Supporting information

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

Yann Corre,a,e Wissam Iali,c Mustapha Hamdaoui,c Xavier Trivelli,d Jean-Pierre Djukic,c Francine Agbossou-Niedercorn,a,b,e Christophe Michon,a,b,e*

a Université Lille Nord de France, 59000 Lille, France
b CNRS, UCCS UMR 8181, 59655 Villeneuve d’Ascq, France
c Institut de Chimie de Strasbourg, UMR 7177, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France
d UGSF CNRS, UMR 8576, Université Lille Nord de France, 59655 Villeneuve d’Ascq Cedex France
e ENSCL, UCCS-CCM-CCCF UMR 8181, (Chimie-C7) CS 90108, 59652 Villeneuve d’Ascq Cedex, France
Fax : +33-320436585, Email : christophe.michon@enscl-lille.fr

I) General remarks. 2
II) General procedures. 2
III) Characterization of compounds. 2
IV) Synthesis and characterization of complexes 8a-b and 9a-b. 8
V) Structural studies. 10
VI) Preliminary study of the reaction mechanism 14
VII) References. 17
VIII) 1H, 13C NMR spectra of isolated compounds. 20
IX) HRMS spectra. 83
I) General Remarks.

All solvents were dried using standard methods and stored over molecular sieves (4 Å). All silver salts were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere and were repeated at least twice. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. Flash chromatography was carried out with Macherey silica gel (Kieselgel 60). $^1$H (300, 600 and 900 MHz), $^{13}$C (75 and 126 MHz), $^{19}$F (282 MHz) and $^{11}$B (128 MHz) spectra were acquired on Bruker Avance I and II spectrometers. Chemical shifts (δ) are reported downfield of Me$_4$Si in ppm and coupling constants are expressed in Hz. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. HRMS-ESI analyses were performed at CUMA-Pharm. Dept.-University Lille Nord de-France. Ir(III) pre-catalysts were prepared following related procedures. Reagents were prepared as reported.

II) 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$_2$Cl$_2$ 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.

III) Characterization of compounds.

$N$-(1-phenylethyl)aniline 5a

$^1$H NMR (300 MHz, CDCl$_3$): δ = 1.51 (d, $^3$J = 6.3 Hz, 3H, CH$_3$), 4.10 (1s, 1H, NH), 4.49 (q, $^3$J = 6.69 Hz, 1H, CH), 6.51 (d, $^3$J = 8.6 Hz, 2H, H$_{Ar}$), 6.64 (t, $^5$J = 7.2 Hz, 1H, H$_{Ar}$), 7.09 (m, 2H, H$_{Ar}$), 7.24 (m, 1H, H$_{Ar}$), 7.34 (m, 4H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 25.1 (CH$_3$), 52.7 (CH), 113.5 (2CH), 117.4 (CH), 125.9 (2CH), 127.0 (CH), 128.8 (2CH), 129.2 (2CH), 145.3 (C), 147.4 (C, CN).

4-methoxy-$N$-(1-phenylethyl)aniline 5b

$^1$H NMR (300 MHz, CDCl$_3$): δ = 1.50 (d, $^3$J = 6.7 Hz, 3H, CH$_3$), 3.70 (1s, 3H, OCH$_3$), 3.77 (bs, 1H, NH), 4.43 (q, $^3$J = 6.7 Hz, 1H, CH), 6.48 (d, $^3$J = 8.9 Hz, 2H, H$_{Ar}$), 7.29 (d, $^3$J = 9.0 Hz, 2H, H$_{Ar}$), 7.21 (m, 1H, H$_{Ar}$), 7.29 (m, 4H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 25.2 (CH$_3$), 54.4 (OMe), 55.9 (CH), 114.7 (2CH), 114.9 (2CH), 126.0 (2CH), 126.9 (CH), 128.7 (2CH), 141.8 (C, CN), 145.7 (C), 152.1 (C, OMe).
4-fluoro-\(N\)-(1-phenylethyl)aniline 5c

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta = 1.50 (d, \_J^H = 6.7 \text{ Hz}, 3\text{H, CH}_3), 4.41 (q, \_J^H = 6.7 \text{ Hz}, 1\text{H, CH}), \\
& 6.44 (m, 2\text{H, H}_A), 6.78 (m, 2\text{H, H}_A), 7.31 (m, 5\text{H, H}_A).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta = 25.2 (\text{CH}_3), 54.3 (\text{CH}), \\
& 114.3 (d, J_{C,F} = 7.3 \text{ Hz}), 115.5 (d, J_{C,F} = 22.2 \text{ Hz}), 125.9 (2\text{CH}), 127.1 (\text{CH}), 128.8 (2\text{CH}), 143.6 (d, J_{C,F} = 1.1 \text{ Hz}), 145.1 (\text{C, CN}), 156.0 (d, J_{C,F} = 233.4 \text{ Hz}).
\end{align*}
\]

2-bromo-\(N\)-(1-phenylethyl)aniline 5d

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta = 1.57 (d, \_J^H = 6.8 \text{ Hz}, 3\text{H, CH}_3), 4.51 (q, \_J^H = 6.7 \text{ Hz}, 1\text{H, CH}), \\
& 4.74 (bs, 1\text{H, NH}), 6.38 (dd, \_J = 1.5, 8.1 \text{ Hz}, 1\text{H, H}_A), 6.50 (m, 1\text{H, H}_A), 6.98 (m, 1\text{H, H}_A), 7.22 (m, 1\text{H, H}_A), 7.32 (m, 4\text{H, H}_A).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta = 25.3 (\text{CH}_3), 53.7 (\text{CH}), \\
& 109.4 (\text{C}), 112.8 (\text{CH}), 117.9 (\text{CH}), 125.8 (2\text{CH}), 127.2 (\text{CH}), 128.4 (2\text{CH}), 132.3 (\text{CH}), 143.9 (\text{C}), 144.6 (\text{C}).
\end{align*}
\]

2-ethyl-\(N\)-(1-phenylethyl)aniline 5e

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta = 1.37 (s, 3\text{H, CH}_3 \text{ Et}), 1.61 (d, \_J^H = 6.59 \text{ Hz}, 3\text{H, CH}_3), 2.63 (q, \_J^H = 7.54 \text{ Hz}, 2\text{H, CH}_2), \\
& 4.06 (bs, 1\text{H, NH}), 4.58 (q, \_J^H = 6.59 \text{ Hz}, 1\text{H}), 6.44 (dd, \_J^H = 1.00 \text{ Hz}, 1\text{H, H}_A), 7.38 (m, 1\text{H, H}_A), 7.73 (m, 4\text{H, H}_A), 7.40 (dd, \_J^H = 1.5, 7.9 \text{ Hz}, 1\text{H, H}_A), 111.5 (\text{CH}), 117.1 (\text{CH}), 125.9 (2\text{CH}), 126.9 (2\text{CH}), 127.3 (\text{C}), 127.8 (\text{CH}), 128.7 (2\text{CH}), 144.5 (\text{C}), 145.4 (\text{C}).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta = 13.0 (\text{CH}_3 \text{ Et}), 24.1 (\text{CH}_2), 25.4 (\text{CH}_2), \\
& 53.4 (\text{CH}), 113.4 (2\text{CH}), 117.3 (\text{C}), 126.6 (2\text{CH}), 129.2 (2\text{CH}), 144.0 (\text{C}), 147.6 (\text{C, CN}).
\end{align*}
\]

