Interplay of Polarity and Confinement in Asymmetric Catalysis with Chiral Rh Diene Complexes in Microemulsions

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1 General experimental

Chemicals and solvents were used as received from the supplier unless stated otherwise. Anhydrous solvents were obtained by distillation under a nitrogen atmosphere using suitable drying agents. Ethyl acetate and hexanes were distilled prior to their use as eluents in column chromatography. Solvents for catalysis and the 3.1 M KOH solution were degassed by bubbling nitrogen through them. All NMR spectra were recorded on a Bruker Avance 300 (1H, 300 MHz; 13C, 75 MHz), Avance 500 (1H, 500 MHz; 13C, 126 MHz) or a Avance 700 (1H, 700 MHz; 13C, 176 MHz) spectrometer at room temperature. The NMR spectra were referenced to tetramethylsilane (δ = 0.00 ppm) and calibrated on the respective residual solvent peaks. Infrared spectra were recorded on a Bruker Vektor22 spectrometer equipped with an MKII golden gate single reflection diamant ATR system. All mass spectra were recorded with a Bruker Daltonics micro-TOF-Q using electrospray ionization (ESI) with nitrogen as carrier gas. The melting points of the synthesized compounds were determined with a Stuart SMP10 melting-point apparatus. Specific rotation values [α]D were determined with a Perkin Elmer Polarimeter 241 at 20 °C using the sodium D-line (λ = 589 nm). All HPLC chromatograms were recorded on a Shimadzu LC-20AT setup consisting of a LC-20A pump, a DGU-20A5 degasser, a SIL-20A autosampler and an SPD-20A UV-Vis detector operating at λ = 235 nm. For the mobile phase n-heptane/isopropanol mixtures were used. The chromatograms were evaluated with the program LCsolution v.1.21 from LabSolutions. The utilized column, volumetric ratios of the solvents in the mobile phase, operating conditions and retention times are shown below the respective compound. Microemulsions were analyzed by small angle X-Ray scattering (SAXS) at the high-brilliance beamline ID02 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The X-ray wavelength was set to λ = 1.01 Å and the sample to detector distance to 1 m yielding a q-range from 0.008 to 0.650 nm⁻¹, where \( q = 4\pi \sin(\theta/2)/\lambda \) is the absolute value of the scattering vector. The microemulsion were transferred into mark capillaries from Hilgenberg (glass no. 14, 1.0 mm diameter, wall thickness 0.01 mm) and the capillaries were carefully flame sealed to avoid composition changes due to evaporation. Measurements were performed at \( T = 60 \) °C with an exposure time of 300 ms. Details on the data acquisition procedure are described elsewhere. Finally, scattering of a water filled capillary was subtracted from the normalized data of the samples.
2 Experimental procedures

General procedure for the synthesis of chiral diene ligands (L1, L2) [GP 1]

The chiral diene ligands L1 and L2 were synthesized according to ref.[2]

General procedure for the synthesis of chiral rhodium complexes ([Rh(L1)Cl], [Rh(L2)Cl]2) [GP 2]

The chiral rhodium complexes [Rh(L1)Cl] and [Rh(L2)Cl]2 were synthesized according to ref..[2]

General procedure for the anion exchanges with silver salts ([Rh(L1)OH]2SbF6, [Rh(L2)OAc], [Rh(L2)OTf], [Rh(L2)OTs], [Rh(L2)PO2F2], [Rh(L2)OH]2SbF6) [GP 3]

According to ref.,[3] [Rh(L2)Cl]2 (20.0 mg, 20.4 µmol) was dissolved in CH2Cl2 (5 mL) and the respective silver salt (51.0 mmol) was added. The reaction mixture was stirred for 30 min at room temperature and filtered through a short pad of Celite®. The solvent was removed under reduced pressure and the crude product was washed with hexanes (5 mL). The respective complex was used without further purification.

For a better understanding, the synthesis of the cationic complex [Rh(L1)OH]2SbF6 is shown in Scheme S1. An overview of the synthesis of complexes that contain L2 is given in Scheme 1 in the main text.

Scheme S1. Synthesis of [Rh(L1)OH]2SbF6.

General procedure for the anion exchanges with AOT and SDS ([Rh(L2)AOT], [Rh(L2)SDS]) [GP 4]

To a solution of [Rh(L2)OAc] (30.0 mg, 58.4 µmol) in toluene (1.6 mL) was added water (1.4 mL) and the respective surfactant (58.4 µmol). The reaction mixture was stirred for 30 min at room temperature and the organic layer was decanted. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The respective complex was obtained without further purification.

General procedure for the rhodium-catalyzed 1,2-addition in dioxane (3) [GP 5]

According to ref.,[4] under a nitrogen atmosphere the respective chiral rhodium complex (10.0 µmol) was dissolved in degassed dioxane (1.6 mL), 3.1 M KOH (12.9 µL, 40.0 µmol) was added and the reaction mixture was stirred for 5 min at room temperature. The reaction mixture was heated to 60 °C, triphenylboroxine 2 (74.8 mg, 0.24 mmol) and the N-tosylimine 1 (58.8 mg, 0.20 mmol) were added and the reaction mixture was stirred for 24 h at 60 °C. The solution was diluted with EtOAc (2 mL), filtered through a short pad of silica and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (hexanes / EtOAc = 10 : 1).
General procedure for the rhodium-catalyzed 1,2-addition in microemulsions (3) [GP 6]

Under a nitrogen atmosphere n-octyl-β-D-glucopyranoside (C₆G₁, 0.285 g), sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 15.0 mg) and the respective rhodium complex (10.0 µmol) were dissolved in a mixture of degassed toluene (0.98 mL) and degassed water (0.85 mL). 3.1 M KOH (12.9 µL, 40.0 µmol) was added and the reaction mixture was stirred for 5 min at room temperature. The reaction mixture was heated to 60 °C, triphenylboroxine 1 (74.8 mg, 0.24 mmol) and the N-tosylimine 1 (58.8 mg, 0.20 mmol) were added and the reaction mixture was stirred for 24 h at 60 °C. EtOAc (3 mL) was added, the solution was filtered through a short pad of silica and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (hexanes / EtOAc = 10 : 1).

(R)-4-Isopropyl-3-((1R,2S,3R,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl)-oxazolidin-2-one (L1-H₂)

Side product in the synthesis of L1 according to GP 1; white solid (4 %), column chromatography on silica (hexanes / EtOAc = 10 : 1) followed by recrystallization from hexanes / EtOAc; Rf = 0.17 (hexanes / EtOAc = 10 : 1, UV); Smp.: 163 °C; [α]D²⁰ = −116.4° [c = 10 mg/mL, CH₂Cl₂]; ¹H NMR (500 MHz, CDCl₃): δ = 7.21–7.14 (m, 2H, o-ArH), 7.13–7.07 (m, 3H, p-ArH, m-ArH), 6.72 (dd, J = 3.0, 4.9 Hz, 1H, 5-H), 6.13 (dd, J = 3.0, 4.9 Hz, 1H, 5-H), 4.32–4.19 (m, 2H, 2-H, 3'-H), 4.09–4.01 (m, 2H, 2-H, 2'-H), 3.96 (dd, J = 2.0, 9.2 Hz, 1H, 2'-H), 3.21–3.10 (m, 1H, 1-H), 3.00–2.91 (m, 1H, 4-H), 1.75 (dsep, J = 1.8, 7.2 Hz, 1H, 4'-H), 1.59 (dt, J = 1.4, 9.8 Hz, 1H, 7-H), 1.55 (dt, J = 1.4, 9.8 Hz, 1H, 7-H), 0.70 (d, J = 7.3 Hz, 3H, 5'-H), –0.17 (d, J = 7.3 Hz, 3H, 5'-H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 173.4 (C-6'), 153.5 (C-1'), 141.1 (i-C₉H₉), 138.6 (C-6), 134.5 (C-5), 129.7 (o-C₆H₅), 126.8 (p-C₆H₅), 62.9 (C-2'), 58.5 (C-3'), 54.2 (C-2), 51.4 (C-3), 50.3 (C-7), 50.1 (C-4), 47.1 (C-1), 28.2 (C-4'), 18.4 (C-5'), 18.3 (C-5') ppm; FT-IR (ATR): v = 2966 (m), 2873 (w), 1764 (s), 1691 (s), 1601 (w), 1568 (w), 1489 (m), 1465 (m), 1388 (s), 1369 (m), 1363 (m), 1335 (m), 1301 (m), 1250 (s), 1203 (vs), 1152 (m), 1114 (m), 1120 (m), 1093 (m), 1063 (s), 1039 (m), 1012 (w), 978 (m), 945 (w), 922 (m), 910 (m), 884 (w), 847 (w), 828 (w), 795 (w), 781 (m), 766 (w), 747 (m), 736 (s), 703 (vs), 690 (vs), 668 (w), 632 (w), 606 (w), 534 (m), 500 (w), 474 (w), 423 (w) cm⁻¹; LRMS (ESI): m/z = 197.1 [C₁₃H₁₃O⁺], 260.1 [C₁₃H₁₉NO₃⁺], 326.2 [M + H⁺], 348.2 [M + Na⁺]; HRMS (ESI): calcd. for [C₂₀H₂₃NO₃Na⁺] 348.1570, found [M + Na⁺] 348.1570.

