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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 with sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate, $NaBArF_{24}$, as an additive. By using a slight excess of the organosilane reagent, the 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 species with non-coordinating $BArF_{24}$ counterion gave the highest catalytic activities.

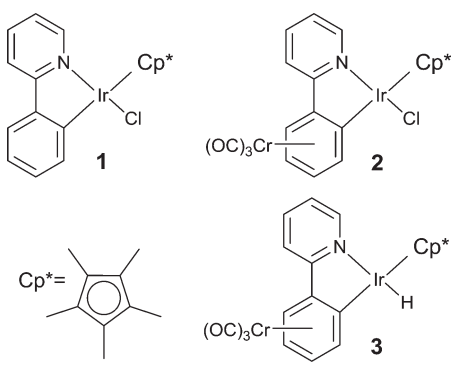
Introduction

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 under mild reaction conditions without any autoclave pressure, is an interesting alternative to hydrogenation, provided that 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 properties 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 catalysts 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 have stated the efficiency of such iridacycles for hydrogenation reactions.[2h,i,3e–h]

Hence, considering the interest of some of us in 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.

Results and discussion

Screening of catalysts, additives and reaction conditions was performed on the hydrosilylation of *N*-phenylethylideneaniline **4a** and we rapidly noticed that 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 gave good yields and were the most interesting solvents, considering their polarity and high boiling point (entries 3–6). The use of toluene and tetrahydrofuran implied lower yields (entries 7–9). By changing the couteranion of the



Scheme 1 Studied iridacycles.

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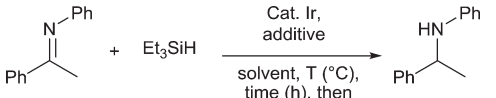
† Electronic supplementary information (ESI) available: Experimental procedures, analytical data, NMR spectra, and HRMS spectra. CCDC 1031536. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cy01233j

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



4a 1 eq. 1.2 eq. **5a**

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

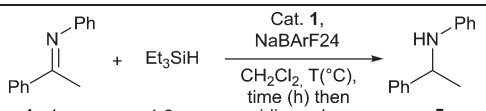
[a] Measured by ^{1}H NMR after work-up. [b] TCE: 1,1′,2,2′-tetrachloroethane. [c] THF: tetrahydrofuran. [d] 8% yield in 40 h. [e] $NaBArF_{24}$: sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate.

Ir(III) catalyst, we confirmed that the less coordinating the anion was, the higher the yields were (entries 10–15). The activity increased according to the following order: $BF_4^- < PF_6^- < SbF_6^- \ll BArF_{24}^-$.

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 the 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 of 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 the catalyst activity, *i.e.* turnover number (TON), increased (entries 1–4). By operating at 0.1 mol% of **1**, the yield of **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 that a higher concentration of the reaction medium could decrease the yield by 10 to 20%, as well as the catalyst activity (entries 1, 2, 5, 6, 8, and 9). At 0.05 mol% loading, catalyst **1** remained quite active at room temperature, affording 88% yield of **5a** and a TON of 1760 within 24 hours (entries 11–13). Finally, using a 0.01 mol% catalyst loading resulted in an important decrease in **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 the 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 the 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

Table 2 Effects of catalyst and additive loadings

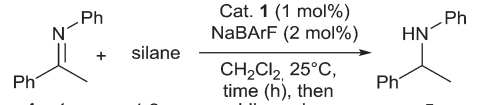


4a 1 eq. 1.2 eq. **5a**

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 of product/mol of catalyst).

Table 3 Screening of the silane reagent



4a 1 eq. 1.2 eq. **5a**

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

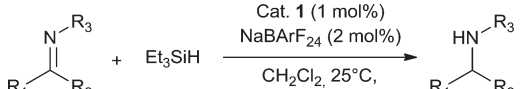
[a] According to ref. 4 and www.sigmaaldrich.com. [b] Measured by ^1H NMR after work-up. [c] 1,1,3,3-Tetramethyldisiloxane. [d] PMHS: polymethylhydroxysiloxane.

reagents used, polymethylhydroxysiloxane (PMHS) showed poor results, but we were glad to reach a quantitative yield using the tetramethyldisiloxane reagent (entries 8–9).

