Supporting Information: Mechanistic Understanding of the Heterogeneous, Rhodium-Cyclic (Alkyl)(Amino)Carbene-Catalyzed (Fluoro-)Arene Hydrogenation

Daniel Moock,^[a] Mario P. Wiesenfeldt, ^{[a]‡} Matthias Freitag, ^{[a]‡} Satoshi

Muratsugu, ^[b] Satoru Ikemoto, ^[b] Robert Knitsch, ^[c] Jacob Schneidewind, ^[d] Wolfgang Baumann, ^[d] Andreas H. Schäfer, ^[e] Alexander Timmer,^[e] Mizuki Tada,^[b,f] Michael Ryan Hansen,^[c]Frank Glorius^[a]*

^[a]Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

^[b]Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602 Aichi, Japan

^[c]Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 28/30, 48149 Münster, Germany

^[d]Leibniz-Institut für Katalyse e. V., Albert-Einstein-Strasse 29a, 18059 Rostock, Germany ^[e]nanoAnalytics GmbH, Heisenbergstrasse 11, 48149 Münster, Germany

^[f]Research Center for Materials Science (RCMS) & Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602 Aichi, Japan

*E-mail: glorius@uni-muenster.de

Contents

(A) Materials and methods	3
(B) Preparation the of starting material	5
(C) Catalyst synthesis	6
(D) Synthesis of isotope labeled compounds	9
(E) Catalytic Reactions	15
(F) Kinetic NMR measurements-investigation of induction periods	s50
(G) XPS measurements	53
(H) X-ray absorption fine structure (XAFS) analysis of 4a	57
(I) Powder X-Ray diffraction (XRD)	59
(J) Brunauer-Emmett-Teller (BET) analysis	60
(K) Solid-state NMR studies	61
(L) Analysis of Rh(0) NPs	65
(M) References	71

(A) Materials and methods

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven- or heat-gun-dried glassware. Reaction temperatures are reported as the temperature of the medium surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: *n*-hexane (CaH₂), dichloromethane (CaH₂), diethyl ether (Na-benzophenone), THF (Na-benzophenone), toluene (CaH₂). Ethyl acetate (4 Å molecular sieves, MS) and methanol (3 Å MS) were purchased as dry solvents from commercial suppliers and stored over molecular sieves.

All hydrogenation reactions were carried out in Berghof High Pressure Reactors using hydrogen gas. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR, Combi-Blocks, Chempur and TCI Europe and used as received unless otherwise stated. Used silica gel was obtained from Merck (40–63 mesh) or Evonik (Aerosil 300) Heterogeneous catalysts were obtained from Johnson Matthey (5% Rhodium/C) or Alfa Aesar (5% Rhodium/Al₂O₃, Ruthenium/Al₂O₃, Ruthenium/C).

Analytical thin layer chromatography was performed on Polygram SIL G/UV₂₅₄ plates. Visualization was accomplished with short wave UV light, and KMnO₄ staining solutions followed by heating. Flash chromatography was performed on Merck silica gel (40–63 mesh) by standard technique eluting with solvents as indicated.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 μ m). The major signals are quoted in m/z with the relative intensity in parentheses. The method indicated as '50_40' starts with the injection temperature T0 (50 °C); after holding this temperature for 3 min, the column is heated by 40 °C/min to temperature T1 (290 °C or 320 °C). ESI mass spectra were recorded on a Bruker Daltonics MicroTof spectrometer. GC-FID analysis was

undertaken on an Agilent Technologies 7890B equipped with an HP-5 quartz column (0.32 mm x 30 m, film: 0.25 µm) using flame ionization detection. Method: Initial temperature 50 °C, hold 3 min, increment 10 °C/min, final temperature 300 °C, hold 3 min. ¹H and ¹³C and ¹⁹F NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in the indicated solvents. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; CD₂Cl₂: $\delta_H = 5.32$ ppm, $\delta_C = 53.8$ ppm, (CD₃)₂CO: $\delta_H = 2.05$ ppm, $\delta_C = 29.48$ ppm). ¹⁹F NMR spectra are not calibrated by an internal reference.

(B) Preparation the of starting material

Synthesis of 5 by TBS protection

The TBS protection of 4-fluorophenol was conducted according to the literature.¹

(C) Catalyst synthesis

Synthesis of rhodium-cyclic alkyl amino carbene (CAAC) catalyst 1

The employed rhodium-CAAC catalyst **1** was synthesized according to a modified literature procedure.² A complete procedure starting from commercial cyclohexane carboxaldehyde is given for the synthesis of the ¹³C-enriched complex ¹³C-**1** starting on page S6 of this supporting information.

General procedure 1: Synthesis of rhodium-CAAC derived, silica supported rhodium(0) nanoparticles (Rh/SiO₂)

Rh-CAAC **1** (indicated amount) was filled to an oven-dried 4 mL screw-cap vial equipped with a stirring bar and silica gel (indicated amount, Merck 40–63 mesh). *n*-Hexane (indicated amount) was added under argon atmosphere. The glass vial was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the pressure was set to 50 bar. The reaction mixture was stirred at 25 °C for 24 h. The pressure was carefully released and the autoclave was directly filled with argon. Under an inert atmosphere, the colorless supernatant was carefully removed and the black solid was washed with *n*-hexane (2 x 5 mL), DCM (3 x 5 mL) and EtOAc (3 x 5 mL). To remove residual EtOAc the black residue was washed two more times with *n*-hexane and dried in vacuo.

Synthesis of catalytically active Rh/SiO2 (4a)

Catalytically active Rh(0) NPs/SiO₂ **4a** were formed according to general procedure 1 by stirring Rh-CAAC **1** (2.9 mg, 5.0 μ mol) with silica gel (50 mg, corresponding to 1 wt% rhodium) in hexanes (1 mL).

Synthesis of catalytically active Rh/SiO₂ (4b)

Catalytically active Rh(0) NPs/SiO₂ **4b** were formed according to general procedure 1 by stirring Rh-CAAC **1** (2.9 mg, 5.0 μ mol) with silica gel (150 mg, corresponding to 0.33 wt% rhodium) in hexanes (1 mL) for 3 h.

Synthesis of catalytically active Rh/SiO₂ (4c)

Catalytically active Rh(0) NPs/SiO₂ **4c** were formed according to general procedure 1 by stirring Rh-CAAC **1** (2.9 mg, 5.0 μ mol) with silica gel (150 mg, corresponding to 0.33 wt% rhodium) in hexanes (1 mL).

Synthesis of catalytically active Rh/SiO₂ (4d)

Catalytically active Rh(0) NPs/SiO₂ **4d** were formed according to general procedure 1 by stirring Rh-CAAC **1** (2.9 mg, 5.0 μ mol) with silica gel (450 mg, corresponding to 0.11 wt% rhodium) in hexanes (1 mL).

<u>General procedure 2: Preparation of ligandless, silica-supported rhodium(0)</u> nanoparticles by an impregnation method (**4e–4g**)

SiO₂ (indicated amount, Aerosil 300, calcined at 473 K for 2 h) was suspended in 30 mL of H₂O. An aqueous solution of Rh(NO₃)₃·H₂O (indicated amount, Aldrich, ~36% Rh basis, 2.5 mL total volume) was added to this suspension, and was dried at 343 K. After grinding, the obtained powder was dried at 473 K for 2 h in vacuo and reduced at 623 K for 2 h under 0.53 bar of H₂.

Synthesis of ligandless Rh/SiO2 4e with 0.87 wt% rhodium

Rh/SiO₂ **4e** was synthesized according to general procedure 2 by impregnating a solution of Rh(NO₃)₃·H₂O (56.7 mg, 0.20 mmol) to a suspension of SiO₂ (2.0 g) in water.

Synthesis of ligandless Rh/SiO2 4f with 5.1 wt% rhodium

Rh/SiO₂ **4f** was synthesized according to general procedure 2 by impregnating a solution of Rh(NO₃)₃·H₂O (147.8 mg, 0.51 mmol) to a suspension of SiO₂ (1.0 g) in water.

Synthesis of ligandless Rh/SiO2 4g with 9.9 wt% rhodium

 Rh/SiO_2 **4g** was synthesized according to general procedure 2 by impregnating a solution of $Rh(NO_3)_3 \cdot H_2O$ (312.0 mg, 1.08 mmol) to a suspension of SiO_2 (1.0 g) in water.

(D) Synthesis of isotope labeled compounds

The synthesis of the isotope labeled complex ¹³C-1 started from commercially available ¹³C-isotope labeled benzoic acid **13**. Our previously developed protocol was used to hydrogenate the aromatic ring to obtain cyclohexylcarboxylic acid **14**.³ After isopropylester (**15**) formation, reduction to the aldehyde **16** was conducted. The established route was followed to obtain the desired complex ¹³C-1.



Scheme S1: Synthesis of isotope labeled Rh-CAAC ¹³C-1.

In a glass cylinder 2.96 g of isotope labeled benzoic acid **13** (24.0 mmol, 1.00 equiv.) and 137 mg of Rh-CAAC **1** (0.240 mmol, 1.00 mol%) were dissolved in 48 mL dry DCM (0.5 M) and 2.4 g of powdered and activated 4 Å molecular sieves were added. The glass cylinder was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the pressure was set to 50 bar and the mixture was stirred at 25 °C for 24 h. After careful release of pressure, the obtained black suspension was filtered through celite, eluted with 100 mL of DCM and concentrated in vacuo. The obtained crude product was filtered through celite again and eluted with 100 mL diethyl ether and

concentrated in vacuo to obtain the desired product **14** in quantitative yield as a slightly yellow oil.

2.32 g of **14** (15.0 mmol, 1.00 equiv.) were dissolved in 18 mL isopropanol and stirred in a high-pressure screw-cap vial. Under argon atmosphere 100 μ L of concentrated H₂SO₄ were added, the vessel was sealed and heated to 80 °C for 17 h. Upon cooling to r.t. ice was added and 30 mL of saturated NaHCO₃ solution were added. The aqueous phase was extracted with diethyl ether (3 x 50 mL) and the combined organic fractions were washed with brine (50 mL), dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash chromatography using a mixture of ethyl acetate in pentane with a gradient of 1:99 to 100:0 (ethyl acetate/pentane, *v/v*). The desired product **15** was obtained as a colorless oil in 69% yield (1.78 g, 10.4 mmol). 19% of the starting material was recovered. Obtained analytical data was consistent with the literature.⁴

15 ¹H NMR (300 MHz, CDCl₃) δ 5.13–4.90 (m, 1H), 2.24 (tdt, *J* = 11.0, 7.2, 3.6 Hz, 1H), 1.94–1.83 (m, 2H), 1.80–1.69 (m, 2H), 1.67–1.59 (m, 1H), 1.49–1.35 (m, 2H), 1.34–1.24 (m, 2H), 1.21 (d, *J* = 6.2 Hz, 6H) 1.21–1.17 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ <u>175.9</u>, 29.2 (d, *J* = 1.6 Hz), 26.0, 25.6, 25.6, 22.0, 15.4.

