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Supporting Information

Helically Chiral NHC-Gold(I) Complexes: Synthesis, Chiroptical Properties and Electronic Features of the [5]Helicene-Imidazolylidene Ligand

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Supporting Information

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1. General methods

Experiments were performed using standard Schlenk techniques. Column chromatography purifications were performed in air over silica gel (Macherey Nagel 60 M, 0.04–0.063 mm). Irradiation reactions were conducted using a Heraeus TQ 150 mercury vapor lamp. All reactions were monitored by TLC analysis and visualizations were accomplished by irradiation with a UV light at 254 nm and 356 nm. THF was dried using Na/Benzophenone method. Dry toluene was obtained from an MB-SPS-800 distillation machine and was degassed by an argon bubbling at least 30 minutes before use. Potassium carbonate and grounded 4Å molecular sieves were dried in a 110°C oven for several days and stored at the same temperature. Sodium *tert*-butoxide was bought from common providers and bulk powder was stored in a Schlenk tube under Ar sealed with a Teflon cap. Other reagents or solvents were purchased from usual providers and were used as received unless otherwise noted.

¹H and ¹³C {¹H} NMR spectra were recorded at room temperature either on a Bruker Avance I 300 MHz, Bruker Avance III 300 MHz or 400 MHz spectrometer equipped with a tunable BBFO probe. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. ¹H and ¹³C NMR chemical shifts were determined using residual signals of the deuterated solvents: deuterated dichloromethane (¹H δ = 5.32 ppm, ¹³C δ = 54.0 ppm) and deuterated chloroform (¹H δ = 7.26 ppm, ¹³C δ = 77.16 ppm). The terms s, d, t, q, hept, m indicate respectively singlet, doublet, triplet, quartet, heptuplet, multiplet; b is for broad; dd is doublet of doublets, dt – doublet of triplets, td – triplet of doublets. Assignment of proton and carbon signals is based on COSY, NOESY, edited-HSQC, and HMBC experiments. ¹H dipolar couplings were studied using NOESY sequence, with a 500 or 800 ms mixing time. High-resolution mass spectrometry (HR-MS) measurements were performed by the CRMPO, University of Rennes 1. IR spectra were recorded on a Perkin-Elmer Spectrum Two (ATR measurements) and on a Jasco FT/IR-4600 (CH₂Cl₂ measurements using a cell with BaF₂ windows) spectrometers.

UV-visible (UV-vis, in M⁻¹cm⁻¹) and electronic circular dichroism (ECD, in M⁻¹cm⁻¹) were measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility. Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1 - Campus de Villejean-35043 Rennes Cedex, France).

2. Synthetic procedures

[5]Helicene-imidazole $\mathbf{4}^{[1]}$ and benzimidazole $\mathbf{7}^{[2]}$ were prepared as reported in the literature. Unless otherwise specified, NHC-gold(I) complexes were prepared under air with technical grade solvents following Nolan *et al.*^[3]

N-(3,5-Dimethylphenyl)-[5]helicene-imidazole 5



In a round-bottom flask were placed 4Å molecular sieves, [5]helicene-imidazole **4** (59.3 mg, 0.22 mmol), 3,5-dimethylphenylboronic acid (69.2 mg, 0.46 mmol), and anhydrous copper(II) acetate (61.3 mg, 0.33 mmol) followed by dichloromethane (analytical grade, 3 mL) and triethylamine (0.1 ml, 0.71 mmol). The reaction mixture was then stirred at room temperature for 63 hours. The crude mixture was then filtered over a Celite© pad washed with CH_2Cl_2 and further purified by column chromatography (SiO₂, *n*-Heptane/EtOAc = 1:0 to 8:2) to afford the desired product **5** as a white powder (68 mg, 83% yield)

¹H NMR (400 MHz, CDCl₃) δ = 9.23 – 9.15 (m, 1H, 26), 8.13 (s, 1H, 5), 8.00 – 7.95 (m, 3H, 19, 20, 29), 7.92 (d, J = 8.6, 1H, 23), 7.86 (d, J = 8.6, 1H, 22), 7.82 (d, J = 4.4, 1H, 12), 7.80 (d, J = 4.6, 1H, 13), 7.62 (ddd, J = 8.0, 6.9, 1.3, 1H, 28), 7.54 (ddd, J = 8.4, 6.9, 1.5, 1H, 27), 7.23 (s, 2H, 7, 11), 7.16 (s, 1H, 9), 2.47 (s, 6H, 24, 25); ¹³C NMR (101 MHz, CDCl₃) δ = 140.7, 140.2, 138.8, 136.3, 133.1, 132.3, 132.0, 131.0, 130.8, 130.5, 130.1, 128.3, 127.8, 127.2, 126.8, 126.5, 126.3, 125.5, 125.3, 124.1, 123.6, 122.5, 111.2, 21.5; HR-MS (ESI, CH₃OH / CH₂Cl₂ = 90/10) [M+Na]⁺ (C₂₇ H₂₀ N₂ Na): calculated for 395.15187 m/z, found 395.1523 (Δ = 1 ppm).

N-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazol-1-ium iodide [(rac)-6].HI



In a dried Schlenk tube was placed acetonitrile (7 mL). After 3 vacuum/argon cycles, **5** (85 mg, 0.22 mmol) was introduced. Then, an excess of methyl iodide was added. The reaction mixture was then sealed with a Teflon Cap and heated at 110°C overnight. The resulting heterogenous mixture was cooled down to room temperature and the solvent was stripped off. The solid was then washed with Et_2O and EtOAc to afford pure iodide salt **[(rac)-6].HI** as a light-brown solid (105 mg, 89 % yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 10.77 (s, 1H, 5), 8.38 – 8.30 (m, 1H, 27), 8.19 (d, *J* = 8.9, 1H, 23), 8.14 – 8.05 (m, 4H, 13, 19, 20, 30), 8.00 (d, *J* = 8.6, 1H, 12), 7.90 (d, *J* = 8.9, 1H, 22), 7.73 – 7.60 (m, 4H, 7, 11, 28, 29), 7.32 (s, 1H, 9), 3.60 (s, 3H, 24), 2.50 (s, 6H, 25, 26); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 141.5, 141.3, 133.5, 133.2, 133.2, 133.1, 132.8, 131.5, 131.2, 131.1, 129.9, 129.5, 129.2, 129.0, 128.0, 127.8, 127.8, 126.4, 125.6, 124.5, 123.3, 116.9, 112.7, 39.7, 21.6; **HR-MS (ESI, CH₃OH / CH₂Cl₂ = 90/10)** [M]⁺ (C₂₈ H₂₃ N₂): calculated for 387.18557 m/z, found 387.1858 (Δ = 1 ppm).

