BIAN-Aluminium-Catalysed Imine Hydrogenation

Jennifer Pölker, Dieter Schaarschmidt, Josef Bernauer, Matteo Villa, and Axel Jacobi von Wangelin*
Inhalt

1. General experimental methods ................................................................. 2
2. Synthesis and characterization of ligands and complexes ....................... 3
3. Preparation of Imines ................................................................................ 13
4. Catalytic Reactions .................................................................................. 18
5. Mechanistic investigation ......................................................................... 25
6. NMR-spectra ............................................................................................ 32
7. References .................................................................................................. 48
1. General experimental methods

**Chemicals and Solvents.** If not indicated, commercial reagents were used without purification. For catalytic reactions, exclusively dried solvents were used. Liquid substrates were distilled prior to use (Kugelrohr). The solvents of the reactions were used from an SPS 5 from MBraun. THF was distilled over sodium and benzophenone prior to use. Stock solutions of LiAlH$_4$, $i$Bu$_2$AlH, $i$Bu$_3$Al, Et$_3$Al, LDA, and Li[$(BuO)AlH$] were used from Sigma Aldrich. All catalyzed reactions were performed under an atmosphere of dry argon using standard Schlenk and glovebox techniques.

**Gas chromatography with mass-selective detector.** *Agilent* 6890N Network GC-System, mass detector 5975 MS. Column: BPX5 (30m x 0.25 mm x 0.25µm) from SGE, carrier gas: H$_2$.

**Gas chromatography with FID.** *Agilent* 7820A GC-Systems. Column: HP 5 19091J 413 (30 m x 0.32 mm x 0.25 μm) from Agilent, carrier gas: H$_2$. GC-FID was used for catalyst screening (calibration with internal standard n-pentadecane and analytically pure samples) and the determination of GC-yields.

**NMR.** $^1$H and $^{13}$C nuclear magnetic resonance spectra were recorded on a *Bruker* FourierHD 300 (300 MHz $^1$H; 75 MHz $^{13}$C). Chemicals shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS). Coupling constants (J) are reported in Hertz (Hz). The following abbreviation have been used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd= doublet of doublet, dt = doublet of triplet.

**Elemental Analyses (CHN):** Elemental Analyses (EA) were performed with a Vario micro cube elemental analyzer.

**High resolution mass spectrometry (HRMS).** The spectra were recorded by the MS Department at the Department of Chemistry, University of Hamburg. Either an SCIEX QTRAP 550 or an ESI-Q-TOF from Bruker maXis was used. Abbreviations used in MS spectra: M – molar mass of target compound, ESI - electrospray Liquid injection field desorption ionization (LIFDI) mass spectrometry: Mass spectra were recorded on a Joel AccuTOF GCX in LIFDI mode.

**Autoclaves for hydrogenation reactions**

A high pressure reactor (Parr®), which was loaded in the glovebox, was used for hydrogenation reactions. Hydrogen gas was purchased from Linde (99.9992%). For kinetic experiments, a sampling device was used that was directly attached to the high-pressure reactor to sample microliter probes under reaction conditions. For every sample the first 20 drops were disposed of.

**IR spectroscopy**

The samples were measured with an Cary630 ATR-FT-IR spectrometer from Agilent under nitrogen atmosphere.

**Column chromatography and Thin-Layer-Chromatography**

For column chromatography, silica gel 60 A (0.035-0.070mm) from Acros was used. TLC was performed using aluminium plates with a layer (0.2 mm) of silica gel 60 and fluorescent indicator UV$_{254}$.
2. Synthesis and characterization of ligands and complexes

Synthesis of N, N'-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diimine (dipp₂BIAN) 1

```
O
+ 2
 MeCN, 80 °C, 6 h
```

The reaction was performed following the procedure of Dastgir et al.\textsuperscript{[1]}
Acenaphthenequinone (95%, 7.05 g, 38.7 mmol) was suspended in acetonitrile (150 mL) and heated under reflux (80 °C) for 60 min. Acetic acid (100 mL) was then added and heating was continued until most of the acenaphthenequinone had dissolved. To this hot suspension 2,6-diisopropylphenylaniline (90%, 16.0 g, 17.0 mL, 89.9 mmol) was added over a period of 30 min and the mixture was heated under reflux for another 5 h and then cooled to room temperature. The resulting orange solid was then filtered, washed with pentane (3 x) and dried in air.

\textsuperscript{1}H-NMR(300 MHz, CDCl\textsubscript{3}) [ppm] = 7.87 (d, \(J = 8.3\) Hz, 2H), 7.36 (t, \(J = 7.7\) Hz, 2H), 7.31 – 7.21 (m, 6H), 6.63 (d, \(J = 7.2\) Hz, 2H), 3.03 (m, 4H), 1.24 (d, \(J = 6.8\) Hz, 12H), 0.97 (d, \(J = 6.8\) Hz, 12H).

GC-MS (EI, 70 eV, m/z): 500 [M]\textsuperscript{+}, 485, 457, 427, 341, 324, 310, 282, 254, 174, 132, 91, 65.

The data correspond to the literature values.\textsuperscript{[2]}

Synthesis of N,N'-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine (dipp₂BIANH\textsubscript{2}) 2

```
1) 2 equiv. K
2) MeOH
THF, r.t., 24 h
```

Under argon atmosphere dipp₂BIAN (1.00 g, 2.00 mmol) was suspended in absolute THF (15 mL) and to this suspension was then added potassium (157 mg, 4.02 mmol). After stirring for 24 h at room temperature MeOH (1 mL) was added, the reaction mixture was filtered, and the filtrate was evaporated to dryness. The solid residue was extracted with hexane (20 mL) and the solvent was removed in vacuo to give a violet solid.

\textsuperscript{1}H-NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) [ppm] = 7.25 – 7.16 (m, 8H), 6.92 (dd, \(J = 8.3\), 7.0 Hz, 2H), 6.50(d, \(J = 7.0\) Hz, 2H), 4.99 (s, 2H), 3.55 (m, 4H), 1.19 (d, \(J = 6.8\) Hz, 12H), 1.09 (d, \(J = 6.8\) Hz, 12H).

The data correspond to the literature values.\textsuperscript{[3]}
Synthesis of aluminium complex 3

To the solution of dipp$_2$BIANH$_2$ (0.50 g, 0.99 mmol) in diethyl ether (15 mL) was added LiAlH$_4$ (38 mg, 1.00 mmol). The reaction mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure and the solid residue was washed with heptane (20 mL). The title compound was obtained as a green solid material (555 mg, 0.81 mmol, 81%). Single crystals of the title compound were obtained by recrystallization from diethyl ether at $-20$ °C.

EA Anal. calcd (%) for C$_{44}$H$_{62}$AlLiN$_2$O$_2$: C, 77.16; H, 9.12; N, 4.09.
Found: C, 77.13; H, 8.75; N, 4.06

LIFDI-MS (m/z) calculated for C$_{36}$H$_{42}$AlLiN$_2$ [3 - (OEt)$_2$]: 536.33, found: 536.41 [M$^+$].

IR (ATR, cm$^{-1}$): $\nu = 3782.3$, 3627.7; 3507.8; 3427.1; 3227.4; 2955.8; 2862.5; 2347.5; 2124.4; 1921.1; 1684.5; 1429.5; 1338.3; 1177.4; 1060.3; 924.24; 759.82.

IR (ATR in Et$_2$O, cm$^{-1}$): $\nu = 3818.3$; 3713.2; 3630.1; 3567.7; 3521.1; 3460.4; 3314.7; 3053.0 2955.4; 2762.1, 2706.5, 2598.1, 2501.4, 2348.6, 2265.6; 2210.6; 2156.9; 1974.7; 1903.2, 1753.1, 1661.9; 588.6; 1505.5, 1425.4, 1335.6, 1175.9, 1056.3, 998.85, 924.23, 862.15, 804.64; 760.79.

