24}$ (mol%)	[**4a**] (mmol.l^{-1})	Time (h)	Temperature (°C)	Yield (%)[a]	TON[b]
1	1	2	0.077	0.5	25	100	100
2	1	2	0.039	0.5	25	100	100
3	0.5	1	0.039	0.5	25	84	168
4	0.5	1	0.039	2	25	100	200
5	0.1	0.2	0.39	0.5	25	30	300
6	0.1	0.2	0.39	2	25	78	780
7	0.1	0.2	0.39	24	25	100	1000
8	0.1	0.2	0.77	0.5	25	18	180
9	0.1	0.2	0.77	2	25	58	580
10	0.1	0.2	0.77	24	25	100	1000
11	0.05	0.1	0.77	0.5	25	37	740
12	0.05	0.1	0.77	2	25	56	1120
13	0.05	0.1	0.77	24	25	88	1760
14	0.01	0.02	0.77	24	25	39	3915
15	0.01	0.02	0.77	24	40	68	6826
16	0.01	0.02	0.77	24	60	90	9000

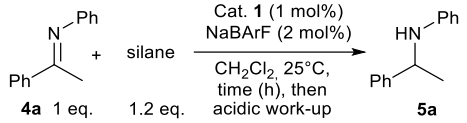
[a] Measured by ^{1}H NMR after work-up. [b] TON, turnover number (mol product / mol catalyst).

BF_4^- < PF_6^- < SbF_6^- << $BArF_{24}^-$. Hence, sodium salts with specific anions were efficient to displace chlorides and afford an active catalyst (entries 11-15). Indeed, the use of tetrakis[(3,5-trifluoromethyl)phenyl]borate, e.g $BArF_{24}$ anion, proved to be critical in drastically reducing reaction times from 20 to 0.25 hour, that is to say a hundred fold decrease. Interested by such an effect, we studied in detail the activity of our catalytic system in order to find the best loadings in catalyst **1** and $NaBArF_{24}$ additive (Table 2). When the catalyst loading was reduced from 1 to 0.5 mol%, 2 hours were needed to complete the hydrosilylation of imine **4a** at room temperature but catalyst activity, i.e. turnover number (TON), increased (entries 1-4). By operating at 0.1 mol% of **1**, the yield in **5a** was still high within 2 hours and a 24 hour reaction time allowed quantitative yields and TONs of 1000 (entries 5-10). When we decreased further the catalyst loading, we noticed a higher concentration of the reaction medium could decrease the yield of 10 to 20% as well as the catalyst activity (entries 1, 2, 5, 6, 8, 9). At 0.05 mol% loading, catalyst **1** remained quite active at room temperature affording 88% yield of **5a** and 1760 TON within 24 hours (entries 11-13). Finally, using a 0.01 mol% catalyst loading resulted in an important decrease of **5a** yield at room temperature (entry 14). However, by increasing the reaction temperature to 40°C or even 60°C, high yields and up to 9000 TON could be achieved (entries 15, 16). To the best of our knowledge, species **1** is among the most active Ir(III) catalysts for hydrosilylation reactions.[7] Morever, by using 1.2 equivalents of reducing agent, iridacycle **1** appeared to be sustainable as compared to catalysts requiring 3 equivalents of silane.

Various silane reagents could be used for the hydrosilylation of **4a** (Table 3). Whereas triethoxysilane reagent afforded **5a** in a poor yield, triethylsilane proved to be an efficient hydrosilylation agent for a moderate cost (entries 1-2). The use of expensive phenyl-, diphenyl- and triphenylsilane led also to good yields (entries 3-5). Sterically hindered 1,1,1,3,5,5,5-heptamethyltrisiloxane afforded **5a** in a poor yield and so did the electron-poor trichlorosilane (entries 6-7). Finally, among the inexpensive and green hydrosilylation reagents, polymethylhydroxysiloxane (PMHS) led to poor results but we were glad to reach a quantitative yield using tetramethyldisiloxane reagent (entries 8-9).