Isotope labeled cyclohexanecarboxaldehyde **16** was synthesized according to a modified literature procedure.⁵ To a solution of ester **15** (2.74 g, 16.0 mmol, 1.00 equiv.) in 160 mL dry THF, 51 mL of a 0.44 M solution of lithium di*iso*butyl-*t*-butoxyaluminum hydride in THF was added dropwise at 0 °C under an argon

atmosphere. The resulting mixture was allowed to warm to r.t. and stirred overnight. 160 mL of a 1 N HCl solution was added to the reaction mixture and it was extracted with diethyl ether (2 x 160 mL). The organic layer was dried over MgSO₄ and the product mixture concentrated under reduced pressure. The desired product **16** was obtained as colorless oil in sufficient purity and 90% yield (1.62 g, 14.5 mmol). Due to its high volatility the product was directly used in the next step without further purification. Obtained analytical data was consistent with the literature.⁶

 $\stackrel{\circ}{H} \longrightarrow 16^{-1}\text{H NMR (400 MHz, CDCl_3) } \delta 9.61 (d, J = 168.1 \text{ Hz}, 1\text{H}), 1.98-1.83 (m, 1\text{H}), 1.82-1.59 (m, 4\text{H}), 1.53-1.12 (m, 6\text{H}).$

The following steps of Rh-CAAC **1** synthesis were conducted according to a modified literature procedure.² NMR data is given for proof of successful labelling with ¹³C and is in good accordance with the literature.

A suspension of cyclohexane carboxaldehyde **16** (1.62 g, 14.4 mmol, 1.00 equiv.), 2,6-diisopropylaniline (2.55 g, 14.4 mmol, 1.00 equiv.), and MgSO₄ (2.60 g) in toluene (29 mL, 0.5 M) were refluxed overnight in an oven-dried Schlenk flask under argon atmosphere. Upon full conversion of the aldehyde, the mixture was filtered and all volatiles were removed under reduced pressure. The crude mixture was dissolved in a small amount of diethyl ether, filtrated over a plug of neutral alumina and volatiles were removed under reduced pressure, yielding aldimine **17** as an off-white powder in 31% yield (1.22 g, 4.46 mmol).



17 ¹H NMR (300 MHz, CDCl₃) δ 7.48 (dd, J = 155.2, 4.9 Hz, 1H), 7.13–7.01 (m, 3H), 2.92 (hept, J = 6.9 Hz, 2H), 2.52–2.39 (m, 1H), 2.04–1.91 (m, 2H), 1.88–1.78 (m, 2H), 1.78–1.68 (m, 2H), 1.46–1.36

(m, 3H), 1.30–1.24 (m, 1H), 1.19–1.10 (m, 12H).

Without further purification, the aldimine **17** (1.20 g, 4.40 mmol, 1.00equiv.) was dissolved in dry diethyl ether (15 mL) under an atmosphere of argon in a dry Schlenk flask. A solution of *n*-butyl lithium (4.62 mmol, 1.05 equiv.) in diethyl ether (2.89 mL, 1.6 M) was added dropwise to the solution of the aldimine at -78 °C. After stirring for 15 min at this temperature, the mixture was allowed to warm up to room temperature and stirred for further three hours at that temperature. At -78 °C, 3-bromo-2-methylpropene (0.653 g, 4.84 mmol, 1.10 equiv.) was added via a syringe in one go. Stirring was continued for 15 min at -78 °C after which the mixture was allowed to warm up to room temperature. After filtration through neutral alumina, elution with pentane and removal of volatiles under reduced pressure the desired alkylation product **18** was obtained as a light-yellow oil in 63% yield (0.911 g, 2.79 mmol).



3H), 1.68–1.50 (m, 6H), 1.44–1.31 (m, 2H), 1.16 (d, *J* = 6.9 Hz, 12H).

The obtained oil of **18** was dissolved in acetonitrile (5 mL) in a dry Schlenk flask. A solution of 4 M HCl in 1,4-dioxane (1.4 mL, 5.5 mmol, 2.0 equiv.) was added at -78 °C dropwise. After stirring for further 15 min at this temperature, the reaction mixture was heated to 50 °C and stirred overnight. All volatiles were removed in vacuo and the residue was washed using pentanes and diethyl ether. Pyrrolidinium salt ¹³C-**2** was obtained as a white powder (0.87 g, 2.4 mmol, 88%).



¹³C-**2** ¹H NMR (400 MHz, CDCl₃) δ 10.89 (d, J = 190.9 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 2.72–2.54 (m, 4H), 2.41 (d, J = 2.1 Hz, 2H), 1.98–1.89 (m, 2H), 1.75–1.66 (m, 3H), 1.64–1.57 (m, 1H), 1.53 (s, 6H), 1.48–1.38 (m, 2H), 1.34 (d, J = 6.7

Hz, 6H), 1.28 (d, J = 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ <u>193.7</u>, 144.6, 131.9,

129.0, 125.4, 82.4 (d, *J* = 4.8 Hz), 53.6 (d, *J* = 35.7 Hz), 45.8, 33.8, 30.1, 29.1, 26.9, 24.2, 22.3, 21.4 (d, *J* = 3.3 Hz).

Rhodium-COD-chloride precursor (247 mg, 0.500 mmol, 0.50 equiv.), pyrrolidinium salt 13 C-2 (381 mg, 1.05 mmol, 1.05 equiv.) and KHMDS (299 mg, 1.50 mmol, 1.50 equiv.) were added to a Schlenk tube under argon atmosphere. Dry THF (25 mL) was added dropwise over 20 min to the solids at -78 °C. The suspension was stirred for 10 min at -78 °C, after which the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. After stirring for 16 h at room temperature, the suspension was filtered, concentrated, dry loaded on silica gel and purified twice by column chromatography (pentane/diethyl ether = 9:1 and pentane/diethyl ether = 19:1). After evaporation of the solvents, the complex was precipitated from a concentrated solution in dichloromethane with pentane to yield the desired complex as yellow powder in 50% yield (284 mg, 0.496 mmol).



¹³C-1 ¹H NMR (500 MHz, CDCl₃) δ 7.45 (dd, J = 7.8, 1.8 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.14 (dd, J = 7.5, 1.8 Hz, 1H), 5.24 (t, J = 8.2 Hz, 1H), 4.62 (q, J = 7.8 Hz, 1H), 3.90 (hept, J = 6.4 Hz, 1H),

3.48–3.41 (m, 1H), 2.93–2.84 (m, 2H), 2.64–2.54 (m, 2H), 2.54–2.46 (m, 1H), 2.31– 2.25 (m, 1H), 2.18–2.10 (m, 1H), 2.04–1.98 (m, 2H), 1.97–1.91 (m, 1H), 1.82–1.76 (m, 3H), 1.74 (d, J = 6.4 Hz, 3H), 1.71–1.64 (m, 1H), 1.61–1.52 (m, 3H), 1.50 (s, 3H), 1.49–1.29 (m, 5H), 1.25 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 6.7 Hz, 3H), 1.20 (s, 3H), 0.95 (d, J = 6.7 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ <u>273.0</u> (d, J = 44.6 Hz), 148.3 (d, J = 1.1 Hz), 146.4 (d, J = 1.7 Hz), 137.0 (d, J = 2.6 Hz), 129.0, 126.5, 124.1, 101.3 (dd, J = 6.1, 3.1 Hz), 98.3 (dd, J = 5.4, 5.4 Hz), 78.2 (d, J = 2.2 Hz), 71.8 (d, J = 15.2 Hz), 64.8 (d, J = 21.5 Hz), 64.7 (d, J = 14.5 Hz), 45.7, 41.8 (d, J = 2.0 Hz), 38.1 (d, J = 1.7Hz), 35.0, 33.7, 31.0, 30.3, 28.9, 28.3, 28.0, 26.6, 26.4, 26.1, 25.9, 25.5, 24.6, 24.1 (d, J = 3.4 Hz), 22.6 (d, J = 4.0 Hz).



Synthesis of isotope labeled pyrrolidine species ¹³C-3 started from ¹³C-2. 47.4 mg of lithium aluminum hydride (1.25 mmol, 2.50 equiv.) were added portion wise to a solution of 182 mg of ¹³C-2 (500 µmol, 1.00 equiv.) in 1 mL dry THF at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, allowed to warm to r.t. and stirred for another 16 h. The mixture was filtered through celite, mixed with 4 mL of ice water and extracted with DCM (3 x 5 mL). The combined organic fractions were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified via flash chromatography using pentanes. The clean product ¹³C-3 was obtained as a white solid in 82% yield (134 mg, 409 µmol).

The synthesis of the unlabeled species was conducted with the same protocol. Obtained analytical data was consistent with the literature.⁷



¹³C-3 ¹H NMR (300 MHz, CDCl₃) δ 7.22–7.15 (m, 1H), 7.14–7.09 (m, 2H), 3.61 (hept, J = 6.9 Hz, 2H), 3.24 (d, J = 135.0 Hz, 2H), 1.81 (d, J = 2.1 Hz, 2H), 1.72–1.61 (m, 2H), 1.54 (tq, J = 6.6, 3.9, 3.4 Hz, 4H), 1.42 (d, *J* = 10.6 Hz, 4H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.12–1.08 (m, 12H);

¹³C NMR (75 MHz, CDCl₃) δ 152.4, 139.3, 126.4, 123.9, 64.9, 62.3 (d, J = 5.0 Hz), 41.5 (d, *J* = 35.2 Hz), 39.5, 28.8, 28.4, 26.6, 26.2, 24.2 (d, *J* = 2.0 Hz), 23.2.

(E) Catalytic Reactions

General procedure 3: Catalytic hydrogenation reactions

The catalyst (indicated amount) and solid additives (if applicable) were filled into an oven-dried 4 mL screw-cap vial, equipped with oven-dried silica gel (if applicable). Solvent (indicated amount), substrate (indicated amount, 1.00 equiv.) and liquid additives (if applicable) were added under argon atmosphere. The glass vial was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the pressure was set to 50 bar and the mixture was stirred at 25 °C for 24 h. Upon completion of the reaction time, the pressure was carefully released and the reaction outcome was analyzed.

Evaluation of the AgBF₄-activated catalyst in the hydrogenation of the model substrate 5

Following a procedure by Bullock *et al.* a hydrogenation of the test substrate 5 was carried out in *n*-hexane or THF, respectively.⁸

Experimental procedure: Rh-CAAC 1 (8.6 mg, 15 μ mol, 3.0 mol%) and silver tetrafluoroborate (2.9 mg, 15 μ mol, 3.0 mol%) were filled to an oven-dried 4 mL screw-cap vial equipped with a stirring bar. Solvent (1 mL) was added under argon atmosphere and the resulting mixture was stirred for 30 min at r.t. The reaction mixture was filtered through a glass frit syringe directly into the reaction vessel (4 mL screw cap vial) and the starting material **5** (118 μ L, 113 mg, 500 μ mol, 1.00 equiv.) was added. The glass vial was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the pressure was set to 7 bar. The reaction mixture was stirred at 25 °C for 24 h. The pressure was carefully released and 1.00 equiv. of mesitylene (60.0 mg,

 $69\,\mu$ L, $500\,\mu$ mol) was added as internal standard and the reaction outcome was analyzed via GC-FID.