N-(1-phenylpropyl)aniline 5f

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta = 0.96 (t, \_J^H = 7.4 \text{ Hz}, 3\text{H, CH}_3 \text{ Et}), 1.83 (m, 2\text{H, CH}_2), 4.06 (bs, \_J^H = 7.54 \text{ Hz}, 2\text{H, CH}_2), \\
& 4.23 (t, \_J^H = 6.7 \text{ Hz}, 1\text{H, CH}), 6.52 (d, \_J^H = 7.7 \text{ Hz}, 2\text{H, H}_A), 6.63 (t, \_J^H = 7.3 \text{ Hz}, 1\text{H, H}_A), 7.08 (t, \_J^H = 7.9 \text{ Hz}, 2\text{H, H}_A), \\
& 7.21 (m, 1\text{H, H}_A), 7.31 (m, 4\text{H, H}_A).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta = 10.9 (\text{CH}_3), 31.8 (\text{CH}_2), 59.9 (\text{CH}), 113.4 (2\text{CH}), 117.3 (\text{CH}), 126.6 (2\text{CH}), 127.1 (\text{CH}), 128.6 (2\text{CH}), 129.2 (2\text{CH}), 144.0 (\text{C}), 147.6 (\text{C, CN}).
\end{align*}
\]

N-benzhydrylaniline 5g

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta = 0.96 (t, \_J^H = 7.4 \text{ Hz}, 3\text{H, CH}_3 \text{ Et}), 1.83 (m, 2\text{H, CH}_2), 4.06 (bs, \_J^H = 7.54 \text{ Hz}, 2\text{H, CH}_2), \\
& 4.23 (t, \_J^H = 6.7 \text{ Hz}, 1\text{H, CH}), 6.52 (d, \_J^H = 7.7 \text{ Hz}, 2\text{H, H}_A), 6.63 (t, \_J^H = 7.3 \text{ Hz}, 1\text{H, H}_A), 7.08 (t, \_J^H = 7.9 \text{ Hz}, 2\text{H, H}_A), \\
& 7.21 (m, 1\text{H, H}_A), 7.31 (m, 4\text{H, H}_A).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta = 10.9 (\text{CH}_3), 31.8 (\text{CH}_2), 59.9 (\text{CH}), 113.4 (2\text{CH}), 117.3 (\text{CH}), 126.6 (2\text{CH}), 127.1 (\text{CH}), 128.6 (2\text{CH}), 129.2 (2\text{CH}), 144.0 (\text{C}), 147.6 (\text{C, CN}).
\end{align*}
\]
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 63.2\) (CH), 113.7 (2CH), 117.9 (CH), 127.5 (2CH), 127.7 (4CH), 128.9 (4CH), 129.3 (2CH), 143.1 (2C), 147.6 (C, CN).

**N-cyclohexylaniline 5h**

\[\text{C-NH-Ph} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.25\) (m, 6H), 1.75 (m, 2H), 2.06 (m, 2H), 3.25 (non, \(^3J = 3.7\) Hz, 1H), 6.59 (d, \(^3J = 7.6\) Hz, 2H\(_{\text{Ar}}\)), 6.67 (t, \(^3J = 7.3\) Hz, 1H\(_{\text{Ar}}\)), 7.16 (t, \(^3J = 7.9\) Hz, 2H\(_{\text{Ar}}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 25.2\) (2CH\(_2\)), 26.1 (CH\(_2\)), 33.5 (2CH\(_2\)), 51.9 (CH), 113.4 (2CH), 117.1 (CH), 129.5 (2CH), 147.4 (C).

**N-benzyl-1-phenylethanamine 5i**

\[\text{HN-Bn-NH-Ph} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.27\) (d, \(^3J = 6.3\) Hz, 3H, CH\(_3\)), 1.78 (bs, 1H, NH), 3.51 (dd, \(^3J = 13.2\) Hz, 2H, CH\(_2\)), 3.71 (q, \(^3J = 6.6\) Hz, 1H, CH), 7.17 (m, 10H, H\(_{\text{Ar}}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 24.5\) (CH\(_3\)), 51.7 (CH\(_2\)), 57.6 (CH), 126.9 (2CH), 127.0 (1CH), 127.1 (1CH), 128.3 (2CH), 128.5 (2CH), 128.6 (2CH), 140.5 (C), 145.5 (C).

**N-(4-methylpentan-2-yl)aniline 5j**

\[\text{HN-Bn-NH-Ph} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.94\) (d+d, \(^3J = 6.9\) Hz, 6H), 1.16 (d, \(^3J = 6.5\) Hz, 3H, CH\(_3\)), 1.27 (pent, d, \(^3J = 7.1\) Hz, 1H), 1.48 (hex, \(^3J = 7.1\) Hz, 1H), 1.76 (hept, \(^3J = 6.8\) Hz, 1H, CH), 6.59 (d, \(^3J = 7.7\) Hz, 2H, H\(_{\text{Ar}}\)), 6.66 (t, \(^3J = 7.3\) Hz, 1H, H\(_{\text{Ar}}\)), 7.16 (t, \(^3J = 7.8\) Hz, 2H, H\(_{\text{Ar}}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 21.2\) (CH\(_3\)), 22.7 (CH\(_3\)), 23.1 (CH\(_3\)), 25.3 (CH), 46.7 (CH\(_2\)), 47.1 (CH), 113.3 (2CH), 116.9 (CH), 129.4 (2CH), 147.8 (C).

**N-(1-phenylethyl)cyclohexanamine 5k**

\[\text{HN-Bn-NH-Ph} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.21\) (m, 5H), 1.29 (d, \(^3J = 6.6\) Hz, 3H, CH\(_3\)), 1.49 (m, 1H), 1.64 (m, 3H), 1.93 (m, 1H), 2.24 (m, 1H), 3.92 (q, \(^3J = 6.6\) Hz, 1H, CH), 7.23 (m, 2H, H\(_{\text{Ar}}\)), 7.33 (m, 3H, H\(_{\text{Ar}}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 25.0\) (CH\(_3\)), 25.1 (CH\(_2\)), 25.4 (CH\(_2\)), 26.3 (CH\(_2\)), 33.3 (CH\(_2\)), 34.6 (CH\(_2\)), 53.8 (CH), 54.6 (CH), 126.6 (2CH), 126.8 (CH), 128.5 (2CH), 146.3 (C).

