Electronic Supplementary Information for Catalysis Science & Technology

Catalytic hydrogenation of liquid alkenes with a silica grafted hydride

pincer iridium(III) complex: Support for a heterogeneous mechanism

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Supporting Information

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1. General

Materials. Solvents were dried and degassed by standard methods. All manipulations were carried out under inert atmosphere by means of standard Schlenk techniques under argon or in a glove box in argon, unless otherwise stated. Dihydrogen (5.0), ethene (3.5), and propene (2.5), were purchased by PanGas and used without further purification. 1-Decene, *trans*-5-decene, cyclohexene, 3,3-dimethyl-1-butene, and 4-phenyl-1-butene were purchased from Aldrich, and 1-dodecene and styrene from Fluka. Deuterated solvents were purchased by Armar Chemicals, dried and stored over activated molecular sieves, and degassed by several freeze-pump-thaw cycles.

NMR Measurements. Chemical shifts (δ) are given in ppm and coupling constants are given in Hz. Solution NMR spectra were recorded on Bruker DPX 200, DPX 250, AVANCE III 300, AVANCE III 400, or AVANCE DPX 500 spectrometers. ¹H and ¹³C chemical shifts were measured relative to the residual resonance of the deuterated solvent. The signal of the residual protio methyl group of [D₁₀]*p*-xylene was set at δ 2.296 in the ¹H NMR and at δ 20.90 in the ¹³C NMR spectrum. ³¹P NMR spectra were referenced to external 85 % H₃PO₄. Solid-state ¹H MAS, ¹³C CP MAS and {¹H}³¹P MAS NMR spectra were recorded on a Bruker AVANCE I 400 with a conventional double resonance 2.5 mm probe head or a conventional triple resonance 4 mm probe head in double resonance mode. The samples were filled in a glove box into a zirconia rotor and tightly closed. The spinning frequency was set at 20.00 kHz (2.5 mm rotor) or 10.00 kHz (4 mm rotor). ³¹P NMR chemical shifts are referenced to (NH₄)H₂PO₄. All the spectra were baseline-corrected.

GC Measurements. GC measurements were performed on a ThermoFinningan Trace GC Ultra instrument equipped with an FID detector (30 m β -dex column).

Elemental Analyses. C and H analyses were performed at the Micro-Laboratory of the Laboratory of Organic Chemistry, ETH Zurich.

2. Catalytic Hydrogenation of 1-Decene

Figure S1. Reaction profile of the hydrogenation of 1-decene catalysed by **2** (in pentane suspension and followed by GC) and "spit test" (dashed line) after 90 min at 56.8 % yield.



Recovery of Catalyst 2. In a typical catalytic run of 1-decene hydrogenation, the reaction was stopped after 50 min. The solid catalyst was recovered, washed with pentane (5 mL) and dried in vacuum. The $\{^{1}H\}^{31}P$ MAS NMR spectrum of the recovered material appears identical to the spectrum of the same catalyst before the catalytic reaction, as shown in Figures 2A (before catalysis) and 2B (after catalysis).

Reuse of Catalyst 2. After a standard catalytic 1-decene hydrogenation, the solid catalyst was deposited on the bottom of the reaction Schlenk tube and the liquid phase separated. The remaining wet solid was re-suspended in pentane (5 mL) and separated again (the same procedure was repeated three times. Then, the catalyst was reused in a catalytic 1-decene hydrogenation run. The activity observed in the second run is reduced of approximately 25 % (Figure 3). However, the sampling done during the first run determined the removal of an amount of solid catalyst that can be estimated to be 16 % of the total amount. Therefore, the lower activity during the second run is almost completely accounted for.

Catalytic Hydrogenation of 1-Decene with 3. The molecular catalyst [IrH(POSS)(PO-COP)] (**3**) (12 mg, 8.4 μ mol) was introduced in a 20 mL Young Schlenk tube equipped with a Teflon-coated stirring bar under argon and dissolved in pentane (5 mL). The Schlenk was purged with dihydrogen (1 bar abs.) for 1 min, and the reaction solution was stirred at room temperature for 10 min, whereupon the solution colour changed from red to light yellow. Then, 1-decene (38 μ L, 201 μ mol) was added to the stirred solution by means of a microsyringe through a rubber septum. Samples of the reaction mixture (approximately 0.15 mL) were periodically withdrawn, filtered over silica, and analysed by GC (Figure S2).





Figure S3. Hydrogenation of 1-decene by 1 (pentane solution, monitored by GC).



3. Isomerization of 1-Decene

The isomerization of 1-decene under catalytic hydrogenation conditions was monitored by GC (Figure S4). The isomers were not attributed.