Crystal structure, CCDC 2145612.

ORTEP diagram (50% probability level) of the molecular structure of 3 with the atom-numbering scheme. Isopropyl substituents, H atoms of the ligand backbone and of diethylether omitted for clarity:
Selected bond lengths (Å), angles (°): C(11)-C(12) 1.429(4), C(11)-N(1) 1.397(3), C(13)-N(1) 1.418(3) N(1)-Al(1) 1.842(2), Al(1)-H(1AL) 1.56(3), Li(1)-H(1AL) 2.01(3), Li(1)-Al(1) 2.608(5), O(1)-Li(1) 1.898(5); C(11)-N(1)-C(13) 122.3(2), C(11)-N(1)-Al(1) 105.73(16), N(1)-Al(1)-N(2) 92.61(9), N(1)-Al(1)-H(1AL) 113.7(10), N(1)-Al(1)-Li(1) 132.70(12), H(1AL)-Al(1)-H(2AL) 98.7(14), O(1)-Li(1)-H(1AL) 104.4(8), O(1)-Li(1)-O(2) 129.3(3).

---

Crystal and intensity collection data for 3

| Chemical formula         | C_{44}H_{62}AlLiN_{2}O_{2} |
|--------------------------|-----------------------------|
| Formula weight           | 684.87                      |
| Temperature / K          | 123.00                      |
| Wavelength / Å           | 1.54184                     |
| Crystal system, space group | monoclinic, P2_{1/n}      |
| a / Å                    | 11.0627(5)                  |
| b / Å                    | 17.8984(11)                 |
| c / Å                    | 21.6065(10)                 |
| α / °                    | 90                          |
| β / °                    | 95.684(4)                   |
| γ / °                    | 90                          |
| V / Å³                   | 4257.2(4)                   |
| ρ_{calc} / g·cm⁻³        | 1.069                       |
| F(000)                   | 1488                        |
| Crystal size / mm        | 0.24 x 0.19 x 0.05          |
| Z                        | 4                           |
| Max. and min. transmission | 0.994, 0.970               |
| μ / mm⁻¹                 | 0.674                       |
| θ / °                    | 4.112-73.599                |
| Index ranges             | -13≤h≥13, -22≤k≥19, -26≤l≥18 |
| Total / unique reflections | 22786 / 8357               |
| Data / restraints / parameters | 8357 / 84 / 477           |
| R_{int}                  | 0.0409                      |
| R₁, wR₂ [l≥2σ(I)]        | 0.0659, 0.1645              |
| R₁, wR₂ (all data)       | 0.1023, 0.1928              |
| Goodness-of-fit S on F²  | 1.018                       |
| Largest diff. peak and hole / eÅ⁻³ | 0.413, -0.276           |
Scheme 1 $^1$H-NMR spectra of 3 (400 MHz, toluene-$d_8$) at varying temperatures.

DOSY NMR Experiments were carried out to determine the solution structure of 3 from its diffusion constant. Unfortunately, the peaks in benzene-$d_6$ were very broad.

Scheme 2 DOSY-$^1$H-NMR experiment spectra of compound 3 (400 MHz, benzene-$d_6$)
Scheme 3 DOSY-\textsuperscript{1}H-NMR experiment spectra of compound 3 (400 MHz, thf-\textit{d}_8)

Evans NMR experiments of 3 in benzene-\textit{d}_6 showed no paramagnetic behavior:

Scheme 4 Evans \textsuperscript{1}H-NMR spectra of compound 3 (400 MHz, benzene-\textit{d}_6) with capillary of benzene-\textit{d}_6/benzene.
Scheme 5 $^1$H-NMR spectra of compound 3 (400 MHz, toluene-$d_8$).

Scheme 6 $^1$H-NMR spectra of compound 3 (400 MHz, Et$_2$O-$d_{10}$).
Scheme 7 $^1$H-NMR spectra of compound 3 (400 MHz, Et$_2$O-d$_{10}$, zoomed in).

Scheme 8 IR Spectra of 3 in solid state (orange) and in Et$_2$O solution (blue).
Synthesis of aluminium complex 4

To the solution of complex 3 (500 mg, 0.73 mmol) in thf (5 mL) was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The title compound was obtained as a green solid material (quantitative yield).

$^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 7.04 – 6.98 (m, 4H), 6.97 – 6.91 (m, 4H), 6.58 – 6.55 (m, 2H), 6.52 – 6.47 (m, 2H), 6.49 (dd, $J = 8.2$, 6.7 Hz, 1H), 5.54 (d, $J = 6.6$ Hz, 2H), 4.02 (hept, $J = 6.9$ Hz, 4H), 3.39 (q, $J = 7.0$ Hz, 10H), 1.19 (d, $J = 6.9$ Hz, 12H), 1.12 (t, $J = 7.0$ Hz, 10H), 1.05 (d, $J = 6.9$ Hz, 12H).

$^1$H NMR (300 MHz, benzene-$d_6$) $\delta$ 7.31 (m, 6H), 7.07 (m, 2H), 6.89 (m, 2H), 6.28 (d, $J = 6.8$ Hz, 2H), 4.38 (h, $J = 6.6$ Hz, 1H), 4.23 (m, 1H), 4.14 (p, $J = 6.8$ Hz, 1H), 3.84 (m 1H), 3.37 (s, 10H), 1.53 (dt, $J = 22.5$, 7.1 Hz, 6H), 1.45 (d, $J = 6.9$ Hz, 6H), 1.41 (dd, $J = 6.9$, 2.3 Hz, 12H), 1.27 (dd, $J = 6.9$, 4.3 Hz, 10H).

IR (ATR, cm$^{-1}$): $\nu$ = 3854.9, 3576.0, 3199.1, 2956.6, 2864.3, 2462.3, 2321.4, 2068.0, 1749.7, 1426.9, 1320.5, 1176.2, 1039.4; 883.3; 757.8.

IR (ATR in THF, cm$^{-1}$): $\nu$ = 3789.0, 3651.4, 3572.3, 3143.7, 3054.0, 2957.0, 2864.5, 2798.5, 2703.1, 2576.7, 2518.7, 2406.2, 2346.8, 2243.5, 2152.4, 2035.1, 1904.4, 1736.4, 1676.9, 1587.9, 1506.9, 1425.8, 1325.1, 1263.4, 1175.0, 1105.0, 1041.2, 885.9, 798.2, 690.8.

The data correspond to the literature values $^{[4]}$.

Scheme 9 IR Spectra of 4 in solid state or in solution.
Synthesis of (DippBIAN)Al(H)(thf) (5)

\[
\begin{array}{c}
\text{(DippBIAN)Al(H)(thf)} \\
\end{array}
\]

\[
\begin{array}{c}
thf, \text{rt, 1h} \\
\end{array}
\]

\[\begin{array}{c}
thf, \text{rt, 1h} \\
\end{array}\]

\[\begin{array}{c}
\text{IR (ATR, cm}^{-1}\text{): } \nu = 2959.1, 2864.7, 2322.1, 2108.5, 1863.3, 1433.1, 1317.6, 1038.2, 922.1, 761.0. \\
The data match with literature values.}\]

\[\begin{array}{c}
\end{array}\]

**Thermal stability of complex 3**

Detection of \(\text{H}_2\) gas evolution by heating complex 3. In an argon-filled glovebox, a Schlenk flask (10 mL) was charged with a magnetic stir bar, complex 3 (25 mg, 0.4 mmol) and toluene (1 mL). Another schlenk flask (10 mL) was charged with a magnetic stir bar, styrene (0.4 mmol) and Pd-C (10 mol%) in hexane (1 mL). The two Schlenk flasks were connected by a short condensation bridge. The first flask containing the Al-complex was placed in an oil bath and heated to 100 °C. After cooling to room temperature, the Pd-containing mixture was diluted with ethyl acetate and water was added. The organic phase was dried over MgSO\(_4\) and analyzed by GC-MS and GC-FID. Quantitative GC-FID analysis documented no catalytic turnover and only minimal yield of ethylbenzene (~5%).

