

## Electronic Supplementary Information

### Controlled Entry to a Heterometallic N-Heterocyclic Carbene Helicate

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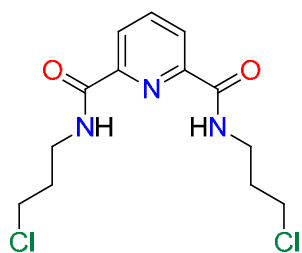
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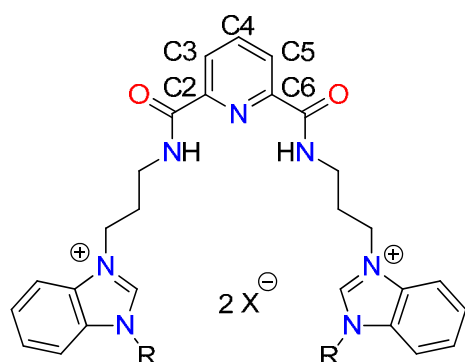
## Experimental Section

**General Considerations.** Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at 298 K on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts ( $\delta$ ) were internally referenced to the residual solvent signals relative to tetramethylsilane. ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on an ElementarVario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore.



**Compound I.** A mixture of 2-chloropropylamine hydrochloride (780 mg, 6.00 mmol) and  $\text{NEt}_3$  (1.35 mL) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) was stirred for 1 h to give the free amine. Pyridine-2,6-dicarboxylic acid chloride (600 mg, 2.90 mmol) was added to this solution, and the reaction mixture was stirred at ambient temperature for 8 h. The solvent was evaporated before  $\text{H}_2\text{O}$  was added. The aqueous layer was extracted with  $\text{CHCl}_3$  ( $3 \times 50$  mL), and the combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Filtration and removal of the solvent from the filtrate gave a crude solid, which was purified by column chromatography ( $\text{SiO}_2$ , hexane/ethyl acetate: 1/1) to give **I** as a white solid (590 mg, 1.90 mmol, 64%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.36–8.34 (2 H, m, Py–H), 8.17 (2 H, br–s, CONH), 8.06–8.01 (1 H, m, Py–H), 3.67–3.66 (8 H, m,  $\text{NHCH}_2$  and  $\text{CH}_2\text{Cl}$ ), 2.19–2.12 (4 H,

m, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CDCl<sub>3</sub>): δ 164.5 (CO), 149.3, 139.8, 125.7 (Py-C), 43.7 (CH<sub>2</sub>Cl), 38.1 (NHCH<sub>2</sub>), 32.6 (CH<sub>2</sub>). Anal. Calcd for C<sub>13</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>: C, 49.07; H, 5.39; N, 13.21. Found: C, 49.31; H, 5.29; N, 12.98. MS (ESI): *m/z* 318 [M]<sup>+</sup>.



**Salt A<sub>Bn</sub>.** To a solution of compound I (159 mg, 0.50 mmol) in CH<sub>3</sub>CN (30 mL), 1-benzylbenzimidazole (260 mg, 1.25 mmol) and NaI (750 mg, 5.00 mmol) was added. After the mixture was heated under microwave

irradiation for 3 h at 150 °C, the solvent was removed under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added. The resulting suspension was filtered through Celite. Solvent of the filtrate was dried off in vacuo. Ethyl acetate (3 × 20 mL) was added to wash the residue, giving the product as a pale yellow powder (450 mg, 0.49 mmol, 98%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.99 (2 H, s, NCHN), 9.40 (2 H, t, <sup>3</sup>*J*(H,H) = 6.1 Hz, NH), 8.19 (3 H, ps-s, Py-H), 8.11 (2 H, d, <sup>3</sup>*J*(H,H) = 8.2 Hz, Ar-H), 7.92 (2 H, d, <sup>3</sup>*J*(H,H) = 7.6 Hz, Ar-H), 7.67–7.60 (4 H, m, Ar-H), 7.52 (4 H, ps-d, Ar-H), 7.43–7.36 (6 H, m, Ar-H), 5.76 (4 H, s, NCH<sub>2</sub>Ph), 4.62 (4 H, t, <sup>3</sup>*J*(H,H) = 7.0 Hz, NCH<sub>2</sub>), 3.51 (4 H, m, <sup>3</sup>*J*(H,H) = 6.4 Hz, NHCH<sub>2</sub>), 2.31 (4 H, m, <sup>3</sup>*J*(H,H) = 6.9 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>): δ 163.4 (CO), 148.4 (C2/6), 142.6 (NCHN), 139.5 (C4), 133.9, 131.2, 130.9, 129.0, 128.7, 128.3, 126.7, 126.6 (Ar-C), 124.3 (C3/5), 113.9, 113.8 (Ar-C), 49.9 (NCH<sub>2</sub>Ph), 45.0 (NCH<sub>2</sub>), 35.9 (NHCH<sub>2</sub>), 28.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). Anal. Calcd for C<sub>41</sub>H<sub>41</sub>I<sub>2</sub>N<sub>7</sub>O<sub>2</sub>: C, 53.67; H, 4.50; N,