We next studied the hydrosilylation of a series of ketimines. Iridacycle catalyst **1** was used with selected reaction conditions in order to perform fast and straightforward reductions (Table 4). The hydrosilylation of *N*-phenylethylideneaniline **4a** and related para- substituted ketimines **4b-c** could be performed readily and afforded the corresponding amines in high isolated yields (entries 1-3). We noticed the substrate reactivity could be influenced by ortho- substituents as hydrosilylation of brominated reagent **4d** required much more time to be completed (entrie 4). However, ortho-alkylated substrate **4e** reacted as well as ketimines **4a-c** (entrie 5). Interestingly, halogenated substrates **4c-d** were reduced without any dehalogenation. Whereas the hydrosilylation of triarylimine **4g** was easily performed (entry 7), the reduction of *N*-phenylpropylideneaniline **4f** required 2 hours to be completed (entry 6). Aliphatic imines which are challenging substrates[2-4] could be also reduced efficiently. Cyclic reagent **4h** reacted easily (entry 8) and dialkylimines **4i-j** required only one hour of reaction to be reduced (entries 9, 10). As already noticed with other catalysts,[8] hydrosilylation of *N*-cyclohexyl imines like **4k** proved to be difficult, most likely because of reagent steric hindrance (entry 11). Indeed, the switch to *N*-butylimine **4l** led in our case to a much more efficient reduction (entry 12).

Table 3. Screening of silane reagent.

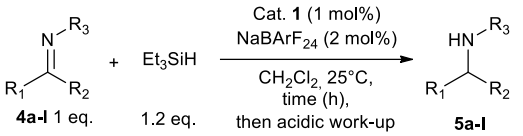


Entry	silane	Cost[a] (€/mmol)	Time (h)	Yield[b] (%)
1	Et_3SiH	0.41	0.25	100
2	$(EtO)_3SiH$	0.79	0.25	8
			17	16
3	Ph_3SiH	1.08	0.25	64
4	Ph_2SiH_2	1.55	0.25	100
5	$PhSiH_3$	1.64	0.25	100
6	$(Me_3SiO)_2SiHMe$	0.38	0.25	6
			17	7
7	Cl_3SiH	0.42	0.25	8
			17	16
8	$[(CH_3)_2SiH]_2O$[c]	0.11	0.25	100
9	PMHS[d]	0.01	0.25	5
			17	13

[a] according[4] and www.sigmaaldrich.com. [b] Measured by ^1H NMR after work-up. [c] 1,1,3,3-tetramethyldisiloxane. [d] PMHS: Polymethylhydroxysiloxane.

The reaction scope was further studied with the hydrosilylation of a series of aldimines. Iridacycle catalyst **1** and selected conditions were applied for fast and straightforward reactions (Table 5). The hydrosilylation of *N*-benzylidene aniline **6a** and related ortho- and para- substituted aldimines **6b-g** could be performed readily and afforded the corresponding amines in high isolated yields independently of the reagent substitution (entries 1-7). Indeed, halogenated substrates **6b,d,f** were reduced without any dehalogenation. Regarding the hydrosilylation of *N*-alkylaldimines **6h** and **6i**, reactions were slower but good yields were obtained after 1 to 2 hours of reaction (entries 8-9). Other aryl-, heteroaryl- and alkylaldimines **6j-l** could be reduced in high yields (entries 10-12). Finally, the hydrosilylation of conjugated aldimine **6m** led to **7m$_1$** as the major product through a 1,2-reduction of the imine function. The doubly reduced product **7m$_2$** was isolated as a minor product arising from the additional reduction of the C=C bond (entry 13).

Table 4. Hydrosilylation of ketimines catalysed by cycloiridated complex **1**.



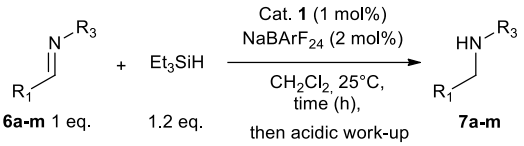
Entry	Reagent	Time (h)	Yield[a] (isolated yield %)[b]
1		0.25	**5a** 100 (87)
2	**4a** R= H	0.25	**5b** 100 (100)
3	**4b** R= *p*-OMe	0.25	**5c** 97 (95)
4	**4c** R= *p*-F	7	**5d** 100 (100)
5	**4d** R= *o*-Br **4e** R= *o*-Et	0.25	**5e** 100 (100)
6	**4f**	2	**5f** 90 (64)
7	**4g**	0.25	**5g** 100 (98) **4/5f**
8	**4h**	0.25	**5h** 100 (37)[c]
9	**4i**	1	**5i** 100 (85)
10	**4j**	1	**5j** 70 (68)
11	**4k**	24	**5k** 34 (-)
12	**4l**	2	**5l** 100 (88)

[a] Measured by ^{1}H NMR after workup. [b] Isolated yield after flash chromatography.
[c] Decomposition of product.