![Diagram](https://example.com/diagram)

(R)-4-Isopropyl-5,5-dimethyl-3-((1R,2S,3R,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one (L2-H₂)

Side product in the synthesis of L2 according to GP 1; colorless solid (9 %); recrystallization from hexanes / EtOAc; Smp.: 146 °C; [α]D²⁰ = −80.3 [c = 10 mg/mL, CH₂Cl₂]; ¹H NMR (500 MHz, CDCl₃): δ = 7.40–7.34 (m, 2H, o-ArH), 7.31–7.23 (m, 3H, m-ArH, p-ArH), 6.89 (dd,
J = 3.0, 5.7 Hz, 1H, 6-H), 6.32 (dd, J = 3.0, 5.7 Hz, 1H, 5-H), 4.37 (dd, J = 3.3, 10.9 Hz, 1H, 2-H), 4.23 (dd, J = 3.3, 10.9 Hz, 1H, 3-H), 4.09 (d, 1H, 4'-H), 3.33–3.27 (m, 1H, 1-H), 3.15–3.09 (m, 1H, 4-H), 1.92 (dsep, J = 1.8, 7.2 Hz, 1H, 5'-H), 1.76–1.69 (m, 2H, 7-H), 1.50 (s, 3H, 3'-H), 1.44 (s, 3H, 3''-H), 0.66 (d, J = 7.0 Hz, 3H, 6'-H), 0.35 (d, J = 7.0 Hz, 3H, 6''-H) ppm; 13C NMR (126 MHz, CDCl3): δ = 173.7 (C-7'), 153.2 (C-1'), 141.1 (i-C₆H), 138.4 (C-6), 134.5 (C-5), 129.9 (o-C₆H), 127.9 (m-C₆H), 126.5 (p-C₆H), 82.6 (C-2'), 66.6 (C-4'), 54.4 (C-2), 51.9 (C-3), 50.3 (C-7), 50.0 (C-4), 47.3 (C-1), 29.5 (C-5), 29.0 (C-3'), 21.2 (C-3''), 19.8 (C-6'), 15.6 (C-6''') ppm; FT-IR (ATR): ν = 2972 (w), 2252 (w), 1771 (m), 1689 (m), 1601 (w), 1494 (w), 1454 (w), 1392 (w), 1363 (m), 1338 (m), 1313 (m), 1276 (m), 1252 (m), 1231 (w), 1218 (m), 1193 (w), 1172 (m), 1115 (w), 1069 (w), 1043 (w), 966 (w), 906 (s), 858 (w), 847 (w), 804 (w), 778 (w), 726 (vs), 702 (s), 691 (s), 670 (w), 647 (m), 608 (w), 554 (w), 539 (w), 501 (w), 471 (w), 438 (w), 414 (w) cm⁻¹; LRMS (ESI): m/z = 352.2 [M – H]⁺; HRMS (ESI): calcd. for [C₂₂H₂₇NO₃]⁺ 352.1907, found [M – H]⁺ 352.1906.

![Diagram](attachment:image.png)

**[Rh(L2)OTf]**

Synthesis according to GP 3; yellow solid (quant.); obtained without further purification; [α]D²⁰ = −2.8° [c = 10 mg/mL, CH₂Cl₂]; 1H NMR (500 MHz, THF-d₈): δ = 7.70–7.63 (m, 2H, m-ArH), 7.33–7.23 (m, 3H, o-ArH, p-ArH), 4.85–4.79 (m, 1H, 6-H), 4.51–4.44 (m, 1H, 5-H), 4.35–4.31 (m, 1H, 1-H), 3.99 (d, J = 3.1 Hz, 1H, 4'-H), 3.73–3.67 (m, 1H, 4-H), 2.34–2.21 (m, 1H, 5'-H), 1.59 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.35 (s, 3H, 3'-H), 1.27 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.15 (d, J = 7.3 Hz, 3H, 6'-H), 1.08 (d, J = 7.3 Hz, 3H, 6'-H), 0.55 (s, 3H, 3''-H) ppm; 13C NMR (176 MHz, CDCl₃): δ = 166.6 (C-1'), 159.0 (C-7'), 136.3 (i-C₆H), 129.3 (o-C₆H), 128.8 (p-C₆H), 128.3 (m-C₆H), 119.8 (q, J = 319.9 Hz, CF₃), 88.3 (C-2'), 69.7 (C-4'), 62.8 (d, J = 12.1 Hz, C-3'), 62.0 (d, J = 12.1 Hz, C-6), 60.7 (C-4'), 60.2 (d, J = 6.1 Hz, C-7), 56.71 (C-5), 56.66 (C-1), 41.8 (d, J = 12.1 Hz, C-2), 29.5 (C-5'), 27.6 (C-3'), 21.5 (C-3''), 21.0 (C-6'), 17.4 (C-6'') ppm; FT-IR (ATR): ν = 3304 (w), 2971 (w), 2927 (w), 2883 (w), 2255 (w), 1672 (vs), 1496 (w), 1467 (w), 1444 (w), 1399 (m), 1377 (m), 1317 (m), 1283 (s), 1227 (s), 1202 (s), 1165 (s), 1130 (m), 1080 (w), 1027 (s), 958 (w), 912 (m), 881 (w), 855 (w), 814 (w), 789 (w), 762 (m), 727 (s), 700 (s), 634 (s), 590 (w), 574 (w), 516 (m) cm⁻¹; LRMS (ESI): m/z = 454.09 [M - OTf]⁺, 472.10 [M - OTf + H₂O]⁺; HRMS (ESI): calcd. for [C₂₂H₂₇NO₃Rh]⁺ 454.0884, found [M - OTf]⁺ 454.0885. Anal. Calcd. (%) for C₂₂H₂₇NO₃SF₃Rh: C: 45.78; H: 4.18; N: 2.32. Found: C: 46.08; H: 4.27; N: 2.25. Doublets in the 13C NMR spectrum result from coupling with the rhodium central atom.
[Rh(L2)OTs]

Synthesis according to GP 3; yellow solid (86%); obtained without further purification; $[\alpha]_D^{20} = -13.0^\circ$ [c = 10 mg/mL, CH$_2$Cl$_2$]; $^1$H NMR (700 MHz, CDCl$_3$): $\delta$ = 7.80–7.73 (m, 2H, $\sigma^*$-ArH), 7.69–7.64 (m, 2H, o-ArH), 7.33–7.27 (m, 3H, p-ArH, m-ArH), 7.21–7.15 (m, 2H, m'-ArH), 5.04–5.00 (m, 1H, 6-H), 4.93–4.89 (m, 1H, 5-H), 4.40–4.44 (m, 1H, 1-H), 3.90 (d, $J = 3.6$ Hz, 1H, 4'-H), 3.85–3.82 (m, 1H, 4-H), 2.35 (s, 3H, 1''-H), 2.29–2.21 (m, 1H, 5'-H), 1.67 (dt, $J = 1.3$, 6.9 Hz), 1H, 7-H), 1.43 (dt, $J = 1.3$, 6.9 Hz, 1H, 7-H), 1.35 (s, 3H, 3''-H), 1.15 (d, $J = 7.3$ Hz, 3H, 6''-H), 1.07 (d, $J = 7.3$ Hz, 3H, 6'-H), 0.55 (s, 3H, 3'-H) ppm; $^{13}$C NMR (176 MHz, CDCl$_3$): $\delta$ = 167.2 (C-7'), 158.9 (C-1'), 141.0 (C=C), 140.8 (C=C), 136.9 (C=C), 129.1 (m'-C), 128.9 (m-C), 128.5 (p-C), 127.8 (C=C), 87.7 (C=C), 69.7 (C-C), 62.1 (d, $J = 10.4$ Hz, C-3), 61.7 (C-6), 60.8 (C-4), 60.0 (C-7), 56.7 (C-5), 56.4 (C-1), 41.3 (d, $J = 10.2$ Hz, C-2), 29.5 (C-5'), 27.5 (C-1'), 21.6 (C-3'), 21.5 (C-3'), 20.9 (C-6'), 17.6 (C-6') ppm; FT-IR (ATR): $\tilde{v}$ = 3058 (w), 2967 (w), 2923 (w), 2879 (w), 2245 (w), 1673 (vs), 1600 (w), 1496 (w), 1464 (w), 1444 (w), 1376 (m), 1316 (m), 1262 (m), 1228 (m), 1155 (s), 1105 (s), 1079 (m), 1026 (m), 987 (s), 912 (m), 880 (w), 854 (w), 815 (m), 789 (w), 762 (m), 726 (s), 700 (m), 679 (s), 646 (w), 616 (w), 563 (m), 521 (w) cm$^{-1}$; LRMS (ESI): $m/z$ = 454.1 [M - OTs]$^+$, 472.1 [M - OTs - H$_2$O]$^+$; MS (ESI): neg. ion mode $m/z$ = 365.0 [2 OTs + Na]; HRMS (ESI): calcld. for C$_{29}$H$_{28}$NO$_5$Rh$: 454.0884$, found [M - OTs]$^+$ 454.0886. Anal. Calcd. (%) for C$_{29}$H$_{28}$NO$_5$SRh: 0.5 H$_2$O: C: 54.89; H: 5.24; N: 2.21. Found: C: 54.85; H: 5.26; N: 2.22. Doublets in the $^{13}$C NMR spectrum result from coupling with the rhodium central atom.

[Rh(L2)OAc]

Synthesis according to GP 3; yellow solid (70%); obtained without further purification; $[\alpha]_D^{20} = -12.0^\circ$ [c = 10 mg/mL, CH$_2$Cl$_2$]; $^1$H NMR (700 MHz, CDCl$_3$): $\delta$ = 7.72–7.67 (m, 2H, o-ArH), 7.31–7.26 (m, 2H, m-ArH), 7.25–7.21 (m, 1H, p-ArH), 4.66–4.58 (m, 1H, 6-H), 4.46–4.41 (m, 1H, 5-H), 4.36–4.32 (m, 1H, 1-H), 3.87–3.82 (m, 1H, 4'-H), 3.77–3.72 (m, 1H, 4-H), 2.33–2.24 (m, 1H, 5'-H), 1.91 (s, 3H, 2''-H), 1.60 (dt, $J = 1.3$, 6.9 Hz, 1H, 7-H), 1.35 (s, 3H, 3''-H), 1.32 (dt, $J = 1.3$, 6.9 Hz, 1H, 7-H), 1.16 (d, $J = 7.3$ Hz, 6H, 6'-H), 1.08 (d, $J = 7.3$ Hz, 6H, 6''-H), 0.48 (s, 3H, 3'-H) ppm; $^{13}$C NMR (176 MHz, CDCl$_3$): $\delta$ = 181.3 (C-1''), 168.7 (C-7'), 158.5 (C-1'), 138.0
(i-C$_3$H$_7$), 128.9 (m-C$_6$H$_5$), 128.2 (o-C$_6$H$_5$), 127.7 (p-C$_6$H$_5$), 87.0 (C-2'), 69.6 (C-4'), 60.6 (C-4), 57.6 (C-7), 56.9 (C-6), 54.7 (C-1), 52.7 (C-5), 52.0 (d, J = 10.4 Hz, C-3), 33.2 (d, J = 10.2 Hz, C-2), 29.4 (C-5'), 27.3 (C-2''), 23.5 (C-3'), 21.7 (C-3'), 20.7 (C-6'), 17.7 (C-6') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3058 (w), 2971 (w), 2922 (w), 2251 (w), 1772 (s), 1673 (s), 1571 (s), 1500 (w), 1415 (s), 1361 (m), 1311 (s), 1278 (s), 1247 (m), 1218 (m), 1170 (s), 1118 (m), 1070 (m), 1053 (w), 1032 (w), 1008 (w), 970 (w), 910 (s), 886 (m), 857 (w), 813 (w), 791 (m), 762 (m), 727 (vs), 707 (m), 694 (s), 664 (m), 647 (m), 615 (m), 521 (w), 467 (w), 437 (w), 412 (w) cm$^{-1}$; LRMS (ESI): $m/z$ = 634.2 [M + H + 2HOAc]$^+$; HRMS (ESI): calcld. for [C$_{23}$H$_{27}$NO$_3$Rh]$^+$ 634.1518, found [M + H + 2HOAc]$^+$ 634.1526; Anal. Calcd. (%) for C$_{24}$H$_{28}$NO$_3$Rh: C: 56.15; H: 5.50; N: 2.73. Found: C: 56.03; H: 5.59; N: 2.59. Doublets in the $^{13}$C NMR spectrum result from coupling with the rhodium central atom.

