Experimental and Theoretical Details

Bidentate carbenoid ester coordination in non-planar ruthenium(II) complexes leading to excellent levels of both diastereo- and enantioselectivity in catalytic alkene cyclopropanation

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General experimental details.

All organometallic and catalytic procedures were carried out under an inert atmosphere of argon by using a dual manifold vacuum/argon line and standard schlenk techniques, or in an MBraun glove box. All solvents were predried by refluxing for three days under dinitrogen over the appropriate drying agents (sodium for toluene; potassium for THF; sodium-potassium alloy for diethyl ether, petroleum ether and pentane; calcium hydride for dichloromethane, pyridine and acetonitrile) and degassed before use. Solvents were stored in glass ampoules under argon. All glassware, cannulae and Celite were stored in an oven (>100^{o}C) and flame dried immediately prior to use. Most reagents and chemicals were purchased from Aldrich Chemical Company and used without further purification. Deuterated solvents were freeze-thaw-degassed and dried by refluxing over potassium (or calcium hydride for CD_2Cl_2) before being vacuum distilled to a clean, dry Young′s tap ampoule and being stored in the glove box. Deuterated chloroform was dried over molecular sieves (4Å) in the air.

NMR spectra were recorded on Bruker ACF-250, DPX-300, DPX-400 and ACP-400 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ = 0 ppm). Mass spectra were obtained using a Micromass Autospec mass spectrometer. Infra red spectra were obtained either as Nujol mulls or by evaporation of dichloromethane solutions onto IR plates, using a Perkin-Elmer FTIR spectrometer. Elemental analyses were performed by Warwick Analytical Services on a Leeman Labs CE-440 analyser. GC-MS experiments were on a GC-17A Shimadzu QP-500 analyser using a Chrompak CP-Chirasil-Dex CB column [25m x 0.25 mm, 0.25 μm i.d.]. The conditions were; injection Temp 250^{o}C, column pressure 50 kPa, column flow 1.2 ml/min, linear velocity 36.8 ml/min, split ratio 45, total flow 57 ml/min. Column chromatography was performed using a selection of column widths and 60 nm flash silica. Thin layer chromatography was performed using Polygram 0.25mm silica layer plastic backed plates.

Crystallography.

X-ray structural determinations were obtained using a Siemens SMART (Siemens, 1994) three-circle system with CCD area detector and using the SHELXTL (Sheldrick, 1997) refinement program.

Crystal data for β-*cis*-[RuL^{1}(CH$_3$CN)$_2$].2(CH$_3$CN): $C_{42}H_{46}N_6O_2Ru$, monoclinic, $P2_1/c$, a = 17.9399(11) Å, b = 9.4783(5) Å, c = 23.2630(14) Å, β = 103.498(10)º, U = 3846.4(4) Å^3, Z = 4, D_c = 1.326 g cm^{-3}, T =180(2) K, λ(Mo Kα) = 0.71073 Å. Final R indices [for 5441 reflections with $I > 2\sigma(I)$]: R_1 = 0.0514, wR_2 = 0.1029. GOOF on F^2 = 0.991. Heavy atoms were located by Patterson methods with additional light atoms then found by E-map expansion and successive Fourier syntheses.

DFT Calculations

All DFT calculations employed the Amsterdam Density Functional program version 2.3. Geometries were optimised at the Local Density Functional level with energies subsequently computed with the BP86 gradient corrected functional. Basis sets were triple ζ and polarisation STO expansions on Ru, double ζ and polarisation on the ligand donor atoms and double ζ on the remaining centres.

Synthesis of (±)-H_2L^1- [*N*,*N*'-bis(3-*iso*-propylsalicylidene)-6,6'-dimethylbiphenyl-2,2'-diamine)]

(±)-2,2′-Diamino-6,6′-dimethylbiphenyl (Meisenheimer, J.; Horing, M. *Berichte*, **1927**, *60*, 1425) (1.00 g, 4.72 mmol) and 3-*iso*-propylsalicylaldehyde (1.55 g, 9.43 mmol) were dissolved in ethanol (25 ml) and stirred under reflux for 1 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to –30 °C before the Schiff-base was isolated by vacuum filtration, washed with cold ethanol and dried under reduced pressure.