Results:



Table S1: Control for catalyst activation with AgBF₄ for substrate 5.

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. Numbers do not add up to unity, because cyclohexane and cyclohexanol are formed as byproducts, which co-elute with the solvent and thus cannot be detected. ^{*a*}Optimized conditions using Rh-complex precursor: 1 mol% Rh-CAAC **1**, SiO₂ (1 wt% Rh), 50 bar H₂, 25 °C, 24 h.

<u>Discussion</u>: In the reaction using *n*-hexane as solvent, mainly starting material was recovered, with only traces of a TBS deprotected byproduct (**19**) being formed (**Table S1**, entry 3). The reaction using THF as solvent gave 40% yield of the desired product **6**, with **7** and **20** being major byproducts, which were formed in 19% and 20% yield, respectively (entry 2). This is a significantly lower yield of the desired product **6** when compared to our standard reaction conditions with 1 mol% catalyst loading (87%, entry 1) and drastically increased formation of byproduct (compared to 5% **7** and 4% **20** under standard conditions, entry 1).

This result clearly indicates the important role of the activation of the catalyst precursor **1** with silica gel as support material for substrates bearing challenging functional groups.

Evaluation of the AgBF₄-activated catalyst in the hydrogenation of hexafluorobenzene **10**

A similar control reaction was performed using hexafluorobenzene 10 as a substrate.

Experimental procedure: To a mixture of Rh-CAAC 1 (5.1 mg, 9.0 μ mol, 3.0 mol%) and silver tetrafluoroborate (1.8 mg, 9.0 μ mol, 3.0 mol%) dry THF (1 mL) was added under an argon atmosphere and the resulting mixture was stirred for 30 min at r.t. The reaction mixture was filtered through a glass frit syringe directly into the reaction vessel and the solvent was removed under reduced pressure. *n*-Hexane (2 mL) and the starting material **10** (35.0 μ L, 55.8 mg, 300 μ mol, 1.00 equiv.) were added. The resulting mixture was pressurized with 50 bar hydrogen and stirred at 25 °C for 24 h. Upon completion of the reaction time the pressure was carefully released, the reaction mixture was filtered through a glass frit (elution with dichloromethane and acetone) and the solvent was removed under reduced pressure. Traces of a solid material were isolated, but ¹H- and ¹⁹F-NMR revealed no product formation.

<u>Discussion</u>: In agreement with the results obtained for the hydrogenation of model substrate **5**, the reaction conditions using $AgBF_4$ were not competitive with the ones using silica gel as additive (88% yield under the optimized reaction conditions,⁹ and ca. 40% using the ones described in this paper (page S48).

Test of different support materials

To evaluate the influence of the supporting material 4 Å crushed molecular sieves and different types of alumina were used in hydrogenations with in situ generation of the active catalyst.

Experimental procedure: Rh-CAAC 1 (2.9 mg, 5.0 μ mol, 5 mol%) was reacted with oven-dried support material (50 mg, 1 wt%) and 100 μ mol of substrate 5 (23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) under 50 bar H₂ according to general procedure 3. After release of the pressure, mesitylene (14.0 μ L, 12.1 mg, 100 mmol, 1.00 equiv.) was added and the yield was analyzed by GC-FID (**Table S2**).

Results:





Entry	Additive	Conversion	Yield of 6 [%]	Yield of 7 [%]
			(d.r.)	
1	Silica gel	>99	90 (94:6)	3
2	Crushed 4 Å molecular sieves	>99	96 (94:6)	4
3	Neutral aluminum oxide	>99	87 (94:6)	15
4	Acidic aluminum oxide	>99	84 (94:6)	9
5	Basic aluminum oxide	>99	82 (94:6)	12

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard.

<u>Discussion</u>: All investigated support materials allow for the chemoselective hydrogenation of the test substrate **5**. With neutral, acidic and basic alumina (entries 3–4) higher amounts of defluorination were detected when compared to silica gel and crushed molecular sieves (entries 1 and 2). With silica gel and molecular sieves the same low amount of defluorinated by-product **7** was detected. The yield for molecular sieves as support material was the highest with 96% (entry 2), which is probably due to

the improved preservation of the OTBS group which was observed to be deprotected with acidic silica gel (the resulting by-product cannot be detected via GC-FID). However, both reaction outcomes for entries 2 and 3 can be considered very similar and silica gel was chosen as support material for this study.

Mercury droplet poisoning

Mercury droplet poisoning is a test to distinguish a heterogeneous from a homogenous catalyst system. The argument is as follows: only heterogeneous catalysts should form an amalgam with mercury and as such be poisoned by the presence of a mercury droplet. Homogeneous catalysts are generally not poisoned by mercury. However, this test is notoriously difficult to reproduce.¹⁰

Experimental procedure:



Rh-CAAC 1 (2.9 mg, 5.0 μ mol, 1.0 mol%), silica gel (50 mg, 1 wt%), dry *n*-hexane (1 mL) and substrate **5** (118 μ L, 113 mg, 500 μ mol, 1.00 equiv.) were reacted according to general procedure 3 in presence of one droplet of liquid mercury. Importantly, the mixture was stirred vigorously prior to the transfer to the autoclave. After release of the pressure, the formation of a black solid residue was observed. 1.00 equiv. of mesitylene (69.0 μ L, 60.0 mg, 500 μ mol) was added as internal standard and the reaction outcome was analyzed via GC-FID.

<u>Discussion</u>: No conversion could be observed, which indicates poisoning via formation of an amalgame, thus pointing to a heterogeneous nature of the catalyst. It is however noteworthy that in analogous experiments some conversion was observed. We attribute this to an incomplete poisoning of the catalyst by mercury due to the use of an insufficient amount or insufficient stirring prior to the reaction. Note that 0.1 mol% of the active catalyst are enough to catalyze the complete hydrogenation of the model substrate **5**.

Substoichiometric poisoning with tetrahydrothiophene (THT)

Substroichiometric poisoning studies were conducted using THT. Heterogeneous active catalysts are expected to be completely deactivated by a substoichiometric amount of the catalyst poison since in large heterogenous particles, only a fraction of the rhodium atoms will be exposed to the surface, which is a requirement for catalytic activity.

Experimental procedure: A stock solution of THT (2.2 μ L, 2.2 mg, 25 μ mol) in dry *n*-hexane (10 mL) was prepared in an oven-dried Schlenk flask under argon atmosphere. Rh-CAAC **1** (2.9 mg, 5.0 μ mol, 5.0 mol%), was filled into an oven-dried 9 mL screwcap vial, equipped with 50 mg oven-dried silica gel (5 wt%). Dry *n*-hexane and THT stock solution were added to the vial adding up to a volume of 2 mL, followed by 100 μ mol of substrate **5** (23.5 μ L, 22.6 mg, 1.00 equiv.) under argon atmosphere. The glass vial was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the pressure was set to 50 bar and the mixture was stirred for 24 h at 25 °C. Upon completion of the reaction time the pressure was carefully released and 1.00 equiv. of mesitylene (14.0 μ L, 12.1 mg, 100 μ mol) was added as internal standard and the reaction outcome was analyzed via GC-FID.

S21

Results:

5

6

7

2.5

3.5

5.0

Table S3: Substoichiometric	poisoning	of the catalyst with	tetrahydrothiophene	(THT).
		2		· /

	F 5 5	h-CAAC 1 (5 mol%) 50 mg SiO ₂ (5 wt%) THT (n mol%) 50 bar H ₂ 25 °C, 24 h <i>n</i> -hexane (0.05 M)	OTBS + 0 6 7	TBS
Entry	ТНТ	Conversion	Yield of 6 [%]	Yield of 7 [%]
	(mol%)		(d.r. cis:trans)	
1	0	>99	86 (94:6)	4
2	0.25	>99	85 (93:7)	4
3	0.50	>99	87 (91:9)	5
4	1.5	>99	83 (91:9)	6

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. Numbers do not add up to unity, because cyclohexane and cyclohexanol are formed as byproducts, which co-elute with the solvent and thus cannot be detected.

86

0

0

71 (90:10)

_

_

6

<u>Discussion</u>: A reduced conversion was observed using as low as 2.5 mol% of THT (**Table S3**, entry 5) and a substoichiometric amount of 3.5 mol% of the poison completely suppressed catalytic activity. Note that 5 mol% catalyst was used and as little as 0.1 mol% are sufficient to catalyze complete conversion of the substrate under the optimized reaction conditions. Furthermore, we have identified sulfur-containing compounds in our previous studies to be strong catalyst poisons. It is also noteworthy that THT cannot be hydrogenated during the reaction, which is different for benzothiophene. Hence, this experiment strongly supports a heterogeneous catalysis pathway.

<u>Maitlis' test – catalyst recovery by filtration and evaluation of the catalytic activity</u> for model substrate <u>5</u>

To evaluate the recyclability of the catalytic species, the performance of the active catalyst generated in situ from Rh-CAAC precursor **1** was compared to that of the recovered residue after hydrogenation.

Experimental procedure: Rh-CAAC 1 (2.9 mg, 5.0 μ mol, 5 mol%) was reacted with oven-dried silica gel (50 mg, 1 wt%) and 100 μ mol of substrate 5 (23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) under 50 bar H₂ according to general procedure 3 (**Table S4**, entry 1). After release of the pressure, mesitylene (14.0 μ L, 12.1 mg, 100 mmol, 1.00 equiv.) was added and the yield was analyzed by GC-FID (**Table S3**, entry 1).

The obtained black suspension from this reaction was then further treated as described in general procedure 1.

The isolated solid (Rh/SiO₂ **4**) was then used as catalyst for the hydrogenation of substrate **5** (100 μ mol, 23.5 μ L, 22.6 mg, 1.00 equiv.) in *n*-hexane (1 mL) according to general procedure 3. After the pressure was carefully released, mesitylene (14.0 μ L, 12.1 mg, 100 mmol, 1.00 equiv.) was added, again and the yield was analyzed by GC-FID (entry 2).

Residue **4a**, which was synthesized without substrate, was obtained according to general procedure 1 as described on page S6. The reaction with the isolated solid was conducted according to general procedure 3 with otherwise identical chemicals and amounts compared to the previous experiment for the residue prepared in presence of substrate (**4**).