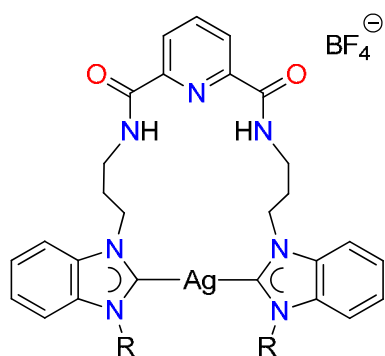
10.68. Found: C, 53.68; H, 4.88; N, 10.59 MS (ESI):  $m/z$  332  $[M - 2 I]^{2+}$ , 790  $[M - I]^+$ .

**Salt A<sub>Me</sub>.** This salt was prepared in analogy to **A<sub>Bn</sub>** from 0.50 mmol of compound **I** with 1-methylbenzimidazole (165 mg, 1.25 mmol) and NaI (750 mg, 5.00 mmol). Yield: 341 mg, 0.45 mmol, 89%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.77 (2 H, s, NCHN), 9.29 (2 H, t, <sup>3</sup>*J*(H,H) = 5.9 Hz, NH), 8.17 (3 H, br-s, Py-H), 8.10–8.18 (2 H, m, Ar-H), 8.00–7.96 (2 H, m, Ar-H), 7.67–7.65 (4 H, m, Ar-H), 4.60 (4 H, t, <sup>3</sup>*J*(H,H) = 6.5 Hz, NCH<sub>2</sub>), 4.06 (6 H, s, NCH<sub>3</sub>), 3.50 (4 H, m, <sup>3</sup>*J*(H,H) = 6.0 Hz, NHCH<sub>2</sub>), 2.28 (4 H, br-s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.3 (CO), 148.3 (C2/6), 142.8 (NCHN), 139.5 (C4), 131.8, 130.8, 126.4 (Ar-C, two are coincident), 124.2 (C3/5), 113.53, 113.47 (Ar-C), 44.8 (NCH<sub>2</sub>), 36.0 (NCH<sub>3</sub>), 33.2 (NHCH<sub>2</sub>), 28.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). Anal. Calcd for C<sub>29</sub>H<sub>33</sub>I<sub>2</sub>N<sub>7</sub>O<sub>2</sub>: C, 45.51; H, 4.35; N, 12.81. Found: C, 45.82; H, 4.37; N, 12.45. MS (ESI):  $m/z$  256  $[M - 2 I]^{2+}$ , 638  $[M - I]^+$ .

**Salt B<sub>Bn</sub>.** Salt **A<sub>Bn</sub>** (890 mg, 0.97 mmol) was mixed with AgBF<sub>4</sub> (380 mg, 1.95 mmol) in CH<sub>3</sub>CN and stirred for 3 h. The precipitation was removed by filtering through Celite. The filtrate was dried in vacuo to afford the product as white powders (747 mg, 0.89 mmol, 92%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  9.35 (2 H, s, NCHN), 8.75 (2 H, t, <sup>3</sup>*J*(H,H) = 5.9 Hz, NH), 8.20 (2 H, ps-d, C(3/5)H), 8.08 (1 H, ps-t, (C4)H), 7.90 (2 H, d, <sup>3</sup>*J*(H,H) = 8.2 Hz, Ar-H), 7.69–7.53 (6 H, m, Ar-H), 7.46–7.39 (10 H, m, Ar-H), 5.60 (4 H, s, NCH<sub>2</sub>Ph), 4.54 (4 H, t, <sup>3</sup>*J*(H,H) = 6.8 Hz, NCH<sub>2</sub>), 3.56 (4 H, m, <sup>3</sup>*J*(H,H) = 6.3 Hz, NHCH<sub>2</sub>), 2.36 (4 H, m, <sup>3</sup>*J*(H,H) = 6.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR (75.48 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  164.9 (CO), 149.7 (C2/6), 142.7 (NCHN), 140.2 (C4), 140.0, 132.7, 132.4, 130.2, 130.1, 129.5, 128.0 (Ar-C, two are coincident), 125.4 (C3/5), 114.7, 114.6 (Ar-C), 51.7 (NCH<sub>2</sub>Ph), 46.3 (NCH<sub>2</sub>), 36.8 (NHCH<sub>2</sub>), 29.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.38 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -74.82, -74.87 (s,  $\text{BF}_4$ ). Anal. Calcd for  $\text{C}_{41}\text{H}_{41}\text{B}_2\text{F}_8\text{N}_7\text{O}_2$ : C, 58.80; H, 4.94; N, 11.71. Found: C, 58.36; H, 4.64; N, 11.68. MS (ESI):  $m/z$  332  $[\text{M} - 2 \text{BF}_4]^{2+}$ , 750  $[\text{M} - \text{BF}_4]^+$ .