![Rh(L2)OAc]

$[\text{Rh(L2)OAc}]$

**[Rh(L2)PO$_2$F$_2$]**

Synthesis according to GP 3; yellow solid (quant.); obtained without further purification; $[\alpha]^2_D$ = $-14.0^\circ$ [c = 10 mg/mL, CH$_2$Cl$_2$]; $^1$H NMR (700 MHz, CDCl$_3$): $\delta$ = 7.73–7.65 (m, 4H, m-ArH), 7.36–7.29 (m, 6H, o-ArH, p-ArH), 4.88–4.80 (m, 2H, 6-H), 4.67–4.59 (m, 2H, 5-H), 4.50–4.43 (m, 4H, 1-H), 3.94 (d, J = 3.1 Hz, 2H, 4'-H), 3.91–3.87 (m, 2H, 4-H), 2.34–2.22 (m, 2H, 5'-H), 1.70 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.45 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.38 (s, 6H, 3'-H), 1.18 (d, J = 7.3 Hz, 6H, 6'-H), 1.10 (d, J = 7.3 Hz, 6H, 6'-H), 0.59 (s, 6H, 3'-H) ppm; $^{13}$C NMR (176 MHz, CDCl$_3$): $\delta$ = 166.9 (C-7'), 159.2 (C-1'), 136.6 (i-C$_3$H$_7$), 129.3 (o-C$_6$H$_5$), 128.7 (p-C$_6$H$_5$), 127.7 (m-C$_6$H$_5$), 88.1 (C-2'), 69.8 (C-4'), 62.6 (C-3), 61.3 (C-6), 60.8 (C-4), 60.2 (C-7), 56.7 (C-1), 56.0 (C-5), 41.8 (C-2'), 29.5 (C-5'), 27.5 (C-3'), 21.6 (C-3'), 20.9 (C-6'), 17.5 (C-6') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2971 (w), 1772 (w), 1673 (vs), 1496 (w), 1467 (w), 1444 (w), 1399 (m), 1377 (m), 1283 (s), 1246 (m), 1229 (m), 1192 (m), 1175 (w), 1130 (s), 1080 (m), 1031 (w), 958 (w), 911 (m), 878 (m), 854 (m), 789 (w), 763 (m), 727 (m), 700 (m), 648 (w), 616 (w), 590 (w), 535 (w), 498 (m) cm$^{-1}$; LRMS (ESI): $m/z$ = 454.1 [M – PO$_2$F$_2$]$^+$, 472.1 [M – PO$_2$F$_2$ + H$_2$O]$^+$; HRMS (ESI): calcld. for [C$_{22}$H$_{26}$F$_2$NO$_3$Rh]$^+$ 454.0884, found [M – PO$_2$F$_2$]$^+$ 454.0882. Anal. Calcd. (%) for C$_{22}$H$_{26}$F$_2$NO$_3$Rh: C: 43.15; H: 4.25; N: 2.19. Found: C: 42.81; H: 4.36; N: 2.18. Doublets in the $^{13}$C NMR spectrum result from coupling with the rhodium central atom.

![Rh(L2)PO$_2$F$_2$]

$[\text{Rh(L2)PO$_2$F$_2$}]$
[Rh(L2)OH₂]SbF₆

Synthesis according to GP 3; yellow solid (79 %); obtained after additional washing step with Et₂O without further purification; [α]²⁰ = 9.8° [c = 10 mg/mL, CH₂Cl₂]; ¹H NMR (700 MHz, THF-d₈): δ = 7.73–7.64 (m, 2H, m-ArH), 7.41–7.30 (m, 3H, o-ArH, p-ArH), 4.83–4.78 (m, 1H, 6-H), 4.53–4.49 (m, 1H, 5-H), 4.48–4.45 (m, 1H, 1-H), 4.14 (d, J = 3.1 Hz, 2H, 4'-H), 3.90–3.85 (m, 1H, 4-H), 2.39–2.29 (m, 1H, 5'-H), 1.67 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.41 (s, 3H, 3'-H), 1.40 (dt, J = 1.3, 6.9 Hz, 1H, 7-H), 1.18 (d, J = 7.3 Hz, 3H, 6'-H), 1.07 (d, J = 7.3 Hz, 3H, 6'-H), 0.68 (s, 3H, 3'-H) ppm; ¹³C NMR (176 MHz, THF-d₈): δ = 167.0 (C-7'), 160.2 (C-1'), 137.6 (i-C₆), 129.8 (o-C₆), 128.9 (p-C₆), 128.2 (m-C₆), 89.9 (C-2'), 70.3 (C-4'), 61.4 (d, J = 10.2 Hz, C-6), 61.2 (C-4), 59.2 (d, J = 5.7 Hz, C-7), 56.4 (C-1), 56.3 (d, J = 12.6 Hz, C-2), 55.5 (d, J = 9.5 Hz, C-5), 37.9 (d, J = 11.5 Hz, C-3), 30.1 (C-5'), 27.4 (C-3'), 21.2 (C-6'), 21.1 (C-3'), 17.0 (C-6') ppm; FT-IR (ATR): ν = 2976 (w), 1669 (s), 1497 (w), 1466 (w), 1444 (w), 1400 (w), 1378 (m), 1317 (w), 1285 (m), 1230 (w), 1193 (w), 1176 (w), 1131 (w), 1096 (w), 1030 (w), 958 (w), 914 (w), 882 (w), 855 (w), 828 (w), 789 (w), 762 (m), 727 (w), 701 (m), 654 (vs), 616 (m), 589 (w), 535 (w), 518 (w), 414 (w) cm⁻¹; LRMS (ESI): m/z = 454.1 [M – SbF₆ – H₂O]⁺; HRMS (ESI): calcd. for [C₂₂H₂₂NO₄Rh]⁺ 454.0884, found [M – SbF₆ – H₂O]⁺ 454.0882. Anal. Calcd. (%) for C₂₂H₂₂NO₄Rh: 0.25 Et₂O: C: 38.02; H: 4.09; N: 1.93. Found: C: 38.23; H: 4.32; N: 1.74. Doublets in the ¹³C NMR spectrum result from coupling with the rhodium central atom.

![Diagram](https://example.com/diagram.png)

[CaH₂NO₄Rh]⁺[SbF₆]⁻

708.11 g/mol

[Rh(L2)OH₂]SbF₆

Synthesis according to GP 4; yellow solid (82 %); [α]²⁰ = −4.7° [c = 10 mg/mL, CH₂Cl₂]; ¹H NMR (500 MHz, CDCｌ₃): δ = 7.74–7.66 (m, 2H, o-ArH), 7.33–7.27 (m, 3H, p-ArH, m-ArH), 4.89–4.80 (m, 1H, 6-H), 4.75–4.66 (m, 1H, 5-H), 4.43–4.36 (m, 1H, 1-H), 4.23–4.07 (m, 3H, CO₂CH₂CH, CH₂CHSO₃), 4.02–3.87 (m, 3H, 4'-H, CO₂CH₂CH), 3.84–3.78 (m, 1H, 4-H), 3.25–2.97 (m, 2H, CH₂CHSO₃), 2.33–2.20 (m, 1H, 5'-H), 1.70–1.61 (m, 2H, 7-H, CH(CH₂)₃CH₃), 1.55–1.48 (m, 1H, CH(CH₂)₃CH₃), 1.42–1.19 (m, 20H, 7-H, 3'-H, CH₂CH₃, CH(CH₂)₃CH₃), 1.16 (d, J = 7.3 Hz, 3H, 6'-H), 1.09 (d, J = 7.3 Hz, 3H, 6'-H), 0.92–0.80 (m, 12H, CH₂CH₃, CH(CH₂)₃CH₃), 0.56 (s, 3H, 3'-H) ppm; ¹³C NMR (126 MHz, CDCｌ₃): δ = 171.2, 171.1, 168.9, 168.6 (C=O₃Ar), 167.4 (C-7'), 158.8 (C-1'), 136.9 (i-C₆), 129.1 (m-C₆), 128.4 (p-C₆), 127.9 (o-C₆), 87.6 (C-2'), 69.7 (C-4'), 68.40, 68.35, 68.33, 68.28 (CO₂CH₂CH), 67.32, 67.29 (CO₂CH₂CH), 62.13 (C-3), 62.08, 62.0 (CH₂CHSO₃), 61.0 (C-6), 60.6 (C-4), 59.6 (C-7), 56.1 (C-1), 56.0 (C-5), 39.6 (C-2), 38.75, 38.72, 38.68, 38.66 (CH(CH₂)₃CH₃), 33.7 (CH₂CHSO₃), 30.40, 30.38, 30.36, 30.21, 30.17, 29.8 (CH(CH₂)₃CH₃), 29.5 (C-5'), 29.00, 28.98 (CH(CH₂)₃CH₃), 27.5 (C-3'), 23.7, 23.6, 23.1, 23.0 (CH₂CH₃), 21.6 (C-3'), 20.8 (C-6'), 17.5 (C-6'), 14.21, 14.15, 11.06, 11.05, 11.02, 11.01, 10.96 (CH₂CH₃, CH(CH₂)₃CH₃) ppm; FT-IR (ATR): ν = 2958 (w), 2927 (m), 2859 (w), 1734 (m), 1675 (vs), 1495 (w), 1463 (w), 1376 (m), S8
1317 (m), 1282 (m), 1227 (m), 1192 (s), 1161 (s), 1132 (m), 1080 (w), 1014 (m), 958 (w), 913 (w), 881 (w), 854 (w), 814 (w), 789 (w), 762 (m), 727 (s), 700 (m), 647 (w), 616 (w), 589 (w), 520 (m) cm\(^{-1}\); LRMS (ESI): \(m/z = 454.1\) [M – C\(_{26}\)H\(_{37}\)O\(_2\)S\(^+\)]\(^+\), 472.1 [M – C\(_{26}\)H\(_{37}\)O\(_2\)S + H\(_2\)O]\(^+\); HRMS (ESI): calcd. for [C\(_{22}\)H\(_{28}\)NO\(_2\)Rh]\(^+\) 454.0884, found [M – C\(_{26}\)H\(_{37}\)O\(_2\)S]\(^+\) 454.0895. Due to signal broadening no rhodium carbon couplings were observed in the \(^{13}\)C NMR spectrum. For the AOT anion multiple sets of \(^{13}\)C NMR signals were observed since commercial AOT contains a mixture of stereoisomers. A \(^1\)H–\(^{13}\)C HSQC NMR spectrum is shown below for clarification (Figure S26).