Yield = 2.23 g, 94%.

^{1}H NMR ($CDCl_3$): δ 12.54 (s, 2H, ArO*H*), 8.42 (s, 2H N=CH), 7.33 (t, *J* = 8, 2H, Ar-H), 7.22 (d, *J* = 8, 2H, Ar-H), 7.03 – 7.20 (m, 6H, Ar-H), 6.79 (t, 2H, *J* = 8, Ar-H), 3.25 (sept, *J* = 7, 2H, C*H*Me_2), 2.04 (s, 6H, Me), 1.17 (d, *J* = 7, 6H, CH*Me*$_2$), 1.15 (d, *J* = 7, 6H, CH*Me*$_2$).

^{13}C NMR ($CDCl_3$): δ 162.2 (N=C), 158.6, 147.1, 136.8, 135.9, 133.2, 129.7, 128.6, 127.4, 127.2, 118.5, 118.3, 116.2 (Ar), 26.4 (*C*HMe_2), 22.3 (CH*Me*$_2$), 22.1 (CH*Me*$_2$), 18.8 (Me).

MS (EI^+) m/z: 504 (M^+).

EA for $C_{34}H_{36}N_2O_2$, Calculated % C, 80.88; H, 7.17; N, 5.60. Found % C, 80.92; H, 7.19; N, 5.55.

Synthesis of (+)-H_2L^1

This was synthesised by the same method as the racemic Schiff-base (±)-H_2L^1 using (+)-2,2′-Diamino-6,6′-dimethylbiphenyl (Meisenheimer, J.; Horing, M. *Berichte*, **1927**, *60*, 1425) (1.00 g, 4.72 mmol) and 3-*iso*-propylsalicylaldehyde (1.55 g, 9.43 mmol).

Yield = 2.05 g, 86%.

Synthesis of (±)-H_2L^2 – [*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-6,6'-dimethylbiphenyl-2,2'-diamine)]

(±)-2,2′-Diamino-6,6′-dimethylbiphenyl (4.00 g, 18.8 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (8.84 g, 37.7 mmol) were dissolved in methanol (150 ml) and stirred under reflux for 5 h to produce a bright yellow crystalline solid. The reaction mixture was cooled to -30°C before the Schiff-base was isolated by vacuum filtration, washed with cold methanol and dried under reduced pressure.

Yield = 11.3 g, 93%.

^{1}H NMR ($CDCl_3$): δ 12.90 (s, 2H, OH), 8.42 (s, 2H, N=CH), 6.91 - 7.30 (m, 10H, Ar-H), 2.10 (s, 6H, Me), 1.26 (s, 18H, ^{t}Bu), (1.19 (s, 18H, ^{t}Bu).

^{13}C NMR ($CDCl_3$): δ 162.9 (N=C), 158.7, 147.3, 140.2, 137.5, 137.1, 134.0, 128.7, 128.6, 127.8, 126.9, 118.6, 115.7 (Ar), 35.42, 34.47, 31.83, 29.65 (^{t}Bu), 20.26 (Me).

MS (EI^+) m/z: 644 (M^+), 629 (M^+-CH_3).

IR (CH_2Cl_2) ν cm^{-1}: 3441, 2955, 2906, 1616, 1567, 1462, 1438, 1391, 1360, 1273, 1249, 1201, 1173, 1025, 978, 946, 877, 831, 809, 770, 740, 643.

EA for $C_{44}H_{58}N_2O_2$, Calculated % C, 81.94; H, 9.07; N, 4.34. Found % C, 81.75; H, 8.67; N, 4.37.

