

- *Supplementary Information* -

Chiral *N*-heterocyclic biscarbenes based on 1,2,4-triazole as ligands for metal-catalyzed asymmetric synthesis

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1 General remarks

The preparation of all metal complexes was carried out under dry argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen.¹ $[\alpha]_D^{20}$ values are given in deg mL dm⁻¹ g⁻¹. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker Avance III 400 spectrometer at room temperature and referenced to the residual solvent signal.² NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were acquired by the Technische Universität München Mass Spectrometry Laboratory using a Finnigan MAT 90 spectrometer equipped with a FAB ionization chamber. The ee values in catalysis were determined by chiral GC using a HP 5890A and a Chirasil-L-Val column for product **6** and an Astec ChiralDEX G-TA column for product **8**.

1.1 Synthesis of (1)³

Formylhydrazine (1.06 g, 18.0 mmol) and triethylorthoformate (5.83 ml, 36.0 mmol) were solved in dry methanol (20 mL) and heated for 3 h at 80 °C. Then 1R,2R-(-)-1,2-diaminocyclohexane (1.00 g, 8.80 mmol) was added. The reaction mixture was held under reflux for 16 h, before the resulting white solid was filtered, washed with ethanol and dried in vacuum.

Yield: 0.33g (68 %). $[\alpha]_D^{20}$ -60.3 (*c* 0.028 in DMSO). Anal. Calcd for C₁₀H₁₄N₆ (218.13): C, 55.03; H, 6.47; N, 38.50. Found: C, 54.95; H, 6.47; N, 38.78. ¹H NMR (400 MHz, DMSO-d⁶): δ 1.47 (m, 2H, ^{c-hex}CH₂), 1.86 (m, 2H, ^{c-hex}CH₂), 1.96 (m, 2H, ^{c-hex}CH₂), 2.10 (m, 2H, ^{c-hex}CH₂), 4.63 (m, 2H, ^{c-hex}CH), 8.39 (s, 4H, NCHN). ¹³C{¹H} NMR (100.5 MHz, DMSO-d⁶): δ 24.1 (^{c-hex}CH₂), 32.5 (^{c-hex}CH₂), 58.3 (^{c-hex}CH), 141.6 (NCHN). MS (ESI): *m/z* = 437.4 (16) [2M+H]⁺, 219.3 (100) [M+H]⁺.

1.2 General procedure for the synthesis of (2)

1 (1.8 mmol), alkyl halide (4.5 mmol) and 1.0 mL MeCN were heated in an ACE pressure tube with a volume of 35 mL at 100 °C for 24 h. The precipitate was isolated by filtration, washed three times with 5 mL THF and pentane and dried under reduced pressure to obtain the solid.

Compound (2^{Me})

Yield: 628 mg (68 %). $[\alpha]_D^{20}$ -25.7 (*c* 0.007 in DMSO). Anal. Calcd for C₁₂H₂₀I₂N₆ (501.98): C, 28.70; H, 4.01; N, 16.74. Found: C, 28.62; H, 3.91; N, 16.46. ¹H NMR (400 MHz, DMSO-d⁶): δ 1.49 (m, 2H, ^{c-hex}CH₂), 1.92 (m, 2H, ^{c-hex}CH₂), 2.08 (m, 2H, ^{c-hex}CH₂), 2.35 (m, 2H, ^{c-hex}CH₂), 4.04 (s, 6H, CH₃), 5.05 (m, 2H, ^{c-hex}CH), 9.19 (s, 2H, NCHN), 10.22 (s, 2H, NCHN).

^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, DMSO- d^6): δ 23.4 ($^{c\text{-hex}}\text{CH}_2$), 31.4 ($^{c\text{-hex}}\text{CH}_2$), 39.1 (CH_3), 60.2 ($^{c\text{-hex}}\text{CH}$), 142.4 (NCHN), 143.2 (NCHN). MS(FAB) m/z (%): 374.8 (24.3) $[\text{M}+\text{I}]^+$, 246.9 (100) $[\text{M}]^{2+}$.