N-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazol-1-ium chloride [(rac)-6].HCl



A glass column was charged with about 9 g of ion exchange DOWEX© resin, activated with 15 mL of HCl 37% then washed with MilliQ water until pH = 7. Salt [(*rac*)-6].HI (105 mg, 0.204 mmol) was then loaded as a liquid deposit (acetone/methanol, 1:1) and slowly eluted through the column with the same eluent. Solvents were then removed under vacuum and the obtained solid was triturated in acetone and Et₂O and finally dried under air. The desired chloride salt [(*rac*)-6].HCl was obtained as a white solid (85 mg, 98% yield).

¹H NMR (300 MHz, CD₂Cl₂) δ = 11.86 (s, 1H, 5), 8.30 (d, *J* = 8.3, 1.2, 1H, 27), 8.18 (d, *J* = 8.8, 1H, 23), 8.15 – 8.05 (m, 4H, 13, 19, 20, 30), 8.01 (d, *J* = 8.6, 1H, 12), 7.91 (d, *J* = 8.8, 1H, 22), 7.74 – 7.66 (m, 1H, 29), 7.66 – 7.61 (m, 1H, 28), 7.59 (d, *J* = 1.6, 2H, 7, 11), 7.34 (s, 1H, 9), 3.65 (s, 3H, 24), 2.52 (s, 6H, 25, 26); ¹³C NMR (75 MHz, CD₂Cl₂) δ = 143.6, 141.6, 133.6, 133.5, 133.2, 133.0, 132.9, 131.6, 131.3, 131.3, 129.9, 129.3, 129.3, 128.9, 128.0, 127.9, 127.7, 126.4, 125.5, 124.6, 123.3, 117.1, 112.9, 39.2, 21.7; HR-MS (ESI, CH₂Cl₂ / CH₃OH = 90/10) [M]⁺ (C₂₈ H₂₃ N₂): calculated for 387.18557 m/z, found 387.1860 (Δ = 1 ppm), the cluster [2M + Cl]⁺ (C₅₆ H₄₆ N₄³⁵Cl) was also detected: calculated for 809.34055 m/z, found 809.3401 (Δ = 1 ppm).

1-(3,5-Dimethylphenyl)-3-methyl-1H-benzimidazol-3-ium iodide [8].HI



In a dried Schlenk tube was placed acetonitrile (6 mL). After 3 vacuum/argon cycles, **7** (106 mg, 0.47 mmol) was added. Under argon, was added an excess of methyl iodide. The reaction mixture was then sealed with a Teflon Cap and was heated at 110°C overnight. The resulting heterogenous mixture was finally allowed to cool to room temperature and the solvent was stripped off. The resulting residue was transferred into a round-bottom flask by dissolution and evaporation of CH₂Cl₂. The solid was then washed with acetone, Et₂O and EtOAc to afford pure iodide salt **[8].HI** as a light-brown solid (164 mg, 94% yield).

¹H NMR (500 MHz, CD₂Cl₂) δ = 10.86 (s, 1H, 5), 7.85 (d, *J* = 8.2, 1H, 15), 7.78 – 7.67 (m, 3H, 12, 13, 14), 7.45 (s, 2H, 7, 11), 7.28 (s, 1H, 9), 4.41 (s, 3H, 16), 2.45 (s, 6H, 17, 18); ¹³C NMR (126 MHz, CD₂Cl₂) δ = 142.0, 141.5, 133.2, 132.9, 132.7, 131.7, 128.3, 128.1, 122.8, 114.3, 113.6, 34.9, 21.5; HR-MS (ESI, CH₃OH / CH₂Cl₂ = 90/10) [M]⁺ (C₁₆ H₁₇ N₂): calculated for 237.13862 m/z, found 237.1387 (Δ = 0 ppm).

[5]Helicenic NHC iridium(I) 1,5-cyclooctadiene chloride complex (rac)-9/(rac)-9'



(*rac*)-9 (*rac*)-9/(*rac*)-9' = 79:21 (*rac*)-9'

In a dried Schlenk tube protected from light with an aluminum foil, was added Ag₂O (4.9 mg, 0.021 mmol) and salt **[(***rac***)-6].HI** (22.8 mg, 0.044 mmol). The solids were degassed by 3 vacuum/argon cycles and further dissolved in dry CH₂Cl₂ (2 mL). The mixture was stirred at r.t. for 2 hours and [Ir(COD)Cl]₂ (14.8 mg, 0.022 mmol) was added. The reaction was then stirred overnight at r.t. and the crude was filtered over a Celite© pad and washed with CH₂Cl₂. The yellow filtrate was evaporated under reduced pressure and the obtained residue was purified by column chromatography (SiO₂, CH₂Cl₂) affording the desired complex as a yellow powder (13.5 mg, 43% yield) and as a mixture of conformers ((*rac*)-9 : (*rac*)-9' = 79% / 21%, determined by ¹H NMR).