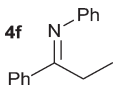
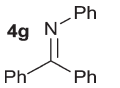
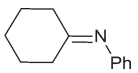
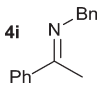
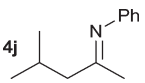
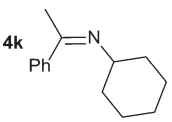
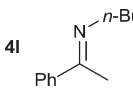
We next studied the hydrosilylation of a series of ketimines. Iridacycle catalyst **1** was used under selected reaction conditions in order to perform fast and straightforward reduction reactions (Table 4). The hydrosilylation of *N*-phenylethylideneaniline **4a** and related *para*-substituted ketimines **4b–c** could be performed readily and afforded the corresponding amines in high isolated yields (entries 1–3). We noticed that the substrate reactivity could be influenced by *ortho*-substituents as hydrosilylation of the brominated reagent **4d** required much more time to be completed (entry 4). However, the *ortho*-alkylated substrate **4e** reacted as well as ketimines **4a–c** (entry 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,[2,2a–i,3,3a–h,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).

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

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



4a-l 1 eq. 1.2 eq. **5a-l**

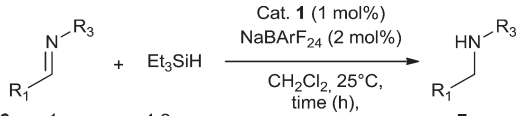
Entry	Reagent	Time (h)	Yield[a] (isolated yield %)[b]
1	**4a** R= H	0.25	**5a** 100 (87)
2	**4b** R= *p*-OMe	0.25	**5b** 100 (100)
3	**4c** R= *p*-F	0.25	**5c** 97 (95)
4	**4d** R= *o*-Br	7	**5d** 100 (100)
5	**4e** R= *o*-Et	0.25	**5e** 100 (100)
6	**4f** 	2	**5f** 90 (64)
7	**4g** 	0.25	**5g** 100 (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)

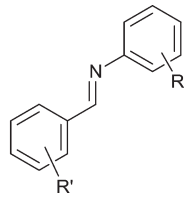
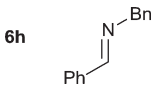
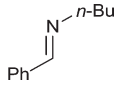
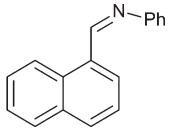
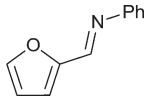
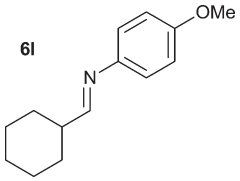
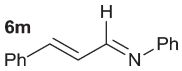
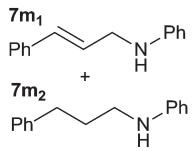
[a] Measured by ^1H NMR after workup. [b] Isolated yield after flash chromatography. [c] Decomposition of product.

corresponding amines in high isolated yields independently of the reagent substitution (entries 1–7). Indeed, halogenated substrates **6b**, **d**, and **f** were reduced without any dehalogenation. Regarding the hydrosilylation of *N*-alkylaldimines **6h** and **6i**, the 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** gave $\mathbf{7m_1}$ as the major product through 1,2-reduction of the imine function. The doubly reduced product $\mathbf{7m_2}$ was isolated as a minor product arising from the additional reduction of the C=C bond (entry 13). It was worth noting that the use of an excess of triethylsilane allowed most of product $\mathbf{7m_1}$ to be reduced to $\mathbf{7m_2}$ 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 obtained from the hydrosilylation of ketimine **4b**

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



Entry	Reagent	Time (h)	Yield[a] (isolated yield %)[b]
1	 **6a** R= H, R'= H	0.25	**7a** 90 (90)
2	**6b** R= *o*-Br, R'= H	0.25	**7b** 100 (100)
3	**6c** R= *o*-Et, R'= H	0.25	**7c** 100 (100)
4	**6d** R= *p*-F, R'= H	0.5	**7d** 97 (84)
5	**6e** R= *p*-OMe, R'= H	0.5	**7e** 100 (89)
6	**6f** R= H, R'= *o*-Br	0.25	**7f** 100 (79)
7	**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	100 (**7m**$_1$ 87 + **7m**$_2$ 13)[c] 100 (**7m**$_1$ 20 + **7m**$_2$ 80)[d]  **7m**$_1$ + **7m**$_2$	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 obtained from imine reduction; **7m**$_2$ is the doubly reduced product. [d] With 2.2 equivalents of triethylsilane.