Compound (2^{MN})

Yield: 799 mg (66 %). $[\alpha]_{\text{D}}^{20}$ -57.1 (c 0.003 in CH_2Cl_2). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{Br}_2\text{N}_6$ (660.45): C, 58.19; H, 4.88; N, 12.72. Found: C, 57.62; H, 4.85; N, 12.57. ^1H NMR (400 MHz, DMSO- d^6): δ 1.48 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 1.93 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.14 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.39 (m, 4H, $^{c\text{-hex}}\text{CH}_2$), 5.05 (m, 2H, $^{c\text{-hex}}\text{CH}$), 5.74 (m, 4H, CH_2Ph), 7.49 (m, 2H, aryl), 7.58 (m, 4H, aryl), 7.94 (m, 8H, aryl), 9.29 (s, 2H, NCHN), 10.47 (s, 2H, NCHN). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, DMSO- d^6): δ = 23.5 ($^{c\text{-hex}}\text{CH}_2$), 31.1 ($^{c\text{-hex}}\text{CH}_2$), 55.4 (NCH $_2$), 60.7 ($^{c\text{-hex}}\text{CH}$), 126.2 (C_{arom}), 126.7 (C_{arom}), 126.9 (C_{arom}), 127.7 (C_{arom}), 127.9 (C_{arom}), 128.5 (C_{arom}), 128.6 (C_{arom}), 130.2 (C_{quat}), 132.6 (C_{quat}), 132.8 (C_{quat}), 142.5 (NCHN), 143.9 (NCHN). MS(FAB) m/z (%): 581.1 (12.6) $[\text{M}+\text{Br}]^+$, 499.2 (100) $[\text{M}]^{2+}$.

1.3 General procedure for the synthesis of (3)

A solution of ditriazolium dihalide **2** (1.0 mmol) in water (2 mL) was added to a solution of potassium hexafluorophosphate (2.0 mmol) in water (0.5 mL). The precipitate was isolated by filtration, washed with diethyl ether (three times with 5 mL), and dried in vacuo overnight yielding the colourless solid product.

Compound (3^{Me})

Yield: 425 mg (79 %). $[\alpha]_{\text{D}}^{20}$ -32.9 (c 0.010 in DMSO). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{F}_{12}\text{N}_6\text{P}_2$ (538.10): C, 26.78; H, 3.75; N, 15.61. Found: C, 26.55; H, 3.63; N, 15.49. ^1H NMR (400 MHz, DMSO- d^6): δ 1.47 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 1.93 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.06 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.32 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 4.03 (s, 6H, CH_3), 4.98 (m, 2H, $^{c\text{-hex}}\text{CH}$), 9.13 (s, 2H, NCHN), 10.12 (s, 2H, NCHN). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, DMSO- d^6): δ 23.4 ($^{c\text{-hex}}\text{CH}_2$), 31.4 ($^{c\text{-hex}}\text{CH}_2$), 38.9 (CH_3), 60.3 ($^{c\text{-hex}}\text{CH}$), 142.4 (NCHN), 143.3 (NCHN). ^{31}P $\{^1\text{H}\}$ NMR (161.8 MHz, CD_2Cl_2): δ - 143.5 (sept). MS(FAB) m/z (%): 392.7 (68.34) $[\text{M}+\text{PF}_6]^+$, 246.9 (100) $[\text{M}]^{2+}$.

Synthesis of (3^{MN})