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.39 (d, *J* = 8.0, 0.2H, 13'), 8.29 (d, *J* = 8.5, 1H, 13), 8.13 – 8.00 (m, 3H), 8.03 – 7.89 (m, 2H), 7.89 – 7.78 (m, 4H), 7.80 – 7.73 (m, 1H), 7.71 – 7.59 (m, 2H), 7.58 – 7.47 (m, 1H), 7.27 – 7.20 (m, 1H), 4.76 (td, *J* = 3.9, 0.1H, C(sp²) (*rac*)-9'), 4.62 (td, *J* = 7.7, 3.3, 1H, C(sp²) (*rac*)-9), 4.49 – 4.39 (m, 0.2 H, C(sp²) (*rac*)-9'), 4.40 – 4.29 (m, 1H, C(sp²) (*rac*)-9), 3.51 (s, 0.7H, N-CH₃ (*rac*)-9'), 3.47 – 3.40 (m, 0.8H), 3.41 (s, 3H, N-CH₃ (*rac*)-9), 2.79 – 2.70 (m, 0.2H, C(sp³) (*rac*)-9'), 2.60 (td, J=7.4, 3.5, 1H, C(sp³) (*rac*)-9), 2.52 (s, 1H, CH₃ (*rac*)-9'), 2.50 (s, 6H, CH₃ (*rac*)-9), 2.43 – 2.29 (m, 1H), 2.19 – 2.05 (m, 1H), 2.06 – 1.77 (m, 2H), 1.76 – 1.65 (m, 1H), 1.65 – 1.56 (m, 0.7H), 1.52 – 1.41 (m, 0.4H), 1.38 – 1.26 (m, 1H); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 192.3 (C^{carbene} (*rac*)-9), 192.0 (C^{carbene} (*rac*)-9'), 139.3, 139.2, 138.3, 138.1, 134.9, 134.7, 134.1, 133.6, 132.6, 132.5, 132.3, 131.7, 131.7, 131.5, 130.9, 130.4, 130.3, 128.9, 128.9, 128.7, 128.4, 128.1, 127.8, 127.6, 127.1, 127.1, 127.0, 126.6, 126.5, 126.4, 126.3, 126.2, 126.2, 125.9, 125.7, 124.9, 124.7, 124.5, 124.1, 116.0, 111.9, 111.1, 86.4, 85.5, 84.7, 84.4, 54.2, 53.0, 52.0, 51.6, 40.6, 39.6, 35.2, 34.3, 32.9, 32.5, 30.5, 29.9, 29.4, 29.2, 21.7, 21.6; HR-MS (ESI, CH₂Cl₂) [M]⁺⁺ (C₃₆ H₃₄ N₂ ³⁵Cl ¹⁹³Ir): calculated for 722.20344 m/z, found 722.2027 (Δ = 1 ppm).

Model NHC iridium(I) 1,5-cyclooctadiene chloride 10



In a dried Schlenk tube protected from light with an aluminum foil, was added Ag₂O (11.3 mg, 0.049 mmol) and salt **[8].HI** (35.5 mg, 0.097 mmol). The solids were degassed by 3 vacuum/argon cycles, further dissolved in dry CH₂Cl₂ (2 mL). The mixture was stirred at r.t. for 1h30 and [Ir(COD)Cl]₂ (33 mg, 0.049 mmol) was added. The reaction was then stirred overnight at r.t. and the crude was filtered over a Celite© pad and washed with CH₂Cl₂. The yellow filtrate was evaporated under reduced pressure and the obtained residue was purified by column chromatography (SiO₂, CH₂Cl₂) affording the desired complex **10** as a yellow powder (40 mg, 72% yield)

¹H NMR (400 MHz, CDCl₃) δ = 7.65 (s, 2H, 9, 13), 7.41 – 7.34 (m, 2H, 14, 17), 7.35 – 7.26 (m, 1H, 16), 7.28 – 7.21 (m, 1H, 15), 7.18 – 7.13 (m, 1H, 11), 4.77 (td, J=7.7, 3.6, 1H, 114), 4.62 – 4.51 (m, 1H, 115), 4.27 (s, 3H, 18), 3.09 – 2.98 (m, 1H, 108), 2.47 (s, 6H, 19, 20), 2.38 (td, J=7.3, 3.6, 1H, 109), 2.33 – 2.11 (m, 2H, 116, 118), 1.92 – 1.76 (m, 1H, 113), 1.73 – 1.55 (m, 3H, 110, 112, 117, 119), 1.42 – 1.19 (m, 1H, 111); ¹³C NMR (101 MHz, CDCl₃) δ = 191.6 (5, C^{Carbene}), 138.6, 137.7, 135.6, 135.2, 129.7, 125.0, 123.1, 122.9, 110.9, 109.7, 86.1, 84.9, 52.3, 52.1, 34.6, 34.5, 32.3, 29.7, 28.9, 21.4; HR-MS (ESI, CH₂Cl₂) [M]⁺⁺ (C₂₄ H₂₈ N₂ ³⁵Cl ¹⁹³Ir): calculated for 572.15649 m/z, found 572.1558 (Δ = 1 ppm).

[5]Helicenic NHC iridium(I) dicarbonyl chloride complex (rac)-11



In a round-bottom flask, was placed complex (rac)-9 (5 mg, 0.01 mmol, as a mixture of conformers) and CH₂Cl₂ (3 mL). Gaseous carbon monoxide was bubbled inside the solution for 15 min then volatiles were removed under reduced pressure. The obtained crude was precipitated and triturated with *n*-

pentane then dried under vacuum to afford complex (*rac*)-11 as a yellow powder (7 mg, quantitative yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.43 – 8.37 (m, 1H, 27), 8.09 – 8.01 (m, 3H, 9, 10, 30), 7.99 – 7.93 (m, 3H, 12, 13, 15), 7.69 – 7.62 (m, 2H, 28, 29), 7.57 (d, *J* = 8.6, 1H, 16), 7.41 (s, 2H, 19, 23), 7.30 (s, 1H, 21), 3.45 (s, 3H, 26), 2.50 (s, 6H, 31, 32); ¹³C NMR resolution was not enough to record proper spectra; IR (ATR, cm⁻¹) 2062 (CO), 1979 (CO); IR (solution in CH₂Cl₂, cm⁻¹) 2067 (CO), 1984 (CO); HR-MS (ESI, CH₂Cl₂/CH₃OH = 95/5) [M+H]⁺ (C₃₀ H₂₃ N₂O₂ ³⁵Cl ¹⁹³Ir): calculated for 671.1072 m/z, found 671.1072 (Δ = 0 ppm), [M-Cl]⁺ (C₃₀ H₂₂ N₂O₂ ¹⁹³Ir): calculated for 635.13052 m/z, found 635.1305 (Δ = 0 ppm).



Figure S1. FT-IR spectra of (rac)-11 measured in powder (ATR) (left) and in CH₂Cl₂ (liquid cell with BaF₂ windows (right).

Model NHC iridium(I) dicarbonyl chloride 12



In a round-bottom flask, was placed complex **10** (7 mg, 0.014 mmol) and CH_2Cl_2 (3 mL). Gaseous carbon monoxide was bubbled inside the solution for 15 min then volatiles were removed under reduced pressure. The obtained crude was precipitated and triturated with *n*-pentane and dried under vacuum to afford complex **12** as a brown powder (8 mg, quantitative yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 7.55 (dt, *J* = 8.2, 1.0, 1H, 9), 7.46 (ddd, *J* = 8.2, 7.0, 1.2, 1H, 8), 7.38 (ddd, *J* = 8.3, 7.1, 1.1, 1H, 7), 7.31 (dt, *J* = 8.2, 1.0, 1H, 6), 7.26 (s, 2H, 11, 15), 7.23 (s, 1H), 4.20 (s, 3H, 18), 2.43 (s, 6H, 19, 20); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 183.2 (2, C^{carbene}), 182.2, 168.6, 140.0, 137.3,

135.8, 135.2, 131.6, 126.0, 124.9, 124.8, 112.4, 111.4, 35.8, 21.6; IR (ATR, cm⁻¹) 2062 (CO), 1980 (CO); IR (solution in CH₂Cl₂, cm⁻¹) 2068 (CO), 1986 (CO); HR-MS (ESI, CH₂Cl₂ / CH₃OH = 95/5) [M+H]⁺ (C₁₈ H₂₇ N₂ O₂ ³⁵Cl ¹⁹³Ir): calculated for 521.06025 m/z, found 521.0601 (Δ = 0 ppm).