**Thermal stability of complex 3**: Complex 3 (25 mg, 0.4 mmol, 1 eq) was heated as solid in a pressure tube to 100°C for 24 h. The resulting solid was analyzed by IR spectroscopy. There were no changes in the IR spectrum recorded before/after thermal treatment.

**IR (ATR, cm\(^{-1}\))**: \(\nu = 3796.0, 3675.2, 3503.5, 3464.4, 3207.3, 2956.4, 2862.5, 2337.4, 2165.0, 1906.5, 1684.6, 1430.1, 1337.8, 1177.7, 1060.9, 924.7, 760.9.\)

**Thermal stability of complex 3 in the presence of \(\text{H}_2\)**: Complex 3 (25 mg, 0.4 mmol) was heated in THF in a Young-NMR tube in the presence of \(\text{H}_2\) (1 bar) to 100°C for 24 h. \(^1\)H NMR spectra were recorded which displayed identical signals before/after thermal treatment.

\[\begin{array}{c}
\text{IR (ATR, cm}^{-1}\text{): } \nu = 3796.0, 3675.2, 3503.5, 3464.4, 3207.3, 2956.4, 2862.5, 2337.4, 2165.0, 1906.5, 1684.6, 1430.1, 1337.8, 1177.7, 1060.9, 924.7, 760.9. \\
The data match with literature values.}\]

\[\begin{array}{c}
\end{array}\]
Complex 3 (25 mg, 0.4 mmol, 1 eq) was heated in Et₂O (0.5 mL) in an autoclave with hydrogen (50 bar) to 100°C for 24 h. The resulting solid was analyzed by IR spectroscopy. The IR spectra of samples before/after thermal treatment were nearly identical.

**IR (ATR, cm⁻¹):** ν = 3810.6; 3650.1, 3507.6, 3452.1, 3242.1, 2960.3, 2862.7, 2386.2, 1703.9, 1432.5, 1318.9, 1178.6, 1061.6, 923.9, 760.9
3. Preparation of Imines

The reaction was performed following the procedure of Guzen *et al.*[^5^]
Aldehyde (5 mmol), Aniline (5 mmol) and Silica (1.0 g) were mixed in ethanol (5 mL) and
irradiated in the water bath of an ultrasonic cleaner at room temperature for a period of 10
minutes. After completion of the reaction, the mixture was filtered, and the filtrate was
evaporated under reduced pressure. The purification of the compounds was done by
recrystallization in either hexane or ethanol.

1-(4-chlorophenyl)-N-phenylmethanimine

\[
\text{C}_{13}\text{H}_{10}\text{ClN} \quad 215.68 \text{ g/mol}
\]

\(^1\text{H NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.44\) (s, 1H), 8.05 – 7.76 (m, 2H), 7.54 – 7.35 (m,
4H), 7.34 – 7.16 (m, 3H).

\text{GC-MS}\) (EI, 70 eV, m/z): 215 [M]^+, 180, 152, 125, 104, 91, 77, 51.

The data correspond to the literature values[^6^].

1-(4-(tert-butyl)phenyl)-N-phenylmethanimine

\[
\text{C}_{17}\text{H}_{19}\text{N} \quad 237.35 \text{ g/mol}
\]

\(^1\text{H NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.35\) (s, 1H), 7.82 – 7.69 (m, 2H), 7.47
– 7.37 (m, 2H), 7.38 – 7.25 (m, 2H), 7.21 – 7.06 (m, 3H), 1.28 (s,
9H).

\text{GC-MS}\) (EI, 70 eV, m/z): 237 [M]^+, 222, 206, 180, 147, 133, 119, 104, 91, 77.

The data corresponds to the literature values[^7^].

4-((phenylimino)methyl)benzonitrile

\[
\text{C}_{14}\text{H}_{10}\text{N}_2 \quad 206.25 \text{ g/mol}
\]

\(^1\text{H NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.52\) (s, 1H), 8.03 (d, \(J = 8.3\) Hz, 2H),
7.78 (d, \(J = 8.4\) Hz, 2H), 7.50 – 7.36 (m, 2H), 7.36 – 7.18 (m, 3H).

\text{GC-MS}\) (EI, 70 eV, m/z): 206 [M]^+, 178, 153, 117, 104, 77, 65, 51.

The data correspond to the literature values[^8^].
1-(3-chlorophenyl)-N-phenylmethanimine

\[
\text{Cl} \quad \text{N} \quad \text{Ph}
\]

C\textsubscript{13}H\textsubscript{10}ClN  215.68 g/mol

\(^1\text{H} \text{NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.33 \ (s, 1H), 7.86 \ (t, J = 1.8 \text{ Hz}, 1H), 7.66 \ (dt, J = 7.1, 1.6 \text{ Hz}, 1H), 7.44 – 7.26 \ (m, 4H), 7.24 – 7.07 \ (m, 3H).

\(\text{GC-MS}\) (El, 70 eV, m/z): 215 [M]+, 180, 152, 125, 91, 77, 65, 51.
The data correspond to the literature values.\[8\]

1-phenyl-N-(4-(trifluoromethoxy)phenyl)methanimine

\[
\text{Ph} \quad \text{N} \quad \begin{array}{c}
\text{OF}_3
\end{array}
\]

C\textsubscript{14}H\textsubscript{10}F\textsubscript{3}NO  265.24 g/mol

\(^1\text{H} \text{NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.33 \ (s, 1H), 7.86 \ (t, J = 1.8 \text{ Hz}, 1H), 7.66 \ (dt, J = 7.1, 1.6 \text{ Hz}, 1H), 7.44 – 7.26 \ (m, 4H), 7.24 – 7.07 \ (m, 3H).

\(\text{GC-MS}\) (El, 70 eV, m/z): 265 [M]+, 196, 167, 141, 115, 91, 69, 51.

\(\text{N-benzyl-1-}(4\text{-methoxyphenyl})\text{methanimine}\)

\[
\text{MeO} \quad \text{N} \quad \text{Bn}
\]

C\textsubscript{15}H\textsubscript{15}NO  225.29 g/mol

\(^1\text{H} \text{NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.25 \ (t, J = 1.4 \text{ Hz}, 1H), 7.68 – 7.63 \ (m, 2H), 7.26 \ (d, J = 4.1 \text{ Hz}, 4H), 7.21 – 7.16 \ (m, 1H), 6.88 – 6.83 \ (m, 2H), 4.72 \ (d, J = 1.4 \text{ Hz}, 2 H), 3.77 \ (s, 3H).

\(\text{GC-MS}\) (El, 70 eV, m/z): 225 [M]+, 194, 134, 117, 91.
The data correspond to the literature values.\[9\]

\(\text{N-benzyl-1-}(4\text{-bromophenyl})\text{methanimine}\)

\[
\text{Br} \quad \text{N} \quad \text{Bn}
\]

C\textsubscript{14}H\textsubscript{12}BrN  274.16 g/mol

\(^1\text{H} \text{NMR}\) (300 MHz, Chloroform-\(d\)) \(\delta 8.27 \ (t, J = 1.5 \text{ Hz}, 1H), 7.61 – 7.55 \ (m, 2H), 7.51 – 7.45 \ (m, 2H), 7.32 – 7.19 \ (m, 5H), 4.74 \ (d, J = 1.4 \text{ Hz}, 2 H).