Results:

	F F $OTBS$ F $OTBS$ OTB	F OTBS	+ OTBS	
	5	6	7	
Entry	Catalyst	Conversion	Yield of 6	Yield of 7
			[%] (d.r.)	[%]
1	Rh-CAAC 1 and SiO ₂	>99	90 (94:6)	3
2	Residue 4 obtained from entry 1	>99	91 (94:6)	4
3	Residue 4a obtained without substrate	>99	89 (94:6)	3

Table S4: Catalytic results obtained in Maitlis' test for substrate 5.

D1

(F 10()

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard.

<u>Discussion</u>: Within the error of measurement, all obtained yields were identical. This indicates that the active catalyst is contained in the black residue obtained after the reaction and therefore is most likely heterogeneous in nature. The active catalyst can be recycled without loss of activity. Additionally, no influence of the substrate on the formation of the active catalyst could be observed.

<u>Maitlis' test – catalyst recovery by filtration and evaluation of the catalytic activity</u> for hexafluorobenzene **10**

Experimental procedure: The catalytic reactions with the in situ prepared catalyst and the catalysts prepared in presence (4') and absence (4a) of substrate were conducted according to general procedures 1 and 3 analogous to the experiment described for the Maitlis' test conducted with substrate 5 (vide supra). After completion of the catalytic reaction, the reaction mixture was filtered through a glass frit and eluted with DCM (30 mL) and acetone (30 mL). The raw product was dryloaded on silica gel and purified using flash chromatography (DCM/acetone, 100:0 to 90:10, v/v) and products 11 and 12 were isolated as pure, white solids.

Results:

	$F + F = F = 1 \mod \text{catalyst} \\ 50 \text{ bar H}_2 \\ F + F = 25 \text{ °C}, 24 \text{ h} \\ n\text{-hexane (0.1 M)} $	$F \xrightarrow{F} F$	+ F	F
	10 0.1 mmol	11	12	
Entry	Catalyst	Conversion	Yield of 11	Yield of 12
			[%]	[%]
1	Rh-CAAC 1 and SiO ₂	>99	39	22
2	Residue 4' obtained from entry 1	>99	42	38
3	Residue 4a obtained without substrate	>99	41	41

Table S5: Catalytic results obtained in Maitlis' test for substrate 10.

<u>Discussion</u>: Analogous to the Maitlis' test conducted for model substrate **5**, identical yields (within experimental error) were obtained for the far more difficult to reduce substrate hexafluorobenzene **10**. Note that a catalyst loading of 1 mol% was used for an improved experimental comparison with the analyzed catalyst batches (vide supra), which performs less good than our previously optimized catalyst loading of 0.5 mol% for this substrate. Nevertheless, this experiment strongly supports the heterogeneous nature of the active catalyst.

<u>Collman's test – 3-phase-reaction</u>

As an additional experiment to test if the catalytically active species is hetero- or homogeneous in nature, a 3-phase-reaction was conducted. With this test the interaction of the catalyst with a substrate bound to a solid phase can be observed. A lack of this interaction would hint to a solid, undissolved catalyst species. Wang resin **21** was chosen as the solid, to which different substrates were attached to.

Experimental procedure:



To a mixture of Wang-resin (**21**, 1.00 g, ~1.5 mmol, ~1.0 equiv.), phenol (4.50 mmol, 3.00 equiv.) and triphenyl phosphine (1.18 g, 4.50 mmol, 3.00 equiv.) in 4methylmorpholine (NMM, 10 mL) in a 25 mL round bottom flask equipped with a stirring bar, 883 μ L of diisopropyl azodicarboxylate (DIAD, 910 mg, 4.50 mmol, 3.00 equiv.) were added dropwise under vigorous stirring. The resulting mixture was supersonicated for 1 h and then further stirred overnight at 25 °C. The mixture was filtered through a glass filter and washed with THF (20 mL), DCM (20 mL), MeOH (20 mL), water (20 mL), MeOH (20 mL) and DCM (20 mL). After removal of solvent residues under reduced pressure the success of the reaction was verified by weighing the loaded resin.



Cleavage was performed by stirring 52 mg of the loaded resin with 4 mL of trifluoroacetic acid (TFA) in 2 mL of DCM in a 4 mL screw-cap vial overnight at 25 °C.

The solid resin was separated by filtration and washed with DCM. The combined filtrate was washed with saturated NaHCO₃ solution, dried over MgSO₄ and concentrated under reduced pressure. 6.1 mg of methyl 4-hydroxybenzoate **25** were isolated in a mixture with the hydrolyzed carboxylic acid **26** in a ratio of 85:15, corresponding to a loading of the resin of 0.77 mmol/g. The obtained NMR data is in good accordance with the literature.^{9,10} In the case of the fluorinated compound no product could be isolated, probably because of its volatility.

0.30H, acid), 6.91–6.83 (m, 1.7H, ester), 6.15–5.50 (bs, 0.85H, ester), 5.83 (s, 0.15H, acid), 3.90 (s, 0.15H, acid), 3.89 (s, 2.55H, ester).



Rh-CAAC 1 (1.2 mg, 2.1 μ mol) was filled into an oven-dried 9 mL screw-cap vial, equipped with 50 mg oven-dried 4 Å molecular sieves, 100 mg resin (77 μ mol, 21 or 23) and dry *n*-hexane (2 mL). In the first two experiments, 100 μ mol of 5 (23.5 μ L, 22.6 mg, 1.00 equiv.) was added to the vial under argon atmosphere. The glass vial was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave

was pressurized and depressurized with hydrogen gas three times before the pressure was set to 50 bar and the mixture was stirred at 25 °C for 24 h. Upon completion of the reaction time the pressure was carefully released and 1.00 equiv. of mesitylene (14.0 μ L, 12.1 mg, 100 μ mol) was added as internal standard and the reaction outcome was analyzed via GC-FID. The solid residue was separated via filtration and washed with *n*-hexane.

<u>Results and Discussion</u>: Formation of a black residue was observed in all three reactions. Hydrogenation of dissolved model substrate **5** gave complete conversion (observed *via* GC-FID) in the first two reactions. Hence, these reactions were not hindered by the present resin species. At the same time, no hydrogenation of the resinbound species could be detected after cleavage in all three solvents (starting material was recovered in near quantitative amounts). This is a strong hint for a heterogeneous, non-dissolved catalyst species, since a reaction between two solid phases in a suspension is unlikely to occur.

Particle formation from Rh complexes bearing CAAC ligands 8 and 9

To test the influence of the CAAC ligand on the appearance and performance of the resulting catalyst, rhodium complexes with ligands **8** and **9** were used as catalyst precursors. The corresponding residues were tested for their catalytic activity.

<u>Experimental procedure:</u> Rh-CAAC(COD)Cl complexes **28** (10 μ mol, 5.2 mg) or **29** (10 μ mol, 6.4 mg) and SiO₂ (100 mg, 1 wt% Rh) were reacted according to general procedure 1 and black residues **4h** and **4i** were obtained.

<u>Results:</u> The obtained black residues were analyzed with transmission electron microscopy (TEM, see p. S65). Analysis shows the formation of a metallic residue in both cases. To compare the amount of small particles formed, the fraction of particles smaller or equal to 3 nm within all analyzed particles ($N_{s/all}$) was calculated. Using complex **28** as precursor, nanoparticles **4h** were obtained, with more particles being of a small size ($N_{s/all} = 16\%$) than those of the standard catalyst **4a** ($N_{s/all} = 2\%$, **Figure S1a**) When using complex **29** as a precursor, larger aggregates were obtained predominantly ($N_{s/all} = 2\%$, **Figure S1b**).



Figure S1: Alternative CAAC ligands **8** and **9**, their corresponding Rh(COD)Cl-complexes **28** and **29** (left), TEM images of residues **4h** and **4i** obtained by stirring these complexes with SiO₂ under hydrogen pressure (center) and histograms of obtained particle sizes of **4h** and **4i**, respectively (right, 211 and 122 particles were examined, respectively).

<u>Discussion</u>: Under otherwise identical conditions, the different precursors produced particles with different appearance. This shows that the CAAC ligand in the precursor complex has an influence on the properties of the obtained particles.

Catalytic performance of 28, 29, 4h and 4i in the hydrogenation of test substrate 5

The performances of the complexes **28** and **29** and that of the obtained corresponding particles **4h** and **4i** were evaluated (**Table S6**).

<u>Experimental procedure:</u> Complex **28** (0.53 mg, 1.0 μ mol, 1 mol%) or **29** (0.66 mg, 1.0 μ mol, 1 mol%), respectively, and SiO₂ (10 mg, 1 wt%) with substrate **5** (23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 3. Analogously, **4h** (10 mg, 1 mol% Rh) or **4i** (10 mg, 1 mol%) and substrate **5** (23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 3.

Results:

	Rh source (1 mol%) 10 mg SiO ₂ (1 wt%) OTBS 50 bar H ₂	ОТВ	s	BS	УОН .	С ОН
F	25 °C, 24 h <i>n</i> -hexane (0.1 M)	F	+	F F	F	\checkmark
5		6	7		19	20
Entry	Rh source	Conversion	Yield of 6	Yield of	Yield of	Yield of
			[%] (d.r.)	7 [%]	19 [%]	20 [%]
1	Rh-COD-8-Cl	>99	78 (92:8)	5	-	-
2	Rh-COD-9-Cl	90	80 (94:6)	4	-	-
3	4h recovered from entry 1	56	51 (92:8)	5	-	-
4	4i recovered from entry 2	0	-	-	-	-
5^a	1	>99	87 (93:7)	5	-	4

Table S6: Control reactions with Rh-COD-Cl complexes derived from CAACs 8 and 9.

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. Numbers do not add up to unity, because cyclohexane and cyclohexanol are formed as byproducts, which co-elute with the solvent and thus cannot be detected. ^{*a*}Optimized conditions using Rh-complex precursor: 1 mol% Rh-CAAC **1**, SiO₂ (1 wt% Rh), 50 bar H₂, 25 °C, 24 h.

<u>Discussion</u>: The observed yields for product **6** are slightly lower, when compared to the standard catalyst (entry 5). When using complex **29** as precursor, full conversion could not be observed after full 24 h of reaction time. When the isolated residues **4h** and **4i** were collected, washed and used as the catalyst in a new reaction, a significantly reduced conversion (entry 3) or full loss of activity (entry 4) was observed. These results stay in contrast to the catalyst recovery experiment for complex **1** (**Table S4**) and highlight the importance of CAAC **1a** during the formation of the active catalyst.

Particle formation by in situ reduction of Rh-CAAC 1 with NaBH₄

To investigate the influence of the reducing agent on the formation of rhodium NPs from complex **1**, sodium borohydride was used for the reduction of Rh^I in **1** in presence and absence of silica gel, respectively.