Figure S2. FT-IR spectra of **12** measured in powder (ATR) (left) and in CH₂Cl₂ (liquid cell with BaF₂ windows (right).

3-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazole-2-selenone (rac)-13



Method A:^[4] In a dried Schlenk tube, was placed salt **[(***rac***)-6].HI** (13.5 mg, 0.026 mmol) and elemental selenium powder (7.4 mg, 0.093 mmol). After 3 vacuum/argon cycles, dried THF (1 mL) was added and the suspension was cooled down to -78°C. A NaHMDS solution (0.03 mL, 1.0 M in THF) was added dropwise and the obtained mixture was allowed to heat up to r.t. then stirred overnight. The solvent was stripped off and the obtained residue was dissolved in CH₂Cl₂ and filtered over a Celite© pad and evaporated. The filtrate was purified by column chromatography (SiO₂, *n*-Heptane/EtOAc = 1:0 to 9:1) to afford the desired product (*rac*)-13 as a grey powder (3.8 mg, 32% yield). **Method B**:^[5] In a screw-capped vial, was placed salt **[(***rac***)-6].HI** (9.2 mg, 0.018 mmol), elemental selenium powder (3.5 mg, 0.044 mmol) and acetone (technical grade, 1 mL). The mixture was stirred at 40°C for 15 min. NEt₃ (8 μ L, 0.057 mmol) was then added and the obtained mixture was heated to 60°C and stirred overnight. Then, the heterogenous mixture was filtered through a plug of silica gel, washed with CH₂Cl₂ then EtOAc. The solvents were removed under reduced pressure and the obtained wax was dried under vacuum to afford the desired product (*rac*)-13 as a fine yellow powder (5.3 mg, 63% yield).

¹H NMR (400 MHz, Acetone-*d₆*) δ = 8.39 (d, *J* = 8.5, 1H, 28), 8.19 – 8.11 (m, 2H, 20, 31), 8.11 – 8.02 (m, 2H, 21, 23), 7.99 – 7.92 (m, 2H, 14, 24), 7.72 – 7.65 (m, 1H, 30), 7.61 – 7.53 (m, 1H, 29), 7.39 (d, *J* = 8.6, 1H, 13), 7.30 (s, 2H, 8, 12), 7.27 (s, 1H, 10), 3.17 (s, 3H, 25), 2.46 (s, 6H, 26, 27); ¹³C NMR (101 MHz, Acetone-*d₆*) δ = 169.8 (5, C=Se), 149.3, 140.3, 138.1, 135.1, 133.3, 133.0, 132.4, 132.1, 132.0, 131.7, 129.4, 129.4, 128.9, 127.4, 127.2, 127.1, 127.1, 126.7, 125.5, 124.9, 115.8, 111.8, 40.3, 21.3; ⁷⁷Se NMR (76 MHz, CDCl₃) δ = 106.2; ⁷⁷Se NMR (76 MHz, Acetone-*d₆*) δ = 133.0; HR-MS (ASAP, 230°C) [M+H]⁺ (C₂₈ H₂₃ N₂⁸⁰Se): calculated for 467.10209 m/z, found 467.1021 (Δ = 0 ppm).

1-(3,5-Dimethylphenyl)-3-methyl-benzimidazole-2-selenone 14



In a dried Schlenk tube, was placed salt **[8].HI** (38.9 mg, 0.106 mmol) and elemental selenium powder (31.8 mg, 0.4 mmol). After 3 vacuum/argon cycles, dried THF (2 mL) was added and the suspension was cooled down to -78°C. A NaHMDS solution (0.12 mL, 1.0 M in THF) was added dropwise and the obtained solution was allowed to heat up to r.t. then stirred overnight. The solvent was then stripped off and the obtained residue was dissolved in CH_2Cl_2 , filtered over a Celite[®] pad and evaporated. The residue was dissolved several times in Et_2O to precipitate the remaining inorganic impurities while the supernatant was removed with a pipette. The combined liquid layers were finally evaporated to afford the desired product **14** as a white crystalline solid (27 mg, 81% yield).

¹H NMR (400 MHz, Acetone-*d*₆) δ = 7.54 (d, *J* = 8.0, 0.8, 1H, 16), 7.33 (t, *J* = 8.2, 7.5, 1.1, 1H, 15), 7.23 (t, *J* = 8.4, 7.4, 1.1, 1H, 14), 7.19 (s, 1H, 10), 7.13 (s, 2H, 8, 12), 7.02 (d, *J* = 8.0, 0.9, 1H, 13), 3.94 (s, 3H, 17), 2.39 (s, 6H, 18, 19); ¹³C NMR (101 MHz, Acetone-*d*₆) δ = 169.1 (5, C=Se), 140.0, 137.7, 135.2, 134.6, 131.3, 126.7, 124.4, 124.3, 110.9, 110.7, 33.5, 21.2; ⁷⁷Se NMR (76 MHz, CDCl₃) δ = 91.5; ⁷⁷Se NMR (76 MHz, Acetone-*d*₆) δ = 112.7; HR-MS (ESI, CH₂Cl₂ / CH₃OH = 90/10) [M+Na]⁺ (C₁₆ H₁₆ N₂ Na ⁸⁰Se): calculated for 339.03709 m/z, found 339.0368 (Δ = 1 ppm).