(Table 4). We could unambiguously characterize dechlorinated Ir(III) complex **1**, *i.e.* cationic species **8a**, along with its $BArF_{24}$ anion and the hydrolysed reaction product **5b** (Fig. 1 and the ESI†). Hence, though the reaction mixture was not quenched, the simple use of methanol for solubilizing the mass analysis sample resulted in 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 possible ionization of such species during the analysis or because of the 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, 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 with respect to the 2-phenyl pyridine ligand. This 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 was confirmed by X-ray diffraction analysis, two iridacycle entities being bridged by a chloride and with a single $BArF_{24}$ anion (Table 6 and Fig. S1 in the ESI†). Iridacycles **8a–b** were then tested on the hydrosilylation of *N*-phenylethylideneaniline **4a** (Table 6). 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 catalysts **8a** and **8b**, respectively (entries 1–3). In addition, cationic acetonitrile iridacycles **9a–d** were prepared using a related procedure[11] (see Table 6 and the ESI†). The coordination of acetonitrile to iridium was confirmed unambiguously at the liquid state by DOSY ^{1}H and ^{2}D-^{15}N-HMBC NMR experiments (see Fig. S2 and S3 in the ESI†). Acetonitrile $BArF_{24}$ complex **9a** proved to catalyse the hydrosilylation of ketimine **4a** in a fair 82% yield (Table 6, entry 4). However, complexes **9b–d** bearing SbF_6, PF_6 and BF_4 anion, respectively, gave much lower yields (Table 6, entries 5–8). Hence, we showed that *in situ*-generated catalysts were more active as compared to isolated cationic iridacycles. In both cases, the catalyst activity and productivity strongly depended on the counterion and the non-coordinating $BArF_{24}$ anion proved to be the most suitable one. Interestingly, such an anion effect was already observed for iridium-catalysed hydrogenation 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 ESI†). The first one is based on the Chalk–Harrod mechanism which implies an iridium activation of the silane reagent by oxidative addition.[9]

The second reaction pathway considers the activation of the substrate through a silane–iridium adduct wherein another silane molecule participates in the hydride transfer.[10] When complex **8a** was allowed to react with a stoichiometric 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 information (see Fig. S4–S7 in the ESI†). Hence, at this stage, further