**Salt B<sub>Me</sub>**. This salt was prepared in analogy to **B<sub>Bn</sub>** from **A<sub>Me</sub>** (742 mg, 0.97 mmol) and  $\text{AgBF}_4$  (380 mg, 1.95 mmol). Yield: 645 mg, 0.94 mmol, 97%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ): 9.14 (2 H, s, NCHN), 8.54 (2 H, t,  $^3J(\text{H,H}) = 5.6$  Hz, NH), 8.16 (2 H, ps-d, C(3/5)H), 8.05 (1 H, t,  $^3J(\text{H,H}) = 7.5$  Hz, C(4)H), 7.87–7.85 (2 H, m, Ar-H), 7.74–7.73 (2 H, m, Ar-H), 7.61–7.58 (4 H, m, Ar-H), 4.52 (4 H, t,  $^3J(\text{H,H}) = 6.8$  Hz, NCH<sub>2</sub>), 4.00 (6 H, s, NCH<sub>3</sub>), 3.54 (4 H, m,  $^3J(\text{H,H}) = 6.3$  Hz, NHCH<sub>2</sub>), 2.33 (4 H, m,  $^3J(\text{H,H}) = 6.5$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  164.8 (CO), 149.5 (C2/6), 142.9 (NCHN), 140.3 (C4), 133.2, 132.2, 127.83, 127.79 (Ar-C), 125.4 (C3/5), 114.3, 114.1 (Ar-C), 46.2 (NCH<sub>2</sub>), 37.0 (NCH<sub>3</sub>), 34.1 (NHCH<sub>2</sub>), 29.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.38 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -74.87, -74.93 (s,  $\text{BF}_4$ ). Anal. Calcd for  $\text{C}_{29}\text{H}_{33}\text{B}_2\text{F}_8\text{N}_7\text{O}_2$ : C, 50.83; H, 4.85; N, 14.31. Found: C, 50.97; H, 4.78; N, 14.28. MS (ESI):  $m/z$  256  $[\text{M} - 2 \text{BF}_4]^{2+}$ , 598  $[\text{M} - \text{BF}_4]^+$ .

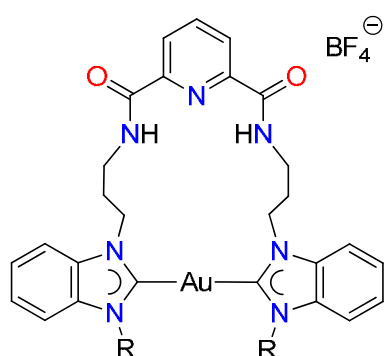


**Silver(I) dicarbene complex 1<sub>Bn</sub>**. A mixture of salt **B<sub>Bn</sub>** (84 mg, 0.10 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (20 mL) before  $\text{Ag}_2\text{O}$  (28 mg, 0.12 mmol) was added. The mixture was heated at 60 °C with stirring for 5 h. The

resulting suspension was dried in vacuo before  $\text{CH}_2\text{Cl}_2$  (100 mL) was added and filtered. The filtrate was consequently extracted with water ( $5 \times 100$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the product was obtained as a white solid (86 mg, 0.10 mmol, 99%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.57 (2 H, br-s, NH), 7.73 (2 H, br-s, C(3/5)H), 7.60 (3 H, br-s, (C4)H and Ar-H), 7.40 (4 H, br-s, Ar-H), 7.34 (2 H, t,  $^3J(\text{H,H}) = 7.6$  Hz, Ar-H), 7.22–7.19 (6 H, m, Ar-H), 7.16–7.15 (4 H, m, Ar-H), 5.30 (4 H, br-s,  $\text{NCH}_2\text{Ph}$ ), 4.45 (4 H, br-s,  $\text{NCH}_2$ ), 3.47 (4 H, br-s,  $\text{NHCH}_2$ ), 2.20 (correct integration is not obtained due to overlapping with  $\text{H}_2\text{O}$  signal, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.48 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  164.4 (CO), 149.5 (C2/6), 139.8 (C4), 136.9, 134.7, 134.5, 129.9, 129.2, 128.4, 125.29, 125.26 (Ar-C), 124.8 (C3/5), 113.0 (Ar-C, two are coincident), 53.0 ( $\text{NCH}_2\text{Ph}$ ), 48.6 ( $\text{NCH}_2$ ), 37.7 ( $\text{NHCH}_2$ ), 30.3 (br-s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), the carbene signal was not obtained despite prolonged measuring.  $^{19}\text{F}$  NMR (282.38 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -74.83, -74.89 (s,  $\text{BF}_4$ ). Anal. Calcd for  $\text{C}_{41}\text{H}_{39}\text{AgBF}_4\text{N}_7\text{O}_2$ : C, 57.50; H, 4.59; N, 11.45. Found: C, 57.67; H, 4.35; N, 11.38. MS (ESI):  $m/z$  768  $[\text{M} - \text{BF}_4]^+$ .