\(^{13}\text{C} \text{NMR}\) (75 MHz, CDCl\(_3\)) \(\delta 160.6, 139.0, 135.1, 131.8, 129.7, 128.6, 128.0, 127.1, 125.2, 65.04.

\(\text{GC-MS}\) (El, 70 eV, m/z): 274 [M]+, 155, 117, 105, 91, 79, 77.
**N-benzyl-1-(4-(trifluoromethyl)phenyl)methanimine**

\[
\begin{align*}
\text{C}_{15}\text{H}_{12}\text{F}_{3}\text{N} & \quad 263.26 \text{ g/mol} \\
{^1}\text{H NMR} & \quad (300 \text{ MHz, Chloroform-d}) \; \delta 8.37 (t, J = 1.5 \text{ Hz}, 1\text{H}), 7.83 (d, J = 8.1 \text{ Hz}, 2\text{H}), 7.60 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.33 - 7.20 (m, 5\text{H}), 4.79 (d, J = 1.4 \text{ Hz}, 2\text{H}). \\
\text{GC-MS} & \quad (\text{EI}, 70 \text{ eV, m/z}): 263 [\text{M}]^{+}, 195, 172, 159, 104, 91, 77.
\end{align*}
\]

The data correspond to the literature values.[10]

**N-benzyl-2-ethylhexan-1-imine**

\[
\begin{align*}
\text{C}_{15}\text{H}_{23}\text{N} & \quad 217.36 \text{ g/mol} \\
{^1}\text{H NMR} & \quad (300 \text{ MHz, Chloroform-d}) \; \delta 7.47 (\text{dt}, J = 6.8, 1.4 \text{ Hz}, 1\text{H}), 7.29 - 7.13 (m, 5\text{H}), 4.51 (d, J = 1.3 \text{ Hz}, 2\text{H}), 2.20 - 2.04 (m, 1\text{H}), 1.50 - 1.14 (m, 8\text{H}), 0.91 - 0.74 (m, 6\text{H}). \\
{^{13}}\text{C NMR} & \quad (75 \text{ MHz, CDCl}_3) \; \delta 170.4, 139.5, 128.4, 127.8, 126.8, 66.1, 46.7, 31.9, 29.4, 25.4, 22.8, 14.0, 11.7. \\
\text{GC-MS} & \quad (\text{EI}, 70 \text{ eV, m/z}): 217 [\text{M}]^{+}, 188, 174, 160, 146, 118, 91.
\end{align*}
\]

**Benzaldehyde oxime**

\[
\begin{align*}
\text{C}_{15}\text{H}_{10}\text{O} & \quad 135 \text{ g/mol} \\
{^1}\text{H NMR} & \quad (300 \text{ MHz, Chloroform-d}) \; \delta 7.98 (s, 1\text{H}), 7.52 - 7.45 (m, 2\text{H}), 7.31 - 7.24 (m, 3\text{H}), 3.89 (s, 3\text{H}). \\
{^{13}}\text{C NMR} & \quad (75 \text{ MHz, CDCl}_3) \; \delta 148.6, 132.2, 129.8, 128.7, 123.7, 62.0. \\
\text{GC-MS} & \quad (\text{EI}, 70 \text{ eV, m/z}): 135 [\text{M}]^{+}, 104, 77.
\end{align*}
\]

The data correspond to the literature values.[11]

---

The reaction was performed following the procedure of Dubost et al.[11] Benzaldehyde (1.06 g, 10.0 mmol) was added to a mixture of the alkyl hydroxylamine-hydrochloride (12.0 mmol) and pyridine (0.98 g, 40 mmol) in 30 mL dichloromethane (DCM). After stirring for 1 hour at room temperature, the solvent was removed in vacuo. The residue was dissolved in a small amount of DCM and filtered over silica. DCM was distilled off to give a colorless liquid.

\[
\begin{align*}
\text{C}_{15}\text{H}_{10}\text{O} & \quad 135 \text{ g/mol} \\
{^1}\text{H NMR} & \quad (300 \text{ MHz, Chloroform-d}) \; \delta 7.98 (s, 1\text{H}), 7.52 - 7.45 (m, 2\text{H}), 7.31 - 7.24 (m, 3\text{H}), 3.89 (s, 3\text{H}). \\
{^{13}}\text{C NMR} & \quad (75 \text{ MHz, CDCl}_3) \; \delta 148.6, 132.2, 129.8, 128.7, 123.7, 62.0. \\
\text{GC-MS} & \quad (\text{EI}, 70 \text{ eV, m/z}): 135 [\text{M}]^{+}, 104, 77.
\end{align*}
\]

The data correspond to the literature values.[11]
**N,1-diphenylethan-1-imine**

The reaction was performed following the procedure of Barluenga et al.\textsuperscript{[13]} Acetophenone (3.60 g, 30 mmol) was dissolved in 20 mL dry Toluene. Aniline (2.79 g, 30 mmol) and p-toluenesulfonic acid monohydrate (57.0 mg, 0.3 mmol) were added. The mixture was refluxing for 8 h in a dean stark apparatus. When no more water was evolving, the reaction was allowed to cool to room temp. and the solvent was distilled off. The residue was mixed with pentane, cooled to 8 °C, and the product crystallized as yellow solid.

\[ ^1\text{H NMR} \ (300 \text{ MHz, Chloroform-d}) \delta 8.16 \ (s, 1H), 7.64 - 7.56 \ (m, 2H), 7.48 - 7.30 \ (m, 8H), 5.24 \ (s, 2H). \]

\[ ^1\text{C NMR} \ (75 \text{ MHz, CDCl}_3) \delta 149.2, 137.6, 132.3, 130.0, 128.8, 128.6, 128.5, 128.1, 127.2, 76.5. \]

The data correspond to the literature values.\textsuperscript{[12]}

**N-benzylidene-4-methylbenzenesulfonamide**

The reaction was performed following the procedure of Frias et al.\textsuperscript{[14]} Benzaldehyde (0.74 g, 7.0 mmol, 1.2 eq), pyrrolidine (48 μl, 10%) and 4-methylbenzenesulfonamide (0.993 g, 5.8 mmol, 1.0 eq) were solved in dry DCM (18 mL) with molecular sieves (4A). The mixture was heated to reflux in a sealed pressure tube for 24 hours. The reaction mixture was filtered through a pad of celite. The solvent was removed in vacuo and the product was obtained as colourless solid.

\[ ^1\text{H NMR} \ (300 \text{ MHz, Chloroform-d}) \delta 9.03 \ (s, 1H), 7.98 - 7.85 \ (m, 4H), 7.68 - 7.56 \ (m, 1H), 7.55 - 7.43 \ (m, 2H), 7.38 - 7.32 \ (m, 2H), 2.44 \ (s, 3H). \]

The data correspond to the literature values.\textsuperscript{[14]}
Benzyl-benzylidene carbamate

\[
\text{H}_2\text{N}^\text{Cbz} + \text{Ph} = \text{O} + \text{PhSO}_2\text{Na} \xrightarrow{\text{formic acid}} \text{Cbz}^\text{NH} + \text{PhSO}_2\text{Ph} \xrightarrow{\text{K}_2\text{CO}_3} \text{N}^\text{Cbz}
\]

The reaction was performed following the procedure of Tillman et al.\textsuperscript{[13]} Bezylcarbamate (2.33 g, 16 mmol) and bezenesulfonic acid sodium salt (5.1 g, 31 mmol) were suspended in methanol/water (15 mL/30 mL). The aldehyde (2.39 mL, 24 mmol) was added in one portion, followed by the formic acid (2.4 mL). The reaction mixture was stirred for 3 days and then filtered and washed with water (25 mL) and diethyl ether (25 mL). The product was dried and used without further purification.