[5]Helicenic NHC gold(I) chloride complex (rac)-1



In a screw-capped vial protected from light with an aluminum foil, were placed salt (*rac*)-7 (21.7 mg, 0.051 mmol), [AuCl(Me₂S)] (15.4 mg, 0.052 mmol) and dried K_2CO_3 (22.6 mg, 0.163 mmol). The solids were dissolved in acetone (technical grade, 1 mL) and the mixture was stirred at 60°C for 1 hour under

air. After completion of the reaction, the solvent was stripped off and the heterogenous violet/brown mixture was directly filtered on a silica gel plug and washed with CH_2Cl_2 . After evaporation under reduced pressure, the desired gold chloride complex (*rac*)-**1** was obtained as a white powder by precipitation with Et_2O and drying under vacuum (30 mg, 94% yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.32 (d, *J* = 8.3, 1H, 29), 8.12 – 8.05 (m, 2H, 24, 32), 8.05 – 8.01 (m, 1H, 25), 7.99 – 7.92 (m, 3H, 15, 21, 22), 7.69 – 7.63 (m, 1H, 31), 7.63 – 7.57 (m, 1H, 30), 7.58 (d, *J* = 8.6, 1H, 14), 7.39 (s, 2H, 9, 13), 7.31 (s, 1H, 11), 3.38 (s, 3H, 26), 2.50 (s, 6H, 27, 28); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 140.7, 137.4, 134.1, 132.8, 132.6, 132.3, 132.1, 131.6, 129.2, 129.1, 128.1, 127.4, 127.3, 127.2, 126.6, 126.4, 126.0, 125.4, 124.8, 116.7, 112.6, 40.8, 21.7. One quaternary carbon and the carbenic carbon cannot be seen. The C^{carbene} was identified at 178.3 ppm with ¹H-¹³C heteronuclear coupling with 26; HR-MS (ESI, CH₃OH / CH₂Cl₂ = 90/10) [M+Na]⁺ (C₂₈ H₂₂ N₂ ³⁵Cl Na Au): calculated for 641.10293 m/z, found 641.1029 (Δ = 0 ppm).

[5]Helicenic NHC phenyacetylide gold(I) complex (rac)-2



In a round-bottom flask, were placed (*rac*)-**1** (47 mg, 0.075 mmol) and dried K_2CO_3 (36.4 mg, 0.26 mmol) and the solids were dissolved in methanol (2 mL). Phenylacetylene (25 µl, 0.22 mmol) was added dropwise and the reaction mixture was stirred at 70°C for 2 hours. After completion of the reaction, the solvent was stripped off and the obtained mixture was directly filtered over a basic alumina plug and washed with CH₂Cl₂. After evaporation under reduced pressure, the desired gold acetylide complex (*rac*)-**2** was obtained as a white powder by precipitation with Et₂O and drying under vacuum (42 mg, 81% yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.40 – 8.32 (m, 1H, **36**), 8.08 (t, *J* = 8.4, 2H, **31**, **39**), 8.05 – 7.99 (m, 1H, **32**), 7.98 – 7.90 (m, 3H, **22**, **28**, **29**), 7.69 – 7.63 (m, 1H, **38**), 7.63 – 7.59 (m, 1H, **37**), 7.59 – 7.51 (m, 1H, **21**), 7.42 (s, 2H, **16**, **20**), 7.32 (s, 1H, **18**), 7.31 – 7.25 (m, 2H, **10**, **14**), 7.21 – 7.09 (m, 3H, **11**, **12**, **13**), 3.42 (s, 3H, **33**), 2.52 (s, 6H, **34**, **35**); ¹³C NMR (**101** MHz, CD₂Cl₂) δ = 194.5 (**5**, C^{carbene}), 140.6, 137.6, 137.6, 134.4, 132.7, 132.6, 132.5, 132.3, 132.2, 131.9, 131.7, 130.4, 130.3, 129.1, 129.0, 128.4, 128.1, 127.3, 127.2, 127.2, 126.8, 126.5, 126.4, 126.3, 126.1, 126.1, 125.5, 125.5, 124.9, 116.7, 112.5, 104.8, 40.4, 21.7; HR-MS (ESI, CH₃OH / CH₂Cl₂ = **90/10**) [M+Na]⁺ (C₃₆ H₂₇ N₂ Na Au): calculated for 707.1732 m/z, found 707.1725 (Δ = 1 ppm).

[5]Helicenic NHC carbazolide gold(I) complex (rac)-3



In a dried Schlenk tube, were placed (*rac*)-1 (17.6 mg, 0.028 mmol), 9H-Carbazole (14.2 mg, 0.084 mmol) and NaOtBu (8.4 mg, 0.087 mmol). After 3 vacuum/argon cycles, the solids were dissolved in freshly distilled THF (2 mL) and the reaction mixture was stirred under argon at 70°C overnight. The solvent was stripped off and the obtained mixture was directly filtered over a basic alumina plug and washed with CH_2Cl_2 . After evaporation under reduced pressure, the desired gold carbazolide complex (*rac*)-3 was obtained as a white powder by precipitation with Et_2O , washing with acetone and Et_2O and drying under vacuum (14.7 mg, 69% yield).

¹H NMR (400 MHz, CD₂Cl₂) δ = 8.43 (d, 1H, 41), 8.15 – 8.05 (m, 3H, 32, 33, 44), 8.04 – 7.95 (m, 5H, 15, 23, 29, 30, 38), 7.71 (d, *J* = 8.5, 1H, 22), 7.71 – 7.61 (m, 2H, 42, 43), 7.59 (s, 2H, 17, 21), 7.45 (d, *J* = 8.1, 0.9, 2H, 12, 35), 7.41 (s, 1H, 19), 7.23 (t, *J* = 8.2, 6.9, 1.3, 2H, 13, 36), 6.98 (t, *J* = 7.8, 7.0, 1.0, 2H, 14, 37), 3.58 (s, 3H, 34), 2.58 (s, 6H, 39, 40); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 182.5 (5, C^{carbene}), 150.1, 140.8, 137.8, 134.3, 132.9, 132.7, 132.6, 132.3, 132.0, 131.7, 129.2, 129.0, 128.2, 127.4, 127.3, 127.3, 126.5, 126.5, 126.4, 126.1, 125.5, 124.9, 124.4, 124.2, 120.7, 119.9, 119.9, 116.8, 116.6, 114.1, 112.5, 111.2, 40.6, 21.8; HR-MS (ESI, CH₂Cl₂) [M+H]⁺ (C₄₀ H₃₁ N₃ Au): calculated for 750.21781 m/z, found 750.2171 (Δ = 1 ppm).

3. NMR Spectra



Figure S3. ¹H NMR spectrum of **5** in CDCl₃ at 298 K (400 MHz).



Figure S4. ¹³C NMR spectrum of **5** in $CDCI_3$ at 298 K (101 MHz).