**N-Benzylbutan-1-amine 5l**

\[\text{HN-Bn-NH-Ph} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.87\) (t, \(^3J = 1.0\) Hz, 3H, CH\(_3\)_n-Bu\(_1\)), 1.29 (m, 2H, CH\(_2\)), 1.37 (d, \(^3J = 6.6\) Hz, 3H, CH\(_3\)), 1.46 (m, 2H, CH\(_2\)), 2.45 (m, 2H, CH\(_2\)), 3.76 (q, \(^3J = 6.6\) Hz, 1H, CH), 7.23 (m, 2H, H\(_{\text{Ar}}\)), 7.33 (m, 3H, H\(_{\text{Ar}}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.1\) (CH\(_3\)), 20.6 (CH\(_2\)), 24.4 (CH\(_3\)), 32.4(CH\(_2\)), 47.5(CH\(_2\)), 58.6 (CH), 126.7 (2CH), 127.0 (CH), 128.5 (2CH), 145.4(C).
**N-benzylaniline 7a***

![N-benzylaniline structure]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 4.03 (bs, 1H, NH), 4.35 (s, 2H, CH$_2$), 6.65 (d, $^3J =$ 8.2 Hz, 2H, H$_{Ar}$), 6.75 (t, $^3J =$ 7.3 Hz, 1H, H$_{Ar}$), 7.17 (t, $^3J =$ 7.4 Hz, 2H, H$_{Ar}$), 7.35 (m, 5H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 48.4 (CH$_2$), 112.9 (2CH), 117.7 (1CH), 127.3 (1CH), 127.6 (2CH), 128.7 (2CH), 129.3 (2CH), 139.5 (C), 148.3 (C, CN).

**N-benzyl-2-bromoaniline 7b***

![N-benzyl-2-bromoaniline structure]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 4.42 (s, 2H, CH$_2$), 4.86 (bs, 1H, NH), 6.61 (m, 2H, H$_{Ar}$), 7.14 (m, 1H, H$_{Ar}$), 7.34 (m, 5H, H$_{Ar}$), 7.46 (dd, $^3J =$ 1.41, 7.82 Hz, 1H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 48.2 (CH$_2$), 109.9 (C), 111.9 (CH), 118.2 (CH), 127.4 (2CH), 127.5 (CH), 128.6 (CH), 128.9 (2CH), 132.5 (CH), 138.7 (C), 144.8 (C).

**2-ethyl-N-(1-phenylethyl)aniline 7c***

![2-ethyl-N-(1-phenylethyl)aniline structure]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 1.37 (s, 3H, CH$_3$), 1.61 (d, $^3J =$ 6.59 Hz, 3H, CH$_3$), 2.63 (q, $^3J =$ 7.54 Hz, 2H, CH$_2$), 4.0 (bs, 1H, NH), 4.58 (q, $^3J =$ 6.59 Hz, 1H), 6.44 (dd, $^3J =$ 1.00 Hz, 1H, H$_{Ar}$), 6.70 (td, $^3J =$ 7.39 Hz, 1H, H$_{Ar}$), 7.0 (m, 1H, H$_{Ar}$), 7.12 (m, 1H, H$_{Ar}$), 7.27 (m, 1H, H$_{Ar}$), 7.38 (m, 4H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 13.0 (CH$_3$), 24.1 (CH$_2$), 25.4 (CH$_3$), 53.4 (CH), 111.5 (CH), 117.1 (CH), 125.9 (2CH), 126.9 (2CH), 127.3 (C), 127.8 (CH), 128.7 (2CH), 144.5 (C), 145.4 (C).

HRMS (EI): calculated for C$_{16}$H$_{20}$N (M+), 226.3407; found, 226.15903.

**N-(4-Fluorophenyl)benzenemethanamine 7d***

![N-(4-Fluorophenyl)benzenemethanamine structure]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 3.83 (br s, 1H, NH), 4.31 (s, 2H, CH$_2$), 6.66 (m, 2H, H$_{Ar}$), 6.89 (m, 2H, H$_{Ar}$), 7.33 (m, 5H, H$_{Ar}$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 3.83 (br s, 1H, NH), 4.31 (s, 2H, CH$_2$), 6.66 (m, 2H, H$_{Ar}$), 6.89 (m, 2H, H$_{Ar}$), 7.33 (m, 5H, H$_{Ar}$).

**N-(4-Methoxyphenyl)benzenemethanamine 7e***

![N-(4-Methoxyphenyl)benzenemethanamine structure]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 3.47 (bs, 1H, NH), 3.76 (s, 3H, OCH$_3$), 4.30 (s, 2H, CH$_2$), 6.63 (m, 2H, H$_{Ar}$), 6.80 (m, 2H, H$_{Ar}$), 7.34 (m, 5H, H$_{Ar}$).
\[1^3C\text{ NMR (75 MHz, CDCl}_3\): \delta = 49.4 (CH\textsubscript{2}), 55.9 (OCH\textsubscript{3}), 114.3 (2CH), 115.1 (2CH), 127.3 (CH), 127.7 (2CH), 128.7 (2CH), 139.8 (C), 142.6 (C), 152.4 (C).\]

\textit{N-(2-bromobenzyl)aniline 7f\textsuperscript{16}}

\[\text{H}N\text{Ph}\]
\[\text{Br}\]
\[\text{H}N\text{Ph}\]

\[\text{H}N\text{Ph}\]
\[\text{OMe}\]

\[1^H\text{ NMR (300 MHz, CDCl}_3\): \delta = 4.24 (bs, 1H, NH), 4.43 (s, 2H, CH\textsubscript{2}), 6.64 (m, 2H, H\textsubscript{Ar}), 6.75 (tt, \textsuperscript{2}J = 7.3 Hz, 1H, H\textsubscript{Ar}), 7.17 (m, 3H, H\textsubscript{Ar}), 7.27 (q, \textsuperscript{3}J = 1.0 Hz, 1H, H\textsubscript{Ar}), 7.43 (m, 1H, H\textsubscript{Ar}), 7.58 (dd, \textsuperscript{3}J = 7.9 Hz, 1H, H\textsubscript{Ar}).\]

\[1^3C\text{ NMR (75 MHz, CDCl}_3\): \delta = 48.6 (CH\textsubscript{2}), 113.2 (2CH), 118.1 (CH), 123.4 (C), 127.7 (CH), 128.8 (CH), 129.4 (CH), 129.5 (2CH), 132.9 (CH), 138.2 (C), 147.7 (C).\]

\textit{N-(2-methoxybenzyl)aniline 7g\textsuperscript{16}}

\[\text{H}N\text{Ph}\]
\[\text{O}\]
\[\text{Me}\]

\[1^H\text{ NMR (300 MHz, CDCl}_3\): \delta = 3.88 (s, 3H, OCH\textsubscript{3}), 4.36 (s, 2H, CH\textsubscript{2}), 6.71 (m, 3H, H\textsubscript{Ar}), 6.93 (m, 2H, H\textsubscript{Ar}), 7.19 (m, 1H, H\textsubscript{Ar}), 7.27 (m, 1H, H\textsubscript{Ar}), 7.33 (dd, \textsuperscript{3}J = 7.3 Hz, 1H, H\textsubscript{Ar}).\]

\[1^3C\text{ NMR (75 MHz, CDCl}_3\): \delta = 43.7 (CH\textsubscript{2}), 55.4 (OCH\textsubscript{3}), 110.4 (CH), 113.4 (2CH), 117.6 (CH), 120.7 (CH), 127.4 (C), 128.5 (CH), 129.1 (CH), 129.3 (2CH), 148.4 (C), 157.6 (C).\]