\(\text{K}_2\text{CO}_3\) (1.6 g, 11.4 mmol, 6 eq) was weighed into a flame-dried schlenk tube. Sulphone (1.9 mmol, 1.0 eq) and thf (10 mL) were added. The reaction mixture was refluxed under argon for 15 hours. After cooling down, the suspension was filtered through a glass frit. The filtrate was concentrated in vacuo and the imine was isolated in quantitative yield.

\(^{1}\text{H} \text{NMR}\quad (300 \text{ MHz, Chloroform-}d) \delta 8.95 (s, 1H), 7.92 (s, 2H), 7.63 - 7.53 (m, 1H), 7.53 - 7.43 (m, 4H), 7.43 - 7.29 (m, 4H), 5.32 (s, 2H).

The data correspond to the literature values.\textsuperscript{[15]}
4. Catalytic Reactions

**Imine Hydrogenations**

![Chemical diagram: Ph-N=Ph + H2 → Cat. toluene, T, 24 h → Ph-N-Ph]

**Optimization procedure:** Under argon, a stir bar, the imine (0.250 mmol) and catalyst (10 mol%) were charged into a glass vial, toluene (0.15 mL) was added and the vial sealed with a rubber septum. The solution was thoroughly mixed, the septum of the vial was punctured with a needle and the vial placed into a pressure reactor. Hydrogen gas was purged through the reactor. 47 bar H₂ and heating to 100 °C were applied to give a final pressure of 50 bar H₂. After 24 h of stirring the reaction, the gas was released, the vials retrieved and water (1 mL) was added. The organic phase was extracted with ethyl acetate and dried over NaSO₄. Conversions and yields were determined by quantitative GC-FID vs. n-pentadecane as internal standard.

| Entry | Cat. (mol%) | T [°C] | H₂ [bar] | Yield [%][a] |
|-------|-------------|--------|----------|--------------|
| 1     | 3 (10)      | 100    | 100      | >95          |
| 2     | 3 (5)       | 100    | 100      | 73           |
| 3     | 3 (3)       | 100    | 100      | 50           |
| 4     | 3 (1)       | 100    | 100      | 9            |
| 5     | 3 (10)      | 100    | 50       | >95 (65[b])  |
| 6     | 3 (10)      | 70     | 50       | 38           |
| 7     | 3 (10)      | 100    | 30       | 55           |
| 8     | 3 (10)      | 25     | 50       | 18           |
| 9     | 3 (10)      | 85     | 25       | 78 (39[b])   |
| 10    | DiBAl-H (10)| 100    | 100      | 94           |
| 11    | DiBAl-H (10)| 100    | 50       | 36           |
| 12    | iBu₃Al (10) | 100    | 50       | 19           |
| 13    | Et₂Al (10)  | 100    | 50       | 12           |
| 14    | (n-octyl)₂Al (10) | 100 | 50 | 21 |
| 15    | Li[(tBuO)₂AlH] (10) | 100 | 50 | 9 |
| 16    | LiAlH₄ (10) | 100    | 50       | 50           |
| 17    | LiAlH₄ (10) + dippBIAN (10) | 100 | 50 | 29 |
| 18    | LiAlH₄ (10) + Et₂O (30) | 100 | 50 | 56 |
| 19    | LiAlH₄ (10) + dippBIANH₂ (10) + Et₂O (30) | 100 | 50 | >95 |
| 20    | LiHmds (10) | 100    | 50       | 87           |
General procedure: Under argon, a stir bar, the imine (0.250 mmol) and catalyst (10 mol%) were charged into a glass vial, toluene (0.15 mL) was added and the vial sealed with a rubber septum. The solution was thoroughly mixed, the septum of the vial was punctured with a needle and the vial placed into pressure reactor. Hydrogen gas was purged through the reactor. 47 bar H₂ and heating to 100 °C were applied to give a final pressure of 50 bar H₂. After 24 h of stirring the reaction, the gas was release, the vials retrieved and water (1 mL) was added. The organic phase was extracted with Et₂O (3 x 1 mL) and dried over Na₂SO₄. The drying agent was filtered off and the clear solution was treated with HCl (1 mL, 1.0 M in Et₂O) to give the ammonium salts via filtration.

N-benzylaniline 8a
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.

\[
\begin{align*}
\text{C}_{13}\text{H}_{13}\text{N} & \quad 183.25 \text{ g/mol} \\
^1\text{H NMR} & \quad (300 \text{ MHz, Methanol-}\text{d}_4) \delta 7.57 – 7.50 (\text{m, 3H}), 7.46 – 7.39 (\text{m, 7H}), 4.61 (\text{s, 2H}). \\
^13\text{C NMR} & \quad (75 \text{ MHz, Methanol-}\text{d}_4) \delta 136.2, 131.8, 131.5, 131.3, 131.0, 130.8, 130.1, 124.3, 57.0. \\
\text{GC-MS} & \quad (\text{EI, 70 eV, m/2}): 183 [\text{M}]^+, 106, 91, 65, 51.
\end{align*}
\]

The data match a commercial sample and correspond to the literature values.\textsuperscript{[16]}

N-(4-chlorobenzyl)aniline 8b
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.

\[
\begin{align*}
\text{C}_{13}\text{H}_{12}\text{ClN} & \quad 217.70 \text{ g/mol} \\
^1\text{H-NMR} & \quad (300 \text{ MHz, Methanol-}\text{d}_4) \delta 7.61 – 7.30 (\text{m, 9H}), 4.60 (\text{s, 2H}).
\end{align*}
\]
$^{13}$C-NMR (75 MHz, Methanol-$d_4$) δ 136.9, 133.2, 131.4, 131.3, 130.9, 130.3, 124.1, 55.9.

**GC-MS** (EI, 70 eV, m/z): 217 [M]$^+$, 182, 125, 90, 77, 65, 51.
The data correspond to the literature values.$^{[16]}$

**$N$-(4-(tert-butyl)benzyl)aniline 8c**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

$^1$H-NMR (300 MHz, Methanol-$d_4$) δ 7.56 – 7.29 (m, 9H), 4.55 (s, 2H), 1.31 (s, 9H).

$^{13}$C-NMR (75 MHz, Methanol-$d_4$) δ 154.3, 136.6, 131.4, 131.2, 130.8, 129.1, 127.5, 127.1, 126.0, 124.1, 56.7, 35.6, 31.6.

**GC-MS** (EI, 70 eV, m/z): 239 [M]$^+$, 222, 182, 147, 132, 117, 91, 77, 51.
The data correspond to the literature values.$^{[16]}$

**$N$-(3-chlorobenzyl)aniline 8e**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

$^1$H-NMR (300 MHz, Methanol-$d_4$) δ 7.62 – 7.34 (m, 9H), 4.63 (s, 2H).

$^{13}$C-NMR (75 MHz, Methanol-$d_4$) δ 135.9, 134.0, 131.8, 131.5, 131.3, 130.9, 130.3, 129.8, 126.0, 124.0, 55.9.

**GC-HRMS** (CI, m/z): found 218.0729 [M+H]$^+$ (calculated 218.0731).
The data correspond to the literature values.$^{[16]}$

**$N$-benzyl-4-(trifluoromethoxy)aniline 8g**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

$^1$H-NMR (300 MHz, Methanol-$d_4$) δ 7.45 – 7.39 (m, 9H), 4.59 (s, 2H).

$^{13}$C-NMR (75 MHz, Methanol-$d_4$) δ 136.1, 132.5, 131.0, 130.7, 130.2, 125.3, 123.8, 55.7.

**GC-MS** (EI, 70 eV, m/z): 267 [M]$^+$, 190, 176, 161, 139, 115, 91, 81, 68, 63.
The data correspond to the literature values.$^{[16]}$
**N-benzyl-2-methylpropan-2-amine 8h**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

![Structural formula of N-benzyl-2-methylpropan-2-amine 8h]

C$_{11}$H$_{17}$N  163.26 g/mol

$^1$H-NMR (300 MHz, Methanol-d$_4$) δ 7.56 – 7.44 (m, 5H), 4.18 (s, 2H), 1.47 (s, 9H).