\[
\text{C}_{42}\text{H}_{62}\text{NO}_{10}\text{SRh}
\]

875.92 g/mol

[Rh(L2)AOT]

**[Rh(L2)SDS]**

Synthesis according to GP 4; yellow solid (90%); \([\alpha]_D^{20^\circ} = -7.2^\circ\) [c = 10 mg/mL, CH\(_2\)Cl\(_2\)]; \(^1\)H NMR (700 MHz, CDCl\(_3\)): \(\delta = 7.71–7.65\) (m, 2H, o-Ar\(\tilde{H}\), 7.33–7.27 (m, 3H, p-Ar\(\tilde{H}\), m-Ar\(\tilde{H}\), 4.97–4.91 (m, 1H, 6-H), 4.81–4.74 (m, 1H, 5-H), 4.45–4.38 (m, 1H, 1-H), 4.09–4.01 (m, 2H, CH\(_3\)(CH\(_2\))\(_{11}\)), 3.92 (d, \(J = 3.1\) Hz, 4'-H), 3.87–3.82 (m, 1H, 4-H), 2.31–2.23 (m, 1H, 5'-H), 1.73–1.65 (m, 3H, 7-H, CH\(_3\)(CH\(_2\))\(_{11}\)), 1.43 (dt, \(J = 1.3, 6.9\) Hz, 1H, 7-H), 1.41–1.34 (m, 5H, 3'-H, CH\(_3\)(CH\(_2\))\(_{11}\)), 1.31–1.20 (m, 16H, CH\(_2\)(CH\(_2\))\(_{11}\)), 1.17 (d, \(J = 7.3\) Hz, 3H, 6'-H), 1.09 (d, \(J = 7.3\) Hz, 3H, 6'-H), 0.86 (t, \(J = 7.2\) Hz, 3H, CH\(_3\)(CH\(_2\))\(_{11}\)), 0.57 (s, 3H, 3'-H) ppm; \(^{13}\)C NMR (176 MHz, CDCl\(_3\)): \(\delta = 167.1\) (C-7'), 158.9 (C-1'), 136.9 (C-Ar), 129.2 (m-C\(_\tilde{A}\)), 128.5 (p-C\(_\tilde{A}\)), 127.8 (o-C\(_\tilde{A}\)), 87.8 (C-2'), 69.7 (C-4'), 69.2 (CH\(_3\)(CH\(_2\))\(_{11}\)), 63.3 (C-3), 61.9 (C-6), 60.8 (C-4), 59.9 (C-7), 56.7 (C-5), 56.4 (C-1), 41.2 (C-2), 32.0, 29.77, 29.74, 29.72, 29.68 (CH\(_3\)(CH\(_2\))\(_{11}\)), 29.52 (C-5'), 29.45, 29.42, 29.39 (CH\(_3\)(CH\(_2\))\(_{11}\)), 27.5 (C-3'), 22.8, 25.9 (CH\(_3\)(CH\(_2\))\(_{11}\)), 21.6 (C-3'), 20.9 (C-6'), 17.6 (C-6'), 14.2 (CH\(_3\)(CH\(_2\))\(_{11}\)) ppm; FT-IR (ATR): \(\tilde{\nu} = 2923\) (m), 2853 (m), 1674 (vs), 1543 (w), 1495 (w), 1465 (w), 1444 (w), 1398 (m), 1376 (m), 1314 (m), 1283 (m), 1246 (m), 1227 (m), 1227 (m), 1171 (s), 1130 (m), 1079 (w), 958 (m), 912 (m), 881 (w), 855 (w), 789 (m), 762 (m), 726 (s), 699 (s), 646 (w), 616 (m), 576 (m), 536 (w), 521 (w), 476 (w) cm\(^{-1}\); LRMS (ESI): \(m/z = 454.1\) [M – C\(_{12}\)H\(_{26}\)SO\(_4\)]\(^+\); 472.1 [M – C\(_{12}\)H\(_{26}\)SO\(_4\) + H\(_2\)O]\(^+\); HRMS (ESI): calcd. for [C\(_{22}\)H\(_{28}\)NO\(_2\)Rh]\(^+\) 454.0884, found [M – C\(_{12}\)H\(_{26}\)SO\(_4\)]\(^+\) 454.0884. Due to signal broadening no rhodium carbon couplings were observed in the \(^{13}\)C NMR spectrum.
\( \text{N-}((4\text{-Chlorophenyl})(\text{phenyl})\text{methyl})\text{-}4\text{-methylbenzenesulfonamide (3)} \)

Synthesis according to GP 6; colorless solid (61 %, 90% ee \((R)\) according to chiral HPLC); column chromatography on SiO\(_2\) (hexanes/EtOAc 10 : 1).

\( R_f = 0.55 \) (hexanes/EtOAc 5 : 1, UV); m.p.: 115 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.59-7.51 \) (m, 2H, \( \sigma'-\text{Ar} \)), 7.24–7.11 (m, 7H, \( \sigma-\text{Ar} \), \( \sigma''-\text{Ar} \), \( \rho'-\text{Ar} \)), 7.10–7.00 (m, 4H, \( \rho-\text{Ar} \), \( \rho''-\text{Ar} \)), 5.53 (d, \( J = 7.2 \) Hz, 1H, CH\(_2\)), 4.96 (d, \( J = 7.2 \) Hz, 1H, NH), 2.39 (s, 3H, CH\(_3\)) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 143.6 \) (\( \rho-\text{ArC} \)), 140.2 (\( \iota''-\text{ArC} \)), 139.1 (\( \rho'-\text{ArC} \)), 137.3 (\( \iota'-\text{ArC} \)), 133.6 (\( \iota-\text{ArC} \)), 129.6 (\( m-\text{ArC} \)), 128.9 (\( m'-\text{ArC} \)), 128.9 (\( m''-\text{ArC} \)), 128.9 (\( \iota''-\text{ArC} \)), 128.8 (\( \rho''-\text{ArC} \)), 128.0 (\( \rho'-\text{ArC} \)), 127.4 (\( m''-\text{ArC} \)), 127.3 (\( \sigma''-\text{ArC} \)), 60.9 (CH), 21.6 (CH\(_3\)) ppm. The spectroscopic data were in accordance with the literature.\(^7\) Analytical HPLC: Daicel Chiralcel® OD-H (250 × 4.6 mm, 5 \( \mu \)m), heptane/isopropanol 93 : 7, flow rate: 1.0 mL/min, \( \lambda = 235 \) nm, \( R_t \ ((S)-3) = 14.84 \) min, \( R_t \ ((R)-3) = 18.54 \) min.
3 Microemulsion Characterization

3.1 Phase behavior studies

The phase behavior of the microemulsion systems H\textsubscript{2}O/KOH – toluene – C\textsubscript{8}G\textsubscript{1}/(ionic cosurfactant) – triphenylboroxine 2 / N-tosylimine 1 was determined as a function of the temperature and the surfactant concentration in the overall mixture

\[ \gamma = \frac{m_{\text{C}_8\text{G}_1} (+ m_{\text{ionic co-surfactant}})}{\sum_i m_i} \cdot 100\% \]

while keeping the mass fraction of toluene in the H\textsubscript{2}O/KOH - toluene

\[ \alpha = \frac{m_{\text{toluene}}}{m_{\text{H}_2\text{O}/\text{KOH}} + m_{\text{toluene}}} \cdot 100\% \]

constant at \( \alpha = 50 \) wt.%.

The KOH concentration in the mixture of water and KOH is given by

\[ \varepsilon = \frac{m_{\text{KOH}}}{m_A + m_{\text{KOH}}} \cdot 100\% . \]

Furthermore, we chose to keep the mass ratio of 1 and 2 in respect to the surfactant concentration constant

\[ S = \frac{m_1 + m_2}{m_{\text{C}_8\text{G}_1} (+ m_{\text{ionic co-surfactant}}) + m_1 + m_2} \cdot 100\% . \]

The concentration of the ionic-co surfactant in the overall surfactant mixture is defined by

\[ \delta = \frac{m_{\text{ionic co-surfactant}}}{m_{\text{C}_8\text{G}_1} + m_{\text{ionic co-surfactant}}} \cdot 100\% . \]

All components were weighed into a test tube with a precision of \( \Delta m = \pm 0.001 \) g and a stirring bar was added. Then the test tube was sealed with a polyethylene stopper and placed in a thermostated water bath equipped with a Thermo Electron Model Haake DC30 thermostat which can control the temperature up to \( \Delta T = \pm 0.1 \) K. After homogenization at \( T = 60 \) °C, the number and type of co-existing phases at a specific temperature and without stirring was determined visually. Liquid crystalline phases were identified by the appearance of transmitted light when using crossed polarizers. For each phase, the phase transition temperatures were determined with a precision of \( \Delta T = \pm 0.1 \) K. Finally, the samples were diluted with H\textsubscript{2}O/ KOH and toluene to the next composition and the procedure was repeated until no one-phase region was found. Note that no stock solution of 1 and 2 in toluene could be prepared due to the precipitation of these mixtures at temperatures below 55 °C.\textsuperscript{[2]}
3.2 Additional phase diagrams

The temperature-dependent phase behavior was studied recording \( T(\gamma) \)-sections through the phase space of the system \( \text{H}_2\text{O}/\text{KOH}-\text{toluene-C}_8\text{G}_1\)-triphenylboroxine 2/\( N\)-tosylimine 1 at \( \alpha = 50 \) wt.\%. In Figure S1 the phase diagram obtained in this work (▲) is compared with previous results\(^2\) (○).