**Silver(I) dicarbene complex  $1_{\text{Me}}$ .** This complex was obtained in analogy to  $1_{\text{Bn}}$  from  $\mathbf{B}_{\text{Me}}$  (69 mg, 0.10 mmol) and  $\text{Ag}_2\text{O}$  (28 mg, 0.12 mmol). Yield: 67 mg, 0.10 mmol, 95%.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.02 (2 H, br-s, NH), 8.04 (1 H, t,  $^3J(\text{H,H}) = 7.5$  Hz, (C4)H), 7.90 (2 H, d,  $^3J(\text{H,H}) = 8.2$  Hz, (C3/5)H), 7.83 (2 H, d,  $^3J(\text{H,H}) = 7.6$  Hz, Ar-H), 7.53 (2 H, d,  $^3J(\text{H,H}) = 7.6$  Hz, Ar-H), 7.48–7.41 (4 H, m, Ar-H), 4.75 (4 H, br-s,  $\text{NCH}_2$ ), 3.71 (6 H, s,  $\text{NCH}_3$ ), 3.44 (4 H, br-s,  $\text{NHCH}_2$ ), 2.47 (4 H, br-s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  162.3 (CO),

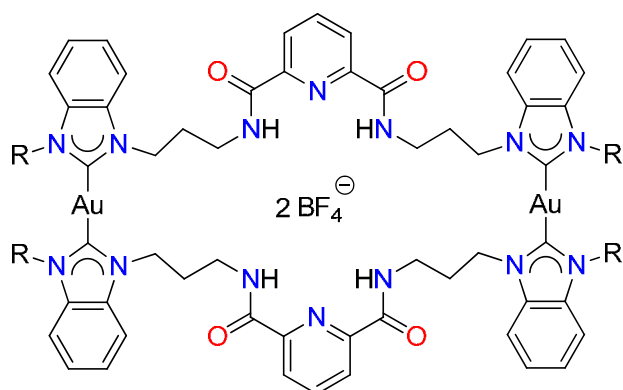
148.0 (C2/6), 139.3 (C4), 133.8, 133.2, 123.95, 123.92 (Ar-C), 123.4 (C3/5), 112.3, 111.6 (Ar-C), 47.2 (NCH<sub>2</sub>), 36.8 (NCH<sub>3</sub>), 35.1 (NHCH<sub>2</sub>), 27.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), the carbene signal was not obtained despite prolonged measuring. <sup>19</sup>F NMR (282.38 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  -72.25, -72.30 (s, BF<sub>4</sub>). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>AgBF<sub>4</sub>N<sub>7</sub>O<sub>2</sub>: C, 49.46; H, 4.44; N, 13.92. Found: C, 49.32; H, 4.48; N, 13.98. MS (ESI): *m/z* 618 [M - BF<sub>4</sub>]<sup>+</sup>.



**Monogold(I) dicarbene complex 2<sub>Bn</sub>.** A solution of [AuCl(tht)] (40 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was slowly added to the solution of complex 1<sub>Bn</sub> (106 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The mixture was kept stirring for 4 h before the precipitation was

removed by centrifuging. The liquid was concentrated to 3 mL and subjected to column chromatography (SiO<sub>2</sub>, CH<sub>3</sub>CN/CHCl<sub>3</sub>, 2:7). Yield of mononuclear complex 2<sub>Bn</sub>: 42 mg, 0.04 mmol, 36%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.89 (2 H, t, <sup>3</sup>*J*(H,H) = 5.2 Hz, NH), 7.99 (2 H, ps-d, C(3/5)H), 7.90 (2 H, t, <sup>3</sup>*J*(H,H) = 7.6 Hz, (C4)H), 7.60 (2 H, d, <sup>3</sup>*J*(H,H) = 8.2 Hz, Ar-H), 7.43 (2 H, t, <sup>3</sup>*J*(H,H) = 7.8 Hz, Ar-H), 7.31 (2 H, t, <sup>3</sup>*J*(H,H) = 7.8 Hz, Ar-H), 7.22–7.21 (6 H, m, Ar-H), 7.12–7.10 (6 H, m, Ar-H), 5.24 (4 H, s, NCH<sub>2</sub>Ph), 4.74 (4 H, t, <sup>3</sup>*J*(H,H) = 6.6 Hz, NCH<sub>2</sub>), 3.69 (4 H, br-s, NHCH<sub>2</sub>), 2.63 (4 H, m, <sup>3</sup>*J*(H,H) = 5.1 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125.77 MHz, CDCl<sub>3</sub>):  $\delta$  191.7 (C<sub>carbene</sub>), 164.0 (CO), 149.4 (C2/6), 139.1 (C4), 135.5, 134.2, 133.9, 129.7, 129.1, 127.5, 125.7 (Ar-C, two are coincident), 124.5 (C3/5), 113.0, 112.5 (Ar-C), 52.6 (NCH<sub>2</sub>Ph), 48.2 (NCH<sub>2</sub>), 37.6 (NHCH<sub>2</sub>), 28.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.38 MHz, CDCl<sub>3</sub>):  $\delta$  -74.50, -74.56 (s, BF<sub>4</sub>). Anal. Calcd for C<sub>41</sub>H<sub>39</sub>AuBF<sub>4</sub>N<sub>7</sub>O<sub>2</sub>: C, 52.08;

H, 4.16; N, 10.37. Found: C, 52.02; H, 3.84; N, 10.53. MS (ESI):  $m/z$  858  $[M - BF_4]^+$ .