$^{13}$C-NMR (75 MHz, Methanol-d$_4$) δ 133.1, 131.0, 130.6, 130.3, 58.7, 46.7, 27.7, 25.8.

HRMS (ESI) (CI, m/z): found 164.1409 [M+H]$^+$ (calculated 164.1434).

The data correspond to the literature values.$^{[19]}$

**N-methyl-1-phenylmethanamine 8i**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

![Structural formula of N-methyl-1-phenylmethanamine 8i]

C$_8$H$_{11}$N  121.18 g/mol

$^1$H-NMR (300 MHz, Methanol-d$_4$) δ 7.53 – 7.43 (m, 5H), 4.19 (s, 2H), 2.72 (s, 3H).

$^{13}$C-NMR (75 MHz, Methanol-d$_4$) δ 132.6, 130.9, 130.7, 130.3, 53.6, 33.1.

HRMS (ESI) (CI, m/z): found 122.0966 [M+H]$^+$ (calculated 122.0964).

The data correspond to the literature values.$^{[19]}$

**Dibenzylamine 8j**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

![Structural formula of Dibenzylamine 8j]

C$_{14}$H$_{15}$N  197.28 g/mol

$^1$H-NMR (300 MHz, Methanol-d$_4$) δ 7.54 – 7.38 (m, 10H), 7.03 – 6.97 (m, 2H), 4.20 (d, $J$ = 10.2 Hz, 4H), 3.82 (s, 3H).

$^{13}$C-NMR (75 MHz, Methanol-d$_4$) δ 162.2, 132.5, 131.1, 130.8, 130.3, 52.1.

HRMS (ESI) (CI, m/z): found 198.1288 [M+H]$^+$ (calculated 198.1277).

The data correspond to the literature values.$^{[20]}$

**N-benzyl-1-(4-methoxyphenyl)methanamine 8k**
Treated with 1.0 M HCl in Et$_2$O for isolation. NMR measured of protonated form.

![Structural formula of N-benzyl-1-(4-methoxyphenyl)methanamine 8k]

C$_{15}$H$_{17}$NO  227.31 g/mol

$^1$H-NMR (300 MHz, Methanol-d$_4$) δ 7.53 – 7.38 (m, 7H), 7.03 – 6.97 (m, 2H), 6.93 (d, $J$ = 10.2 Hz, 4H), 3.82 (s, 3H).

$^{13}$C-NMR (75 MHz, Methanol-d$_4$) δ 162.2, 132.7, 132.5, 131.1, 130.7, 130.3, 124.1, 115.6, 55.8, 51.8, 51.6.
GC-MS (EI, 70 eV, m/z): 227 [M]⁺, 226, 196, 136, 121, 106, 91, 77, 67, 52.
The data correspond to the literature values.²¹

*N*-benzyl-1-(4-bromophenyl)methanamine 8l
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.

![Structural formula of 8l](image)

C₁₄H₁₂BrN  276.18 g/mol

¹H-NMR  (300 MHz, Methanol-d₄) δ 7.66 – 7.60 (m, 1H), 7.53 – 7.38 (m, 8H), 4.26 – 4.21 (m, 4H).

¹³C-NMR  (75 MHz, Methanol-d₄) δ 133.5, 133.0, 132.4, 131.8, 131.1, 130.8, 130.3, 52.2, 52.1, 51.4.

HRMS (ESI)  (Cl, m/z): found 276.0388 [M+H]⁺ (calculated 276.0382).
The data correspond to the literature values.²²

*N*-benzyl-1-(4-(trifluoromethyl)phenyl)methanamine 8m
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.

![Structural formula of 8m](image)

C₁₅H₁₄F₃N  265.28 g/mol

¹H-NMR  (300 MHz, Methanol-d₄) δ 7.82 – 7.76 (m, 2H), 7.72 – 7.67 (m, 2H), 7.54 – 7.44 (m, 5H), 4.35 (s, 2H), 4.29 (s, 2H).

¹³C-NMR  (75 MHz, Methanol-d₄) δ 132.3, 131.9, 131.1, 130.8, 130.4, 127.2, 127.1, 52.5, 51.4.

HRMS (ESI)  (Cl, m/z): found 266.1149 [M+H]⁺ (calculated 266.1151).

*N*-benzyl-2-ethylhexan-1-amine 8n
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.

![Structural formula of 8n](image)

C₁₅H₂₅N  219.37 g/mol

¹H-NMR  (300 MHz, Methanol-d₄) δ 7.58 – 7.41 (m, 5H), 4.23 (m, 2H), 2.93 (d, J = 6.7 Hz, 2H), 1.71 (h, J = 6.4 Hz, 1H), 1.50 – 1.14 (m, 8H), 0.90 (q, J = 7.4, 6.9 Hz, 6H).

¹³C-NMR  (75 MHz, Methanol-d₄) δ 132.3, 131.3, 130.7, 130.3, 52.7, 51.6, 38.0, 31.3, 29.4, 24.5, 23.9, 14.3, 10.5.

HRMS (ESI)  (Cl, m/z): found 220.2150 [M+H]⁺ (calculated 220.2060).
The data correspond to the literature values.²³

*N*-(1-phenylethyl)aniline 8o
Treated with 1.0 M HCl in Et₂O for isolation. NMR measured of protonated form.
**N<sup>1</sup>,N<sup>2</sup>-dicyclohexylethane-1,2-diamine 8p**
Treated with 1.0 M HCl in Et<sub>2</sub>O for isolation. NMR measured of protonated form.

\[
\text{C}_{14}\text{H}_{28}\text{N}_2 \quad 224.39 \text{ g/mol}
\]

**<sup>1</sup>H-NMR**
(300 MHz, Methanol-<sup>d</sup>4) δ 3.40 (s, 4H), 3.23 – 3.10 (m, 2H), 2.16 (m, 4H), 1.98 – 1.81 (m, 4H), 1.73 (d, J = 12.5 Hz, 2H), 1.49 – 1.15 (m, 10H).

**<sup>13</sup>C-NMR**
(75 MHz, Methanol-<sup>d</sup>4) δ 59.1, 41.7, 30.3, 26.0, 25.4.

**HRMS (ESI)** (Cl, m/z): found 225.2357 [M+H]<sup>+</sup> (calculated 225.2325).

The data correspond to the literature values.\[^{[24]}\]

**N-(1-(naphthalen-2-yl)ethyl)aniline 8q**
Treated with 1.0 M HCl in Et<sub>2</sub>O for isolation. NMR measured of protonated form.

\[
\text{C}_{18}\text{H}_{17}\text{N} \quad 247.34 \text{ g/mol}
\]

**<sup>1</sup>H-NMR**
(300 MHz, Methanol-<sup>d</sup>4) δ 8.02 – 7.80 (m, 4H), 7.64 – 7.26 (m, 8H), 5.01 (q, J = 6.9 Hz, 1H), 1.90 (d, J = 6.9 Hz, 3H).

**<sup>13</sup>C-NMR**
(75 MHz, Methanol-<sup>d</sup>4) δ 135.2, 135.1, 134.5, 133.9, 131.2, 131.0, 130.2, 129.4, 129.2, 128.8, 128.3, 128.0, 125.5, 124.8, 64.9, 18.8.

**GC-MS** (El, 70 eV, m/z): 247 [M]<sup>+</sup>, 232, 155, 127, 93, 77.

The data correspond to the literature values.\[^{[25]}\]

**Phenylmethanamine 9r/9s/9t**
Treated with 1.0 M HCl in Et<sub>2</sub>O for isolation. NMR measured of protonated form.
C\textsubscript{7}H\textsubscript{9}N 107.16 g/mol

\textsuperscript{1}H-NMR  (300 MHz, Methanol-d\textsubscript{4}) \(\delta\) 7.49 – 7.38 (m, 5H), 4.11 (s, 2H).