![Phase Diagram](image)

**Figure S1.** \( T(\gamma) \)-section of the system \( \text{H}_2\text{O}/\text{KOH}-\text{toluene-C}_8\text{G}_1\)-triphenylboroxine 2/\( N\)-tosylimine 1 at \( \alpha = 50 \) wt.\%, \( \varepsilon = 0.33 \) wt.\% and 0.24 mmol of 2 and 0.20 mmol 1 at \( \gamma = 28 \) wt.\%. Data taken from Deimling et al.\(^2\) (○) in comparison to the data from this work (▲). At high temperatures a water-in-oil microemulsion coexists with a water excess phase (2̅), while at intermediate temperatures a one-phase region (1) is formed, which at lower temperatures converts into an oil-in-water microemulsion coexisting with an oil excess phase (2). Almost quantitative agreement was found between the phase diagrams.

As can be seen, there is an almost quantitative agreement between the two phase diagrams. A one-phase region (1) is limited at high temperatures by a water-in-oil microemulsion coexisting with a water excess phase (2̅), and at low temperatures by an oil-in-water microemulsion which coexists with an oil excess phase (2). The optimal microemulsion (\( \bar{X} \)-point), given by the phase inversion temperature \( \bar{T} \) and the minimum concentration of \( C_8\text{G}_1 \) \( \bar{\gamma} \) needed to formulate this microemulsion, is located at about \( \bar{T} = 41 \pm 2 \) °C and \( \bar{\gamma} = 20.5 \pm 0.5 \) wt.\%. Note that for the catalytic reactions, a larger surfactant concentration of 28 wt.% was used to ensure the reaction microemulsion existed over a wide composition and temperature regime.
3.2.1 Phase behavior of the microemulsion doped with cationic surfactants

The following figure shows the phase diagrams obtained when the nonionic starting microemulsion is doped with the cationic surfactant dodecyl trimethylammonium bromide (DTAB). Contrary to our observed trends of increasing efficiency at small co-surfactant fractions of an anionic surfactant, for $\delta_{DTAB} = 5$ wt.% the phase boundaries were shifted to higher surfactant concentrations compared to the non-doped system, see Figure S2, left, with the $X$-point located at $T \approx 25.0 \pm 0.5 \, ^\circ C$ and $\gamma \approx 24.0 \pm 0.5$ wt.%. By increasing the DTAB mass fraction to $\delta_{DTAB}= 10$ wt.% the phase boundaries shift back to lower surfactant concentrations.

Considering that an aqueous KOH solution ($\varepsilon = 0.33$ wt.%) is used in the phase behavior studies to mimic the catalysis conditions, we assumed that the hydroxide ions inhibit the dissociation of DTAB, making it act as a nonionic co-surfactant. This in turn leads to the initial decrease in efficiency. To proof this explanation, the KOH mass fraction in water was reduced by half ($\varepsilon = 0.16$ wt.%) to reduce the shielding of the electrostatic interactions. As a consequence, a significant shift of the phase boundaries to lower surfactant concentrations was found as observed for the two anionic surfactants at higher concentration of KOH.

Figure S2. $T(\gamma)$-section of the system H$_2$O/KOH-toluene-C$_8$G$_1$/DTAB-triphenylboroxine 2/N-tosylimine 1 at $\alpha = 50$ wt.%, $S = 11$ wt.%, $\varepsilon = 0.33$ wt.% and $\varepsilon = 0.16$ wt.%, respectively. Left: While the surfactant mixture became inefficient at $\delta_{DTAB} = 5$ wt.%, the phase boundaries shifted back toward smaller surfactant concentration at $\delta_{DTAB} = 10$ wt. %. Right: The efficiency of the surfactant mixture with $\delta_{DTAB} = 10$ wt. % can be improved by reducing the amount of KOH by half.
3.3 SAXS analysis of microemulsions

The corresponding SAXS scattering data of the investigated microemulsions are shown and described in the main part, see Figure 5. Herein the models used for the evaluation of the scattering data are described.

The size $d_{TS}/2$ of the water/oil domains as well as the correlation length $\xi_{TS}$ of the microemulsions were determined from the analysis of the peak and shoulder of the recorded scattering curves applying the Teubner-Strey model\[^6,7\] taking into account multiple scattering contributions.

\[
I(q) = \frac{l_{0,1}}{(1 - \frac{l_{0,1}}{l_{\max,1}})(\frac{q^2}{q_{\max}^2} - 1)^2} + \frac{l_{0,2}}{(1 - \frac{l_{0,2}}{l_{\max,2}})(\frac{q^2}{4q_{\max}^2} - 1)^2} + \frac{l_{0,2}}{l_{\max,2}}
\]

Here, $l_{0,1} = l_0 \cdot (1 - f \cdot x)$ and $l_{0,2} = l_0 \cdot f \cdot x$ are the intensities of the single and double scattering contributions at $q \to 0$ with $f$ being the fraction of the double scattering and $x$ the broadening due to higher order scattering. The maximum intensities at $q = q_{\max}$ and $q = 2q_{\max}$ of the single and double scattering contributions are given by $l_{\max,1} = l_{\max} (1 - f)$ and $l_{\max,2} = l_{\max} \cdot f$, respectively.

$I_{\max,1}$, $l_{\max,1}$ and $q_{\max}$ are correlated to the coefficients of the order parameter expansion $a_2 = 1/l_{0,1}$, $c_1 = -2c_2 q_{\max}^2$ and $c_2 = (1/l_{0,1} - 1/l_{\max,1})/q_{\max}^4$ from which the periodicity $d_{TS}$ and the correlation length $\xi_{TS}$ can be calculated according to

\[
d_{TS} = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^0.5 - \frac{c_1}{4c_2} \right]^{-0.5}
\]

\[
\xi_{TS} = \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^0.5 + \frac{c_1}{4c_2} \right]^{-0.5}
\]

Applying the above-mentioned analysis, the following parameters, were obtained for each sample (Table S1).

| \(\gamma\) [wt. %] | \(\delta\) [wt. %] | \(q_{\max}\) [Å\(^{-1}\)] | \(l_{\max}\) [cm\(^{-1}\)] | \(l_0\) [cm\(^{-1}\)] | \(f\) | \(x\) | \(d_{TS}\) [Å] | \(\xi_{TS}\) [Å] |
|------------------|------------------|-----------------|-----------------|-----------------|------|----|--------|--------|
| 14               | 5                | 0.029           | 40.0            | 13.2            | 0.045| 1.6 | 206    | 107    |
| 22               | 5                | 0.044           | 12.3            | 3.8             | 0.090| 1.5 | 136    | 74     |
| 28               | 0                | 0.071           | 3.2             | 1.0             | 0    | 0   | 84     | 43     |

The samples specific interface $S/V$ per volume was determined from the large $q$ part of the scattering curve combining film and bulk contrast contributions according to

\[
I(q) = 2\pi \cdot \phi_S \frac{\nu_s (\Delta \rho_s)^2}{q^2} e^{-q^2t^2} + 2\pi \cdot \phi_s \frac{a_s (\Delta \rho_s^B)^2}{q^2} e^{-q^2t^2} + b
\]

With $\phi_S$ the effective volume fraction of the surfactant at the film, $\nu_s$ the volume of a surfactant molecule, $a_s$ the effective area per surfactant molecule, $\Delta \rho_s^F$ and $\Delta \rho_s^B$ the scattering length density differences of the film and bulk contribution, respectively, $t$ being the thickness parameter and $b$ is the incoherent background.
To describe the scattering curves, the equation was simplified as follows

\[ I(q) = q^2 e^{-q^2} \left( z_1 + z_2 q^2 \right) + b \]

with \( z_1 \) and \( z_2 \) are prefactors of the film and bulk scattering contributions, respectively. The experimental values of \( z_1 \) and \( z_2 \) obtained from the fitting were compared to the theoretical values \( z_{1,\text{theo}} \) and \( z_{2,\text{theo}} \) which were calculated assuming that 1) all surfactant molecules reside at the interface and are not solubilized in water or toluene, 2) \( v_s/a_s \approx 10 \, \text{Å} \), and that 3) \( \Delta \rho^F = |\rho_{\text{surface}} - \frac{1}{2}(\rho_{\text{oil}} + \rho_{\text{H}_2\text{O}})| \) and \( \Delta \rho^B = \rho_{\text{H}_2\text{O}} - \rho_{\text{oil}} \) with \( \rho_{\text{CBG1}} = 1.12 \cdot 10^{-5} \, \text{Å}^{-2} \), \( \rho_{\text{AOT}} = 1.02 \cdot 10^{-5} \, \text{Å}^{-2} \), \( \rho_{\text{toluene}} = 8.17 \cdot 10^{-6} \, \text{Å}^{-2} \), \( \rho_1 = 8.77 \cdot 10^{-6} \, \text{Å}^{-2} \), \( \rho_2 = 9.95 \cdot 10^{-6} \, \text{Å}^{-2} \), and \( \rho_{\text{H}_2\text{O}} = 9.71 \cdot 10^{-6} \, \text{Å}^{-2} \).

From the experimental \( z_2 \), the specific interface per volume unit \( S/V \) can be recalculated by

\[ \frac{S}{V} = \phi_s a_s \frac{v_s}{2\pi \Delta \rho^B} \]

Alternatively, \( S/V \) can be determined from \( dTS/2 \) according to geometric models of the bicontinuous structure\cite{8-10} by

\[ \frac{S}{V} = 7 \phi(1 - \phi) \frac{dTS/2}{\rho_{\text{H}_2\text{O}}} \]

with \( \phi \) the volume fraction of oil in the oil/water mixture. Note that the pre-factor 7 was found in previous measurements on model microemulsions stabilized by nonionic surfactants.\cite{11}

The obtained parameters and their theoretical values are summarized in Table S2.

| \( \gamma \) [wt. %] | \( \delta \) [wt. %] | \( t \) [Å] | \( z_{1,\text{theo}} \) [10^{-11} Å^{-3}] | \( z_{2,\text{theo}} \) [10^{-13} Å^{-1}] | \( S/V \) [1/Å] | \( b \) [cm^{-1}] |
|----------------|----------------|---------|-----------------|-----------------|----------------|-----------------|
| 14             | 5              | 2.75    | 6.0             | 7.2             | 2.0            | 1.8             | 0.015           | 0.017           | 0.025          |
| 22             | 5              | 2.70    | 8.5             | 9.4             | 3.5            | 2.3             | 0.028           | 0.026           | 0.030          |
| 28             | 0              | 2.92    | 11.5            | 12.0            | 4.8            | 2.8             | 0.040           | 0.041           | 0.028          |

Comparing the experimental and theoretical values for \( z_1 \) and \( z_2 \) there are small but systematic deviations, where \( z_1 < z_{1,\text{theo}} \) while \( z_2 > z_{2,\text{theo}} \). They may arise through inaccuracy in absolute calibration by differences e.g. in optical path length and wall thickness of the capillaries as well as the definition of the film scattering length density differences \( \Delta \rho^F \).