Figure S5.¹H NMR spectrum of [(rac)-6].HI in CD₂Cl₂ at 298 K (400 MHz).



Figure S6. ${}^{1}H{}^{13}C$ satellites of the imidazolium proton in ${}^{1}H$ NMR and determination of the ${}^{1}J(C,H)$ coupling constant [(rac)-**6**].HI (CD₂Cl₂, 400 MHz, 298 K).



Figure S7. ¹³C NMR spectrum of [(rac)-**6**].HI in CD₂Cl₂ at 298 K (101 MHz).



Figure S8.¹H NMR spectrum of [(rac)-**6**].HCl in CD₂Cl₂ at 298 K (300 MHz).



Figure S9. ¹³C NMR spectrum of [(rac)-**6**].HCl in CD₂Cl₂ at 298 K (75 MHz).



Figure S10. ¹H NMR spectrum of [**8**].HI in CD_2CI_2 at 298 K (500 MHz).



Figure S11. ${}^{1}H_{-}{}^{13}C$ satellites of the imidazolium proton in ${}^{1}H$ NMR and determination of the ${}^{1}J(C,H)$ coupling constant [8].HI (CD₂Cl₂, 400 MHz, 298 K).



Figure S12. ¹³*C NMR spectrum of* [**8**].*HI in CD*₂*Cl*₂ at 298 *K* (125 MHz).



Figure S13. ¹H NMR spectrum of (rac)-**9**/(rac)-**9**' in CD₂Cl₂ at 298 K (400 MHz).



Figure S14. ¹³C NMR spectrum of (rac)-**9**/(rac)-**9**′in CD₂Cl₂ at 298 K (100 MHz).



Figure S15. ¹H NMR spectrum of **10** in CDCl₃ at 298 K (400 MHz).



Figure S16. ¹³C NMR spectrum of **10** in CDCl₃ at 298 K (100 MHz).



Figure S17. ¹H NMR spectrum of (rac)-**11** in CD_2Cl_2 at 298 K (500 MHz).



Figure S18. ¹H NMR spectrum of **12** in CD_2CI_2 at 298 K (400 MHz).



Figure S19. ¹³C NMR spectrum of **12** in CD₂Cl₂ at 298 K (100 MHz).



Figure S20. ¹*H NMR spectrum of (rac)-13 in (CD₃)*₂*CO at 298 K (400 MHz).*



Figure S21. ¹³C NMR spectrum of (rac)-**13** in (CD₃)₂CO at 298 K (100 MHz).



Figure S22. ^{77}Se NMR spectrum of (rac)-13 in CDCl3 at 298 K (76 MHz).



Figure S23. ⁷⁷*Se NMR spectrum of (rac)-13 in (CD₃)*₂*CO at 298 K (76 MHz).*



Figure S24. ¹H NMR spectrum of **14** in $(CD_3)_2CO$ at 298 K (400 MHz).



Figure S25. 13 C NMR spectrum of **14** in (CD₃)₂CO at 298 K (100 MHz).



Figure S26. ^{77}Se NMR spectrum of $\mathbf{14}$ in CDCl3 at 298 K (76 MHz).



Figure S27. ⁷⁷Se NMR spectrum of (rac)-**13** in $(CD_3)_2CO$ at 298 K (76 MHz).



Figure S28. ¹H NMR spectrum of (rac)- $\mathbf{1}$ in CD₂Cl₂ at 298 K (400 MHz).



Figure S29. ¹³C NMR spectrum of (rac)-**1** in CD₂Cl₂ at 298 K (101 MHz) (inset: ¹H-¹³C hetereonuclear correlation between the unresolved carbene signal in ¹³C NMR and the N-CH₃ group in ¹H NMR).



Figure S30. ¹H NMR spectrum of (rac)-2 in CD₂Cl₂ at 298 K (400 MHz).



Figure S31. 13 C NMR spectrum of (rac)-**2** in CD₂Cl₂ at 298 K (101 MHz).



Figure S32. ¹H NMR spectrum of (rac)- $\mathbf{3}$ in CD₂Cl₂ at 298 K (400 MHz).



Figure S33. ¹³C NMR spectrum of (rac)-**3** in CD₂Cl₂ at 298 K (101 MHz).

4. X-ray crystallographic data

X-ray crystallographic data were measured on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator). The structures were solved by dual-space algorithm using the *SHELXT* program [1a], and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*) [2a]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters.

Compound 8: Crystal under study has revealed to be twinned, composed by two different domains founded with the CELL_now program [3a]. Twin law of this non-meroedral twinning is the following : 1.000 0.000 0.328 0.000 -1.000 0.000 0.000 -1.000

The diffraction frames of the data collection were then integrated with SAINT [4a] and TWINABS [5a] program was used for scaling, empirical absorption corrections and generation of HKLF5 type data set. Final structural refinement has been refined using these total integrated intensities, leading to a twinning of 0.43.

- [1a] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8
- [2a] G.M. Sheldrick Acta Cryst. C71 (2015) 3-8
- [3a] G. M. Sheldrick (2008). CELL_NOW. Georg-August-Universität, Göttingen, Germany
- [4a] Bruker (2017). SAINT v.8.38A. Bruker, Madison, Wisconsin, USA
- [5a] G. M. Sheldrick (2012). TWINABS 2012/1. Bruker, Madison, Wisconsin, USA »



Figure S34. ORTEP figures for [(rac)-6].HI, [8].HI, (rac)-9, 10, (rac)-11, 12, 14 (50% probability).



Figure S35. Heterochiral supramolecular arrangement of (rac)-6. Hydrogens and solvent molecules have been omitted for clarity.

Complexe	Helicity (°)	Au-C _{carbene} bond length (Å)	Au-Y bond length (Å)	C _{carbene} -Au-Y dihedral angle (°)	Shortest Au-Au distance (Å)
(<i>rac</i>)- 1	47.87	1.962	2.280	178.30	3.893
(rac)- 2	48.12	2.014	2.021	175.98	3.567
(rac)- 3	54.66	1.991	2.020	173.24	4.026

Table S1. Selected metrics (bond length and angles) for the gold complexes.