Figure S4. Isomerization of 1-decene during hydrogenation (reported in Figure S1) catalysed by **2** and "hot filtration test".



Figure S5. Reaction profile of the hydrogenation of 1-decene catalysed by **2** (in pentane suspension) followed by GC up to 90.2 % yield.



Figure S6. Isomers of 1-decene formed during the hydrogenation reaction shown in Figure S5.



In a control reaction, SBA-15 (85 mg) (unloaded, from the same batch used to prepare 2) was suspended in pentane (5 mL) in a 20 mL-Schlenk tube equipped with a Teflon coated stirring bar under argon, and 1-decene (38 μ L, 201 μ mol) was added to the suspension by means of a microsyringe. Samples of the reaction mixture were periodically withdrawn, filtered over silica, and analysed by GC. No isomerization products were observed over 120 min.

4. Catalytic Hydrogenation of Other Alkenes

Figure S7. Hydrogenation of *trans*-5-decene catalysed by **2** (in pentane suspension and followed by GC) and "hot filtration test" (dashed line) after 240 min at 11.5 % yield.



Figure S8. Reaction profile of the hydrogenation of cyclohexene catalysed by **2** (in pentane suspension and followed by GC) and "hot filtration test" (dashed line) after 240 min at 23.7 % yield.



Figure S9. Reaction profile of the hydrogenation of styrene catalysed by **2** (in pentane suspension and followed by GC) and "hot filtration test" (dashed line) after 90 min at 15.3 % yield.



Figure S10. Reaction profile of the hydrogenation of 4-phenyl-1-butene catalysed by **2** (in pentane suspension and followed by GC) and "hot filtration test" (dashed line) after 120 min at 31.9 % yield.



Figure S11. Isomers of 4-phenyl-1-butene formed during the hydrogenation reaction catalysed by **2** shown in Figure S10.



Figure S12. Hydrogenation of *trans*-5-decene by 1 (pentane solution, monitored by GC).



Figure S13. Hydrogenation of cyclohexene by 1 (pentane solution, monitored by GC).



Figure S14. Hydrogenation of styrene catalysed by 1 (pentane solution, monitored by GC).



Figure S15. Hydrogenation of 4-phenyl-1-butene by 1 (pentane solution, monitored by GC).



5. Catalytic Hydrogenation with [IrH(OSi₈O₁₂*i*Bu₇)(POCOP)] (3) and POSS in Excess

Hydrogenation of 1-Decene with 3 + POSS (10 equiv). The molecular catalyst [IrH(POSS)(POCOP)] (3) (12 mg, 8.4 µmol) and a 10-fold excess of POSS (58 mg, 70 µmol) were introduced in a 20 mL Young Schlenk tube equipped with a Teflon coated stirring bar under argon and dissolved in pentane (5 mL). The Schlenk was purged with hydrogen (1 bar abs.) for 1 min, and the reaction solution was stirred at room temperature for 10 min. whereupon its colour changed from red to light yellow. Then, 1-decene (38 µL, 201 µmol) was added to the stirred solution by means of a microsyringe through a rubber septum. Samples of the reaction mixture (approximately 0.15 mL) were periodically withdrawn, filtered over silica, and analysed by GC (Figure S16).

Figure S16. Reaction profile of the hydrogenation of 1-decene catalysed by **3** in the presence of a 10-fold excess of POSS.



6. Reaction of [IrH(O-SBA-15)(POCOP)] (2) with Ethene

Figure S17. ³¹P NMR spectrum of **2** after exposure to ethene (1.5 bar absolute) for 6 h (162 MHz, 2.5 mm rotor, 20 kHz)



7. Reaction of [IrH(OSi₈O₁₂*i*Bu₇)(POCOP)] (3) with Ethene

Figure S18. Progress of the reaction of **3** with ethene monitored by 31 P NMR spectroscopy (162 MHz) in [D₁₀]*p*-xylene