\textit{Dibenzylamine 7h\textsuperscript{17}}

\[\text{H}N\text{Ph}\]
\[\text{Ph}\]

\[1^H\text{ NMR (300 MHz, CDCl}_3\): \delta = 3.83 (s, 4H, CH\textsubscript{2}), 7.31 (m, 10H, H\textsubscript{Ar}).\]

\[1^3C\text{ NMR (75 MHz, CDCl}_3\): \delta = 53.3 (2CH\textsubscript{2}), 127.1(2CH), 128.3 (2CH), 128.5 (2CH), 140.5 (2C).\]

\textit{N-Benzyl-butyl-amine 7i\textsuperscript{18}}

\[\text{H}N\text{Ph}\]
\[\text{Ph}\]

\[1^H\text{ NMR (300 MHz, CDCl}_3\): \delta = 0.94 (t, \textsuperscript{3}J = 7.3 Hz, 3H, CH\textsubscript{3}), 1.36 (m, 2H, CH\textsubscript{2}), 1.53 (m, 2H, CH\textsubscript{2}), 2.66 (t, \textsuperscript{3}J = 7.2 Hz, 2H, CH\textsubscript{2}), 3.82 (s, 2H, N-CH\textsubscript{2}), 7.31 (m, 5H, H\textsubscript{Ar}).\]

\[1^3C\text{ NMR (75 MHz, CDCl}_3\): \delta = 14.1 (CH\textsubscript{3}), 20.6 (CH\textsubscript{2}), 32.2 (CH\textsubscript{2}), 49.3 (CH\textsubscript{2}), 54.1 (CH\textsubscript{2}), 127.0 (CH), 128.3 (2CH), 128.5 (2CH), 140.5 (2C).\]

\textit{N-(naphthalen-1-ylmethyl)aniline 7j\textsuperscript{14}}

\[\text{H}N\text{Ph}\]
\[\text{Ph}\]

\[1^H\text{ NMR (300 MHz, CDCl}_3\): \delta = 4.03 (bs, 1H, NH), 4.75 (s, 2H, CH\textsubscript{2}), 6.70 (m, 2H, H\textsubscript{Ar}), 6.77 (m, 1H, H\textsubscript{Ar}), 7.21 (m, 2H, H\textsubscript{Ar}), 7.21 (m, 2H, H\textsubscript{Ar}), 7.44 (m, 1H, H\textsubscript{Ar}), 7.54 (m, 3H, H\textsubscript{Ar}), 7.82 (d, \textsuperscript{3}J = 8.10 Hz, 1H, H\textsubscript{Ar}), 7.91 (m, 1H, H\textsubscript{Ar}), 8.09 (m, 1H, H\textsubscript{Ar}).\]
\[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)): \(\delta = 46.7\) (CH\(_2\)), 112.9 (2CH), 117.8 (CH), 123.7(CH), 125.7(CH), 126.0 (CH), 126.2 (CH), 126.5 (CH), 128.3 (CH), 128.9 (CH), 129.5 (2CH), 131.7 (C), 134.1 (C), 134.5 (C), 148.4 (C).

\textit{N-(furan-2-ylmethyl)aniline 7k}\(^{14}\)

\[\text{Fur}\]

\(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.83\) (bs, 1H), 4.34 (d, \(\text{J}= 0.8\) Hz, 2H, CH\(_2\)), 6.26 (qd, \(\text{J}= 3.2\) Hz, 1H, H\(_{\text{furan}}\)), 6.34 (dd, \(\text{J}= 3.3\) Hz, 1H, H\(_{\text{furan}}\)), 6.70 (m, 2H, H\(_{\text{Ar}}\)), 6.78 (m, 1H, H\(_{\text{Ar}}\)), 7.21 (m, 2H, H\(_{\text{Ar}}\)), 7.39 (dd, \(\text{J}= 1.9\) Hz, 1H, H\(_{\text{furan}}\)).

\[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)): \(\delta = 41.5\) (CH\(_2\)), 107.1 (CH), 110.5 (CH), 113.3 (2CH), 129.4 (2CH), 142.1 (CH), 147.6 (C), 152.8 (C).

\textit{N-(cyclohexylmethyl)-4-methoxyaniline 7l}\(^{19}\)

\[\text{OCH}_3\]

\(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.98\) (m, 2H, H\(_{\text{Cy}}\)), 1.24 (m, 3H, H\(_{\text{Cy}}\)), 1.55 (m, 1H, H\(_{\text{Cy}}\)), 1.77 (m, 5H, CH\(_{\text{Cy}}\)), 2.91 (d, \(\text{J}= 6.6\) Hz, 2H, N-CH\(_2\)), 3.75 (s, 3H, OCH\(_3\)), 6.57 (m, 2H, H\(_{\text{Ar}}\)), 6.77 (m, 2H, H\(_{\text{Ar}}\)).

\[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)): \(\delta = 26.0\) (2CH\(_2\)), 26.8 (CH\(_2\)), 31.4 (2CH\(_2\)), 37.8 (CH), 51.8 (CH\(_2\)), 56.0 (OCH\(_3\)), 114.1 (2CH), 115.1 (2CH), 142.9 (C), 151.8 (C).

\textit{N-cinnamylaniline 7m}\(^{20}\)

\(\text{Ph} = \text{Ph}\)

\(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.83\) (bs, 1H), 3.94 (dd, \(\text{J}= 4.1\) Hz, 2H), 6.30 (t+t, \(\text{J}= 5.8\) Hz, 1H), 6.69 (m, 4H), 7.22 (m, 3H), 7.35 (m, 4H).

\[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)): \(\delta = 46.4\) (CH\(_2\)), 113.2 (2CH), 117.8 (CH), 126.5 (2CH), 127.2 (CH), 127.7 (CH), 128.7 (2CH), 129.4 (2CH), 131.7 (CH), 137.0 (C), 148.2 (C).

\textit{N-(3-phenylpropyl)aniline 7m}\(^{21}\)

\(\text{Ph} = \text{Ph}\)

\(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.96\) (pent, \(\text{J}= 7.7\) Hz, 2H), 2.74 (t, \(\text{J}= 6.8\) Hz, 2H), 3.15 (d, \(\text{J}= 7.1\) Hz, 2H), 3.62 (bs, 1H), 6.59 (d, \(\text{J}= 8.6\) Hz, 2H), 6.69 (t, \(\text{J}= 7.3\) Hz, 1H), 7.19 (m, 5H), 7.29 (m, 2H).

\[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)): \(\delta = 31.2\) (CH\(_2\)), 33.6 (CH\(_2\)), 43.6 (CH\(_2\)), 112.9 (2CH), 117.4 (CH), 126.1 (CH), 128.5 (2CH), 128.6 (2CH), 129.4 (2CH), 141.9 (C), 148.5 (C).
IV) Synthesis and characterization of complexes 8a-b and 9a-b.