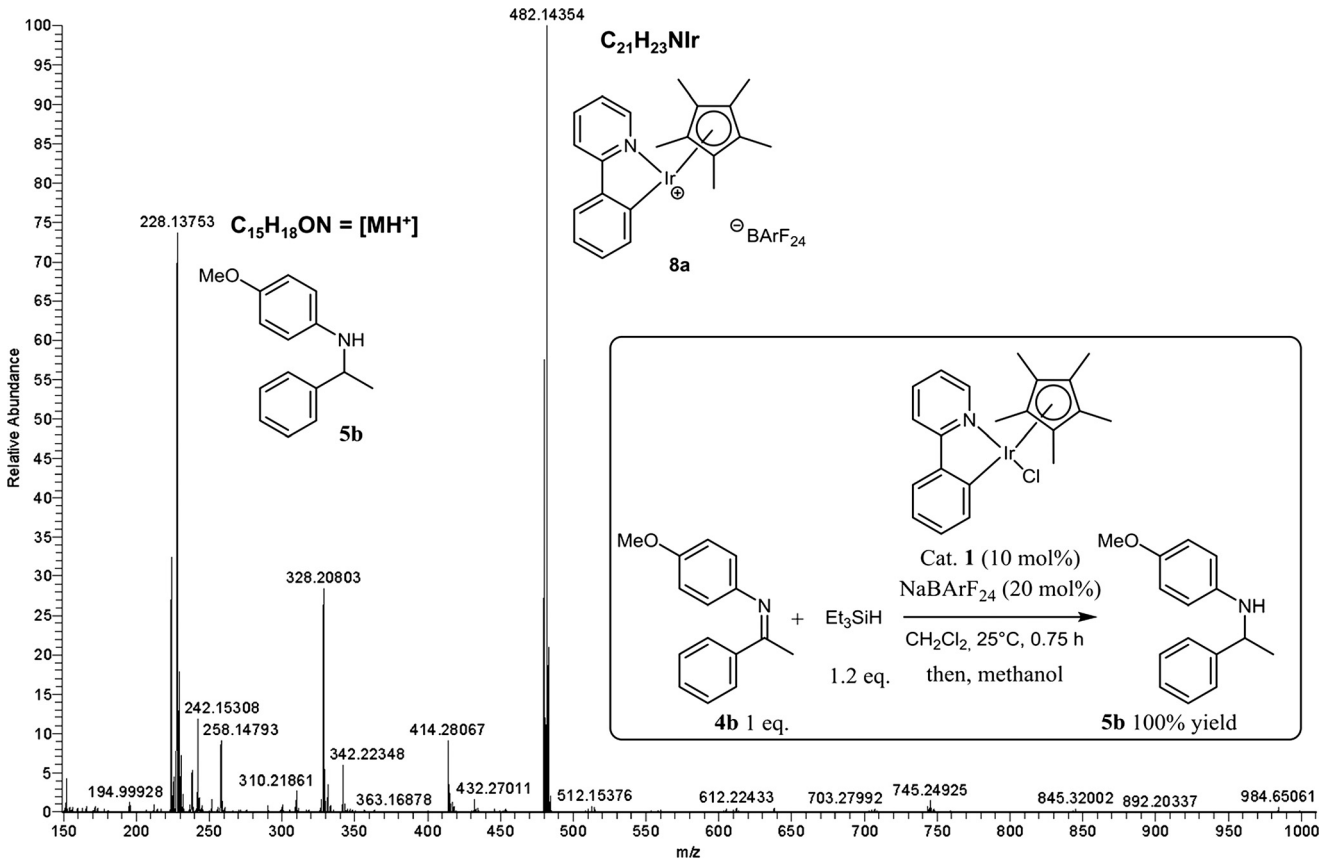
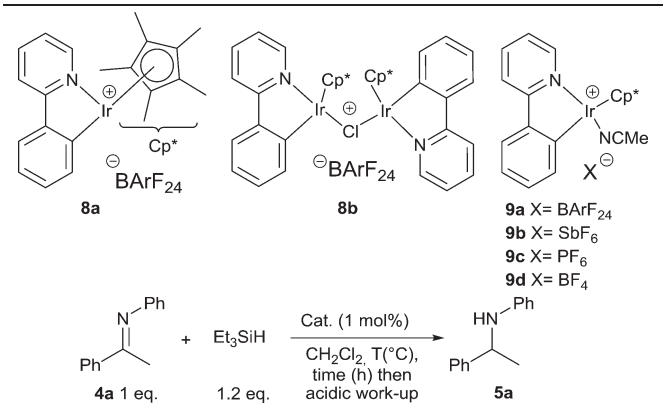


Fig. 1 ESI(+)-MS analysis in methanol of the crude mixture resulting from the hydrosilylation of reagent **4b**.

Table 6 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.

investigations on the reaction mechanism proved to be difficult.

Conclusions

The combined use of an Ir(III) metallacycle and $NaBArF_{24}$ as a catalyst was successfully applied for the hydrosilylation of various ketimines and aldimines. By using a slight excess of an affordable organosilane reagent, the reactions proceeded rapidly and efficiently, at low catalyst loadings and under 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 species with non-coordinating $BArF_{24}$ counterion gave the highest catalytic activities. Considering the high efficiency of such cationic cyclometallated Ir(III) catalysts, 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, the imine reagent (0.15 mmol, 1 eq.), the selected iridium(III) catalyst (x mol%) and the additive

(2x mol%) were introduced in a Schlenk tube. Under nitrogen, the solvent (2 mL) was added followed by the 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 ^1H NMR. At the end of the reaction, the solvent was evaporated under vacuum and the crude product was directly purified by flash chromatography or by preparative TLC.