	[(<i>rac</i>)-6].HI	[8].HI	(rac)- 9	10	12
Empirical Formula	C ₂₈ H ₂₃ IN ₂ ● CH ₂ Cl ₂	$C_{16}H_{17}IN_2$	$C_{36}H_{34}CIIrN_2$	$C_{24}H_{28}CIIrN_2$	$C_{18}H_{26}CIIrN_2O_2$
CCDC number	2085972	2085973	2086202	2086203	2086204
Formula Weight	599.31	364.21	722.30	572.13	519.98
Temperature (K)	150	150	150	150	150
Wavelenght (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
Space Group	C2/c	P21/c	<i>P</i> -1	Pbca	<i>P</i> -1
a (Å)	29.179(4)	10.8827(14)	7.5502(11)	14.1044(16)	8.5209(6)
b (Å)	8.1815(12)	11.2420(15)	11.232(3)	16.0957(15)	14.7543(9)
c (Å)	21.986(3)	12.6771(15)	18.367(4)	18.991(2)	15.9605(10)
α (°)	90	90	77.346(8)	90	111.063(2)
β (°)	99.880(5)	101.022(5)	79.074(8)	90	92.649(2)
γ (°)	90	90	71.436(8)	90	106.753(4)
Volume (ų)	5170.8(13)	1522.3(3)	1428.5(5)	4311.3(8)	1767.6(2)
Z	8	4	2	8	4
Color	colourless	colourless	yellow	yellow	green
$ ho_{ m calculated}$ (g.cm ⁻³)	1.540	1.589	1.679	1.763	1.954
Absorption coefficient (mm ⁻¹)	1.466	2.093	4.795	6.329	7.716
Tmin	0.708	0.580	0.292	0.088	0.255
Tmax	0.916	0.882	0.487	0.181	0.462
F (000)	2400	720	716	2240	992
Crystal size (mm)	0.350 x 0.220 x	0.260 x 0.210 x	0.430 x 0.370 x	0.530 x 0.400 x	0.290 x 0.250 x
, , ,	0.060	0.060	0.150	0.270	0.100
θ range for data collection (°)	2.542 to 27.535	2.442 to 27.508	2.292 to 27.668	2.199 to 27.507	2.463 to 27.597
	-37 ≤ h ≤ 37	-14 ≤ h ≤ 13	-9 ≤ h ≤ 8	-18 ≤ h ≤ 18	-11 ≤ h ≤ 11
Limiting indices	-8 ≤ k ≤ 10	0 ≤ k ≤ 14	$-14 \le k \le 14$	-20 ≤ k ≤ 19	-19 ≤ k ≤ 19
	-28 ≤ l ≤ 28	0 ≤ l ≤ 16	-23 ≤ l ≤ 23	-24 ≤ l ≤ 23	-19 ≤ l ≤ 20
Data completeness	97.5%	98.7%	99.6%	99.4%	97.9%
Reflection collected	33516	3457	33483	23588	50754
Reflections uniques	5825 [R(int) = 0.0572]	3457	6643 [R(int) = 0.0545]	4925 [R(int) = 0.0921]	8018 [R(int) = 0.0405]
Data / restraints / parameters	5825 / 0 / 310	3457 / 0 / 176	6643 / 0 / 361	4925 / 0 / 256	8018 / 0 / 439
Goodness-on-fit on F ²	1.094	1.089	1.026	1.054	1.168
Final <i>R</i> indices	R1 = 0.0443,	R1 = 0.0311,	R1 = 0.0247,	R1 = 0.0467,	R1 = 0.0275,
[I > 2σ]	wR2 = 0.1088	wR2 = 0.0748	wR2 = 0.0603	wR2 = 0.1073	wR2 = 0.0586
	R1 = 0.0609,	R1 = 0.0376,	R1 = 0.0288,	R1 = 0.0744,	R1 = 0.0334,
R indices (all data)	wR2 = 0.1187	wR2 = 0.0776	wR2 = 0.0622	wR2 = 0.1271	wR2 = 0.0621
Largest diff peak and	2.157 and -	0.468 and -	1.313 and -	2.292	1.627
hole (eÅ ⁻³)	1.145	1.091	1.819	and -1.866	and -1.523

Table S2. X-ray crystallographic data

		1	1
	(rac)- 1	(rac)- 2	(rac)- 3
Empirical Formula	C ₂₈ H ₂₂ AuClN ₂ • CH ₂ Cl ₂	$C_{36}H_{27}AuN_2$	$C_{40}H_{30}AuN_3$
CCDC number	2085969	2085970	2085971
Formula Weight	703.82	684.56	749.63
Temperature (K)	150	150	150
Wavelenght (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space Group	C2/c	P-1	P21/c
a (Å)	22.953(2)	10.7486(11)	14.6402(9)
b (Å)	15.8832(17)	12.3503(12)	13.5945(9)
c (Å)	15.4461(18)	12.5806(12)	16.2108(9)
α (°)	90	87.492(3)	90
β (°)	111.559(4)	66.568(3)	112.724(2)
γ (°)	90	66.219(3)	90
Volume (Å ³)	5237.3(10)	1388.6(2)	2975.9(3)
Z	8	2	4
Color	colourless	colourless	green
$ ho_{ m calculated}$ (g.cm ⁻³)	1.785	1.637	1.673
Absorption coefficient (mm ⁻¹)	5.945	5.325	4.978
Tmin	0.068	0.568	0.117
Tmax	0.172	0.766	0.370
F (000)	2736	672	1480
Crystal size (mm)	0.440 x 0.340 x 0.240	0.240 x 0.180 x 0.050	0.600 x 0.450 x 0.200
heta range for data collection (°)	2.931 to 27.484	3.265 to 27.484	2.961 to 27.484
	-29 ≤ h ≤ 29	-13 ≤ h ≤ 13	-18 ≤ h ≤ 19
Limiting indices	-20 ≤ k ≤ 20	-16 ≤ k ≤ 16	-17 ≤ k ≤ 17
	-20 ≤ l ≤ 20	-16 ≤ ≤ 16	-18 ≤ ≤ 21
Data completeness	99.9%	99.8%	99.8%
Reflection collected	32205	31422	31299
Reflections uniques	6001 [R(int) = 0.0424]	6371 [R(int) = 0.0392]	6809 [R(int) = 0.0489]
Data / restraints / parameters	6001 / 3 / 326	6371 / 0 / 355	6809 / 0 / 400
Goodness-on-fit on F ²	1.034	1.098	1.038
Final <i>R</i> indices	<i>R</i> 1 = 0.0258,	<i>R</i> 1 = 0.0202,	<i>R</i> 1 = 0.0267,
[I > 2σ]	wR2 = 0.0592	wR2 = 0.0414	wR2 = 0.0629
Pindicos (all data)	R1 = 0.0318,	R1 = 0.0245,	R1 = 0.0362,
k indices (all data)	wR2= 0.0623	wR2 = 0.0428	wR2 = 0.0678
Largest diff peak and hole (eÅ ⁻³)	0.934 and -1.500	0.788 and -1.001	1.563 and -1.873

5. Chiral HPLC separations

Analytical chiral HPLC separation for 1

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

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Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IH	Heptane / isopropanol / dichloromethane (80/10/10)	9.45 (-)	2.20	12.37 (+)	3.19	1.45	5.64



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.45	4189	49.89	2.20		
12.37	4207	50.11	3.19	1.45	5.64
Sum	8396	100.00			

Preparative separation for 1:

• Sample preparation: About 26 mg of **1** are dissolved in 4.5 mL of a mixture of dichloromethane and hexane (1/1).