Synthesis of complex 8a:

In a glovebox, iridium(III) complex 1 (40 mg, 7.7.10^-5 mmol, 1 eq.) and NaBArF$_{24}$ (1 eq) were introduced in a Schlenk tube. Under nitrogen, degassed CH$_2$Cl$_2$ (1 mL) was added. The reaction mixture was stirred during 30 minutes at room temperature and then filtered through dry Celite which was further washed with CH$_2$Cl$_2$. Solvent was removed under reduced pressure to afford complex 8a as a red powder (quantitative).

Elemental analysis: calculated for C$_{53}$H$_{35}$BF$_{24}$IrN$+0.5$ CH$_2$Cl$_2$: C, 46.31; H, 2.59; N, 1.01; measured C, 46.47; H, 2.99; N, 0.90. HMRS-ESI (m/z): [M]$^+$ calcd for C$_{21}$H$_{23}$IrN: 482.14489, found: 482.14543 (100%); [M]$^-$ m/z calcd for C$_{32}$H$_{12}$BF$_{24}$: 863.06543 [M], measured: 863.06150 (100%).

Synthesis of complex 8b:

A mixture of iridium(III) complex 1 (50 mg, 0.097 mmol) and NaBArF$_{24}$ (43 mg, 0.048 mmol) was stirred at room temperature for two hours in freshly distilled acetone (1 mL) and CH$_2$Cl$_2$ (1 mL) resulting in a marked change in color from deep orange to lemon yellow. Upon concentration of the solvent, the residue was washed with cold pentane to afford a red powder after removal of the solvents under reduced pressure. The remaining solid was recrystallized using CH$_2$Cl$_2$/pentane (46.6 mg, 52%).

$^1$H NMR (600 MHz, 253 K, CDCl$_3$) $\delta$ 8.44 (m, 2H, H$_{-}$C=N), 7.77 (m, 2H, H$_{Ar}$), 7.69-7.63 (m, 5H, H$_{BArF24}$), 7.55 (d, 1H, H$_{Ar}$), 7.52 (m, 4H, H$_{Ar}$), 7.30 (t, 1H, H$_{Ar}$), 7.24 (t, 1H, H$_{Ar}$), 7.17-7.08 (m, 3H, H$_{BArF24}$), 7.08-7.04 (m, 30H, Cp-Me$_5$).

$^{13}$C (126 MHz, 293 K, CDCl$_3$) $\delta$ 167.0, 162.0 (q, 4C, $^1$J$_{B-C}$ = 50.0, BArF), 151.8, 144.9, 138.9, 138.4, 134.9 (bs, 8CH$_{ortho}$ BArF), 131.2, 129.0 (q, 8C-CF$_3$, $^2$J$_{C-F}$ = 31.8 Hz), 125.0 (q, 8CF$_3$, $^1$J$_{C-F}$= 272.2 Hz), 123.8, 123.6, 123.0, 121.4, 118.8, 117.6 (bs, 4CH$_{para}$ BArF), 89.6 (Cp-Me$_5$), 8.4 (Cp-Me$_5$).

$^{19}$F (282 MHz, 298 K, CDCl$_3$) $\delta$ -65.28. $^{11}$B (128 MHz, 298 K, CDCl$_3$) $\delta$ -6.62. HRMS-ESI (m/z): [M]$^+$ calcd for C$_{42}$H$_{46}$ClIr$_2$N$_2$: 999.2593; found, 999.2580; [M]$^-$ calcd for C$_{32}$H$_{12}$BF$_{24}$: 863.0649; found, 863.0670.

Elemental analysis: calculated for C$_{74}$H$_{58}$BClF$_{24}$Ir$_2$N$_2$ + 2 CH$_2$Cl$_2$: C, 44.93; H, 3.08; N, 1.38; measured C, 45.00; H, 2.90; N, 1.20.
Synthesis of complexes 9a-d:
In a glovebox, iridium(III) complex 1 (40 mg, 7.7.10⁻⁵ mmol, 1 eq.) was added to NaBArF₂₄ (1 eq) (or AgBF₄ or AgPF₆ or AgSbF₆) in a Schlenk tube. Under nitrogen, degassed CH₂Cl₂ (1 mL) was added. The reaction mixture was stirred during 30 minutes at room temperature. Then, CH₃CN (7 µL, 1.5 eq.) was added. After 30 minutes, the reaction mixture was filtered through dry Celite which was further washed with CH₂Cl₂. After all, solvent was removed under reduced pressure. The complex obtained was recristallized twice with acetone/n-Hexane for 9a, CH₂Cl₂/n-Hexane for 9c or 9d and CH₂Cl₂/cyclohexane for 9b, to give a solid: pale yellow powder (9a, 85% yield), yellow powder (9b, 83% yield), yellow powder (9c, 77% yield), orange powder (9d, 70% yield).

Complex 9a

\[
\begin{align*}
&\text{N} \quad \text{Ir} \\
&\begin{array}{c}
Cp^* \\
\text{NMe} \\
\text{BArF}_{24}
\end{array}
\end{align*}
\]

\(^1\text{H} \text{NMR} (300 \text{ MHz, CD}_2\text{Cl}_2): \delta = 1.66 (s, 15H, CH₃-Cp*), 2.23 (s, 2H, CH₃-CN), 7.20 (m, 2H, HAr), 7.25 - 7.33 (m, 1H, HAr), 7.57 (s, 4H, HAr + 8HAr BArF \text{ para}), 7.74 (m, 10H, 2HAr + 8HAr BArF \text{ meta}), 7.83 (m, 1H, HAr), 7.92 (m, 1H, HAr), 8.61 (d, 1H, J = 6 Hz, HAr).

\(^13\text{C} \text{NMR} (75 \text{ MHz, CD}_2\text{Cl}_2): \delta = 4.3 (\text{CH}_3\text{-CN}), 9.1 (5\text{CH}_3\text{-Cp*}), 92.0 (5\text{C-Cp*}), 118.1 (bs, 4\text{CH}_{\text{para}} \text{BArF}), 118.6 (C, \text{Me-CN}), 120.5 (CH), 124.2 (CH), 124.7 (CH), 125.1 (CH), 125.2 (q, 8\text{CF}_3, {^1}\text{J}_{\text{C-F}} = 255.0 \text{ Hz}), 129.4 (q, 8\text{C-CF}_3, {^2}\text{J}_{\text{C-F}} = 31.5Hz), 130.6 (C), 132.4 (CH), 135.4 (bs, 8\text{CH}_{\text{ortho}} \text{BArF}), 136.3 (CH), 139.9 (CH), 145.3 (C), 152.1 (CH), 156.8 (C), 162.4 (q, 4C, {^1}\text{J}_{\text{B-C}} = 49.5, \text{BArF}), 168.3(C).

\(^19\text{F} \text{NMR} (282 \text{ MHz, CD}_2\text{Cl}_2): -62.9.

Elemental analysis: calculated for C₅₅H₃₈BF₂₄IrN₂, C, 47.67; H, 2.76; N, 2.02; measured C, 47.20; H, 3.09; N, 1.52.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₃H₂₆IrN₂, 523.17197; found, 523.17141 (100); [M]⁺ calcd for C₂₁H₂₃IrN, 482.14543; found, 482.14523 (32); [M]⁻ calcd for C₃₂H₁₂BF₂₄, 863.06433; found, 863.06599.