It was worth noting the use of an excess of triethylsilane allowed most of product **7m1** to be reduced into **7m2** within 18 hours (entry 14).

As a preliminary study regarding the possible active species involved in the catalytic process and the mechanism of such hydrosilylation reaction,[9,10] we performed an analysis by electrospray ionization mass spectroscopy on the reaction mixture issued from the hydrosilylation of ketimine **4b** (Table 4). We could unambiguously characterized dechlorinated Ir(III) complex **1**, i.e. cationic species **8**, along with its $BArF_{24}$ anion and the hydrolysed reaction product **5b** (Figure 1 and the Supporting Information). Hence, though the reaction mixture was not quenched, the simple use of methanol for the solvation of the mass analysis sample led to the hydrolysis of the hydrosilylated reaction product and afforded amine **5b**. In addition, the mass analysis conditions didn't allow any hydride complex like **3** to be observed, probably because of the

Table 5. Hydrosilylation of aldimines catalysed by cycloiridated complex **1**.



Entry	Reagent	Time (h)	Yield[a] (isolated yield %)[b]
1		0.25	**7a** 90 (90)
2		0.25	**7b** 100 (100)
3	**6a** R= H, R'= H	0.25	**7c** 100 (100)
4	**6b** R= *o*-Br, R'= H	0.5	**7d** 97 (84)
5	**6c** R= *o*-Et, R'= H	0.5	**7e** 100 (89)
6	**6d** R= *p*-F, R'= H	0.25	**7f** 100 (79)
7	**6e** R= *p*-OMe, R'= H **6f** R= H, R'= *o*-Br **6g** R= H, R'= *o*-OMe	0.25	**7g** 100 (95)
8	**6h**	2	**7h** 100 (73)
9	**6i**	1	**7i** 100 (62)
10	**6j**	0.5	**7j** 100 (79)
11	**6k**	0.25	**7k** 100 (97)
12	**6l**	0.5	**7l** 100 (87)
13	**6m**	7	100 (**7m$_1$** 87 + **7m$_2$** 13)[c]
14		18	100 (**7m$_1$** 20 + **7m$_2$** 80)[d]

[a] Measured by ^{1}H NMR after workup. [b] Isolated yield after flash chromatography.
[c] **7m$_1$** is issued from the imine reduction; **7m$_2$** is the doubly reduced product.
[d] With 2.2 equivalents of triethylsilane.