Yield: 751 mg (95%). $[\alpha]_{\text{D}}^{20}$ -44.1 (c 0.002 in DMSO). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{F}_{12}\text{N}_6\text{P}_2$ (790.57): C, 48.62; H, 4.08; N, 10.63. Found: C, 48.38; H, 4.11; N, 10.52. ^1H NMR (400 MHz, DMSO- d^6): δ = 1.47 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 1.94 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.11 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 2.38 (m, 2H, $^{c\text{-hex}}\text{CH}_2$), 4.97 (m, 2H, $^{c\text{-hex}}\text{CH}$), 5.72 (m, 4H, CH_2Ph), 7.46 (m, 2H, aryl), 7.58 (m, 4H, aryl), 7.92 (m, 8H, aryl), 9.24 (s, 2H, NCHN), 10.30 (s, 2H, NCHN). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, DMSO- d^6): δ = 23.3 ($^{c\text{-hex}}\text{CH}_2$), 30.9 ($^{c\text{-hex}}\text{CH}_2$), 55.2 (NCH $_2$), 60.8 ($^{c\text{-hex}}\text{CH}$), 126.1 (C_{aryl}), 126.8 (C_{aryl}), 127.0 (C_{aryl}), 127.7 (C_{aryl}), 127.9 (C_{aryl}), 128.5 (C_{aryl}), 128.7 (C_{aryl}), 130.1 (C_{quat}), 132.6 (C_{quat}), 132.9 (C_{quat}), 142.5 (NCHN), 144.0 (NCHN). ^{31}P $\{^1\text{H}\}$ NMR

(161.8 MHz, CD₂Cl₂): δ - 144.2 (sept). MS(FAB) *m/z* (%): 645.2 (59.7) [M+PF₆]⁺, 499.2 (100) [M]²⁺.

1.4 General procedure for the preparation of the biscarbene complexes (4)

NaH (12.16 mg, 0.51 mmol) was dissolved in ethanol (5 mL) and slowly added to a suspension of [RhCl(COD)]₂ (50.0 mg, 0.10 mmol) in ethanol (5 mL). The reaction mixture was stirred for 30 min at room temperature before the chiral di-1,2,4-triazolium di(hexafluorophosphate) salt **3** (0.21 mmol) was added. After stirring for 16 h at 40 °C, the solvent was reduced in vacuo. The remaining solid was dissolved in dichloromethane, the solution was filtrated, and then the solvent was removed under reduced pressure to obtain the pure product. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a solution of complex **4** in dichloromethane.

Synthesis of (4^{Me})

Yield: 111 mg (91 %). [α]_D²⁰ +64.1 (*c* 0.004 in CH₂Cl₂). Anal. Calcd for C₂₀H₃₀F₆N₆PRh (602.12): C, 39.88, H, 5.02, N, 13.95. Found: C, 40.03, H, 5.10, N, 14.13. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.56 – 1.82 (m, 3H, ^{c-hex}CH₂), 2.0 (m, 1H, ^{c-hex}CH₂), 2.12 – 2.53 (m, 11H, 4H ^{c-hex}CH₂, 7H, COD_{allyl}), 2.65 (m, 1H, COD_{allyl}), 3.83 (s, 3H, CH₃), 4.11 (s, 3H, CH₃), 4.41 (m, 1H, ^{c-hex}CH), 4.52 (m, 2H, COD_{vinyl}), 4.90 (m, 1H, COD_{vinyl}), 5.01 (m, 1H, COD_{vinyl}), 6.80 (m, 1H, ^{c-hex}CH), 8.03 (s, 1H, NCHN), 8.12 (s, 1H, NCHN). ¹³C {¹H} NMR: (100.5 MHz, CD₂Cl₂): δ 24.5 (^{c-hex}CH₂), 25.8 (^{c-hex}CH₂), 29.2 (^{c-hex}CH₂), 29.7 (^{c-hex}CH₂), 30.2 (COD_{allyl}), 32.3 (COD_{allyl}), 32.5 (COD_{allyl}), 37.2 (COD_{allyl}), 39.4 (CH₃), 41.6 (CH₃), 61.3 (^{c-hex}CH), 62.7 (^{c-hex}CH), 89.6 (d, ¹J_{Rh-C} = 7.6 Hz, COD_{vinyl}), 90.6 (d, ¹J_{Rh-C} = 8.4 Hz, COD_{vinyl}), 90.9 (d, ¹J_{Rh-C} = 7.6 Hz, COD_{vinyl}), 93.6 (d, ¹J_{Rh-C} = 7.6 Hz, COD_{vinyl}), 140.1 (NCHN), 144.9 (NCHN), 178.9 (d, ¹J_{Rh-C} = 50.5 Hz, carbene), 183.2 (d, ¹J_{Rh-C} = 52.0 Hz, carbene). ³¹P {¹H} NMR (161.8 MHz, CD₂Cl₂): δ - 143.9 (sept). MS(FAB) *m/z* (%): 456.8 (100) [M]⁺, 348.7 (38.77) [M-COD]⁺.