For the specific interface \( S/V \), within an experimental error, an almost quantitative agreement between the experimental and the values based on the periodicity \( dTS/2 \) was found.
## 4 X-ray crystal structure analysis

|                  | L2-H₂   | L1-H₂   |
|------------------|---------|---------|
| **formula**      | C₂₂H₂₂NO₃ | C₂₀H₂₀NO₃ |
| **formula weight (g/mol)** | 353.44 | 325.39 |
| **crystal size (mm)** | 0.410 × 0.314 × 0.220 | 0.475 × 0.431 × 0.054 |
| **temperature (K)** | 135(2) | 140(2) |
| **wavelength λ (Å)** | 1.54178 | 0.71073 |
| **crystal system** | orthorhombic | monoclinic |
| **space group**   | P2₁2₁2₁ | P2₁ |
| **unit cell dimension** | | |
| a (Å)            | 8.4948(4) | 6.5249(6) |
| b (Å)            | 11.2864(5) | 9.9262(9) |
| c (Å)            | 19.8460(10) | 26.262(2) |
| α (deg)          | 90 | 90 |
| β (deg)          | 90 | 95.647(5) |
| γ (deg)          | 90 | 90 |
| V (Å³)           | 1902.75(16) | 1692.7(3) |
| Z                | 4 | 4 |
| **Dc (g/cm³)**   | 1.234 | 1.277 |
| **μ (mm⁻¹)**     | 0.648 | 0.085 |
| **F(000)**       | 760 | 696 |
| **theta range for data collection** | 4.507 to 66.360 | 1.558 to 26.424 |
| **index ranges** | –10≤h≤9, –13≤k≤12, –23≤l≤22 | –8≤h≤8, –12≤k≤12, –32≤l≤32 |
| **reflection collected/unique** | 17555 / 3272 [R(int) = 0.0336] | 32657 / 6801 [R(int) = 0.0571] |
| **completeness to theta** | 66.360, 99.2 % | 25.242, 98.8 % |
| **max. and min. transmission** | 0.9169 and 0.7917 | 0.7386 and 0.5967 |
| **refinement methods** | Full-matrix least-squares on F² | |
| **data/restraints/parameter** | 3272 / 0 / 240 | 6801 / 1 / 437 |
| **GOF on F²**    | 1.019 | 1.032 |
| R₁, wR₂ [l > 2σ(l)] | 0.0244, 0.0634 | 0.0522, 0.1218 |
| R₁, wR₂ (all data) | 0.0247, 0.0637 | 0.0801, 0.1326 |
| **absolute structure parameter** | 0.05(5) | 0.6(6) |
| **extinction coefficient** | 0.0026(3) | |
| **largest diff. peak and hole (e/Å³)** | 0.158 and –0.107 | 0.334 and -0.243 e.A⁻³ |

[a] The cif files were deposited with the reference numbers CCDC 2099410 (L2-H₂) and CCDC 2099412 (L1-H₂).
Figure S3. ORTEP drawing of hydrogenation product L2-H$_2$ in the solid state.

Figure S4. ORTEP drawing of hydrogenation product L1-H$_2$ in the solid state.
|                     | [Rh(L2)OTf] | [Rh(L2)OTS] |
|---------------------|-------------|-------------|
| formula             | C_{23}H_{25}F_{3}NO_{6}RhS | C_{29}H_{32}NO_{6}RhS |
| formula weight (g/mol) | 603.41     | 625.52      |
| crystal size (mm)   | 0.353 x 0.176 x 0.138  | 0.240 x 0.074 x 0.074 |
| temperature (K)     | 135(2)      | 135(2)      |
| wavelength λ (Å)    | 0.71073     | 0.71073     |
| crystal system      | orthorhombic | orthorhombic |
| space group         | P2₁2₁2₁     | P2₁2₁2₁     |
| unit cell dimension |              |             |
| a (Å)               | 9.1187(3)   | 11.9733(5)  |
| b (Å)               | 12.3256(4)  | 12.3130(5)  |
| c (Å)               | 20.8042(8)  | 18.1704(8)  |
| α (deg)             | 90          | 90          |
| β (deg)             | 90          | 90          |
| γ (deg)             | 90          | 90          |
| V (Å³)              | 2338.26(14) | 2678.8(2)   |
| Z                   | 4           | 4           |
| Dc (g/cm³)          | 1.714       | 1.551       |
| μ (mm⁻¹)            | 0.885       | 0.760       |
| F(000)              | 1224        | 1288        |
| theta range for data collection | 1.920 to 30.618 | 1.998 to 28.328 |
| index ranges        | -13sh≤12, -17sk≤17, -29sl≤29 | -13sh≤15, -16sk≤14, -24sl≤24 |
| reflection collected/unique | 29570 / 7184 [R(int) = 0.0432] | 35659 / 6641 [R(int) = 0.0429] |
| completeness to theta | 25.242, 100.0 % | 25.242, 100.0 % |
| max. and min. transmission | 0.7528, 0.6944 | 0.9830, 0.8256 |
| refinement methods  | Full-matrix least-squares on F² |             |
| data/restraints/parameter | 7184 / 0 / 320 | 6641 / 0 / 348 |
| GOF on F²           | 1.007       | 1.018       |
| R₁, wR₂ [I > 2σ(I)] | 0.0274, 0.0506 | 0.0303, 0.0523 |
| R₁, wR₂ (all data)  | 0.0342, 0.0525 | 0.0427, 0.0550 |
| absolute structure parameter | -0.004(11) | -0.018(10) |
| largest diff. peak and hole (e/Å³) | 0.332, -0.454 | 0.494, -0.325 |

[a] Cif files were deposited with reference numbers CCDC 2099413 ([Rh(L2)OTf]) and CCDC 2099414 ([Rh(L2)OTS]).
**Figure S5.** ORTEP drawing of $[\text{Rh(L_2)OTf}]$ in the solid state.

**Figure S6.** ORTEP drawing of $[\text{Rh(L_2)OTs}]$ in the solid state.
Table S5. Crystal data and structural refinement details for Rh complexes [Rh(L2)OAc] and [Rh(L2)PO2F2].

|                        | [Rh(L2)OAc]                        | [Rh(L2)PO2F2]                        |
|------------------------|------------------------------------|------------------------------------|
| formula                | C25H29Cl3NO5Rh                     | C22H25F2NO5PRh                     |
| formula weight (g/mol) | 632.75                             | 555.31                             |
| crystal size (mm)      | 0.432 × 0.129 × 0.060               | 0.263 × 0.200 × 0.074              |
| temperature (K)        | 135(2)                             | 140(2)                             |
| wavelength λ (Å)       | 0.71073                             | 0.71073                             |
| crystal system         | monoclinic                         | orthorombic                         |
| space group            | P2₁                                | P2₁P2₁P2₁                          |
| unit cell dimension    |                                    |                                    |
| a (Å)                  | 8.8257(5)                          | 8.9521(4)                          |
| b (Å)                  | 10.5657(6)                         | 11.7838(6)                         |
| c (Å)                  | 14.4268(8)                         | 20.9278(10)                        |
| α (deg)                | 90                                 | 90                                 |
| β (deg)                | 105.919(2)                         | 90                                 |
| γ (deg)                | 90                                 | 90                                 |
| V (Å³)                 | 1293.70(13)                        | 2207.67(18)                        |
| Z                      | 2                                  | 4                                  |
| Dc (g/cm³)             | 1.624                              | 1.671                              |
| μ (mm⁻¹)               | 1.007                              | 0.898                              |
| F(000)                 | 644                                | 1128                               |
| theta range for data collection | 2.400 to 28.362           | 1.946 to 28.318                     |
| index ranges           | −7hs±11, −14ks±14, −19ls±19        | −11hs±11, −15ks±15, −27ls±27       |
| reflection collected/unique | 24723 / 6437 [R(int) = 0.0409] | 29795 / 5484 [R(int) = 0.0278] |
| completeness to theta  | 25.242, 100.0 %                    | 25.242, 99.9 %                     |
| max. and min. transmission | 0.9600, 0.7554               | 0.9698, 0.8447                    |
| refinement methods     | Full-matrix least-squares on F²    |                                    |
| data/restraints/parameter | 6437 / 1 / 322                  | 5484 / 20 / 303                     |
| GOF on F²              | 1.010                              | 1.049                              |
| R₁, wR₂ [I > 2σ(I)]    | 0.0327, 0.0536                     | 0.0242, 0.0529                     |
| R₁, wR₂ (all data)     | 0.0474, 0.0566                     | 0.0300, 0.0549                     |
| absolute structure parameter | −0.019(13)                      | −0.019(8)                          |
| extinction coefficient | 0.0015(4)                          | n / a                              |
| largest diff. peak and hole (e/Å³) | 0.693, −0.580        | 0.701, −0.518                      |

[a] Cif files were deposited with reference numbers CCDC 2099419 ([Rh(L2)OAc]) and CCDC 2099420 ([Rh(L2)PO2F2]).
Figure S7. ORTEP drawing of \( \text{[Rh(L2)OAc]} \) in the solid state.

Figure S8. ORTEP drawing of \( \text{[Rh(L2)PO_2F_2]} \) in the solid state.
| Property                              | Value                                           |
|--------------------------------------|-------------------------------------------------|
| formula                              | $\text{C}_{22}\text{H}_{27}\text{F}_6\text{NO}_4\text{RhSb} \cdot \text{CH}_2\text{Cl}_2$ |
| formula weight (g/mol)               | 793.03                                          |
| crystal size (mm)                    | $0.240 \times 0.090 \times 0.061$               |
| temperature (K)                      | 140(2)                                          |
| wavelength ($\lambda$ Å)             | 0.71073                                         |
| crystal system                       | tetragonal                                      |
| space group                          | P4$_3$                                          |
| unit cell dimension                  |                                                 |
| $a$ (Å)                              | 10.0072(3)                                      |
| $b$ (Å)                              | 10.0072(3)                                      |
| $c$ (Å)                              | 28.1618(13)                                     |
| $\alpha$ (deg)                       | 90                                              |
| $\beta$ (deg)                        | 90                                              |
| $\gamma$ (deg)                       | 90                                              |
| $V$ ($\text{Å}^3$)                   | 2820.2(2)                                       |
| $Z$                                  | 4                                               |
| $D_\text{c}$ (g/cm$^3$)              | 1.868                                           |
| $\mu$ (mm$^{-1}$)                    | 1.802                                           |
| $F(000)$                             | 1560                                            |
| theta range for data collection      | 2.035 to 28.396                                 |
| index ranges                         | $-12\leq h \leq 13, -13\leq k \leq 13, -37\leq l \leq 37$ |
| reflection collected/unique          | 55460 / 7042 [R(int) = 0.0519]                  |
| completeness to theta                | 25.242, 100.0 %                                 |
| max. and min. transmission           | 0.9167, 0.7157                                  |
| refinement methods                   | Full-matrix least-squares on $F^2$              |
| data/restraints/parameter            | 7042 / 25 / 381                                 |
| GOF on $F^2$                         | 1.043                                           |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$]    | 0.0326, 0.0580                                  |
| $R_1$, $wR_2$ (all data)            | 0.0433, 0.0600                                  |
| absolute structure parameter         | 0.000(8)                                        |
| largest diff. peak and hole ($e/\text{Å}^3$) | 0.469, −0.562                                  |

[a] Cif files were deposited with reference numbers CCDC 2099421 ([Rh(L2)OH2]SbF6 · CH2Cl2).
**Figure S9.** ORTEP drawing of [Rh(L2)OH2]SbF6 in the solid state.
Figure S10. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of hydrogenation product L2-H$_2$. 
Figure S11. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of hydrogenation product L2-H$_2$.