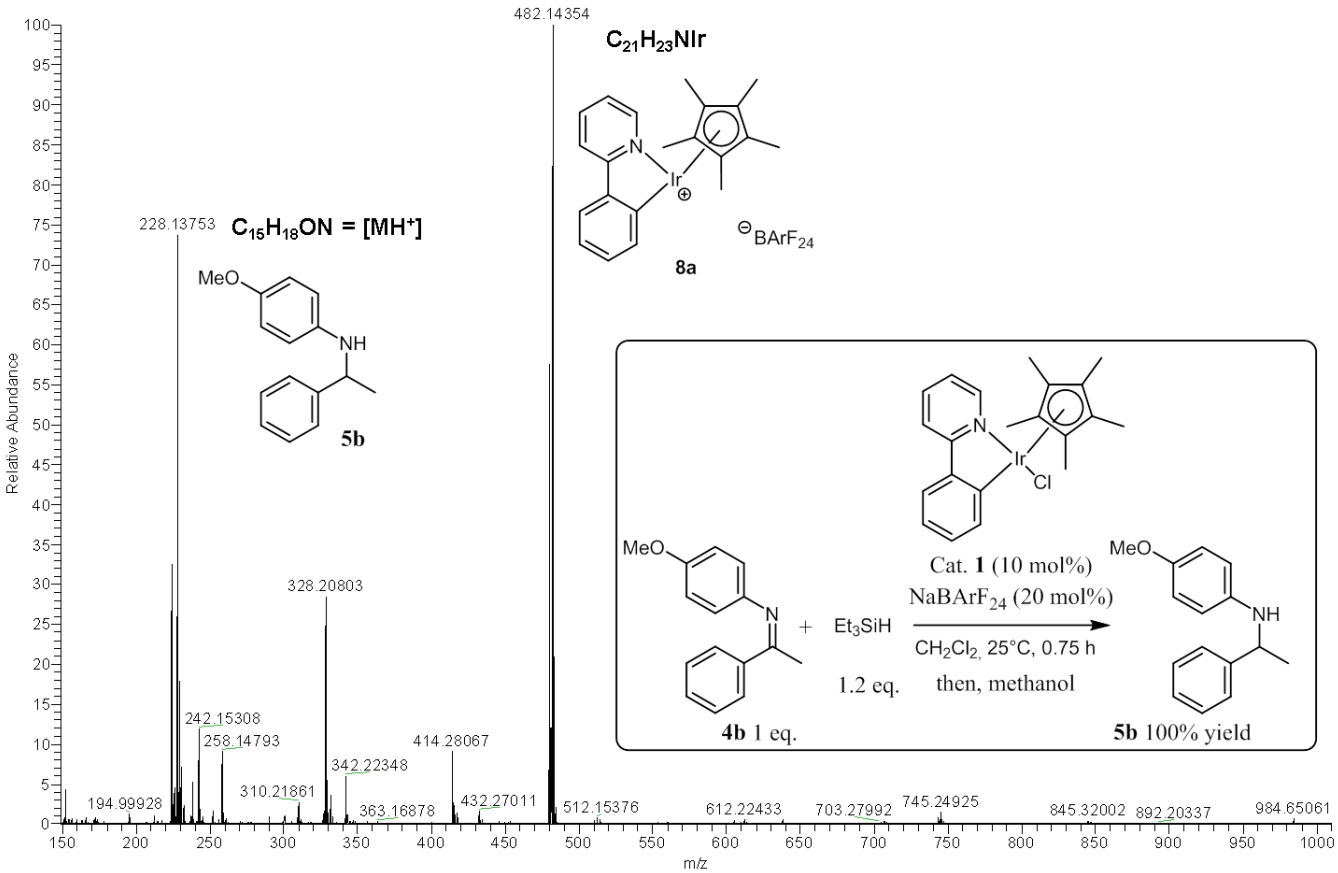


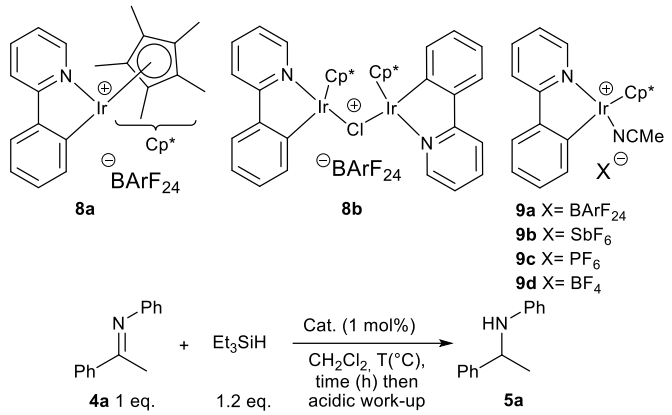
Figure 1. ESI(+)-MS analysis in methanol of the crude mixture resulting from the hydrosilylation of reagent **4b**.

possible ionization of such species during the analysis or because of reaction with alcoholic solvents and air atmosphere.