Experimental procedure:

In situ preparation of rhodium particles in presence of SiO₂:

To Rh-CAAC **1** (28.6 mg, 50.0 μ mol, 1.00 equiv.) in dichloromethane/toluene (1:1 ν/ν , 10.0 mL) and SiO₂ (250 mg) a solution of NaBH₄ (18.9 mg, 500 μ mol, 10.0 equiv. in 3 mL H₂O) was added dropwise at r.t. while stirring. The reaction mixture turned black immediately. After 18 h stirring at 25 °C, the solids were isolated by centrifugation. The solvent was decanted off and the gray product was washed with DCM (3 x 5 mL) and pentane (3 x 5 mL) and dried in vacuum.

In situ preparation of rhodium particles in absence of SiO₂:

To Rh-CAAC **1** (28.6 mg, 50.0 μ mol, 1.00 equiv.) in dichloromethane/toluene (1:1 ν/ν , 10.0 mL) a solution of NaBH₄ (18.9 mg, 500 μ mol, 10.0 equiv. in 3 mL H₂O) was added dropwise at r.t. while stirring. The reaction turned black after approximately 30 min. After 18 h stirring at 25 °C, the solids were precipitated by adding excess methanol and subsequent centrifugation. The solvent was decanted off and the black solid residue was washed with DCM (3 x 5 mL) and pentane (3 x 5 mL) and dried in vacuum.

The catalytic performance of the obtained rhodium residues was tested under standard reaction conditions with 5 mol% rhodium loading, with substrate **5** (23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) according to general procedure 3 (**Table S7**).

Results:

	F OTBS -	Rh (5 mol%) (SiO ₂) 50 bar H ₂ 25 °C, 24 h n-hexane (0.1 M)	F OTBS +	OTBS	
	5	(-)	6	7	
Entry	Rh source	SiO ₂	Conversion	Yield of 6	Yield of 7
				[%]	[%]
1^a	Rh-CAAC 1	1 wt%	>99	87	5
2	in situ reduction of 1	1 wt%	>99	62	34
3	in situ reduction of 1	-	0	-	-

 Table S7: Control reactions with preformed Rh residues derived from complex 1.

Yields were determined via GC-FID against mesitylene as internal standard. ^aOptimized conditions using 1 mol% Rh-CAAC **1**.

<u>Discussion</u>: The observed performance differed significantly from the optimized conditions using **1** or **4a** as catalyst in both experiments. With identical silica loading in the preformed sample, an increased amount of defluorination was observed (34% **7** instead of 5%). In the absence of silica during catalyst formation, the preformed catalyst showed no catalytic activity, giving no conversion. These results reveal an important role of hydrogen and SiO₂ during the formation of the active catalyst as opposed to a hydride source as the reducing agent.

Experimental procedure for the hydrogenation of test substrates using Rh-CAAC

1

The hydrogenation of model substrate **5** (100 μ mol, 23.5 μ L, 22.6 mg, 1.00 equiv.) with Rh-CAAC **1** (1.0 μ mol, 0.57 mg, 1 mol%) and silica gel (10 mg, 1 wt% rhodium) in dry *n*-hexane (1 mL) was conducted according to general procedure 3. Upon completion of the reaction time, the pressure was carefully released and 1.00 equiv. of mesitylene (14.0 μ L, 12.1 mg, 100 μ mol) was added as internal standard and the reaction outcome analyzed via GC-FID.

Alternatively, 5 mol% of Rh-CAAC **1** (5.0 μ mol, 2.9 mg) and silica gel (50 mg, 1 wt% rhodium) or 5 mol% of Rh-CAAC **1** (5.0 μ mol, 2.9 mg) and silica gel (10 mg, 5 wt% rhodium) were used.

Experimental procedure for the hydrogenation of test substrates using modifiers



Preparation and evaluation of modified catalyst – general procedure 4: Non-soluble catalysts (1 or 5 mol% rhodium) were placed in an oven-dried 4 mL screw-cap vial equipped with a stirring bar. Dry *n*-hexane (0.5 mL) was added under argon atmosphere. Solutions of **2** (0.05 M in DCM) and/or **3** (0.05 M in *n*-hexane) were added in relative amounts (0–1.00 equiv.) to the used rhodium. The resulting mixture was stirred for 30 min, before the solvent was removed thoroughly under reduced pressure. To this mixture, substrate **5** (100 µmol, 23.5 µL, 22.6 mg, 1.00 equiv.) and dry *n*-hexane (1 mL) were added and it was reacted according to general procedure 3. Upon completion of the reaction time, the pressure was carefully released and 1.00 equiv. of mesitylene (14.0 µL, 12.1 mg, 100 µmol) was added as internal standard and the reaction outcome was analyzed via GC-FID.

<u>Preparation and evaluation of modified catalyst – general procedure 5:</u> Soluble rhodium complexes (indicated amount) and silica gel (indicated amount) were placed in an ovendried 4 mL screw-cap vial equipped with a stirring bar. Dry *n*-hexane (0.5 mL) was added under argon atmosphere. Solutions of **2** (0.05 M in DCM) and/or **3** (0.05 M in *n*-hexane) were added in relative amounts (0–1.00 equiv.) to the used rhodium. The resulting mixture was stirred for 30 min, before the solvent was removed thoroughly under reduced pressure. To this mixture, substrate **5** (100 µmol, 23.5 µL, 22.6 mg, 1.00 equiv.) and dry *n*-hexane (1 mL) were added and it was reacted according to general procedure 3.

Addition of modifiers to reactions using the catalyst precursor Rh-CAAC 1

To investigate the influence of the observed modifiers **2** and **3** on the hydrogenation of test substrate **5**, these were added in varying ratios with a total of 1 equiv. to the Rh-CAAC **1** catalyzed reaction (**Table S8**).

Experimental procedure: Rh-CAAC 1 (1.0 μ mol, 0.57 mg, 1 mol%), SiO₂ (10 mg, 1 wt% rhodium) and mixtures of 2 and 3 (0–1 equiv., respectively) were reacted with substrate 5 according to general procedure 5.

Results:

2

3

4

5

6

0

0.33

0.50

0.67

1.0



53

0

0

0

0

5

33 (92:8)

Table S8: Catalytic results obtained with Rh-CAAC 1 with 2 and 3 as reaction additives.

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard.

1.0

0.67

0.50

0.33

0

<u>Discussion</u>: While the formation of a black residue was observed in every case, the addition of the modifiers entirely diminished the reactivity of the formed residue in almost any modifier ratio (entries 3–6). It is worth noting, that some reactivity was preserved when exclusively 1 equiv. of species **3** was used (entry 2). Thus, together with the one equivalent of CAAC **1** derivatives liberated from the complex precursor, a total of two resulting equivalents of modifiers significantly reduced catalytic activity, showing the impact of the modifiers on the catalytic results.
Under standard, optimized reaction conditions, using Rh-CAAC **1** as catalyst, a maximum of 1 equiv. of CAAC **1a** derivatives can form during the reaction. To mimic this reaction environment more closely, a total of 1 equiv. of modifiers with respect to the amount of rhodium was not exceeded in further experiments.

Modifying commercially available Rh/Al2O3

Studies on the influence of the modifiers 2 and 3 with commercial sources of heterogeneous Rh catalysts were performed.

Experimental procedure: A commercial sample of rhodium on alumina (10.3 mg, 5 mol%, 5 wt% rhodium) and mixtures of **2** and **3** (0–0.5 equiv. relative to rhodium, respectively) were reacted with substrate **5** according to general procedure 5.

Results:

	F OTBS	Rh/alumina (5 mol%, 5 wt%) modifier 50 bar H ₂ 25 °C, 24 h <i>n</i> -hexane (0.1 M)	F FOTBS	+ OTBS	
	5		6	7	
Entry	Equivalents of 2	Equivalents of 3	Conversion	Yield of 6 [%]	Yield of 7 [%]
1^a	-	-	>99	90	3
2	-	-	>99	52	44
3	0	0.50	>99	45 (92:8)	40
4	0.17	0.33	>99	56 (93:7)	32
5	0.25	0.25	>99	56 (93:7)	25
6	0.33	0.17	>99	68 (93:7)	25
7	0.50	0	>99	75 (93:7)	25
8	0	1.0	>99	40 (94:6)	55
9	0.33	0.67	>99	58 (93:7)	39
10	0.50	0.50	>99	63 (93:7)	33
11	0.67	0.33	>99	76 (93:7)	19
12	1.0	0	>99	75 (92:8)	18

Table S9: Catalytic results obtained with Rh/Al₂O₃, modified with 2 and 3.

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. ^{*a*}**4a** was used as the catalyst.

<u>Discussion</u>: When using the commercial Rh source (**Table S9**, entry 2) instead of **4a** (entry 1) a significantly lower yield was observed for product **6**. At the same time an increased amount of defluorination to **7** was detected. The addition of a total of 0.5 equiv. of mixtures of modifiers pyrrolidinium **2** and pyrrolidine **3** improved yields

and decreased byproduct formation (entries 4–7). Increasing the fraction of **2** relative to **3** gradually increased the yield of product **6**. At the same time, the yield of the defluorinated byproduct **7** decreased to 25% at a 1:1 ratio of modifiers and did not further decrease when the fraction of **2** was further increased. Results for using one total equivalent of modifiers are similar (entries 8–12) but could not match the results originally obtained with **4a** (entry 1).

These results indicate, that **2** plays a major role in catalyst modulation, while **3** was not observed to have a major contribution. However, the nature of rhodium in the commercial sample might significantly differ to Rh-CAAC **1** derived particles **4a** and a different support material is present (alumina instead of silica gel). Therefore, the analysis of a rhodium source that is closer to the original system was needed (vide infra).

[Rh(COD)Cl]₂ derived particles as active catalyst

As the synthesis of the commercial rhodium samples might significantly differ from the conditions employed when using the catalyst precursor 1 and another support material was used, the influence of the modifiers 2 and 3 was further investigated on particles obtained from $[Rh(COD)Cl]_2$ as precursor in presence of silica gel.

Synthesis of the [Rh(COD)Cl]₂ derived residue: [Rh(COD)Cl]₂ (5.0 μ mol, 2.5 mg) and SiO₂ (100 mg, 1 wt% rhodium) were stirred in *n*-hexane (2 mL) under 50 bar hydrogen pressure at 25 °C for 24 h. The resulting black suspension was filtered and the residue was dried in vacuo (yield 93 mg).

Experimental procedure for catalytic reactions using the $[Rh(COD)Cl]_2$ derived residue: The $[Rh(COD)Cl]_2$ derived residue (10 mg, 1 mol% Rh) and modifiers **2** and/or **3** (adding up to a total of 1 equiv. of modifier relative to the amount of rhodium) were reacted with the substrate **5** (0.10 mmol, 23.5 µL, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) according to general procedure 4.