Synthesis of (+)-H_2L^2

This was synthesised by the same method as the racemic Schiff-base (±)-H_2L^2 using (+)-2,2′-Diamino-6,6′-dimethylbiphenyl (1.00 g, 4.72 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (2.21 g, 9.44 mmol). Yield = 2.52 g, 83%.

Synthesis of (+)-H_2L^3- [*N*,*N*'-bis(3,5-dichlorosalicylidene)-6,6'-dimethylbiphenyl-2,2'-diamine)]

This was synthesised by the same method as the racemic Schiff-base (±)-H_2L^2 using (+)-2,2′-Diamino-6,6′-dimethylbiphenyl (1.00 g, 4.72 mmol) and 3,5-dichlorosalicylaldehyde (1.80 g, 9.40 mmol).

Yield = 2.44 g, 93%.

^{1}H NMR ($CDCl_3$): δ 12.85 (s, 2H, ArO*H*), 8.42 (s, 2H, N=CH), 7.40 (t, *J* = 6, 2H, Ar-H), 7.33 (s, 2H, Ar-H), 7.31 (d, *J* = 6, 2H, Ar-H), 7.15 (s, 2H, Ar-H), 7.12 (d, *J* = 6, 2H, Ar-H), 2.03 (s, 6H, Me).

^{13}C NMR ($CDCl_3$): δ 160.24 (N=C), 155.9, 145.9, 137.8, 133.8, 132.8, 130.2, 130.0, 129.4, 123.5, 122.9, 120.7, 115.8 (Ar), 20.19 (Me).

MS (EI^+): m/z 558 (M^+).

IR (CH_2Cl_2) ν cm^{-1}: 3069, 2978, 2917, 1615, 1559, 1447, 1377, 1352, 1294, 1264, 1208, 1180, 1101, 1020, 976, 944, 863, 854, 802, 776, 739, 705, 689.

EA for $C_{28}H_{20}N_2O_2Cl_4$, Calculated % C, 60.24; H, 3.61; N, 5.02. Found % C, 60.00; H, 3.61; N, 4.67.

Synthesis of Na_2L^n.xTHF (n = 1-3)

Synthesis of (±)- or (+)-Na_2L^1.xTHF

THF (25 ml) was added to a mixture of the Schiff-base (±)- or (+)-H_2L^1 (1.00 g, 1.99 mmol) and sodium hydride (0.48 g, 19.9 mmol). The reaction mixture was connected to a bubbler and stirred at room temperature. Once hydrogen evolution had stopped the solution was filtered to remove excess sodium hydride and the filtrate was evaporated to dryness *in vacuo* to afford a bright yellow solid. The amount of THF (x) in the material was deduced by careful integration of an ^{1}H NMR spectrum recorded in deuterated pyridine.

Yield = 100%.

^{1}H NMR (d-pyridine): δ 8.48 (s, 2H, N=CH), 7.12 – 7.26 (m, 4H, Ar-H), 6.98 (d, *J* = 8, 2H, Ar-H), 6.91 (t, 8, 2H, Ar-H), 6.59 (d, *J* = 8, 2H, Ar-H), 6.46 (t, *J* = 8, 2H, Ar-H), 3.60 – 3.69 (m, variable, C*H*Me_2, THF), 2.06 (s, 6H, Me), 1.60 – 1.64 (m, variable, THF), 1.02 (d, *J* = 8, 6H, CH*Me*$_2$), 0.93 (d, *J* = 8, 6H, CH*Me*$_2$).

Synthesis of (±)- or (+)-Na_2L^2.xTHF

This was synthesised by the same method as for (±)- or (+)-Na_2L^1.xTHF using (±)- or (+)-H_2L^2 (2.85 g, 4.4 mmol) and sodium hydride (1.06 g, 44.2 mmol).

Yield = 100%.