In order to compare in-situ generated and isolated catalysts, cationic iridacycle **8a** was isolated. Whereas **8a** could be characterized by elemental analysis and HRMS, ^{1}H and ^{13}C NMR spectra proved to suffer from strong dynamic effects. The latter were induced by the rapid switch of the pentamethylcyclopentadienyl fragment from endo to exo positions as respect to the 2-phenyl pyridine ligand. That phenomenon was already observed on related iridacycles and predicted by calculations by some of us.[5b] Complex **8b** could also be synthesized and its molecular structure confirmed by X-ray diffraction analysis, two iridacycle entities being bridged by a chloride and with a single $BArF_{24}$ anion (Table 5 and Figure S1 in the Supporting Information). Iridacycles **8a-b** were then tested on the hydrosilylation of *N*-phenylethylideneaniline **4a** (Table 5). Though the in-situ prepared catalyst involving chlorinated iridacycle **1** and $NaBArF_{24}$ afforded amine **5a** quantitatively, moderate yields of 27% and 39% were observed using respectively catalyst **8a** and **8b** (entries 1-3). In addition, cationic acetonitrile iridacycles **9a-d** were prepared using a related procedure[11] (see Table 5 and the Supporting Information). Coordination of the acetonitrile to the iridium was confirmed unambiguously at the liquid state by DOSY ^{1}H and ^{2}D-^{15}N-HMBC NMR experiments (see Figures S2 and S3 in the Supporting Information). Acetonitrile $BArF_{24}$ complex **9a** proved to catalyse the hydrosilylation of ketimine **4a** in a fair 82% yield (Table 5, entry 4). However, complexes **9b-d** bearing respectively SbF_6, PF_6 and BF_4 anion led to much lower yields (Table 5, entries 5-8). Hence, we showed in-situ generated catalysts were more active as compared to isolated cationic iridacycles. In both cases, the catalyst activity and productivity were strongly depending on the counterion and non-coordinative $BArF_{24}$ anion proved to be the most suitable. Interestingly, such anion effect was already observed for iridium catalysed hydrogenations of alkenes and imines[12a-b] and the nature of the cation was previously shown to influence the catalytic activity of ruthenium catalysed hydrogenation of ketones.[12c]

Regarding the reaction mechanism and on the basis of the bibliography, two pathways may be considered for the hydrosilylation reaction catalysed by iridium (III) (see Schemes S1 and S2 in the Supporting Information). A first one is based on the Chalk-Harrod mechanism which implies an iridium activation of the silane reagent by oxidative addition.[9]

Table 5. Hydrosilylation of imine **4a** by catalysts **8a-b**, **9a-d**.



Entry	Cat. (mol%)	Additive (mol%)	Time (h)	T (°C)	Yield (%)[a]
1	**1** (1)	$NaBArF_{24}$ (2)[b]	0.25	25	100
2	**8a** (1)	none	0.25	25	27
3	**8b** (1)	none	0.25	25	39
4	**9a** (1)	none	0.25	25	82
5	**9b** (1)	none	20	25	43
6	**9c** (1)	none	20	25	24
7	**9d** (1)	none	20	25	<5
8	**9d** (1)	none	20	40	24

[a] Measured by ^{1}H NMR after work-up. [b] $NaBArF_{24}$: sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate.

A second reaction pathway consideres the activation of the substrate through a silane-iridium adduct whereas another silane molecule participates in the hydride transfer.[10] When complex **8a** was allowed to react with a stoechiometric amount of triethylsilane, the ^{1}H NMR analysis of the resulting mixture showed several mono and dihydride species without any coordinated hydrogen according T1 measurements.[13] Unfortunately, additional ^{29}Si INEPT and DEPT45 NMR experiments didn't provide significant informations (see Figures S4-S7 in the Supporting Information). Hence, at this stage, further investigations of the reaction mechanism proved to be difficult.

Conclusions

The combined use of an Ir(III) metallacycle and $NaBArF_{24}$ was successfully applied as catalyst for the hydrosilylation of various ketimines and aldimines. By using a slight excess of an affordable organosilane reagent, reactions proceeded rapidly and efficiently, at low catalyst loadings and in very mild reaction conditions. Several examples of cationic Ir(III) catalysts could be synthesized, characterized and tested for the hydrosilylation of imines. In-situ generated catalysts proved to be more active as compared to isolated ones and non-coordinative $BArF_{24}$ anion was the most adapted in order to reach high catalytic activities. Considering the high efficiency of such cationic cyclometallated Ir(III) catalyst, further applications and developments can be reasonably foreseen. Other studies from our laboratories will be reported soon.

Experimental Section

General procedure for the catalysis

In a glovebox, imine reagent (0.15 mmol, 1 eq.), selected iridium(III) catalyst (x mol%) and additive (2x mol%) were introduced in a Schlenk tube. Under nitrogen, solvent (2 mL) was added followed by silane reagent (0.18 mmol, 1.2 eq.). The reaction mixture was then heated at 25°C under stirring. In order to follow the progress of the reaction, aliquots (0.1 mL) were taken at defined times, filtered through Celite with a CH_2Cl_2 wash (3 mL), evaporated under vacuum and analysed by ^{1}H NMR. At the end of the reaction, solvent was evaporated under vacuum and the crude product was directly purified by flash chromatography or by preparative TLC.

Acknowledgements

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Notes and references

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