Complex 9b

\[
\begin{align*}
&\text{N} \quad \text{Ir} \\
&\begin{array}{c}
Cp^* \\
\text{NMe} \\
\text{SbF}_6
\end{array}
\end{align*}
\]

\(^1\text{H} \text{NMR} (300 \text{ MHz, CDCl}_3): \delta = 1.70 (s, 15H, CH₃-Cp*), 2.29 (s, 3H, CH₃-CN), 7.16 (m, 1H, J = 6.0 Hz, HAr), 7.25 (t, 1H, HAr), 7.34 (t, 1H, J = 6.0 Hz, HAr), 7.72 (d+d, 2H, J = 6.0 Hz, 7.88 (m, 2H, HAr), 8.80 (d, 1H, J = 6.0 Hz, HAr).

\(^13\text{C} \text{NMR} (75 \text{ MHz, CDCl}_3): \delta = 3.7 (CH₃-CN), 8.8 (5CH₃-Cp*), 91.4 (5C-Cp*), 118.6 (C, Me-CN), 119.5 (CH), 124.0 (CH), 124.3 (CH), 124.5 (CH), 131.6 (CH), 135.9 (CH), 139.3 (CH), 145.0 (C), 152.8 (CH), 156.7 (C), 167.0 (C).

\(^19\text{F} \text{NMR} (282 \text{ MHz, CDCl}_3): -63.3.

Elemental analysis: calculated for C₂₃H₂₆SbF₆IrN₂, C, 36.42; H, 3.46; N, 3.69; measured C, 37.17; H, 3.44; N, 4.02.
HRMS-ESI (m/z): [M]^+ calcd for C_{23}H_{26}IrN\_2, 523.17197; found, 523.17060 (100); [M]^+ calcd for C_{21}H_{23}IrN, 482.14543; found, 482.14431 (41); [M]^− calcd for SbF\_6, 234.89479; found, 234.89442 (100).

**Complex 9c**

![Complex 9c](image)

\(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.62\) (s, 15H, CH\(_3\)-Cp\(^*\)), 2.24 (s, 3H, CH\(_3\)-CN), 7.15 (t, 1H, \(J = 6\) Hz, H\(_{Ar}\)), 7.25 (t, 1H, \(J = 6\) Hz, H\(_{Ar}\)), 7.29 (m, 1H, H\(_{Ar}\)), 7.65 (d+d, 2H, \(J = 6\) Hz, H\(_{Ar}\)), 7.79 (m, 2H, H\(_{Ar}\)), 8.76 (d, \(J = 6\) Hz, H\(_{Ar}\)).

\(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 3.7\) (CH\(_3\)-CN), 8.8 (5CH\(_3\)-Cp\(^*\)), 91.4 (5C-Cp\(^*\)), 118.8 (C, Me-CN), 119.4 (CH), 124.0 (CH), 124.3 (CH), 131.5 (CH), 135.9 (CH), 139.3 (CH), 145.0 (C), 153.0 (CH), 156.7 (C), 167.0 (C).

\(^{19}F\) NMR (282 MHz, CDCl\(_3\)): -73.1 (d, \(J = 711.3\)).

\(^{31}P\) NMR (121 MHz, CDCl\(_3\)): -144.3 (hept).

Elemental analysis: calculated for C\(_{23}\)H\(_{26}\)PF\(_6\)IrN\_2 + \(\frac{1}{4}\) cyclohexane, C, 42.73; H, 4.21; N, 4.07; measured C, 43.05; H, 4.07; N, 2.92.

HRMS-ESI (m/z): [M]^+ calcd for C\(_{23}\)H\(_{26}\)PF\(_6\)IrN\_2, 523.17197; found, 523.17090 (100); [M]^+ calcd for C\(_{21}\)H\(_{23}\)IrN, 482.14543; found, 482.14426 (46); [M]^− calcd for PF\(_6\), 144.95636; found, 144.95364 (100).

**Complex 9d**

![Complex 9d](image)

\(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.71\) (s, 15H, CH\(_3\)-Cp\(^*\)), 2.36 (s, 3H, CH\(_3\)-CN), 7.16 (m, 1H, H\(_{Ar}\)), 7.26 (m, 1H, H\(_{Ar}\)), 7.38 (m, 1H, H\(_{Ar}\)), 7.72 (m, 2H), 7.87 (m, 2H, H\(_{Ar}\)), 8.9 (d, 1H, \(J = 6\) Hz, H\(_{Ar}\)).

\(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 3.9\) (CH\(_3\)-CN), 8.8 (5CH\(_3\)-Cp\(^*\)), 91.4 (5C-Cp\(^*\)), 119.1 (C, Me-CN), 119.3 (CH), 123.9 (CH), 124.3 (CH), 131.4 (CH), 135.8 (CH), 139.2 (CH), 145.1 (C), 153.2 (CH), 156.8 (C), 166.9 (C).

\(^{19}F\) NMR (282 MHz, CDCl\(_3\)): -152.8.

Elemental analysis: calculated for C\(_{23}\)H\(_{26}\)BF\(_4\)IrN\_2, C, 45.32; H, 4.30; N, 4.60; measured C, 44.76; H, 4.41; N, 2.80.

HRMS-ESI (m/z): [M]^+ calcd for C\(_{23}\)H\(_{26}\)IrN\_2, 523.17197; found, 523.17090 (100); [M]^+ calcd for C\(_{21}\)H\(_{23}\)IrN, 482.14543; found, 482.14453 (71); [M]^− calcd for BF\(_4\), 87.00237; found, 87.00202 (100).
V) Structural studies.
The X-ray structure determination of 8b confirmed the dimeric pattern of the complex, two Cp* iridacycle fragments built on 2-phenyl-pyridine ligands were shown to be bonded to a chloride atom. The compound bears a single positive charge and a single BArF$_2$ anion. See file CCDC 1031536. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: www.ccdc.cam.ac.uk/data_request/cif.