### Digold(I) tetracarbene complex

**3<sub>Bn</sub>**. This complex was isolated in

the yield of 46 mg, 0.02 mmol,

39%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

$\delta$  9.34 (4 H, br-s, NH), 7.80 (4 H, d,

<sup>3</sup> $J$ (H,H) = 7.6 Hz, (C3/5)H), 7.47 (4 H, d, <sup>3</sup> $J$ (H,H) = 8.2 Hz, (C4)H and Ar-H),

7.39–7.38 (4 H, m, Ar-H), 7.34–7.29 (10 H, m, Ar-H), 7.23–7.22 (12 H, m, Ar-H),

7.15 (8 H, br-s, Ar-H), 5.49 (8 H, s, NCH<sub>2</sub>Ph), 4.63 (8 H, t, <sup>3</sup> $J$ (H,H) = 7.1 Hz, NCH<sub>2</sub>),

3.65 (8 H, m, <sup>3</sup> $J$ (H,H) = 5.6 Hz, NHCH<sub>2</sub>), 2.34 (8 H, m, <sup>3</sup> $J$ (H,H) = 6.2 Hz,

CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CDCl<sub>3</sub>):  $\delta$  191.1 (C<sub>carbene</sub>), 164.9 (CO),

149.3 (C2/6), 138.3 (C4), 135.6, 133.9, 133.7, 129.7, 129.1, 127.5, 125.8, 125.7

(Ar-C), 124.5 (C3/5), 112.7, 112.6 (Ar-C), 52.7 (NCH<sub>2</sub>Ph), 47.8 (NCH<sub>2</sub>), 37.7

(NHCH<sub>2</sub>), 30.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.38 MHz, CDCl<sub>3</sub>):  $\delta$  -74.96, -74.98 (s,

BF<sub>4</sub>). Anal. Calcd for C<sub>82</sub>H<sub>78</sub>Au<sub>2</sub>B<sub>2</sub>F<sub>8</sub>N<sub>14</sub>O<sub>4</sub>: C, 52.08; H, 4.16; N, 10.37. Found: C,

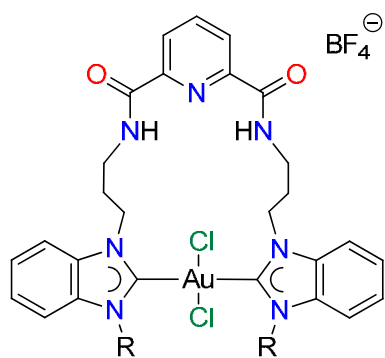
52.24; H, 4.25; N, 10.55. MS (ESI):  $m/z$  858  $[M - 2 BF_4]^{2+}$ .

**Monogold(I) dicarbene complexes 2<sub>Me</sub>**. Complexes **2<sub>Me</sub>** and **3<sub>Me</sub>** were synthesized in analogy to the previous complexes, but purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 30:1). They were further separated by washing with CH<sub>3</sub>CN. Complex **2<sub>Me</sub>** was collected from the CH<sub>3</sub>CN phase and isolated as a white powder upon removal of the solvent (35 mg, 0.04 mmol, 35%). <sup>1</sup>H



NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.20 (2 H, t,  $^3J(\text{H,H}) = 5.4$  Hz, NH), 7.95 (1 H, t,  $^3J(\text{H,H}) = 7.6$  Hz, (C4)H), 7.82 (2 H, d,  $^3J(\text{H,H}) = 7.6$  Hz, (C3/5)H), 7.71 (2 H, d,  $^3J(\text{H,H}) = 7.6$  Hz, Ar-H), 7.47–7.41 (4 H, m, Ar-H), 7.38 (2 H, ps-d, Ar-H), 4.75 (4 H, t,  $^3J(\text{H,H}) = 6.2$  Hz, NCH<sub>2</sub>), 3.65 (6 H, s, NCH<sub>3</sub>), 3.39 (4 H, m,  $^3J(\text{H,H}) = 5.5$  Hz, NHCH<sub>2</sub>), 2.54 (4 H, m,  $^3J(\text{H,H}) = 5.8$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>3</sub>CN):  $\delta$  191.9 (C<sub>carbene</sub>), 163.5 (CO), 149.2 (C2/6), 140.4 (C4), 134.9, 134.1, 125.71, 125.68 (Ar-C), 124.7 (C3/5), 113.3, 112.7 (Ar-C), 48.1 (NCH<sub>2</sub>), 37.9 (NCH<sub>3</sub>), 35.4 (NHCH<sub>2</sub>), 27.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.38 MHz, CD<sub>3</sub>CN):  $\delta$  -75.40, -75.41 (BF<sub>4</sub>). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>AuBF<sub>4</sub>N<sub>7</sub>O<sub>2</sub>: C, 43.90; H, 3.94; N, 12.36. Found: C, 44.02; H, 3.84; N, 12.53. MS (ESI):  $m/z$  706 [M – BF<sub>4</sub>]<sup>+</sup>.