Figure S12. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of hydrogenation product L1-H$_2$.

Figure S13. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of hydrogenation product L1-H$_2$. 
Figure S14. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of Rh complex [Rh(L2)OTs].

Figure S15. $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of Rh complex [Rh(L2)OTs].
Figure S16. $^1$H NMR spectrum (500 MHz, THF-d$_8$) of Rh complex [Rh(L2)OTf].

Figure S17. $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of Rh complex [Rh(L2)OTf].
Figure S18. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of Rh complex [Rh(L2)OAc].

Figure S19. $^1$H NMR spectrum (176 MHz, CDCl$_3$) of Rh complex [Rh(L2)OAc].
Figure S20. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of Rh complex $[\text{Rh}(\text{L2})\text{PO}_2\text{F}_2]$.

Figure S21. $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of Rh complex $[\text{Rh}(\text{L2})\text{PO}_2\text{F}_2]$. 
Figure S22. $^1$H NMR spectrum (700 MHz, THF-d$_8$) of Rh complex [Rh(L2)OH$_2$]SbF$_6$.

Figure S23. $^{13}$C NMR spectrum (176 MHz, THF-d$_8$) of Rh complex [Rh(L2)OH$_2$]SbF$_6$. 
Figure S24. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of Rh complex [Rh(L2)AOT].

Figure S25. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$) of Rh complex [Rh(L2)AOT].
Figure S26. $^1$H–$^{13}$C HSQC NMR spectrum (500 MHz (1H) and 126 MHz (13C), CDCl$_3$) of Rh complex [Rh(L2)AOT].

Figure S27. $^1$H NMR spectrum (700 MHz, CDCl$_3$) of Rh complex [Rh(L2)SDS].
**Figure S28.** $^{13}$C NMR spectrum (176 MHz, CDCl$_3$) of Rh complex [Rh(L2)SDS].

**Figure S29.** $^1$H NMR (300 MHz, CDCl$_3$) of $N$-tosylamide 3.
Figure S30. $^{13}$C NMR (75 MHz, CDCl$_3$) of $N$-tosylamide 3.
6 Additional catalysis experiments in microemulsions

For the initial screening of microemulsions and catalysts a series of experiments with constant concentration of C₆H₄ surfactant (γ = 28 wt.%) and varying SDS cosurfactant concentration δ was carried out (Table S7).

**Table S7.** 1,2-Addition results for the variation of the concentration of SDS in C₆H₄ based microemulsions (γ = 28 wt.%).

| Entry | Catalyst | Solvent | γ [wt. %] | δ [wt. %] | NMR yield [\%][a] | yield [\%][b] | e.r. (R) : (S) |
|-------|----------|---------|-----------|-----------|-------------------|---------------|---------------|
| 1     | [Rh(L1)Cl] | dioxane | -         | -         | 76                | 58            | 96 : 4        |
| 2     | [Rh(L1)Cl] | C₆H₄-ME | 28        | -         | 91                | 86            | 25 : 75      |
| 3     | [Rh(L1)Cl] | C₆H₄ / SDS-ME | 28        | 5         | 96                | 95            | 30 : 70      |
| 4     | [Rh(L1)Cl] | C₆H₄ / SDS-ME | 28        | 10        | 98                | 96            | 35 : 65      |
| 5     | [Rh(L2)Cl] | dioxane | -         | -         | 61                | 54            | 99 : 1       |
| 6     | [Rh(L2)Cl] | C₆H₄-ME | 28        | -         | 73                | 59            | 93 : 7       |
| 7     | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 5         | 84                | 76            | 84 : 16      |
| 8     | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 10        | 86                | 80            | 65 : 35      |
| 9     | [Rh(L2)Cl] | dioxane | -         | -         | 59                | 56            | 90 : 10      |
| 10    | [Rh(L2)Cl] | C₆H₄-ME | 28        | -         | 93                | 79            | 67 : 33      |
| 11    | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 5         | 94                | 84            | 64 : 36      |
| 12    | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 10        | 78                | 75            | 62 : 38      |
| 13    | [Rh(L2)Cl] | dioxane | -         | -         | 9                 | n. d.         | n. d.        |
| 14    | [Rh(L2)Cl] | C₆H₄-ME | 28        | -         | 52                | 32            | 79 : 21      |
| 15    | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 5         | 70                | 65            | 67 : 33      |
| 16    | [Rh(L2)Cl] | C₆H₄ / SDS-ME | 28        | 10        | 57                | 50            | 81 : 19      |

[a] The progress of the reactions was monitored by \(^1\)H NMR spectroscopy using mesitylene as an external standard. 
[b] Isolated yields. [c] C₆H₄-ME: Consisting of 0.600 g C₆H₄, 0.80 mL toluene and 0.70 mL H₂O. [d] C₆H₄ / SDS-ME: Consisting of 0.570 g C₆H₄, 0.030 g SDS, 0.80 mL toluene and 0.70 mL H₂O. [e] C₆H₄ / SDS-ME: Consisting of 0.540 g C₆H₄, 0.060 g SDS, 0.80 mL toluene and 0.70 mL H₂O.

For the monomeric catalyst [Rh(L1)Cl] a reversed enantioselectivity was determined when the catalysis was carried out in microemulsions instead of dioxane (entries 1–4). Furthermore, the yield increased for higher cosurfactant concentrations while the enantioselectivity decreased. When catalysis was carried out in microemulsions with the dimeric rhodium complex [Rh(L2)Cl]₂ the (R)-product 3 was still favored albeit with a lower selectivity (entries 5–8). The addition of anionic SDS cosurfactant led to a similar trend as observed with the monomer regarding yield and selectivity. In case of the tosylate monomer [Rh(L2)OTs] the use of the...
pure C₈G₁ micromemulsion instead of dioxane led to an increase in yield but the enantioselectivity significantly declined (dioxane: 59 %, e.r. 90 : 10; C₈G₁-ME: 93 %, e.r. 67 : 33) (entries 9 and 10). Additional SDS cosurfactant was not beneficial for catalysis since both selectivity and the yield decreased (88 %, e.r. 64 : 36 and 78 %, e.r. 62 : 38) (entries 11 and 12). However, the outcome was different when the acetate complex [Rh(L2)OAc] was employed (entries 13–16). In dioxane only 9 % of the desired product 3 were detected in the ¹H NMR (entry 13). The use of the C₈G₁ microemulsion significantly increased product formation up to 52 % with a moderate selectivity of e.r. 79 : 21 (entry 14). For the highest co-surfactant concentration (δ = 10 wt. %) both selectivity and yield were improved (57 %, e.r. 81 : 19) (entry 16).

Additionally, a series of experiments with constant SDS concentration (δ = 10 wt. %) and varying C₈G₁ concentration was performed (Table S8).

Table S8. 1,2-Addition results for the variation of the C₈G₁ concentration at δ = 10 wt. %.

| Entry | Catalyst | Solvent | γ [wt. %] | δ [wt. %] | NMR yield [%][a] | Yield [%][b] | e.r. (R) : (S) |
|-------|----------|---------|-----------|-----------|----------------|------------|--------------|
| 1     | [Rh(L1)Cl] | C₈G₁ / SDS-ME[c] | 28        | 10        | 98             | 96         | 35 : 65     |
| 2     | [Rh(L1)Cl] | C₈G₁ / SDS-ME [d] | 14        | 10        | 85             | 81         | 21 : 79     |
| 3     | [Rh(L2)OTs] | C₈G₁ / SDS-ME[c] | 28        | 10        | 78             | 75         | 62 : 38     |
| 4     | [Rh(L2)OTs] | C₈G₁ / SDS-ME [d] | 14        | 10        | 88             | 84         | 69 : 31     |
| 5     | [Rh(L2)OAc] | C₈G₁ / SDS-ME[c] | 28        | 10        | 57             | 50         | 81 : 19     |
| 6     | [Rh(L2)OAc] | C₈G₁ / SDS-ME [d] | 14        | 10        | 74             | 70         | 65 : 35     |

[a] The progress of the reactions was monitored by ¹H NMR spectroscopy using mesitylene as an external standard. [b] Isolated yields. [c] C₈G₁ / SDS-ME: Consisting of 0.540 g C₈G₁, 0.060 g SDS, 0.80 mL toluene and 0.70 mL H₂O. [d] C₈G₁ / SDS-ME: Consisting of 0.270 g C₈G₁, 0.030 g SDS, 0.98 mL toluene and 0.85 mL H₂O.

For the monomeric chloro complex [Rh(L1)Cl] the yield was lower for γ = 10 wt. % than for γ = 28 wt. % but the (S)-product 3 was even more favoured at γ = 10 wt. % (98 %, e.r. 35 : 65 and 85 %, e.r. 21 : 79) (entries 1 and 2). The same trend regarding enantioselectivity was observed for the tosylate [Rh(L2)OTs] (78 %, e.r. 62 : 38 and 88 %, e.r. 69 : 31) (entries 3 and 4). For the acetate [Rh(L2)OAc] the yield was higher for γ = 14 wt.% than for γ = 28 wt.% but the enantioselectivity decreased for γ = 14 wt.% (57 %, e.r. 81 : 19 and 74 %, e.r. 65 : 35) (entries 5 and 6).