\textsuperscript{13}C-NMR  (75 MHz, Methanol-d\textsubscript{4}) \(\delta\) 134.5, 130.3, 130.0, 44.4.

The data match those of a commercial sample and correspond to the literature values.\cite{26}
5. Mechanistic investigation

Kinetic experiments

General method for kinetic measurements

N-benzylideneaniline (0.9 mmol, 160 mg) and the aluminium catalyst 3 (10 mol%, 61 mg) were weighed under an argon atmosphere into a glass vial and dissolved in toluene (4.5 mL) and 250 μL pentadecane. The reaction mixture was thoroughly mixed and placed into an autoclave with a capillary device to take samples. The reactor was pressurized to 46 bar H₂ and heated to 100°C (final pressure 50 bar H₂) for 24 h, while the reaction is stirred. Aliquots were taken by a capillary; the first 20 drops of each sample were disposed of. 10 drops were collected and quenched with aqueous K₂CO₃ solution, extracted with ethyl acetate (3 times) and the combined organic phases were dried over Na₂SO₄. The drying agent was filtered off and the conversion was determined by GC-FID measurements with pentadecane as internal standard. To determine the order of reaction with respect to imine, catalyst and H₂, we have varied the concentration of the respective component while keeping the concentrations of other reagents constant. For reaction progress analyses, the samples were taken at 0 min, 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, 5 h, 8 h, 12 h and 24 h. The reaction progress analysis was determined two times by GC-FID and one time by NMR. The values differ only by 2% from each other.

Scheme 11. Reaction progress of the hydrogenation of N-benzylideneaniline with pre-catalyst 3 (10 mol%) in toluene (with pentadecane as internal standard).

For the determination of the reaction order in LiAlH₄, different concentration of LiAlH₄ (1 mol%, 4 mol%, 7 mol%, 10 mol%) were used to determine the reaction rate. The amount of N-benzylideneaniline (0.9 mmol, 160 mg), BIANH₂ (0.09 mmol, 10 mol%, 45 mg), toluene (4.5 mL) and pentadecane (250 μL) were kept constant. The setup of the reaction was the same as already described in the general method for kinetic experiments. To determine only the Hydride mechanism, the end of the plateau was determined by taking
samples from 4 h onwards. Whenever the conversion increased and the hydride mechanism was observed, the samples were taken every 60 min. For 10 mol%, the samples were taken at 5h, 6h, 7h, 8h and 10h. For the concentration of 7 mol%, the samples were taken every 90 min at 13h, 14.5 h, 16h, 17.5h, 19 h. For the concentration of 4 mol %, the samples were taken every 120 min at 16 h, 18 h, 20 h, 22 h and 24h. For the concentration of 1 mol%, the samples were taken every 20 h at 20 h, 40 h, 60 h, 80 h and 100 h. Regression fit with $R^2 = 0.9947$.

Scheme 12: Determination of the reaction order in LiAlH₄.

For the determination of the reaction order in BIANH₂, different concentration of BIANH₂ (0 mol%, 2.5 mol%, 5 mol%, 7.5 mol%, 10 mol%) were used to determine the reaction rate. The amount of N-benzylideneaniline (0.9 mmol, 160 mg), LiAlH₄ (1M solution in toluene, 90 μl, 0.09 mmol, 10 mol%), toluene (4.5mL) and pentadecane (250 μl) were kept constant. The setup of the reaction was the same as already described in the general method for kinetic experiments. To determine only the Hydride mechanism, the end of the plateau was determined by taking samples from 4h on. Whenever the conversion increased and the hydride mechanism was observed, the samples were taken every 60 min at 5 h, 6 h, 7 h, 8 h and 10 h. Regression fit with $R^2 = 0.9708$.

Scheme 13: Determination of the reaction order in $^{\text{Dipp}}$BIANH₂.
For the determination of the reaction order in 3, different concentrations of 3 (2.5 mol%, 5 mol%, 7.5 mol%, 10 mol%) were used to determine the reaction rate. The amount of N-benzylideneaniline (0.9 mmol, 160 mg), toluene (4.5mL) and pentadecane (250 μl) were kept constant. The setup of the reaction was the same as already described in the general method for kinetic experiments. To determine only the Hydride mechanism, the end of the plateau was determined by taking samples from 4h on. Whenever the conversion increased and the hydride mechanism was observed, the samples were taken. For 10 mol% and 7.5 mol % the samples were taken every 60 min at 5 h, 6 h, 7 h, 8 h and 10 h. For the 5 mol% the samples were taken every 120 min (15 h, 17 h, 19 h, 21 h, 23 h) and for 2.5 mol% the samples were taken every 180 min (20 h, 23 h, 26 h, 29 h, 32 h). Regression fit with R² = 0.9884.

Scheme 14: Determination of the reaction order in pre-catalyst 3.

For the determination of the reaction order in N-benzylideneaniline, different concentrations of N-benzylideneaniline (0,5 eq, 0,65 eq, 0,85 eq and 1 eq in respect to the normally used amount (0.9 mmol)) were used to determine the reaction rate. The amount of 3 (61 mg, 0.09 mmol) , toluene (4.5mL) and pentadecane (250 μl) were kept constant. The setup of the reaction was the same as already described in the general method for kinetic experiments. To determine only the Hydride mechanism, the end of the plateau was determined by taking samples from 4h on. Whenever the conversion increased and the hydride mechanism was observed, the samples were taken. The samples were taken every 60 min at 5 h, 6 h, 7 h, 8 h and 10 h. Regression fit with R² = 0.9608.
Scheme 15: Determination of the reaction order in N-benzylideneaniline.

For the determination of conversion towards time at different pressures of hydrogen, the amount of 3 (61 mg, 0.09 mmol), N-benzylideneaniline (0.9 mmol, 160 mg), toluene (4.5mL) and pentadecane (250 μl) were kept constant. The setup of the reaction was the same as already described in the general method for kinetic experiments. To determine only the Hydride mechanism, the end of the plateau was determined by taking samples from 4h on. Whenever the conversion increased and the hydride mechanism was observed, the samples were taken. For 50 bar and 40 bar the samples were taken every 60 min at 5 h, 6 h, 7 h, 8 h and 10 h. For 30 bar the samples were taken every 180 min at 12 h, 15 h, 18 h, 21 h, and 24h. For 20 bar H₂ the samples were taken very 240 min after 13, 17, 21, 25 and 29 h. Regression fit with $R^2 = 0.9947$.

Scheme 16: Determination of the conversion of N-Benzylideneaniline at different H₂ pressures.

For the reactions slope of LiAlH₄ (1M solution in toluene, 90 μl, 0.09 mmol, 10 mol%) the samples were taken at 5min, 30 min, 1h, 4h, 8h, 12 h and 24 h.
Scheme 17. Reaction slope of the hydrogenation of N-benzylideneaniline with LiAlH₄ (10 mol%) in toluene with pentadecane as internal standard.
Experiment for the reversibility of the reaction

In a young-NMR tube, the 1-(4-fluorophenyl)-N-phenylmethanimine (49.8 mg, 0.25 mmol, 1.0 eq), N-benzylaniline (45.8 mg, 0.25 mmol, 1.0 eq) and 3 (17 mg, 0.025 mmol, 10 mol%) were dissolved in benzene-\(d_6\) (0.7mL) and heated up to 60°C for 24 h. There was nearly no product formation of the N-(4-fluorobenzyl)aniline observed in the \(^1\)H and \(^{19}\)F NMR spectra. The small amount of n-(4-fluorobenzyl)aniline can be explained by the stoichiometric reduction of 1-(4-fluorophenyl)-N-phenylmethanimine with the hydrides of catalyst 3. There was no hint of the formation of N,1-diphenylmethanimine.