Synthesis of (4^{MN})

Yield: 145 mg (84 %). [α]_D²⁰ +75.3 (*c* 0.002 in CH₂Cl₂). Anal. Calcd for C₄₀H₄₂F₆N₆PRh (854.22): C, 56.21, H, 4.95, N, 9.83. Found: C, 56.34, H, 4.95, N, 9.46. ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.61 – 2.53 (m, 15H, 8H, ^{c-hex}CH₂, 7H, COD_{allyl}), 2.65 (m, 1H, COD_{allyl}), 4.39 (m, 2H, COD_{vinyl}), 4.53 (m, 1H, ^{c-hex}CH), 4.57 (d, ²J = 15.2 Hz, 1H, NCH₂), 4.63 (d, ²J = 15.6 Hz, 1H, NCH₂), 4.71 (m, 1H, COD_{vinyl}), 5.00 (m, 1H, COD_{vinyl}), 5.10 (d, ²J = 15.6 Hz, 1H, NCH₂), 5.51 (d, ²J = 15.2 Hz, 1H, NCH₂), 6.71 (m, 1H, CH_{aryl}), 6.92 (m, 1H, ^{c-hex}CH), 7.00 (m, 1H, CH_{aryl}), 7.14 (m, 1H, CH_{aryl}), 7.54 (m, 5H, CH_{aryl}), 7.73 (m, 2H, CH_{aryl}), 7.85 (m, 4H, CH_{aryl}), 8.20 (s, 1H, NCHN), 8.23 (s, 1H, NCHN). ¹³C {¹H} NMR (100.5 MHz, CD₂Cl₂): δ = 24.5 (^{c-hex}CH₂), 25.8 (^{c-hex}CH₂), 28.6 (^{c-hex}CH₂), 28.9 (^{c-hex}CH₂), 30.2 (COD_{allyl}), 33.0 (COD_{allyl}), 33.3 (COD_{allyl}), 37.3 (COD_{allyl}), 55.1 (NCH₂), 57.5 (NCH₂), 61.5 (^{c-hex}CH), 63.0 (^{c-hex}CH), 88.3 (d, ¹J_{Rh-C} = 7.7 Hz, COD_{vinyl}), 90.9 (d, ¹J_{Rh-C} = 8.1 Hz, COD_{vinyl}), 91.0 (d, ¹J_{Rh-C} = 7.5 Hz, COD_{vinyl}), 93.8 (d, ¹J_{Rh-C} = 8.8 Hz, COD_{vinyl}), 124.1 (C_{aryl}), 124.9 (C_{aryl}), 125.5 (C_{aryl}),

126.4 (C_{aryl}), 127.0 (C_{aryl}), 127.16 (C_{aryl}), 127.18 (C_{aryl}), 127.4 (C_{aryl}), 128.0 (C_{aryl}), 128.1 ($2 \times C_{\text{aryl}}$), 128.2 (C_{aryl}), 129.1 (C_{aryl}), 129.4 (C_{aryl}), 133.2 (C_{quat}), 133.3 (C_{quat}), 133.41 (C_{quat}), 133.43 (C_{quat}), 133.5 (C_{quat}), 133.9 (C_{quat}), 140.5 (NCHN), 145.2 (NCHN), 180.0 (d, $^1J_{\text{Rh-C}} = 50.5$ Hz, carbene), 184.2 (d, $^1J_{\text{Rh-C}} = 52.8$ Hz, carbene). ^{31}P { ^1H } NMR (161.8 MHz, CD_2Cl_2): δ - 144.3 (sept). MS(FAB) m/z (%): 709.0 (67.6) $[\text{M}]^+$, 601.0 (100) $[\text{M-COD}]^+$.