**Figure S1.** Molecular structure of two chlorobridged iridium complex 8b. Disorders on some CF$_3$ groups were deleted for clarity reason. Another complex and its anion as well as one molecule of dichloromethane and all hydrogen atoms were deleted for clarity reason. Selected bond lengths (Å): Ir3-Cl2 2.479 (3), Ir4-Cl2 2.441 (4), Ir3-N3 2.073 (11), Ir4-N4 2.085 (12) and from the two 2-phenyl-pyridine ligands: Ir3-C53 2.043 (13), Ir4-C74 2.019 (16). CCDC 1031536.
**Compound 8b (CCDC 1031536)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C(<em>{75})H(</em>{60})BCl(<em>3)F(</em>{24})Ir(_2)N(_2)</td>
</tr>
<tr>
<td>Mol. wt</td>
<td>1946.81</td>
</tr>
<tr>
<td>Cryst. Syst.</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>19.0059 (5)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>21.9914 (5)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>22.0920 (7)</td>
</tr>
<tr>
<td>(\alpha) (deg)</td>
<td>114.0030 (10)</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>107.6660 (10)</td>
</tr>
<tr>
<td>(\gamma) (deg)</td>
<td>99.412 (2)</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>7588.0 (4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Color</td>
<td>Red</td>
</tr>
<tr>
<td>Crystal dim. (mm)</td>
<td>0.25×0.20×0.10</td>
</tr>
<tr>
<td>(D_{\text{calc}}) (gcm(^{-3}))</td>
<td>1.4353</td>
</tr>
<tr>
<td>(F_{000})</td>
<td>3800</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>3.712</td>
</tr>
<tr>
<td>Trans. Min. and max</td>
<td>0.43577/0.64126</td>
</tr>
<tr>
<td>(T) (K)</td>
<td>173 (2)</td>
</tr>
<tr>
<td>(hkl) limits</td>
<td>-24,+22/-28,+28/-28,+28</td>
</tr>
<tr>
<td>(2\theta) limits (deg)</td>
<td>1.074/27.504</td>
</tr>
<tr>
<td>Num. of data meas.</td>
<td>34734</td>
</tr>
<tr>
<td>Num. of data with (I &gt; 2 \sigma(I))</td>
<td>17047</td>
</tr>
<tr>
<td>Num. of var.</td>
<td>1734</td>
</tr>
<tr>
<td>(R)</td>
<td>0.0985</td>
</tr>
<tr>
<td>(R_w)</td>
<td>0.2244</td>
</tr>
<tr>
<td>GOF</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Regarding complex 9a, the coordination of acetonitrile to the iridium was confirmed at the liquid state by several analysis. DOSY $^1$H NMR experiment showed similar diffusion coefficient D (D of 8.8-9.1) for the 2-phenyl-pyridine ligand, the pentamethylcyclopentadienyl (Cp*) fragment and the acetonitrile (Figure S2, D in $10^{-10}$ m$^2$/s not calibrated). As expected, BARF anion was bigger (D of 7.7-7.9) and solvents were much more mobile and free: CDHCl$_2$ (D of 30.0) and acetone solvate (D of 28.4).

![Diagram](image)

**Figure S2.** DOSY $^1$H NMR experiment on complex 9a.

The coordination of acetonitrile was also confirmed by 2D-$^{15}$N-HMBC NMR experiment (Figure S3). Chemical shifts were referred to NH$_3$ liquid at 25°C. If $^{15}$N is referred to NH$_3$ liquid at 25°C (0.0 ppm), the $^{15}$N chemical shift in MeNO$_2$ is 380.2 ppm. We observed two $^{15}$N atoms at 211 and 147 ppm (-169.2 and -233.2 ppm with MeNO$_2$ as reference). The chemical shift at 211 ppm correlated with aromatic protons from the 2-phenyl-pyridine ligand (8.60 / 7.91 / 7.22 ppm) and with the aliphatic protons from the pentamethylcyclopentadienyl fragment. Such nitrogen chemical shift is typical of pyridine rings.$^{22}$

The chemical shift at 147 ppm correlated with aliphatic protons from the acetonitrile (at 2.23 ppm) and the pentamethylcyclopentadienyl fragment (at 1.66 ppm). Such nitrogen chemical shift is typical for a coordinated nitrile,$^{23}$ free acetonitrile having a chemical shift at 243 ppm.$^{24}$

Moreover, considering the $^{13}$C NMR spectrum of 9a in CD$_2$Cl$_2$, chemicals shifts were observed at 4.30 (C$_1$) and 118.6 (C$_{IV}$) ppm whereas a free acetonitrile molecule would have carbons shifting at 1.97 (C$_1$) and 116.90 (C$_{IV}$) ppm. Finally, the pentamethylcyclopentadienyl fragment and its 15 protons correlated with both nitrogens through 4 bonds.
Figure S3. 2D-^{15}N-HMBC NMR experiment on complex 9a.
VI) Preliminary study of the reaction mechanism.

Regarding the reaction mechanism, two pathways may be considered for the hydrosilylation of imines catalysed by Ir(III) pre-catalyst 1.

A first one would be based on the Chalk-Harrod mechanism. It may start by the activation of the complex 1 by NaBARF salt which displaces the chloride ligand and affords the cationic catalyst 8 (Scheme S1). The latter may activate the triethylsilane by oxidative addition to afford intermediate A according to previous calculations. In the past, Ir–hydrido intermediate 3 (Scheme 1) was also isolated and may be a key species for the transfer of the hydritic H atom to the electrophilic imine substrate. In the next step, species A may further coordinate the imine reagent 4b thanks to the ring-slippage of Cp* ligand and leads to intermediate B (Scheme S1). Such catalyst activation by shifting from a $\eta^5$ to $\eta^3$ coordination mode of the Ir(III) to the Cp* was already calculated for the hydrosilylation of terminal alkynes by Ir(III) catalyst. In addition, Crabtree et al. proposed recently the activation of an Ir(III) catalyst by loss of a cyclopentadienyl ligand. From intermediate B, the insertion of the imine C=N bond into the Ir-Si bond shall allow the formation of intermediate C (Scheme S1). Finally, a reductive elimination step can afford the reaction product and releases catalytic intermediate 8.

Scheme S1. Proposed reaction pathway 1 for the hydrosilylation of imines using Ir(III) catalyst 1.

On the basis of a possible activating role of the silane, a second reaction pathway can be considered (Scheme S2). Starting from complex 8, the triethylsilane may coordinate the iridium through a single Ir-HSiEt$_3$ sigma bond like in intermediate D, or through a three-center, two-electron "agostic" bond as displayed in intermediate E. In the meantime, imine reagent 4b would be activated by the electrophilic silicium to lead to the cleavage of Si-H bond and afford silyliminium ion G along with neutral iridium hydride F. We noticed a "push-pull" intermediate like D was recently highlighted for the hydrosilylation of ketones with another Ir(III) catalyst and species I was very similar to previously observed Ir-hydrido intermediate 3 (Scheme 1). Finally, the reaction of hydride species F with silyliminium G would afford the corresponding silylamine and cationic complex 8.
Scheme S2. Proposed reaction pathway 2 for the hydrosilylation of imines using Ir(III) catalyst 1.

By performing an ESI-MS analysis of the reaction mixture issued from the hydrosilylation of ketimine 4b, we could characterized complex 8a along with the hydrolysed reaction product 5b (see manuscript, Figure 1). When BArF\textsubscript{24} complex 8a (or a BF\textsubscript{4} counterpart) was prepared in-situ and allowed to react with a stoechiometric amount of triethylsilane, the \textsuperscript{1}H NMR analysis of the resulting sample showed a mixture of several mono and dihydride species whose ratios evolved within 14 hours (Figures S4 and S5). A chemical shift around 4.6 ppm could have been attributed to the presence of hydrogen but T1 (\textsuperscript{1}H) measurements clearly stated no hydrogen was coordinated to the iridium.\textsuperscript{30}

Figure S4. \textsuperscript{1}H NMR spectra along time at 300 K of a stoichiometric mixture of complex 8a and Et\textsubscript{3}SiH.
**Figure S5.** $^1$H NMR spectra at 300 K of a stoichiometric mixture of complex 8a and Et$_3$SiH.