**Digold(I) tetracarbene complex 3<sub>Me</sub>.** This dinuclear complex was collected from the solid phase as a white powder (49 mg, 0.03 mmol, 50%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.02 (4 H, br-s, NH), 7.79 (4 H, d,  $^3J(\text{H,H}) = 7.8$  Hz, (C3/5)H), 7.47–7.44 (14 H, m, (C4)H and Ar-H), 7.37 (4 H, t,  $^3J(\text{H,H}) = 7.5$  Hz, Ar-H), 4.57 (8 H, t,  $^3J(\text{H,H}) = 7.6$  Hz, NCH<sub>2</sub>), 4.02 (12 H, s, NCH<sub>3</sub>), 3.57 (8 H, m,  $^3J(\text{H,H}) = 6.1$  Hz, NHCH<sub>2</sub>), 2.27 (8 H, m,  $^3J(\text{H,H}) = 6.9$  Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  190.8 (C<sub>carbene</sub>), 164.2 (CO), 148.9 (C2/6), 138.3 (C4), 134.2, 133.2, 125.25, 125.22 (Ar-C), 124.2 (C3/5), 111.9, 111.8 (Ar-C), 47.0 (NCH<sub>2</sub>), 37.3 (NCH<sub>3</sub>), 35.3 (NHCH<sub>2</sub>), 30.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.38 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -75.34, -75.40 (BF<sub>4</sub>). Anal. Calcd for C<sub>58</sub>H<sub>62</sub>Au<sub>2</sub>B<sub>2</sub>F<sub>8</sub>N<sub>14</sub>O<sub>4</sub>: C, 43.90; H, 3.94; N, 12.36. Found: C, 44.24; H, 4.25; N, 12.55. MS (ESI):  $m/z$  706 [M – 2 BF<sub>4</sub>]<sup>2+</sup>.

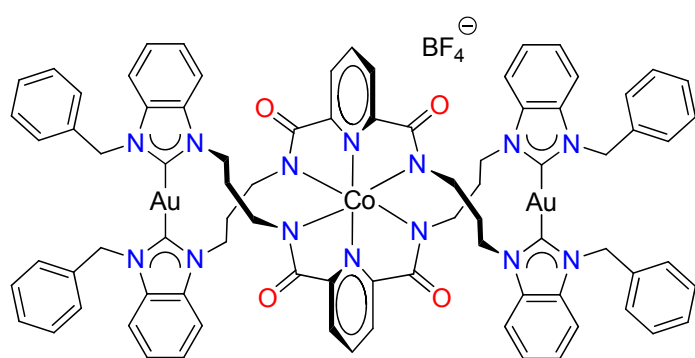


**Monogold(III) dicarbene complexes 4<sub>Bn</sub>.** Complex **2<sub>Bn</sub>** (95 mg 0.10 mmol) and PhICl<sub>2</sub> (33 mg, 0.12 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred for 24 h shielded from light. The solvent was then removed under vacuum, and the residue was washed with

diethyl ether to give the product as a pale yellow solid (90 mg, 0.09 mmol, 89%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.35 (2 H, br-s, NH), 8.25 (2 H, d, <sup>3</sup>J(H,H) = 7.6 Hz, (C3/5)H), 7.96 (1 H, t, <sup>3</sup>J(H,H) = 7.6 Hz, (C4)H), 7.72 (2 H, d, <sup>3</sup>J(H,H) = 7.9 Hz, Ar-H), 7.49 (2 H, br-s, Ar-H), 7.35 (2 H, br-s, Ar-H), 7.25–7.20 (8 H, m, Ar-H), 6.93 (4 H, ps-d, Ar-H), 5.46 (4 H, s, NCH<sub>2</sub>Ph), 4.99 (4 H, br-s, NCH<sub>2</sub>), 3.92 (4 H, br-s, NHCH<sub>2</sub>), 2.64 (4 H, br-s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, CDCl<sub>3</sub>): δ 165.4 (CO), 163.4 (C<sub>carbene</sub>), 149.6 (C2/6), 139.2 (C4), 134.8, 134.3, 133.4, 129.9, 129.4, 126.9, 126.7 (Ar-C, two are coincident), 125.1 (C3/5), 114.1, 113.4 (Ar-C), 52.0 (NCH<sub>2</sub>Ph), 49.1 (NCH<sub>2</sub>), 37.0 (NHCH<sub>2</sub>), 28.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (282.38 MHz, CDCl<sub>3</sub>): δ -73.58, -73.63 (BF<sub>4</sub>). Anal. Calcd for C<sub>41</sub>H<sub>39</sub>AuBCl<sub>2</sub>F<sub>4</sub>N<sub>7</sub>O<sub>2</sub>: C, 48.45; H, 3.87; N, 9.65. Found: C, 48.22; H, 3.84; N, 10.03. MS (ESI): *m/z* 928 [M – BF<sub>4</sub>]<sup>+</sup>.