• Chromatographic conditions: Chiralpak IH (250 x 10 mm), Hexane / isopropanol / dichloromethane (80/10/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 15 times 300 μL, every 6 minutes.

• First fraction: 10 mg of the (P) enantiomer with ee > 98%



RT [min]	Area	Area%			
9.54	3655	99.10			
12.40	33	0.90			
Sum	3689	100.00			

• Second fraction: 10 mg of the (*M*) enantiomer with *ee* > 98 %



Analytical chiral HPLC separation for 2

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.52	2816	45.34	0.87		
7.32	3395	54.66	1.48	1.70	5.18
Sum	6211	100.00			

Preparative separation for 2:

• Sample preparation: About 35 mg of **2** are dissolved in 4 mL of a mixture of dichloromethane and hexane (1/1).

• Chromatographic conditions: Chiralpak IB (250 x 10 mm), Hexane / isopropanol / dichloromethane (80/10/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- Injections (stacked): 20 times 200 μL , every 7 minutes.
- First fraction: 16 mg of the (P) enantiomer with ee > 97.5 %



Analytical chiral HPLC separation for 3

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IA	Heptane / ethanol / dichloromethane (70/20/10)	4.93 (-)	0.67	7.09 (+)	1.40	2.09	7.45



The compound seems unstable and forms the peak at 4.4 min, which is found in all other fractions after preparative separation.

Preparative separation for 3:

• Sample preparation: About 12 mg of compound **3** are dissolved in 2.5 mL of a mixture hexane / dichloromethane (1/1).

• Chromatographic conditions: Chiralpak IA (250 x 10 mm), Hexane / ethanol / dichloromethane (70/20/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 100 times 250 µL, every 5.5 minutes.

• First fraction: 3.2 mg of the first eluted enantiomer with ee > 92%



• Second fraction: 4.7 mg of the second eluted enantiomer with ee > 84%



6. Photophysical studies

Absorption spectra in solution were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Samples for emission measurements were contained within quartz cuvettes of 1 cm pathlength modified to allow connection to a high-vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using aqueous $[Ru(bpy)_3]Cl_2$ as the standard $(\Phi_{lum} = 0.040)$.^[6] The luminescence lifetimes of the complexes were measured by multichannel scaling (MCS) following excitation into the lowest-energy absorption band with a microsecond pulsed xenon lamp. The emitted light was detected at 90° using a Hamamatsu R928 photomultiplier tube, Peltier-cooled to -20 °C, after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is \pm 10% or better. Under air-equilibrated conditions, the intensity of phosphorescence is negligible and certainly too weak to determine a lifetime. We were not able to determine the lifetime of the fluorescence around 400 nm. Using a 374 nm laser diode in conjunction with a time-correlated single photon counting set-up, the detected light was too weak and/or the decay too short to reliably deconvolute the lifetime from the instrument response function. The spectra and lifetimes at 77 K were recorded using the same equipment in a glass of EPA (= diethyl ether / isopentane / ethanol, 2:2:1 v/v) contained within 4 mm diameter quartz tubes in a Dewar.

Table S3. UV-Vis an	d emission data	for the helicenic	c gold compl	exes 1 and 2.
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Complex	Absorption	Emission	Φ	Tphos,	Emission at 77 K ^e		
	(ε / M ⁻¹ cm ⁻¹) ^α	Amax / IIIII	~ 10	7 μs	λ _{max} / nm	τ / μs	
1	268 (36239), 293 (41594), 302 (41847), 314 (34455), 370 (2497), 390 (1963)	393, 415, 439 (Fluo) 514, 551, 602sh (Phos)	0.46	800 (Phos)	511, 546, 592, 642, 700	52 000	

2 280 (42795), 291 393, 415, 439 (47380), 318 (37200), (Fluo) 371 (2828), 391 (2166) (Phos)	1.6	1500 (Phos)	511, 546, 592, 644, 704	19 000
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^a In CH₂Cl₂ at 295 ± 1 K. ^b In deoxygenated CH₂Cl₂ at 295 ± 1 K. $\lambda_{max} = \lambda_{(0,0)}$ ^c Quantum yield in deoxygenated CH₂Cl₂ at 295 ± 1 K were measured using [Ru(bpy)₃]Cl_{2(aq)} as the standard, for which $\Phi = 0.04$.^{[6] d} Lifetime of the phosphorescence band in deoxygenated CH₂Cl₂ at 295 ± 1 K, recorded at $\lambda_{em} = 550$ nm estimated uncertainty in the values is around ±10% ^e In diethyl ether / isopentane / ethanol, 2:2:1, v/v/v; the lifetimes indicated again refer to the phosphorescence, $\lambda_{em} = 550$ nm.

7. Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm) in a 1 or 10 cm cell, thermostated with a Peltier controlled cell holder. Specific rotations are given in $10^{-1} \text{ deg} \cdot \text{cm}^2 \cdot \text{g}^{-1}$, and molar rotations are given in $10^{-3} \text{ deg} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. Specific and molar rotations of the stereoisomers of **1** and **2** were measured in CH₂Cl₂ at 25°C with an uncertainty of ± 6%.

	Conc. (mol.L ⁻¹)	$[\alpha]_D^{25}$ (10 ⁻¹ deg.cm ² .g ⁻¹)	$[\phi]_D^{25}$ (10 ⁻³ deg.cm ² .mol ⁻¹)
(P)- 1	3.4 × 10 ⁻⁴	+ 880	+ 5420
(M)- 1	4.7×10^{-4}	- 895	- 5550
(P)- 2	4.2×10^{-4}	+ 940	+ 6420
(M)- 2	4.1×10^{-4}	- 830	- 5700

Table S4. Specific and molar rotations values for **1** and **2** enantiomers.

8. References

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