8. X-Ray Structures of 6a and 6b

[Ir(C₂H₄)(POCOP)] (6a). Red crystals of **6a** were obtained from a *p*-xylene solution. Crystal data for C₂₄H₄₃IrO₂P₂: plate (0.07 × 0.05 × 0.03 mm), triclinic, *P*–1, cell dimensions (100 K) a = 8.5336(10), b = 11.7835(14), c = 13.3762(15) Å, $\alpha = 100.381(2)$ °, $\beta = 95.958(2)$ °, $\gamma = 103.944(2)$ °, and V = 1.268.7(35) Å³ with Z = 2, $D_{\rm C} = 1.617$ Mg/m³, $\mu = 5.405$ mm⁻¹ (Mo K., graphite monochromated), $\lambda = 0.71073$ Å, *F*(000) = 620. The data were collected at 100 K on a Bruker AXS SMART APEX platform in the θ range 2.49–29.55°. The structure was solved with SHELXTL using direct methods. Of the 19.459 measured reflections with index ranges $-11 \le h \le 11$, $-16 \le k \le 16$, $-19 \le l \le 19$, 7.478 independent reflections ($R_{\rm int} = 0.0372$) were used in the refinement (full-matrix least squares on F^2) with anisotropic displacement parameters for all non-H atoms. Hydrogen atoms were introduced at calculated positions and refined with the riding model and individual isotropic thermal parameters for each group. Final residuals were $R_1 = 0.0264$ (for 6 577 reflections with $I > 2\sigma(I)$) and w $R_2 = 0.0496$ (all data), GOF = 0.996. Max. and min. difference peaks were +1.31 and -0.047 eÅ⁻³, the largest and mean $\Delta/\sigma = 0.003$ and 0.000.

[Ir(C₃H₆)(POCOP)] (6b). Red crystals of **6b** were obtained by slow evaporation of a toluene solution. Crystal data for C₂₅H₄₅IrO₂P₂: prism (0.44 × 0.24 × 0.23 mm), monoclinic, $P2_1/c$, cell dimensions (100 K) a = 16.2181(9), b = 10.7350(6), c = 15.8712(8) Å, $\beta = 107.894(2)$ °, and V = 2 629.5(2) Å³ with Z = 4, $D_c = 1.596$ Mg/m³, $\mu = 5.218$ mm⁻¹ (Mo K_s, graphite monochromated), $\lambda = 0.71073$ Å, F(000) = 1 272. The data were collected at 100 K on a Bruker AXS SMART APEX platform in the θ range 2.87–38.21°. The structure was solved with SHELXTL using direct methods. Of the 46 673 measured reflections with index ranges $-27 \le h \le 25$, $-17 \le k \le 17$, $-26 \le l \le 26$, 12 703 independent reflections ($R_{int} = 0.0438$) were used in the refinement (full-matrix least squares on F^2) with anisotropic displacement parameters for all non-H atoms. Hydrogen atoms were introduced at calculated positions and S13

refined with the riding model and individual isotropic thermal parameters for each group. Final residuals were $R_1 = 0.0382$ (for 10 320 reflections with $I > 2\sigma(I)$) and w $R_2 = 0.1038$ (all data), GOF = 1.042. Max. and min. difference peaks were +3.97 and -2.80 eÅ⁻³, the largest and mean $\Delta/\sigma = 0.008$ and 0.001.

Figure S19. ORTEP plot of **6b** (ellipsoids at 30% probability). The propene ligand and a $P(^{t}Bu)_{2}$ unit are disordered over two positions (solid: 55%; open: 45%).



Table S1. Selected distances (Å) and angles (°) in 6a and 6b.

	6a	6b
Ir–P(1)	2.2793(7)	2.2793(8)
Ir–P(2)	2.2771(7)	2.2811(8)
Ir–C(1)	2.032(3)	2.031(3)
Ir–C(23)	2.178(3)	2.223(5), 2.182(7)
Ir-C(24)	2.185(3)	2.256(6), 2.165(7)
C(23)–C(24)	1.390(4)	1.399(10), 1.381(13)
P(1)–Ir–P(2)	157.48(3)	156.44(3)
P(1)– Ir – $C(1)$	78.72(8)	78.22(8)
P(2)–Ir–C(1)	78.82(8)	78.30(8)
C(1)–Ir–C(23)	161.07(11)	160.08(18), 162.1(2)
C(1)–Ir–C(24)	161.77(11)	162.8(2), 160.5(3)
C(23)–Ir–P(1)	89.15(9)	111.21(18), 87.2(2)
C(24)–Ir–P(1)	112.21(8)	87.78(18), 114.93(18)
C(23)–Ir–P(2)	112.98(9)	111.21(18), 115.5(2)
C(24)–Ir–P(2)	89.14(8)	87.78(18), 89.2(3)
C(23)–Ir–C(24)	37.16(11)	36.4(2), 37.1(3)

9. Reaction of [Ir(C₂H₄)(POCOP)] (6a) with SBA-15

Figure S20. ³¹P MAS NMR spectrum of the product of the reaction between [IrC₂H₄(POCOP)] (**6a**) and SBA-15 (162 MHz, 4 mm rotor, 10.00 kHz). Asterisks denote spinning side bands.