Reaction of 3 with N-benzylideneaniline in stoichiometric amounts

In a young-NMR tube, the N-benzylideneaniline (5.5 mg, 0.025 mmol, 1.1 eq) and 3 (17 mg, 0.25 mmol, 1.0 eq) were dissolved in thf-\(d_8\) (0.7mL). The \(^1\)H and \(^{13}\)C NMR Spectra auf the compounds shows a Signal for the CH2-group oft he Lithium amide at 4.5 ppm (\(^1\)H NMR) and 51.5 ppm (\(^{13}\)C NMR).

Scheme 18. \(^1\)H-NMR spectra of 3 and N-benzylideneaniline in thf- \(d_8\).
Scheme 19. $^{13}$C-NMR spectra of 3 and N-benzylideneaniline in thf- $d_8$. 
6. NMR-spectra

$^1$H-NMR spectra of 8a in Methanol-$d_4$.

$^{13}$C-NMR spectra of 8a in Methanol-$d_4$. 
$^1\text{H}-\text{NMR}$ spectra of 8b in Methanol-$d_4$.

$^{13}\text{C}[\text{H}]$-NMR spectra of 8b in Methanol-$d_4$. 

S33
$^1$H-NMR spectra of 8c in Methanol-$d_4$.

$^{13}$C(H)-NMR spectra of 8c in Methanol-$d_4$. 
$^{1}H$-NMR spectra of 8e in Methanol-$d_4$.

$^{13}C{[H]}$-NMR spectra of 8e in Methanol-$d_4$. 
$^1$H-NMR spectra of 8g in Methanol-$d_4$.

$^{13}$C{$\text{[H]}$}-NMR spectra of 8g in Methanol-$d_4$. 
$^1$H-NMR spectra of 8h in Methanol-$d_4$.

$^{13}$C{H}-NMR spectra of 8h in Methanol-$d_4$. 
\(^1\)H-NMR spectra of 8i in Methanol-\(d_4\).

\(^{13}\)C\{H\}-NMR spectra of 8i in Methanol-\(d_4\).
$^{1}$H-NMR spectra of 8j in Methanol-d$_4$.

$^{13}$C{H}-NMR spectra of 8j in Methanol-d$_4$. 
$^1$H-NMR spectra of 8k in Methanol-$d_4$.

$^{13}$C{H}-NMR spectra of 8k in Methanol-$d_4$. 
$^1$H-NMR spectra of 8I in Methanol-$d_4$.

$^{13}$C[H]-NMR spectra of 8I in Methanol-$d_4$. 

541
$^1$H-NMR spectra of 8m in Methanol-$d_4$.

$^{13}$C{H}-NMR spectra of 8m in Methanol-$d_4$. 
$^1$H-NMR spectra of 8n in Methanol-$d_4$.

$^{13}$C-$[H]$-NMR spectra of 8n in Methanol-$d_4$. 
\( ^1\text{H}-\text{NMR} \) spectra of 8o in Methanol-\( d_4 \).

\( ^{13}\text{C}\{\text{H}\}-\text{NMR} \) spectra of 8o in Methanol-\( d_4 \).
$^1$H-NMR spectra of 8p in Methanol-$d_4$.

$^{13}$C$^1$H-NMR spectra of 8p in Methanol-$d_4$. 
$^1$H-NMR spectra of 8q in Methanol-$d_4$.

$^{13}$C(H)-NMR spectra of 8q in Methanol-$d_4$. 
$^1$H-NMR spectra of 9 in Methanol-$d_4$.

$^{13}$C[H]-NMR spectra of 9 in Methanol-$d_4$. 
7. References

[1] S. Dastgir, K. S. Coleman, A. R. Cowley, M. L. H. Green, Organometallics 2010, 29, 4858–4870.

[2] A. Paulovicova, U. El-Ayaan, K. Shibayama, T. Morita, Y. Fukuda, Eur. J. Inorg. Chem. 2001, 2001, 2641–2646.

[3] I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, Russ. Chem. Bull. 2004, 53, 2744–2750.

[4] V. G. Sokolov, T. S. Koptseva, M. V. Moskalev, A. V. Piskunov, M. A. Samsonov, I. L. Fedushkin, Russ. Chem. Bull. 2017, 66, 1569;

[5] K. P. Guzen, A. S. Guarezemini, A. T.G. Órfão, R. Cella, C. M.P. Pereira, H. A. Stefani, Tetrahedron Lett. 2007, 48, 1845–1848.

[6] R. Torregrosa, I. M. Pastor, M. Yus, Tetrahedron 2005, 61, 11148–11155.

[7] R. Fertig, T. Irrgang, F. Freitag, J. Zander, R. Kempe, ACS Catal. 2018, 8, 8525–8530.

[8] D. Yadav, B. Bhanage, Synlett 2014, 25, 1611–1615.

[9] O.-Y. Lee, K.-L. Law, D. Yang, Org. Lett. 2009, 11, 3302–3305.

[10] E. C. Volpe, P. T. Wolczanski, E. B. Lobkovsky, Organometallics 2010, 29, 364–377.

[11] E. Dubost, C. Fossey, T. Cailly, S. Rault, F. Fabis, J. Org. Chem. 2011, 76, 6414–6420.

[12] T. J. Donohoe, L. P. Fishlock, P. A. Procopiou, Org. Lett. 2008, 10, 285–288

[13] J. Barluenga, A. Jiménez-Aquino, F. Aznar, C. Valdés, J. Am. Chem. Soc. 2009, 131, 4031–4041.

[14] M. Frias, A. C. Carrasco, A. Fraile, J. Aleman; Chem. Eur. J. 2018, 24, 3117–3121.

[15] A. L. Tillman, J. Ye, D. J. Dixon; Chem. Commun. 2006, 1191–1193.

[16] D. B. Bagal, R. A. Watile, M. V. Khedkar, K. P. Dhake, B. M. Bhanage, Catal. Sci. Technol. 2012, 2, 354–358.

[17] A. Afanasenko, S. Elangovan, M. C. A. Stuart, G. Bonura, F. Frusteri, K. Barta, Catal. Sci. Technol. 2018, 8, 5498–5505.

[18] J. P. Patel, A.-H. Li, H. Dong, V. L. Korlipara, M. J. Mulvihill, Tetrahedron Lett. 2009, 50, 5975–5977.

[19] N. L. Lampland, M. Hovey, D. Mukherjee, A. D. Sadow; ACS Catal., 2015, 5, 4219–4226.

[20] Y. Corre, X. Trivelli, F. Capet, J. P. Djukic, F. A. Niedercom, C. Michon;
ChemCatChem. 2017, 9, 2009-2017.

[21] C. J. Smith, C. D. Smith, N. Nikbin, S. V. Ley, I. R. Baxendale, Org. Biomol. Chem. 2011, 9, 1927–1937.

[22] C. Edinger, S. R. Waldvogel, Eur. J. Org. Chem. 2014, 5144-5148.

[23] H. Kato, I. Shibata, Y. Yasaka, S. Tsunoi, M. Yasuda, A. Baba, Chem. Commun. 2006, 4189–4191.

[24] S. M. Opalka, J. Kyoon Park, A. R. Longstreet, D. T. McQuade; Org. Lett. 2013, 15, 996–999.

[25] Z. Wang, X. Ye, S. Wei, P. Wu, A. Zhang, J. Sun, Org. Lett. 2006, 8, 999–1001.

[26] T. D. Nixon, M. K. Whittlesey, J. M.J. Williams, Tetrahedron Lett. 2011, 52, 6652–6654.