**Monogold(III) dicarbene complexes 4<sub>Me</sub>.** This complex was prepared in analogy to complex **4<sub>Bn</sub>** from complex **2<sub>Me</sub>** (79 mg, 0.10 mmol) and PhICl<sub>2</sub> (33 mg, 0.12 mmol). Yield: 67 mg, 0.08 mmol, 78%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> with several drops of CD<sub>3</sub>OD): δ 10.4 (the integral was not correct due to fast exchange with the CD<sub>3</sub>OD solvent, br-s, NH), 8.21 (2 H, ps-d, (C3/5)H), 7.94 (1 H, t, <sup>3</sup>J(H,H) = 7.6 Hz,

(C4)H), 7.74 (2 H, d,  $^3J(\text{H,H}) = 7.6$  Hz, Ar-H), 7.59 (1 H, br-s, Ar-H), 7.54–7.53 (5 H, m, Ar-H), 4.96 (4 H, br-s, NCH<sub>2</sub>), 4.22 (6 H, s, NCH<sub>3</sub>), 3.85 (4 H, br-s, NHCH<sub>2</sub>), 2.61 (4 H, br-s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz, CDCl<sub>3</sub> and several drops of CD<sub>3</sub>OD):  $\delta$  165.8 (CO), 162.4 (C<sub>carbene</sub>), 149.6 (C2/6), 139.2 (C4), 135.3, 133.9, 126.6 (Ar-C, two are coincident), 125.2 (C3/5), 113.8, 112.3 (Ar-C), 49.1 (NCH<sub>2</sub>), 37.3 (NCH<sub>3</sub>), 35.0 (NHCH<sub>2</sub>), 28.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.38 MHz, CDCl<sub>3</sub> several drops of CD<sub>3</sub>OD):  $\delta$  -74.67, -74.73 (BF<sub>4</sub>). Anal. Calcd for C<sub>29</sub>H<sub>31</sub>AuBCl<sub>2</sub>F<sub>4</sub>N<sub>7</sub>O<sub>2</sub>: C, 40.30; H, 3.62; N, 11.34. Found: C, 40.12; H, 3.84; N, 11.43. MS (ESI):  $m/z$  776 [M – BF<sub>4</sub>]<sup>+</sup>.



#### Au<sup>I</sup>Co<sup>III</sup> Helicate 5.

CoCl<sub>2</sub>·6H<sub>2</sub>O (71 mg, 0.30 mmol) and 30 equivalents of NaH (360 mg, 9.00 mmol, 60% dispersion in mineral

oil) were stirred in dry THF for 0.5 h. A solution of complex **3<sub>Bn</sub>** (567 mg, 0.30 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> was then added. After stirring the reaction mixture for 3 h under N<sub>2</sub>, the mixture was stirred in air for 0.5 h. The volatiles were removed in vacuo and CH<sub>2</sub>Cl<sub>2</sub> was added to dissolve the product. The CH<sub>2</sub>Cl<sub>2</sub> phase was extracted with H<sub>2</sub>O (5 × 10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> to give the crude product, which was washed with hexane (5 × 10 mL). The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and toluene and slow evaporation afforded the crystalline product as yellow solids (474 mg, 0.25 mmol, 85%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>, 298K) spectrum is shown in Figure SIII.  $^{13}\text{C}\{^1\text{H}\}$

NMR (100.82 MHz, CDCl<sub>3</sub>):  $\delta$  190.1 (C<sub>carbene</sub>), 169.5 (CO), 157.2 (C2/6), 138.5 (C4), 135.5, 133.9, 133.7, 129.8, 129.7, 128.9, 127.9, 126.0 (Ar-C), 123.2 (C3/5), 113.4, 112.2 (Ar-C), 52.9 (NCH<sub>2</sub>Ph), 49.3 (NCH<sub>2</sub>), 43.4 (CONCH<sub>2</sub>), 31.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).  
<sup>19</sup>F NMR (282.38 MHz, CDCl<sub>3</sub>):  $\delta$  -74.89, -74.95 (s, BF<sub>4</sub>). Anal. Calcd for C<sub>82</sub>H<sub>74</sub>Au<sub>2</sub>BCoF<sub>4</sub>N<sub>14</sub>O<sub>4</sub>: C, 52.97; H, 4.01; N, 10.55. Found: C, 52.67; H, 4.34; N, 10.39. HRMS (ESI): *m/z* 1771.4702 (calcd for [M – BF<sub>4</sub>]<sup>+</sup> 1771.4675).