^{1}H NMR (d-pyridine): δ 8.30 (s, 2H, N=CH), 7.20 (s, 2H, Ar-H), 6.68 (bs, 4H, Ar-H), 6.25 (bs, 2H, Ar-H), 3.64 (m, variable, THF), 1.69 (s, 6H, Me), 1.30 (s, 18H, ^{t}Bu), 1.30 (m, variable, THF), 1.07 (s, 18H, ^{t}Bu).

Synthesis of (+)-Na_2L^3.xTHF

This was synthesised by the same method as for (±)- or (+)-Na_2L^1.xTHF using (+)-H_2L^3 (0.50 g, 0.900 mmol) and sodium hydride (0.22 g, 8.90 mmol).

Yield = 100%.

^{1}H NMR (d-pyridine): δ 8.44 (s, 2H, N=CH), 7.22 (s, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 6.88 (t, 2H, Ar-H), 6.86 (s, 2H, Ar-H), 6.47 (m, 2.0H, Ar-H), 3.45 (m, variable, THF),

1.89 (s, 6.1H, Me), 1.41 (m, variable, THF).

Synthesis of (±)- or (+)-[$RuL^1(CH_3CN)_2$]

The disodium salt (±)- or (+)-Na_2L^1.xTHF (0.24 g, 0.40 mmol) and [{RuCl(μ-Cl)(η^6-C_6H_6)}$_2$] (0.10 g, 0.20 mmol) were stirred in acetonitrile (25 ml) at room temperature overnight. The resulting red precipitate was filtered and washed with cold acetonitrile. The red solid was extracted into dichloromethane and filtered to remove NaCl. The solvent was removed *in vacuo* to leave a dark red solid.

Yield 0.18 g, 66%.

Recrystallisation from an acetonitrile solution of the complex by overnight cooling to 5ºC produced red crystals of the complex [$RuL^1(CH_3CN)_2$] suitable for X-ray structural determination.

^{1}H NMR (CD_2Cl_2): δ 8.10 (s, 1H, N=CH), 7.66 (s, 1H, N=CH), 7.08 (t, *J* = 7, 1H, Ar-H), 6.90 – 6.97 (m, 5H, Ar-H), 6.80 (d, *J* = 7, 1H, Ar-H), 6.59 – 6.64 (m, 3H, Ar-H), 6.23 (t, *J* = 7, 1H, Ar-H), 6.10 (t, *J* = 7, 1H, Ar-H), 3.33 (sept, *J* = 7, 1H, C*H*Me$_2$), 3.20 (sept, *J* = 7, 1H, C*H*Me$_2$), 2.20 (s, 3H, C*H$_3$*CN), 1.99 (s, 3H, Me), 1.84 (s, 3H, Me), 1.65 (s, 3H, C*H$_3$*CN), 1.12 (d, *J* = 8, 3H, *C*H*Me$_2$*), 1.06 (d, *J* = 8, 6H, CH*Me$_2$*), 0.89 (d, *J* = 8, 3H, CH*Me$_2$*).

^{13}C NMR (CD_2Cl_2): δ 163.6 (N=C), 160.5 (N=C), 154.5, 153.1, 142.4, 142.3, 138.3, 137.7, 133.6, 131.9, 131.0, 128.5, 128.3, 127.8, 127.3, 127.0, 126.8, 123.5, 123.4, 123.2, 122.4, 121.9, 119.3, 116.5, 112.2, 112.0 (Ar), 28.3 (*C*HMe$_2$), 27.6 (*C*HMe$_2$), 23.5, 23.0, 22.5, 22.4 (CH*Me$_2$*), 20.7 (Me), 20.2 (Me), 4.5 (*C*H$_3$CN), 3.7(*C*H$_3$CN).

IR (Nujol) ν cm^{-1}: 2252, 1596, 1570, 1528, 1458, 1428, 1377, 1198, 1144, 1105, 775, 748.

MS (EI$^+$) m/z: 685 (M$^+$), 603 (M$^+$ - 2 x CH_3CN).