Results:

F	Rh pa (1 mo OTBS	articles/SiO ₂ bl%, 1 wt%) ifier (1 eq.) 0 bar H ₂ $^{\circ}$ C, 24 h $^{\circ}$ C, 24 h	F OTBS	+OTE	3S + F	OH + F	ОН
5	<i>11-116</i>		6	7		19	20
Entry	Equivalents	Equivalents	Conversion	Yield of 6	Yield of	Yield of	Yield of
	of 2	of 3		[%] (d.r.)	7 [%]	19 [%]	20 [%]
1^a	-	-	>99	87 (93:7)	5	-	4
2	0	0	94	73 (92:8)	5	-	traces
3	1.0	0	35	27 (94:6)	2	-	-
4	0.67	0.33	0	-	-	-	-
5	0.50	0.50	7	3 (-)	-	-	-
6	0.33	0.67	0	-	-	-	-
7	0	1.0	5	5 (-)	-	-	-

Table S10: Control reactions with preformed Rh particles from [Rh(COD)Cl]₂ on SiO₂ as the catalyst.

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. Numbers do not add up to unity, because cyclohexane and cyclohexanol are formed as byproducts, which co-elute with the solvent and thus cannot be detected. ^{*a*}Optimized conditions using complex precursor: 1 mol% Rh-CAAC **1**, SiO₂ (1 wt% Rh), 50 bar H₂, 25 °C, 24 h.

<u>Discussion</u>: Comparison of the reaction using the [Rh(COD)Cl]₂ derived residue (**Table S10**, entry 2) with Rh-CAAC **1** precursor (entry 1) shows a reduced yield of the desired fluorinated cyclohexane **6**. The reactivity of the [Rh(COD)Cl]₂ derived residue significantly diminished when adding 1 equiv. of the modifiers **2** and **3** in almost any ratio (entries 3–7). This is in sharp contrast to the synthesized rhodium particles (**4e**, vide infra) with a size distribution similar to Rh-CAAC **1** derived **4a**, where significant reactivity remained in presence of varying amounts of the modifiers (see **Table S11**). Hence, particles obtained from [Rh(COD)Cl]₂ as precursor show different properties to those obtained under optimized hydrogenation reaction conditions using precursor complex **1**.

Catalyst formation from [Rh(COD)Cl]₂ in presence of modifiers:



<u>Experimental procedure</u>: [Rh(COD)Cl]₂ precursor (0.50 μ mol, 0.25 mg, 1 mol%)) and modifiers **2** and/or **3** (adding up to a total of 1 equiv. of modifier relative to the amount of rhodium) were reacted with the substrate **5** (0.10 mmol, 23.5 μ L, 22.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) according to general procedure 5.

<u>Results and Discussion</u>: When the catalytic residue was not preformed but modifiers were added to the reaction mixture containing $[Rh(COD)Cl]_2$ precursor, SiO₂ and substrate 5, no conversion of the starting material could be detected for all ratios of modifiers 2 and 3. For total amounts of 2 below 0.5 equiv. the formation of a black residue could be observed, above 0.5 equiv. no residue formed (white solid, yellow solution).

Evaluation of rhodium particles on silica gel with a controlled size distribution as active catalyst

To mimic the conditions obtained with in situ catalyst preparation from Rh-CAAC **1** as precursor more closely, synthesized rhodium NPs (**4e–g**, see general procedure 2) with a similar, controlled size distribution when compared to catalyst **4a** and three different weight fractions of rhodium were tested in catalytic hydrogenations.

Experimental procedure: Catalysts **4e** (11.8 mg, 1 mol%, 0.87 wt% rhodium or 59.1 mg, 5 mol%, 0.87 wt% rhodium), **4f** (10.1 mg, 5 mol%, 5.1 wt% rhodium) or **4g** (5.2 mg, 5 mol%, 9.9 wt% rhodium) and mixtures of **2** and **3** (0–1.0 equiv. relative to rhodium, respectively) were reacted with substrate **5** according to general procedure 5.

Results:

Table S11: Catalytic results obtained with Rh/SiO ₂ 4e-	g with varying Rh loadings
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Entry	Rh loading	Equivalents	Equivalents	Conversion	Yield of	Yield of
	<i>n</i> (wt%)	of 2	of 3		6 [%] (d.r.)	7 [%]
1^a	1.0	-	-	>99	90 (93:7)	3
2	0.87	-	-	>99	57 (89:11)	29
3 ^b	0.87	-	-	>99	66 (87:13)	18
4 ^{<i>b</i>}	5.1	-	-	>99	59 (89:11)	23
5 ^b	9.9	-	-	>99	68 (88:12)	23
6	0.87	0.10	-	>99	50 (90:10)	27
7	0.87	0.30	-	92	50 (90:10)	19
8	0.87	1.0	-	79	55 (91:9)	9
9	0.87	0	1.0	>99	66 (89:11)	26
10	0.87	0.33	0.67	>99	75 (91:9)	14
11	0.87	0.50	0.50	83	57 (91:9)	9
12	0.87	0.67	0.33	92	61 (91:9)	11
13	0.87	1.0	0	79	55 (91:9)	9
14	0.87	0.25	0.25	99	82 (93:7)	10
15	0.87	0.15	0.15	>99	80 (91:9)	8
16	0.87	0.05	0.05	>99	68 (90:10)	17

Yields and d.r. values were determined via GC-FID against mesitylene as internal standard. Numbers do not add up to unity, because cyclohexane and cyclohexanol are formed as byproducts, which co-elute with the solvent and thus cannot be detected. ^{*a*}**4a** was used as the catalyst. ^{*b*}5 mol% Rh was used.

<u>Discussion</u>: Despite the similar size distribution and Rh loading (relative to SiO₂) catalyst **4e** (**Table S11**, entry 2) performed significantly worse than catalyst **4a** (entry 1), both in terms of yield and amount of defluorination. Furthermore, different Rh loadings on the silica gel (**4e–g**) have shown similar reactivity (entries 3–5). Since pyrrolidinium **2** appeared to act as the major modifier of catalytic activity in control reactions with Rh/Al₂O₃ and [Rh(COD)Cl]₂ (**Table S9** and **Table S10**), substoichiometric amounts were tested with the Rh particles (entries 6–8 and **Figure**)

S2, top left). With increasing amounts of 2 diminished conversions and yield of defluorinated byproduct 7 were observed, while the product yield remained at a comparatively low 50-55% (cf. entry 1).

Next, mixtures of both observed modifiers **2** and **3** were tested in stoichiometric amount relative to rhodium (entries 9–13 and **Figure S2**, bottom left). One equivalent (in total) was chosen here, since only a maximum of one equivalent of CAAC **1a** derived species can be present in standard catalyst **4a**, and because a higher amount was observed to stop catalytic reactivity (cf. **Table S8**). With different ratios varying amounts of conversion, product yield and defluorination were detected. However, no clear trend could be observed in the data. Leaning on the observed relative amounts of both modifier species of 1:1 in XPS (cf. **Figure S4**), and a comparably low yield of defluorinated product **7** at this ratio, an equimolar amount was chosen for further studies.

Decreasing the total amount of modifier from 1 equiv. to 0 equiv. gradually increased conversion (entries 2, 11, 14–16), which further demonstrated that the modifiers reduce the catalytic activity (**Figure S2**, bottom right). The amount of defluorination decreased from 0 to 0.3 equiv. of modifiers and reached a plateau at this amount. It is noteworthy that full conversion was still observed in presence of 0.3 equiv. of the modifiers (entry 15).



Figure S2: Plots of yields for 5, 6 and 7 for different amounts of modifiers 2 and 3. Top left shows the influence of 2 for varying equivalents relative to rhodium; Bottom left shows yields for a varying ratio of 2 to 3, dashed lines indicate results for unmodified Rh NPs; Bottom right shows yields for varying amounts of modifiers in a 1:1 ratio, dashed lines indicate results obtained with **4a** as catalyst.

<u>Discussion</u>: 0.3 equiv. of modifiers **2** and **3** in a 1:1 ratio applied to catalyst **4e** were identified as optimized conditions. When keeping the remaining reaction conditions (pressure, temperature, reaction time, solvent, concentration) unaltered, the modified modified catalyst **4e'** performed very similar to the active catalyst **4a** in the hydrogenation of **5**.

Application of the optimized modified conditions on the hydrogenation of hexafluorobenzene **10**

To investigate if the bottom-up synthesized heterogeneous catalyst system can hydrogenate more demanding substrates chemoselectively, hexafluorobenzene **10** was chosen as a second model substrate.

Experimental procedures:

Soluble Rh-CAAC **1** (0.57 mg, 1.0 μ mol, 1 mol%), silica gel (44 mg, 0.23 wt% rhodium) with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 3. After completion of the catalytic reaction, the reaction mixture was filtered through a glass frit and eluted with DCM (30 mL) and acetone (30 mL). The raw product was dryloaded on silica gel and purified using flash chromatography (DCM/acetone, 100:0 to 90:10, *v*/*v*) and products **11** and **12** were isolated as pure, white solids.

Non-soluble, dried Rh/C (0.93 mg, 1 mol%, 10 wt% rhodium), with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 4. Isolation of **11** and **12** proceeded as previously describe (vide supra).

Non-soluble, dried Rh/Al₂O₃ (2.1 mg, 1 mol%, 5.0 wt% rhodium), with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 4. Isolation of **11** and **12** proceeded as previously describe (vide supra).

Non-soluble, dried Ru/C (1.0 mg, 1 mol%, 10 wt% ruthenium), with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 4. Isolation of **11** and **12** proceeded as previously describe (vide supra).

Non-soluble, dried Ru/Al₂O₃ (2.0 mg, 1 mol%, 5.0 wt% ruthenium), with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) in dry *n*-hexane (1 mL) were reacted according to general procedure 4. Isolation of **11** and **12** proceeded as previously describe (vide supra).

Non-soluble **4e** (11.8 mg, 1 mol%, 0.87 wt% rhodium), with substrate **10** (100 μ mol, 11.5 μ L, 18.6 mg, 1.00 equiv.) and optionally, modifier **2** (0.15 μ mol, 0.15 mol%) and modifier **3** (0.15 μ mol, 0.15 mol%) in dry *n*-hexane (1 mL) were reacted according to general procedure 4. Isolation of **11** and **12** proceeded as previously described.

Results:



Table S12: Hydrogenation of hexafluorobenzene 10 with different cataly	ysts.
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Entry	Catalyst	Metal loading	Additive	Conversion	Yield of	Yield of
		(wt%)			11 [%]	12 [%]
1^a	Rh-CAAC 1/4Å MS	0.34	-	>99	3413	-
2^a	Rh-CAAC 1/SiO ₂	0.34	-	>99	33	-
3^b	Rh-CAAC 1/SiO ₂	0.11	-	>99	88 ⁹	-
4	Rh-CAAC 1/SiO ₂	0.23	-	>99	39	22
5	Rh/C (activated)	10	-	99	_ C	_ c
6	Rh/Al ₂ O ₃	5.0	-	>99 ^d	_ C	_ c
7	Ru/C (activated)	10	-	$>99^{d}$	_ c	_ c
8	Ru/Al ₂ O ₃	5.0	-	>99 ^d	_ C	_ c
9	Rh/SiO ₂ 4e'	0.87	0.15 equiv. of 2 0.15 equiv. of 3	>99	29	8
10	Rh/SiO ₂ 4e	0.87	-	>99	4	57

^{*a*}0.5 mol% catalyst, 0.07 M. ^{*b*}0.5 mol% catalyst, 0.5 M. ^{*c*}Traces of unknown fluorinated products were detected. ^{*d*}Conversions and yields were determined by ¹⁹F-NMR spectroscopy using 1,2,4,5-tetrafluorobenzene as internal standard.