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Notes and references

1 (*a*) K. S. Hayes, *Appl. Catal., A*, 2001, **221**, 187–195; (*b*) J. J. Brunet and D. Neibecker, in *Catalytic Heterofunctionalization from Hydroamination to Hydrozirconation*, ed. A. Togni and H. Grutzmacher, Wiley-VCH, Weinheim, Germany, 2001, pp. 10–20; (*c*) S. A. Lawrence, in *Amines: Synthesis, Properties and Applications*, Cambridge University Press, Cambridge, 2004; (*d*) S. Doye, in *Science of Synthesis*, ed. D. Enders and E. Schaumann, Thieme, Stuttgart, 2009, vol. 40a, pp. 241–304; (*e*) T. E. Mueller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795–3892; (*f*) J. Hannedouche and E. Schulz, *Chem. – Eur. J.*, 2013, **19**, 4972–4985.

2 (*a*) F. Spindler and H.-U. Blaser in *Transition Metals for Organic Synthesis*, ed. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2nd edn, 2004, vol. 2, p. 113; (*b*) H.-U. Blaser and F. Spindler in *Handbook of Homogeneous Hydrogenation*, ed. J. G. de Vries and C. J. Elsevier, Wiley-VCH, Weinheim, 2007, vol. 3, p. 1193; (*c*) H.-U. Blaser, C. Malan, B. Pugin, F. Spinder, H. Steiner and M. Studer, *Adv. Synth. Catal.*, 2003, **345**, 103–151; (*d*) W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029–3069; (*e*) T. C. Nugent and M. El-Shazly, *Adv. Synth. Catal.*, 2010, **352**, 753–819; (*f*) A. Fabrello, A. Bachelier, M. Urrutigoïty and P. Kalck, *Coord. Chem. Rev.*, 2010, **254**, 273–287; (*g*) J.-H. Xie, S.-F. Zhu and Q.-L. Zhou, *Chem. Rev.*, 2011, **111**, 1713–1760; (*h*) P. A. Dub and T. Ikariya, *ACS Catal.*, 2012, **2**, 1718–1741; (*i*) B. Villa-Marcos, W. Tang, X. Wu and J. Xiao, *Org. Biomol. Chem.*, 2013, **11**, 6934–6939.

3 (*a*) S. Gladiali and E. Alberico in *Transition Metals for Organic Synthesis*, ed. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2004, vol. 2, p. 145; (*b*) S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201–2237; (*c*) J. S. M. Samec and J.-E. Bäckvall, *Chem. – Eur. J.*, 2002, **8**, 2955–2961; (*d*) C. P. Casey and J. B. Johnson, *J. Org. Chem.*, 2003, **68**, 1998–2001; (*e*) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Organometallics*, 2008, **27**, 2795–2802; (*f*) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Chem. – Asian J.*, 2008, **3**, 1479–1485; (*g*) C. Wang, B. Villa-Marcosa and J. Xiao, *Chem. Commun.*, 2011, **47**, 9773–9785; (*h*) D. Talwar, X. Wu, O. Saidi, N. P. Salguero and J. Xiao, *Chem. – Eur. J.*, 2014, **20**, 12835–12842.

4 (*a*) O. Riant, N. Mostefaï and J. Courmarcel, *Synthesis*, 2004, 2943–2958; (*b*) B. Marciniec, H. Maciejewski, C. Pietraszuk and P. Pawluć in *Hydrosilylation: A Comprehensive Review on Recent Advances*, ed. B. Marciniec, Springer, Heidelberg, 2009; (*c*) R. Malacea, R. Poli and E. Manoury, *Coord. Chem. Rev.*, 2010, **254**, 729–752; (*d*) D. Addis, S. Das, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 6004–6011; (*e*) D. Bézier, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19–33.

5 (*a*) W. Iali, F. La Paglia, X.-F. Le Goff, D. Sredojevic, M. Pfeffer and J.-P. Djukic, *Chem. Commun.*, 2012, **48**, 10310–10312; (*b*) J.-P. Djukic, W. Iali, M. Pfeffer and X.-F. LeGoff, *Chem. – Eur. J.*, 2012, **18**, 6063–6078; (*c*) J.-P. Djukic, W. Iali, M. Pfeffer and X.-F. LeGoff, *Chem. Commun.*, 2011, **47**, 3631–3633; (*d*) J.-P. Djukic, C. Boulho, D. Sredojevic, C. Scheeren, S. Zaric, L. Ricard and M. Pfeffer, *Chem. – Eur. J.*, 2009, **15**, 10830–10842; (*e*) C. Scheeren, F. Maasarani, A. Hijazi, J.-P. Djukic, M. Pfeffer, S. D. Zaric, X.-F. LeGoff and L. Ricard, *Organometallics*, 2007, **26**, 3336–3345.