2 Catalytic hydrogenation

Catalyst was dissolved in 1,2-dichloroethane (5 mL). Substrate (**5**) or (**7**) was added in one portion. The resulting solution was transferred to the autoclave (volume = 100 mL). The indicated pressure of hydrogen and temperature were set. After the mixture was stirred at 60 °C for 20 h, the autoclave was opened and the solvent removed in vacuo. The resulting residue was purified by flash chromatography.

3 Crystallographic Data⁴⁻¹¹

Crystal data and details of the structure determination are presented in Table 1. Preliminary examination and data collection were carried out on an area detecting system (APEX II, κ -CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Three data sets were measured in rotation scan modus with $\Delta\phi/\Delta\Omega = 1.00^\circ$. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas all hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens) and refined with isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme. Two crystallographically independent cationic molecules along with their PF_6^- counterions were found. One of the anions is disordered. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.

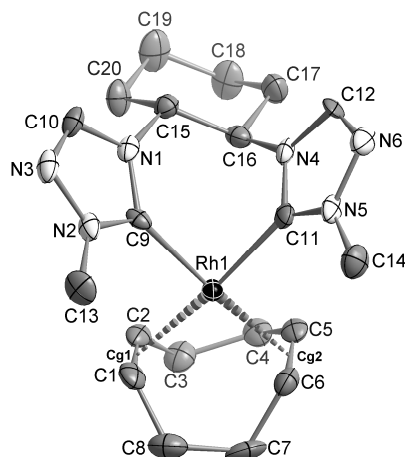


Figure S1. Molecular structure of the cation in 4^{Me} . The counter ion PF_6^- , and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50 % probability level.¹¹ Selected bond lengths (Å) and angles (°): Rh1-C9 2.036(7), Rh1-C11 2.042(7), Rh1-Cg1 2.099, Rh1-Cg2 2.111, Rh1-C1 2.212(6), Rh1-C2 2.200(5), Rh1-C5 2.212(6), Rh1-C6 2.229(7), C9-Rh1-C11 83.2(3), Cg1-Rh1-Cg2 86.4, N1-C9-N2 102.5(5), N2-C9-Rh1 129.7(5), N1-C9-Rh1 127.8(5), N4-C11-N5 104.8(6), N4-C11-Rh1 116.8(5), N5-C11-Rh1 138.3(6).

Table S1. Crystallographic details of 4^{Me} .

formula	$\text{C}_{20}\text{H}_{30}\text{N}_6\text{Rh}, \text{F}_6\text{P}$
CCDC number	781746
M_r (g/mol)	602.38
Crystal description	yellow fragment
Crystal dimensions (mm^3)	0.46 x 0.20 x 0.03
Temperature (K)	173(2)
crystal system, space group	triclinic, $P1$ (No.: 1)
a (Å)	9.8816(11)
b (Å)	10.9635(12)
c (Å)	11.8619(10)
α (°)	111.530(3)
β (°)	90.034(4)
γ (°)	99.352(2)
V (Å ³)	1177.0(2)
Z	2
d_{calc} (g/cm ³)	1.700
F_{000}	612
μ (mm ⁻¹)	0.862
Index ranges ($\pm h, \pm k, \pm l$)	11/-11, 13/-13, 13/-11
θ ranges (°)	1.85-25.41

Collected reflections	7295
Unique reflections [all data]	6818
$R_{\text{int}}/R_{\sigma}$	0.0486/0.0649
Unique reflections [$I_0 > 2 \sigma(I_0)$]	6818
Data/Restraints/Parameter	7295/0/617
GoF (on F^2)	1.007
R_1/wR_2 [$I_0 > 2 \sigma(I_0)$]	0.0313/0.0762
R_1/wR_2 [all data]	0.0348/0.0768
Max./Min. residual electron density	0.537/-0.367

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