<u>Discussion:</u> Previously published,¹³ and optimized reaction conditions gave 34% yield of **11** when using only 0.5 mol% of the catalyst and 150 mg molecular sieves as support material (**Table S12**, entry 1). While an almost identical result was obtained with silica gel (entry 2), increasing the silica amount threefold to 450 mg increased the yield to 88% (entry 3, previously published).⁹ To ensure comparability to the experiments in this work, 1 mol% catalyst loading was chosen for a benchmark experiment (entry 4). In this experiment, Rh-CAAC **1** with silica gel gave a 39% yield of the desired product. Commercial heterogeneous hydrogenation catalysts only provided traces of the desired product (if at all, **Table S12**, entries 5–8).¹³ In some cases traces of unknown fluorinated compounds were detected. The bottom-up synthesized catalyst **4e'** provided a 29% isolated yield of **11** (entry 9), which corresponds to 74% of the performance under the given conditions when using complex **1** as pre-catalyst. The successful hydrogenation of the demanding substrate **10** with the designed catalyst system shows the potential of the bottom-up synthesis approach.

(F) Kinetic NMR measurements-investigation of induction periods

In situ high-pressure NMR study of the hydrogenation of 5 catalyzed by $1 + SiO_2$

160 µl of **5** (154 mg, 680 µmol) were filled into a Schlenk flask under argon along with 3.8 mg of complex **1** (6.7 µmol, 1.0 mol%), 108 mg of SiO₂ and 2.3 ml of cyclohexane d_{12} (degassed and dried over 3 Å molecular sieves). The obtained light-yellow suspension (colorless liquid phase, light-yellow solid) was transferred under argon into a high-pressure 10 mm sapphire NMR tube connected to a custom made high-pressure gas circulation assembly.¹⁴ Inside of the NMR spectrometer (Bruker, 400 MHz) the assembly was pressurized with 20 bar of H₂ (the setup rendered a pressure of 50 bar infeasible) and H₂ gas was continuously bubbled through the reaction suspension via an internal capillary (flow rate: 1 ml/min) at room temperature. The time of first introduction of H₂ was used as the starting point for the reaction. In regular intervals the gas circulation was interrupted to record ¹H NMR spectra (using the cyclohexane solvent peak as internal shift reference, 1.38 ppm). After 8 h the gas circulation was stopped and the reaction assembly was allowed to sit overnight under H₂ atmosphere. Upon removal of the NMR tube the next day a dark suspension was observed (colorless liquid phase, dark brown solid).

In situ high-pressure NMR study of hydrogenation of 5 catalyzed by 4a

160 µl of **5** (154 mg, 680 µmol) were filled in a Schlenk flask under argon along with 106 mg of Rh/SiO₂ **4a** prepared from complex **1** and SiO₂ (1.0 mol% of Rh with respect to **5**, 0.66 wt%) and 2.3 ml of cyclohexane- d_{12} (degassed and dried over 3 Å molecular sieves) according to general procedure 1. The obtained dark brown suspension (colorless liquid phase, dark brown solid) was transferred under argon into a highpressure 10 mm sapphire NMR tube connected to a custom made high-pressure gas circulation assembly.¹⁴ Inside of the NMR spectrometer (Bruker, 400 MHz) the assembly was pressurized with 20 bar of H₂ and H₂ gas was continuously bubbled through the reaction suspension *via* an internal capillary (flow rate: 1 ml/min) at room temperature. The time of first introduction of H₂ was used as the starting point for the reaction. In regular intervals, the gas circulation was interrupted to record ¹H NMR spectra (using the cyclohexane solvent peak as internal shift reference, 1.38 ppm). The assembly was repressurized with H₂ to 20 bar for several times to compensate for hydrogen consumption and loss through a small leak. After 5.25 h the gas circulation was stopped and the reaction assembly was allowed to sit overnight under H₂ atmosphere. Upon removal of the NMR tube the next day a dark suspension was observed (colorless liquid phase, dark brown solid).

Analysis of in situ NMR data

For each experiment, the obtained ¹H NMR spectra were scaled so that all spectra from one experiment had the same integral across the entire spectrum. Subsequently, the absolute integrals at 6.77 ± 0.03 ppm (protons at 2-position of **5**) and 3.71 ± 0.03 ppm (proton at 1-position of **6**) were determined for all spectra. For each experiment, the obtained starting material and product integrals were normalized (considering that the peak at 6.77 ppm corresponds to two protons while the peak at 3.71 ppm corresponds to one proton), setting the starting material integral at t = 0 min to 1. This normalization yielded the shown time courses for starting material and product concentration for both experiments (**Figure S3**).



Figure S3: Reaction profiles of the substrate **5** and product **6** measured in a pressurized NMR sample tube. Profiles were recorded for reactions starting with complex $1 + SiO_2$ and the preformed catalyst **4a**.

<u>Discussion</u>: The data shows an induction period of approximately 120 min when using complex **1** and silica gel as catalyst system before product formation can be observed. Therefore, **1** cannot be the active catalyst, but has to be transferred to another homo- or heterogeneous species. Opposed to this, using **4a** consumption of **5** and product formation starts immediately, indicating, that the active catalyst is present in **4a**.

(G) XPS measurements

Experimental details: Samples for XPS measurements were prepared by mixing Rh-CAAC 1 (17.1 mg, 29.9 μ mol) with oven-dried SiO₂ (100 mg), corresponding to 2.6 wt% Rh loading, in 2 mL of *n*-hexane according to general procedure 1. The supernatant of the resulting black suspension was carefully removed and the solid residue was washed with *n*-hexane (5 x 4 mL). The gray solid (4a) was dried in vacuo and stored under argon until the measurement.

For x-ray photoelectron spectroscopy (XPS) a K-Alpha from Thermo VG Scientific with monochromatic Al-K_{α} X-ray source was used (75 W, ~400 µm spot diameter). The energy scale and transmission function of the analyzer were calibrated using standard gold, silver and copper samples (similar to ISO 15472:2001 and ISO21270:2004). If not stated differently, spectra were measured using a pass energy of 80 eV for survey spectra and 30 eV for core level spectra. If necessary, charge compensation was done using a combined low energy electron/ion flow source. The energy scale was calibrated towards the aliphatic C-1s peak matching 285 eV (detection limit about 0.1 to 1.0 At% inside the analyzed volume). If not otherwise noted, the results are given in atomic percent. Quantitative information about the surface composition was calculated from survey spectra using the standard Scofield sensitivity factors.¹⁵ The total error was estimated to be typically about 10%.

<u>Discussion</u>: XPS plots for Rh3d, C1s and N1s scans of **4a** are given in **Figure S4**. The binding energy of the Rh3d 5/2 peak is 307.3 eV, indicating that the oxidation state of the formed Rh species is (0). In a Cl2p scan traces of a Cl species could be observed, but the intensity was too low for more detailed investigation. The best obtained fitting for the N1s scan suggests the presence of two distinct nitrogen species at app. 399 eV and 402 eV, respectively. For a comparison the C1s and N1s scans for the precursor complex Rh-CAAC **1** and **1** dispersed in SiO₂ (1 wt% Rh) are given in **Figure S5**. In the latter case no nitrogen signal can be observed because of the very small loading in the sample. The N1s scan of Rh-CAAC **1** shows a signal at 401 eV originating from

the nitrogen in the carbene ligand **1a** in the complex. The fitted signals in the spectrum of **4a** differ significantly in their energy to this signal. The CAAC ligand **1a** is the only nitrogen atom containing source in the prepared sample **4a**. Thus the data suggests two CAAC derived species. To test this assumption, prepared samples of the pyrrolidinium chloride salt **2** and pyrrolidine **3** were analyzed in XPS measurements. The observed signals in the obtained N1s plots align with the fitting of the original measurement (**Figure S6**), thus giving evidence for the identity of the observed species. The observed minor peaks at 401 and 399 eV, respectively, originate from minor impurities of the prepared samples.



Figure S4: XPS-plots of Rh3d, C1s and N1s scans of obtained catalyst 4a.



Figure S5: XPS-plots of C1s and N1s scans of Rh-CAAC **1** (top) and a mixture of Rh-CAAC **1** and SiO₂ (bottom, 1 wt% Rh).



Figure S6: XPS-plots of N1s scans of obtained catalyst 4a (top), 3 (second from top), 2 (second from bottom) and a 1:1-mixture of 3 and 2 (bottom).

(H) X-ray absorption fine structure (XAFS) analysis of 4a

Experimental details: X-ray absorption fine structure (XAFS) spectra at the Rh K-edge were measured in transmission mode at room temperature at the NW10A station of the Photon Factory at KEK-IMSS and BL11S2 station at the Aichi Synchrotron Radiation Center. For the measurement at KEK-IMSS, the energy and current of the electrons in the storage ring were 6.5 GeV and 60 mA, respectively. For the measurement at Aichi Synchrotron Radiation Center, the energy and current of the electrons in the storage ring were 1.2 GeV and 300 mA, respectively. X-rays from the storage ring were monochromatized with a Si(311) double-crystal monochromator in both facilities. Two ionization chambers filled with pure Ar and Kr gases were used to monitor the incident (I₀) and transmitted (I) X-rays, respectively, for the measurement at KEK-IMSS. Two ionization chambers filled with a mixture of Ar and Kr gases (1/1, ν/ν) and a mixture of Ar and Kr gases (9/1, ν/ν) were used to monitor I₀ and IX-rays, respectively, for the measurement at Aichi Synchrotron Radiation Center. Rh foil and Rh₂O₃ (diluted with boron nitride) were used as references.

The XAFS spectra were analyzed using ATHENA and ARTEMIS with IFEFFIT (version 1.2.11).¹⁶ The threshold energy was tentatively set at the inflection point for the Rh K-edge (Rh foil: 23219.8 eV).¹⁷ Background subtraction was performed using the Autobk method and the spline smoothing algorithm in ATHENA.¹⁸ The k^3 -weighted extended XAFS (EXAFS) oscillations were Fourier transformed into *R*-space. Curve-fitting analysis was carried out in the *R*-space. The fitting parameters for each shell were the coordination number (CN), interatomic distance (*R*), Debye–Waller factor (σ^2 : mean-square displacement), and correction-of-edge energy (ΔE_0). For the Rh K-edge, S_0^2 was fixed to be 1 based on the fitting of Rh⁰ foil. Phase shift and backscattering amplitude for Rh-Rh were calculated with FEFF 8 code¹⁹ using structural parameters obtained from the crystal structures of Rh⁰ metal.²⁰

Results:

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Figure S7: (a) k^3 -weighted Rh K-edge EXAFS oscillation, and (b) its Fourier transform ($k = 30-180 \text{ nm}^{-1}$) for **4a** measured at room temperature. Black solid lines in (b) show observed data and red dashed lines show fitted data.