6 (*a*) M.-A. Abadie, X. Trivelli, F. Medina, F. Capet, P. Roussel, F. Agbossou-Niedercorn and C. Michon, *ChemCatChem*, 2014, **6**, 2235–2239; (*b*) C. Michon, M.-A. Abadie, F. Medina and F. Agbossou-Niedercorn, *Catal. Today*, 2014, **235**, 2–13; (*c*) C. Michon, F. Medina, M.-A. Abadie and F. Agbossou-Niedercorn, *Organometallics*, 2013, **32**, 5589–5600; (*d*) F. Medina, C. Michon and F. Agbossou-Niedercorn, *Eur. J. Org. Chem.*, 2012, 6218–6227; (*e*) C. Michon, F. Medina, F. Capet, P. Roussel and F. Agbossou-Niedercorn, *Adv. Synth. Catal.*, 2010, **352**, 3293–3305.

7 (*a*) J. Yang and M. Brookhart, *J. Am. Chem. Soc.*, 2007, **129**, 12656–12657; (*b*) S. Park and M. Brookhart, *Organometallics*, 2010, **29**, 6057–6064; (*c*) S. Park and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 640–653; (*d*) R. Lalrempuia, M. Iglesias, V. Polo, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente and L. A. Oro, *Angew. Chem., Int. Ed.*, 2012, **51**, 12824–12827; (*e*) F. J. Fernández-Alvarez, A. M. Aitani and L. A. Oro, *Catal. Sci. Technol.*, 2014, **4**, 611–624.

8 (*a*) A. V. Malkov, S. Stončius, K. N. MacDougall, A. Mariani, G. D. McGeoch and P. Kočovský, *Tetrahedron*, 2006, **62**,

264–284; (*b*) L. C. M. Castro, J.-B. Sortais and C. Darcel, *Chem. Commun.*, 2012, **48**, 151–153.

9 (*a*) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 1967, **89**, 1640–1647; (*b*) I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics*, 1990, **9**, 3127–3133; (*c*) B. M. Trost and Z. T. Ball, *Synthesis*, 2005, 853–887; (*d*) C. Vicent, M. Viciano, E. Mas-Marzá, M. Sanaú and E. Peris, *Organometallics*, 2006, **25**, 3713–3720.

10 (*a*) M. Iglesias, F. J. Fernández-Alvarez and L. A. Oro, *ChemCatChem*, 2014, **6**, 2486–2489; (*b*) T. T. Metsänen, P. Hrobárik, H. F. T. Klare, M. Kaupp and M. Oestreich, *J. Am. Chem. Soc.*, 2014, **136**, 6912–6915; (*c*) W. Wang, P. Gu, Y. Wang and H. Wei, *Organometallics*, 2014, **33**, 847–857; (*d*) M. Iglesias, P. J. Sanz-Miguel, V. Polo, F. J. Fernández-Alvarez, J. J. Pérez-Torrente and L. A. Oro, *Chem. – Eur. J.*, 2013, **19**, 17559–17566; (*e*) J. Yang, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2008, **130**, 17509–17518.

11 D. L. Davies, O. Al-Duaij, J. Fawcett and K. Singh, *Organometallics*, 2010, **29**, 1413–1420.

12 (*a*) S. P. Smidt, N. Zimmermann, M. Studer and A. Pfaltz, *Chem. – Eur. J.*, 2004, **10**, 4685–4693; (*b*) Y. Schramm, F. Barrios-Landeros and A. Pfaltz, *Chem. Sci.*, 2013, **4**, 2760–2766, and references therein; (*c*) R. Hartmann and P. Chen, *Angew. Chem., Int. Ed.*, 2001, **40**, 3581–3585, and references therein.

13 For example: (*a*) R. H. Crabtree, M. Lavin and L. Bonneviot, *J. Am. Chem. Soc.*, 1986, **108**, 4032–4037; (*b*) T. Komuro, K. Furuyama, T. Kitano and H. Tobita, *J. Organomet. Chem.*, 2014, **751**, 686–694.