$^{29}$Si experiments (INEPT et DEPT45) showed a single silicon species at -22 ppm coupling with 6 protons (Figures S6 and S7).

To summarize, we didn't see any triethylsilane oxidative addition to the iridium, nor Si–H$_{\text{bridged}}$–Ir species.$^{25a}$ At this stage, further investigations on the reaction mechanism proved to be difficult.

**Figure S6.** $^{29}$Si DEPT45 experiment at 300 K of a stoichiometric mixture of complex 8 and Et$_3$SiH.

**Figure S7.** $^{29}$Si INEPT experiment at 300 K of a stoichiometric mixture of complex 8 and Et$_3$SiH.
VII) References


VIII) $^1$H, $^{13}$C NMR spectra of isolated compounds.
IX) HRMS spectra.

YC-449 bis

![HRMS spectra diagram]

**C_{21}H_{23}Nlr = [8^+]**

**C_{16}H_{16}ON = [MH^+]**

![Molecular structure of C_{16}H_{16}ON]

**Catalyst I (10 mol%)**

**NaBARF_{24} (20 mol%)**

**CH_{2}Cl_{2} 25^\circ C, 0.75 h**

**5b 100% yield**
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
Analysis Name: O31989hn.d
Method: esi wide pos.m
Sample Name: MH198
Comment

Acquisition Date: 10/29/2014 7:59:13 AM
Operator: Administrator
Instrument: micrOTOF

Acquisition Parameter
Source Type: ESI
Ion Polarity: Positive
Scan Range: n/a
Capillary: 4500 V
Set Capillary Exit: 80.0 V
Set Skimmer 1: 50.0 V
Nebulizer: 0.4 Bar
Dry Gas: 4.0 l/min
Dry Heater: 180 °C
Corona: 219 nA
Set Hexapole RF: 220.0 V
APCI Heater: 514 °C

Intens x10^5

![Graph showing mass spectrometry data with peaks at m/z 482.1525 and 999.2580 for compound 8b.]

+MS, 0.0-0.1 min #1(1-5)
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
Analysis Name: O31993hn.d
Method: esi low neg.m
Sample Name: MH198 neg
Comment:

Acquisition Date: 10/29/2014 8:39:11 AM
Operator: Administrator
Instrument: micrTOF

Acquisition Parameter
Source Type: ESI
Ion Polarity: Negative
Scan Range: n/a
Capillary: 4500 V
Set Capillary Exit: -160.0 V
Dry Gas: 4.0 l/min
Dry Heater: 180 °C
Nebulizer: 0.4 Bar
Set Hexapole RF: 60.0 V
Corona: 219 nA
APCI Heater: 514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 10/29/2014 8:46:30 AM Page 1 of 1
Mass Spectrum Molecular Formula Report

Analysis Info
Analysis Name: D:\Data\Service masse à partir du 25 mars 2013\O31993hn.d
Method: ESI low neg.m
Sample Name: MH198 neg
Comment:

Acquisition Parameter
Source Type: ESI
Scan Range: n/a
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Negative
Capillary Exit: -160.0 V
Hexapole RF: 60.0 V
Hexapole 1: -24.0 V
Set Corretor Fill: 61 V
Set Pulsar Pull: 801 V
Set Pulsar Push: 801 V
Set Reflector: 1740 V
Set Flight Tube: 8600 V
Set Detector TOF: 2200 V

Intens

-MS. 0.0-0.1min #1(1-4)

C 32 H 12 B 1 F 24 .863.06

<table>
<thead>
<tr>
<th>Sum Formula</th>
<th>Sigma</th>
<th>m/z</th>
<th>Err [ppm]</th>
<th>Mean Err [ppm]</th>
<th>rdb</th>
<th>N Rule</th>
<th>e^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 32 H 12 B 1 F 24</td>
<td>0.04</td>
<td>865.0643</td>
<td>1.05</td>
<td>-1.41</td>
<td>15.50</td>
<td>ok</td>
<td>even</td>
</tr>
<tr>
<td>C 32 H 11 B 1 F 24</td>
<td>0.55</td>
<td>862.0565</td>
<td>-12.24</td>
<td>-7.90</td>
<td>16.00</td>
<td>-</td>
<td>odd</td>
</tr>
</tbody>
</table>

Bruker Daltonics DataAnalysis 3.3
printed: 10/29/2014 8:45:46 AM
Page 1 of 1
YC-557 pos

<table>
<thead>
<tr>
<th>m/z</th>
<th>Intensity</th>
<th>Relative</th>
<th>Theo. Mass</th>
<th>Delta (ppm)</th>
<th>ROE equiv.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>16466</td>
<td>42.23</td>
<td>480.15209</td>
<td>+1.33</td>
<td>11</td>
<td>C21H23N[19]H</td>
</tr>
</tbody>
</table>

714459

96
YC 510p

<table>
<thead>
<tr>
<th>m/z</th>
<th>Intensity</th>
<th>Relative</th>
<th>Theo. Mass</th>
<th>Delta (ppm)</th>
<th>RSD (ppm)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>122.0979</td>
<td>791.0062</td>
<td>11.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212.1434</td>
<td>236.8645</td>
<td>1.09</td>
<td>212.1438</td>
<td>0.18</td>
<td>7.5</td>
<td>C15 H18 N</td>
</tr>
<tr>
<td>224.1486</td>
<td>129.9519</td>
<td>6.09</td>
<td>224.1492</td>
<td>0.92</td>
<td>8.5</td>
<td>C16 H20 N</td>
</tr>
<tr>
<td>225.1875</td>
<td>219.9026</td>
<td>100</td>
<td>226.1908</td>
<td>-1.05</td>
<td>7.5</td>
<td>C16 H20 N</td>
</tr>
<tr>
<td>227.1521</td>
<td>152.3240</td>
<td>17.11</td>
<td>227.1529</td>
<td>3.15</td>
<td>5</td>
<td>C11 H21 Cl2 H5</td>
</tr>
<tr>
<td>m/z</td>
<td>Intensity</td>
<td>Relative</td>
<td>Theo. Mass</td>
<td>Delta (ppm)</td>
<td>RDS equiv</td>
<td>Composition</td>
</tr>
<tr>
<td>------</td>
<td>-----------</td>
<td>----------</td>
<td>------------</td>
<td>-------------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>210.1205</td>
<td>400.2580</td>
<td>11.05</td>
<td>210.1375</td>
<td>1.51</td>
<td>0.5</td>
<td>C15 H18 N</td>
</tr>
<tr>
<td>212.1432</td>
<td>366.5422</td>
<td>100</td>
<td>212.1433</td>
<td>-0.59</td>
<td>7.5</td>
<td>C15 H18 N</td>
</tr>
<tr>
<td>213.1483</td>
<td>348.2820</td>
<td>16.05</td>
<td>213.1471</td>
<td>-2.81</td>
<td>3</td>
<td>C16 H18 O2 N3</td>
</tr>
<tr>
<td>446.2304</td>
<td>966.8464</td>
<td>3.01</td>
<td>446.2301</td>
<td>0.51</td>
<td>-1</td>
<td>C16 H18 O2 N3</td>
</tr>
</tbody>
</table>