Table S13: Structural parameters obtained by curve-fitting analysis of Rh K-edge EXAFS for 4a	ı . <i>a</i>
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Sample	Shell	CN	<i>R</i> [nm]	$\Delta E_0 [eV]$	$\sigma^2 [10^5 \text{ nm}^2]$
Rh ⁰ foil ^b	Rh–Rh	12	0.269 ± 0.001	2 ± 1	5 ± 1
$4\mathbf{a}^{c}$	Rh–Rh	8.7 ± 0.7	0.269 ± 0.003	1 ± 1	6 ± 1

 ${}^{a}k = 30-180 \text{ nm}^{-1}$, R = 0.12-0.30 nm, ${}^{b}S_{0}{}^{2}$ was fitted to be 1. ${}^{c}S_{0}{}^{2}$ was fixed as 1. $R_{f} = 0.9\%$.

<u>Discussion</u>: The found Rh–Rh bond distance in the analyzed particles identifies rhodium to be in the metallic state (oxidation state 0).

(I) Powder X-Ray diffraction (XRD)

XRD patterns were recorded on an X-ray diffractometer (MultiFlex, Rigaku; Cu K_{α}, $\lambda = 1.5418$ Å, 40 kV, 30 mA) at a scan rate of 2° min⁻¹ at 293 K under air.

Results:



Figure S8: (A) XRD pattern for catalyst residue 4a. (B) Enlarged XRD pattern from 35° to 50°.

<u>Discussion</u>: The XRD pattern of catalyst residue **4a** (**Figure S8**) shows peaks at 41.0° and 47.4° , which can be attributed to Rh(111) and Rh(200) in Rh(0) nanoparticles, respectively. The nanoparticle size was estimated based on the Debye-Scherrer equation to be 4.9 nm (curve-fitting was conducted at Rh(111), fitting region 37–45°).

(J) Brunauer-Emmett-Teller (BET) analysis

Nitrogen adsorption was performed on a surface adsorption analyzer (Micromeritics ASAP-2020, Shimadzu) at 77 K. Each sample was degassed at 473 K for 1 h under vacuum before the adsorption measurement. The dead volume was measured with helium after degassing before the adsorption measurement.

<u>Results:</u> The BET surface area was determined for samples **4a** (398 m²g⁻¹), **4b** (395 m²g⁻¹), **4c** (373 m²g⁻¹), and **4d** (379 m²g⁻¹). The surface area of the silica gel used for preparation of these samples was determined to be 422 m²g⁻¹.

<u>Discussion</u>: All determined surface areas are very close to that of the standard (used silica gel). This shows that no severe aggregation occurred after the formation of rhodium nanoparticles and an effect originating from a varying surface area can be excluded.

(K) Solid-state NMR studies

Experimental details: Solid-state MAS NMR studies were conducted on a Bruker Avance I spectrometer at a magnetic-field strength of 9.04 T (¹H 400 MHz) using a MAS rotational frequency of 12.5 kHz in a 4.0 mm NMR double-resonance probe. The ¹³C{¹H} CP/MAS NMR spectra were measured using a 5.8 μ s π /2 pulse on ¹H (43 kHz nutation frequency) for excitation followed by a 1000 μ s spinlock pulse at the same nutation frequency of 43 kHz. The maximum pulse amplitude of the corresponding ¹³C spinlock pulse was ramped from 70% to 100% and optimized with respect to signal intensity of an adamantane reference sample. A recycle delay of 4 s was employed. Acquisition was performed using proton decoupling (SW_FTPPM-15, 43 kHz nutation frequency). The ¹³C chemical shift was referenced using adamantane as a secondary reference (¹H 1.78 ppm).

Results:



Figure S9: (a) and (b) show ¹³C CP/MAS NMR spectra acquired at 9.04 T using a spinning frequency of 12.5 kHz for a fivefold loading of Rh NPs on SiO₂ modified using **2** and **3** in a 1:1 mixture (black line) and in situ generated NPs in a onefold loading on SiO₂ as described in the main text (blue line), respectively. Both spectra were acquired using SWFTPPM proton decoupling.

<u>Discussion</u>: Figure S9 (a) shows ¹³C{¹H} CP/MAS spectra for a fivefold loading of Rh NPs on SiO₂ (4e') modified using 2 and 3 in a 1:1 mixture and for in situ generated NPs in a onefold loading on SiO₂ (4a). Preceding experiments showed that the fivefold loading of Rh NPs in the modified sample did not change the ¹³C{¹H} CP/MAS NMR spectrum and therefore could be used to achieve an improved signal-to-noise ratio. However, for the in situ generated NPs even at a threefold loading of Rh with respect to the standard reaction conditions additional ¹³C species were detected. However, as

the aim of this study was to characterize the actual catalyst employed in the hydrogenation reaction, standard conditions were kept for this sample, leading to a comparably low signal-to-noise ratio for both species (pyrrolidinium and pyrrolidine) diluted on the Rh/SiO₂ surface.

Comparing both samples in Figure S9, it is clear, that the spectrum of the in situ generated NPs **4a** exhibit much larger 13 C linewidths. The respective short T₂ relaxation times can be attributed to paramagnetic relaxation, due to the unpaired electron of Rh atoms (Rh^{0} ; 4d⁸ 5s¹). In the modified sample 4e', where 2 and 3 were exposed to Rh NPs on SiO₂ by solvent evaporation, a different NMR behavior is expected at similar reaction characteristics. Here, during the evaporation of the solvent, a part of the modifiers will also bind to the (diamagnetic) silicate surfaces, with excess not washed away, where no additional relaxation phenomena are expected. Thus, it is reasonable to assume that the sharp ¹³C signals originating from such regions superimpose the broad resonance expected from Rh bound substrates. The different nature of the surface-toligand interaction might also explain the ¹³C chemical shift differences observed for the pyrrolidinium species. While the modifier treated sample **4e**' shows a ¹³C resonance at 193 ppm, which is identical to the ${}^{13}C$ shift in solution NMR (cf. Figure 6), the in situ generated species **4a** shows a ¹³C chemical shift at 186 ppm. Another reason for this chemical shift difference might be the respective counterion of the pyrrolidinium, i.e., the chloride anion of complex 1 could be substituted during the H₂-induced decomposition of this complex by a deprotonated silanol group on the SiO₂ surface. This kind of substitution is less likely for the other sample, where modifier 2 and chloride anions of the CAAC·HCl salt were deposited on the support material during solvent evaporation. In theory, a chemical transformation of 2 under the reductive conditions, for instance via hydrogenation of the aromatic ring, could also be responsible for a different chemical shift of the ¹³C enriched carbon species. However, taking into account previous results reported in literature, reduction of the aromatic ring seems not to occur at the present conditions. The generally observed need of higher reaction temperatures for hydrogenation of more demandingly substituted phenyl moieties³ and earlier literature precedence render this scenario unlikely.²¹

(L) Analysis of Rh(0) NPs

<u>Transmission electron microscopy (TEM) and scanning transmission electron</u> microscopy (STEM) with energy dispersive X-ray spectroscopy (EDS)

TEM and STEM-EDS images were taken using two transmission electron microscopes (JEM-ARM 200F Cold and EM-10000BU, JEOL; accelerating voltage of 200 kV, High Voltage Electron Microscope Laboratory, Institute of Materials and Systems for Sustainability, Nagoya University, Japan). Samples were directly deposited on a Cu microgrid and blown with an air duster to remove excess particles. The particle sizes vary in the different samples. To compare the amount of small particles formed, the fraction of particles smaller or equal to 3 nm within all analyzed particles (N_{s/all} = (number of counted particles with sizes below 3 nm) / (number of all counted particles)) was calculated.

Analysis of Rh(0) NPs 4a

The synthesized particles **4a** were analyzed by TEM and the particle size distribution was obtained (**Figure S10**). $N_{s/all}$ was found to be 2%.



Figure S10: Representative TEM images of **4a**. Black dots represent areas of higher density and correspond to Rh, grey background is the silica support. A lattice structure is visible (0.19 nm Rh(200), 0.22 nm Rh(111)). The Histogram shows the particle size distribution of the prepared system.

Analysis of Rh(0) NPs 4b-4d

The synthesized particles **4b–d** were analyzed by TEM and the particle size distribution was obtained (**Figure S11**).

150 mg SiO₂, 3 h, 4b

150 mg SiO₂, 24 h, 4c

450 mg SiO₂, 24 h, 4d



Figure S11: Representative TEM images of **4b–d**. Black dots represent areas of higher density and correspond to Rh, grey background is the silica support. Histograms show the particle size distribution of the prepared systems.

With 24 h reaction time and 150 mg silica gel (0.33 wt% rhodium) $N_{s/all}(4c)$ is 12%. When reducing the reaction time to 3 h, $N_{s/all}(4b)$ is increased to 32%. Increasing the amount of silica gel three-fold to 450 mg (0.11 wt% rhodium), and keeping the reaction time at 24 h, gives $N_{s/all}(4d) = 24\%$. Compared to catalyst 4a (50 mg, 1 wt% rhodium) with $N_{s/all} = 2\%$, the increase in the amount of silica gel yielded more smaller particles in all three alternative cases.

<u>Discussion</u>: A larger $N_{s/all}$ at 3 h reaction time (compared to 24 h) indicates that rhodium NPs grow over the of time of the reaction. The larger $N_{s/all}$ when using a larger amount of silica gel (450 mg instead of 150 mg or 50 mg) indicates the role of SiO₂ in separating the growing NPs, thus reducing aggregation.

Analysis of Rh(0) NPs 4e, 4f and 4g

The synthesized particles **4e-g** were analyzed by TEM and the particle size distribution was obtained (**Figure S12**). All three samples show a similar, narrow distribution of particle sizes. The number of small particles was determined as follows: $N_{s/all}(4e) = 58\%$, $N_{s/all}(4f) = 41\%$ and $N_{s/all}(4g) = 27\%$.



Figure S12: Representative TEM images of **4e-g**. Black dots represent areas of higher density and correspond to Rh, grey background is the silica support. Histograms show the particle size distribution of the prepared systems.

Analysis of Rh(0) NPs 4h and 4i

In addition to the analysis shown on p. S30 representative TEM images of catalysts **4h** and **4i** are shown in **Figure S13**.



Figure S13: Representative TEM images of **4h** and **4i**. Black dots represent areas of higher density and correspond to Rh, grey background is the silica support.

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