Subsequently the anionic co-surfactant SDS was replaced with AOT and a series of catalyses with varying γ at constant δ = 5 wt. % was carried out (Table S9).
Table S9. Variation of the surfactant mass fraction γ in the C₈G₁ / AOT microemulsion at δ = 5 wt. %.

| Entry | Catalyst   | Solvent       | γ [wt. %] | δ [wt. %] | NMR yield [%][a] | Yield [%][b] | e.r. (R) : (S) |
|-------|------------|---------------|-----------|-----------|------------------|--------------|----------------|
| 1     | [Rh(L1)Cl] | C₈G₁ / AOT-ME | 14        | 5         | 98               | 96           | 59 : 41        |
| 2     | [Rh(L1)Cl] | C₈G₁ / AOT-ME | 21        | 5         | 97               | 93           | 59 : 41        |
| 3     | [Rh(L1)Cl] | C₈G₁ / AOT-ME | 28        | 5         | 95               | 91           | 39 : 61        |
| 4     | [Rh(L1)Cl] | dioxane       | -         | -         | 76               | 58           | 96 : 4         |
| 5     | [Rh(L2)OTs] | C₈G₁ / AOT-ME | 14        | 5         | 76               | 72           | 74 : 26        |
| 6     | [Rh(L2)OTs] | C₈G₁ / AOT-ME | 21        | 5         | 69               | 64           | 91 : 9         |
| 7     | [Rh(L2)OTs] | C₈G₁ / AOT-ME | 28        | 5         | 79               | 74           | 90 : 10        |
| 8     | [Rh(L2)OTs] | dioxane       | -         | -         | 59               | 56           | 90 : 10        |
| 9     | [Rh(L2)OAc] | C₈G₁ / AOT-ME | 14        | 5         | 63               | 61           | 95 : 5         |
| 10    | [Rh(L2)OAc] | C₈G₁ / AOT-ME | 21        | 5         | 56               | 50           | 94 : 6         |
| 11    | [Rh(L2)OAc] | C₈G₁ / AOT-ME | 28        | 5         | 59               | 55           | 93 : 7         |
| 12    | [Rh(L2)OAc] | dioxane       | -         | -         | 9                | n. d.        | n. d.          |
| 13    | [Rh(L2)OTf] | C₈G₁ / AOT-ME | 14        | 5         | 72               | 67           | 94 : 6         |
| 14    | [Rh(L2)OTf] | C₈G₁ / AOT-ME | 21        | 5         | 69               | 65           | 85 : 15        |
| 15    | [Rh(L2)OTf] | C₈G₁ / AOT-ME | 28        | 5         | 77               | 71           | 89 : 11        |
| 16    | [Rh(L2)OTf] | dioxane       | -         | -         | 53               | 53           | 93 : 7         |
| 17    | [Rh(L2)OH₂]SbF₆ | C₈G₁ / AOT-ME | 14        | 5         | 60               | 55           | 86 : 14        |
| 18    | [Rh(L2)OH₂]SbF₆ | C₈G₁ / AOT-ME | 21        | 5         | 74               | 70           | 93 : 7         |
| 19    | [Rh(L2)OH₂]SbF₆ | C₈G₁ / AOT-ME | 28        | 5         | 62               | 55           | 91 : 9         |
| 20    | [Rh(L2)OH₂]SbF₆ | dioxane       | -         | -         | 51               | 45           | 96 : 4         |

[a] The progress of the reactions was monitored by 1H NMR spectroscopy using mesitylene as an external standard. 
[b] Isolated yields. [c] C₈G₁ / AOT-ME: Consisting of 0.285 g C₈G₁, 0.015 g AOT, 0.98 mL toluene and 0.85 mL H₂O.[d] C₈G₁ / AOT-ME: Consisting of 0.426 g C₈G₁, 0.025 g AOT, 0.90 mL toluene and 0.78 mL H₂O.[e] C₈G₁ / AOT-ME: Consisting of 0.57 g C₈G₁, 0.030 g AOT, 0.80 mL toluene and 0.70 mL H₂O.

In case of the chloro monomer [Rh(L1)Cl] the enantioselectivity was highly depending on the C₈G₁ mass fraction γ (entries 1–4). At γ = 14 wt.% and γ = 28 wt.% the (S)-product 3 was favoured (98 %, e.r. 34 : 66 and 95 %, e.r. 39 : 61) but at γ = 21 wt.% and in dioxane the (R)-product 3 was preferentially formed (C₈G₁ / AOT-ME: 97 %, e.r. 59 : 41; dioxane: 76 %, e.r. 96 : 4). The catalysis results were different when [Rh(L2)OTs] was used in the 1,2-addition (entries 5–8). At γ = 14 wt.% the enantioselectivity was significantly lower than in dioxane (C₈G₁ / AOT-ME: 76 %, e. r. 74 : 26; dioxane: 59 %, e. r. 90 : 10). For higher γ values the
selectivity was similar to the catalysis in dioxane but yields were slightly higher. The largest effect of the microemulsion on the 1,2-addition results was observed for [Rh(L2)OAc] (entries 9–12). In dioxane only a low yield of 9 % was detected in dioxane (entry 12) while microemulsions performed much better with surprisingly high enantioselectivity. In case of the triflate [Rh(L2)OTf] enantioselectivities were similar in dioxane and in the C8G1 / AOT microemulsion at γ = 14 wt.% (entries 13 and 16). Only for γ = 21 wt.% and γ = 28 wt.% the selectivity was slightly lower than for the 1,2-addition in dioxane (entries 14 and 15). When the anion was exchanged with weakly coordinating SbF6 the yields were slightly lower in the microemulsions as compared to dioxane (entries 17–20). The optimum for the microemulsion was found at γ = 21 wt.% (74 %, e. r. 93 : 7).
7 Theoretical calculations

7.1 Computational details

All Rh complexes were investigated via Density Functional Theory (DFT) with the functional B3LYP-D3(BJ) which includes dispersion correction\textsuperscript{[12]} with Becke-Johnson damping\textsuperscript{[13]} and a def2-SVP basis set. Geometry optimizations were performed in Turbomole V7.4.1\textsuperscript{[14]} using DL-FIND\textsuperscript{[15]} in Chemshell.\textsuperscript{[16]}

The crystal structures were used as initial geometries for geometry optimization. For the complexes with SDS and AOT as counterion, no crystal structure was available as initial geometry. All geometry optimizations were performed using the conductor-like screening model (COSMO)\textsuperscript{[17]} with a dielectric constant of \(\varepsilon = 2.25\) for dioxane.

The Intrinsic Bond Orbitals (IBOs) in the figures were calculated in IboView\textsuperscript{[18]} based on orbitals at B3LYP-D3(BJ)/def2-SVP level. In IboView, the exponent 2 was chosen for the localization method. All visualisations were also done in IboView. The percentual electron distributions in the IBOs shown in the table S10 were calculated in Turbomole.

For the calculation of the binding energies, single-point calculations at the M06/def2-TZVP level were performed. The binding energies were then calculated from the difference of the electronic energies of the Rh complexes without the counterion and the counterion separated and the Rh complexes with the counterion.

The calculation of the equilibrium constants was performed via the following equation:

\[
k_{eq} = \exp \left( \frac{-\Delta G}{RT} \right)
\]

The free energy G was calculated at 333.15 K within the RRHO (rigid rotor harmonic oscillator) approximation. Vibrational frequencies less than 100 cm\(^{-1}\) were raised to this threshold.

7.2 IBOs Table

Table S10. Percentual electron contribution of the different orbitals of the Rh and the counterion or solvent to the IBO of the bond between the Rh and the counterion or solvent.

| Rh complex | Total /% | s   | p    | d    | f  | Rh | Total /% | s   | p    | d   |
|------------|----------|-----|------|------|----|----|---------|-----|------|-----|
| [Rh(L2)OAc] – O1 | 7.88      | 3.35 | 1.50 | 3.00 | 0.03 | 85.78 | 7.49   | 78.21 | 0.08 |
| [Rh(L2)OAc] – O2 | 9.03      | 3.23 | 1.88 | 3.89 | 0.03 | 85.31 | 7.93   | 77.30 | 0.08 |
| [Rh(L2)OTf]   | 8.39      | 3.23 | 1.74 | 3.37 | 0.04 | 85.60 | 17.24  | 68.30 | 0.06 |
| [Rh(L2)OTs]   | 9.66      | 3.31 | 2.00 | 4.30 | 0.05 | 85.14 | 20.35  | 64.74 | 0.05 |
| [Rh(L2)PO2F2] | 10.12     | 4.27 | 1.82 | 3.98 | 0.05 | 84.72 | 20.56  | 64.12 | 0.04 |
| [Rh(L2)dioxane] | 6.18     | 2.33 | 2.16 | 1.66 | 0.03 | 91.78 | 28.19  | 63.59 | 0.00 |
| [Rh(L2)OH2]  | 8.48      | 3.66 | 2.41 | 2.37 | 0.04 | 91.72 | 35.10  | 56.61 | 0.01 |
| [Rh(L2)SDS]   | 8.60      | 3.12 | 2.27 | 3.17 | 0.05 | 86.79 | 22.82  | 63.93 | 0.04 |
| [Rh(L2)AOT]   | 10.34     | 4.22 | 2.00 | 4.07 | 0.05 | 85.30 | 20.25  | 65.00 | 0.05 |
8 HPLC chromatograms

Figure S31. HPLC chromatogram of racemic N-tosylamide 5 obtained with [Rh(COD)OH]$_2$ with GP 6.

Figure S32. HPLC chromatogram of N-tosylamide 5 obtained with [Rh(L2)OAc] with GP 6.
9 Analysis of kinetics

Herein we describe the analysis of the kinetics in microemulsion and dioxane, shown and discussed in the main part, by using a power law approach. The linear decrease in the fraction of newly formed product 3 ($A_{t \to \infty} - A(t)$) against the time in a log-log plot, indicated a power law behavior, see Figure S28.

**Figure S33.** Double logarithmic representation of the fraction of newly formed product 3 ($A_{t \to \infty} - A(t)$) as a function of the time for different temperatures (left) and surfactant mass fractions (right). The data almost quantitively follow a linear behavior.

Accordingly, we described the formation of $N$-tosylamide 3 by

$$A(t) = A_{t \to \infty} - A(t_0)^m.$$  

Thereby, the slope of the data in the log-log representation, corresponds to the power $m$ of the power-law description, while the intercept $ic$ can be used to determine

$$t_0 = \left(\frac{1}{A_{t \to \infty}}\right)^{m} 10^{ic},$$

which can be considered to be an effective reciprocal rate constant.
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