EA for $C_{38}H_{40}N_4O_2Ru$, Found % C, 65.16; H, 5.59; N, 8.82.

Calculated % C, 66.55; H, 5.88; N, 8.17.

Synthesis of (±)- or (+)-[$RuL^2(CH_3CN)_2$]

This was synthesised by the same method as for (±)- or (+)-[$RuL^1(CH_3CN)_2$] using (±)- or (+)-Na_2L^2.xTHF (0.50 g, 0.65 mmol) and [{RuCl(μ-Cl)(η^6-C_6H_6)}$_2$] (0.16 g, 0.33 mmol)

Yield = 0.32 g, 59%.

^{1}H NMR (CD_2Cl_2): δ 8.12 (s, 1H, N=CH), 7.61 (s, 1H, N=CH), 6.87 – 7.12 (m, 10H, Ar-H), 2.13 (s, 3H, C*H$_3$*CN), 1.97 (s, 3H, Me), 1.84 (s, 3H, Me), 1.70 (s, 3H, C*H$_3$*CN), 1.28 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu), 1.16 (s, 9H, ^{t}Bu), 1.13 (s, 9H, ^{t}Bu).

MS (EI$^+$) m/z: 826 (M^+), 744 (M^+ - 2 x CH_3CN).

Synthesis of (+)-[RuL^3(CH$_3$CN)$_2$]

This was synthesised by the same method as for (±)- or (+)-[RuL^1(CH$_3$CN)$_2$] using (+)-Na$_2$L^3.xTHF (0.50 g, 0.76 mmol) and [{RuCl(μ-Cl)(η^6-C$_6$H$_6$)}$_2$] (0.19 g, 0.38 mmol).

Yield = 0.32 g, 57%.

^{1}H NMR (CD_2Cl_2): δ 8.11 (s, 1H, N=CH), 7.66 (s, 1H, N=CH), 6.95 – 7.19 (m, 6H, Ar-H), 6.57 – 6.71 (m, 4H, Ar-H), 2.31 (s, 3H, C*H*$_3$CN), 2.02 (s, 3H, Me), 1.85 (s, 3H, Me), 1.74 (s, 3H, C*H*$_3$CN).

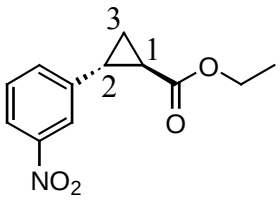
^{13}C NMR (CD_2Cl_2): δ 163.0 (C=N), 160.3 (C=N), 154.1, 152.0, 138.8, 137.9, 133.2, 131.8, 131.7, 130.9, 130.3, 130.0, 129.2, 129.1, 128.5, 127.9, 127.7, 127.3, 125.5, 124.6, 124.2, 123.5, 122.9, 116.5, 116.0, 115.6 (Ar), 20.6 (Me), 20.2 (Me), 5.3 (*C*H$_3$CN), 4.2 (*C*H$_3$CN).

IR (Nujol) ν cm^{-1}: 2264, 1593, 1567, 1500, 1455, 1378, 1309, 1197, 1153, 856, 780, 733.

General Cyclopropanation Procedure

A round bottomed flask modified with a sidearm and teflon stopcock was charged with catalyst (5 mol%) under an atmosphere of argon. The solids were dissolved in toluene (5 ml) with stirring. Alkene (4 equiv.) was added to the flask. A syringe was charged with the required diazoacetate (1 equiv.) dissolved in toluene (5 ml). The contents of the syringe were added to the reaction mixture over 2 h at room temperature using a syringe pump. The reaction mixture was stirred for an additional 15 minutes, filtered through a silica plug, washed with dichloromethane (2 x 5 ml) and concentrated. The excess alkene was either removed *in vacuo* or by columning the reaction mixture (hexane until all alkene was removed then hexane:ethyl acetate in the ratio 25:1 to elute products). The product was identified and *cis/trans* ratios were determined from NMR spectroscopy and GC-MS. Enantiomeric excess were calculated from either chiral GC-MS or by NMR studies using Europium (III) tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorate] ($Eu(hfc)_3$) or both.

(1*R*,2*R*) Ethyl 2-(3-Nitrophenyl)cyclopropane-1-carboxylate

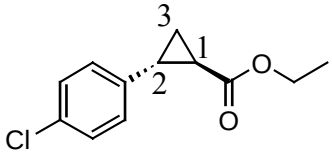


Chiral GC-MS [80°C, 4°/min]: Rt_{cis} 29.8 (minor), 30.0 (major) min.; Rt_{trans} 31.3 (major + minor) min.

D.R. *trans:cis* = 99:1.

E.E. *trans* – 98%, *cis* – *ca.* 53%.

(1*R*,2*R*) Ethyl 2-(4-Chlorophenyl)cyclopropane-1-carboxylate

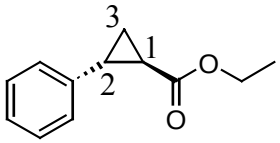


Chiral GC-MS [80°C, 4°/min]: Rt_{cis} 23.6 (minor), 23.8 (major) min.; Rt_{trans} 24.8 (major + minor).

D.R. *trans:cis* = 99:1.

E.E. *trans* – 97%, *cis* – *ca.* 42%.

(1*R*,2*R*) Ethyl 2-phenylcyclopropane-1-carboxylate

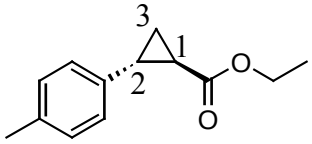


Chiral GC-MS [80°C, 4°/min]: Rt_{cis} 18.0 (minor), 18.3 (major) min.; Rt_{trans} 18.9 (major), 19.1 (minor) min.

D.R. *trans:cis* = 98:2.

E.E. *trans* – 95%, *cis* – *ca.* 36%.

(1*R*,2*R*) Ethyl 2-(4-Methylphenyl)cyclopropane-1-carboxylate

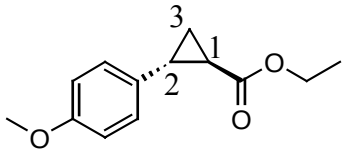


Chiral GC-MS [80°C, 4°/min]: Rt_{cis} 20.0 (minor), 20.4 (major) min.; Rt_{trans} 21.8 (major + minor) min.

D.R. *trans:cis* = 94:6.

E.E. *trans* – 88%, *cis* – *ca.* 4%.

(1*R*,2*R*) Ethyl 2-(4-Methoxyphenyl)cyclopropane-1-carboxylate



Chiral GC-MS [80°C, 4°/min]: Rt_{cis} 24.6 (minor), 25.0 (major) min.; Rt_{trans} 26.5 (major + minor) min.

D.R. *trans:cis* = 96:4.

E.E. *trans* – 86%, *cis* – ≤ 1%.

Chiral Shift reagent experiments

Enantiomeric excess was determined by NMR studies using the chiral shift reagent Europium (III) tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]. Shift reagent was added to the racemic analyte (10.0 mg) in d_6-benzene (0.70 ml) until clean separation of suitable indicator resonances was obtained.

Entry in Table 1	[Eu(hfc)3] / mg	Indicator resonances at *x* / *y* ppm	Relative intergrals
1	10.2	3.56 / 3.48	1 / 79
2	11.0	3.31 / 3.21	1 / 58
3	12.6	3.43 / 3.26	1 / 39
4	10.8	3.26 / 3.13	1 / 13
5	10.8	3.51 / 3.34	1 / 13

Preliminary data for catalysis using L^2 and L^3

Ligand	Alkene	Yield / %	d.r.	e.e. / %
L^2	Styrene	65	95:5	83
L^3	Styrene	61	57:43	76