**Magnetic susceptibility measurements.** Powders of complex **5** were packed into a sample tube (sample weight: 0.0843 g; height: 1.70 cm) and evaluated using a Johnson Matthey magnetic susceptibility balance. The mass susceptibility measures 0 cm<sup>3</sup>.g<sup>-1</sup> indicating a diamagnetic compound. Complex **5** (11 mg, 6.00 mmol) was added into an NMR tube and dissolved in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub> [with 1% (volume) MeOH as reference]. A sealed melting point capillary tube filled with 50  $\mu$ L of CD<sub>2</sub>Cl<sub>2</sub> (with 1% MeOH) was slowly placed on the bottom of the NMR tube. The NMR sample was measured and showed only one signal corresponding to the CH<sub>3</sub> of MeOH.<sup>1</sup>

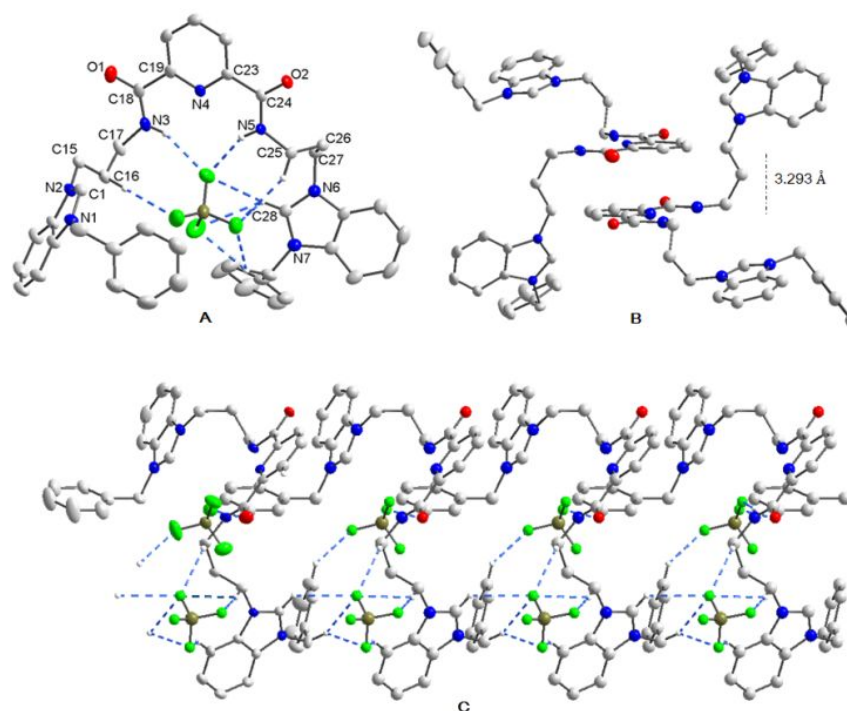
**X-ray Diffraction Studies.** Single crystals of **B<sub>Bn</sub>**·(CH<sub>3</sub>)<sub>2</sub>CO, **2<sub>Me</sub>**, **3<sub>Bn</sub>**·0.5H<sub>2</sub>O and **5**·0.25CH<sub>2</sub>Cl<sub>2</sub> were obtained by slow evaporation of a concentrated solution in CHCl<sub>3</sub> (**B<sub>Bn</sub>**) or CH<sub>2</sub>Cl<sub>2</sub>/toluene (**5**·0.25CH<sub>2</sub>Cl<sub>2</sub>), or diffusion of diethyl ether into a concentrated solution in CH<sub>3</sub>CN (**2<sub>Me</sub>**, **3<sub>Bn</sub>**·0.5H<sub>2</sub>O). X-ray data for them were collected with a Bruker AXS SMART APEX diffractometer, using Mo- or Cu-K $\alpha$

radiation with the SMART suite of Programs.<sup>2</sup> Data were processed and corrected for Lorentz and polarization effects with SAINT,<sup>3</sup> and for absorption effect with SADABS.<sup>4</sup> Structural solution and refinement were carried out with the SHELXTL suite of programs.<sup>5</sup> The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S1.

#### **Discussion of Monogold(III) dicarbene complexes $4_{\text{Bn, Me}}$**

In comparison to the parent complexes, the solubilities of the Au(III) complexes  $4_{\text{Bn, Me}}$  in common organic solvents are significantly decreased. Their  $^1\text{H}$  NMR spectra show even broader signals for the amide and propylene protons at room temperature, which do not sharpen at different temperatures (223–373 K). The ylidene resonances at ~163 ppm are shifted to much higher field in line with the more Lewis acidic  $\text{Au}^{\text{III}}$  centers.<sup>6</sup> Base peaks at  $m/z$  928 and 776 in their ESI mass spectra further corroborate the coordination of two additional chlorido ligands.

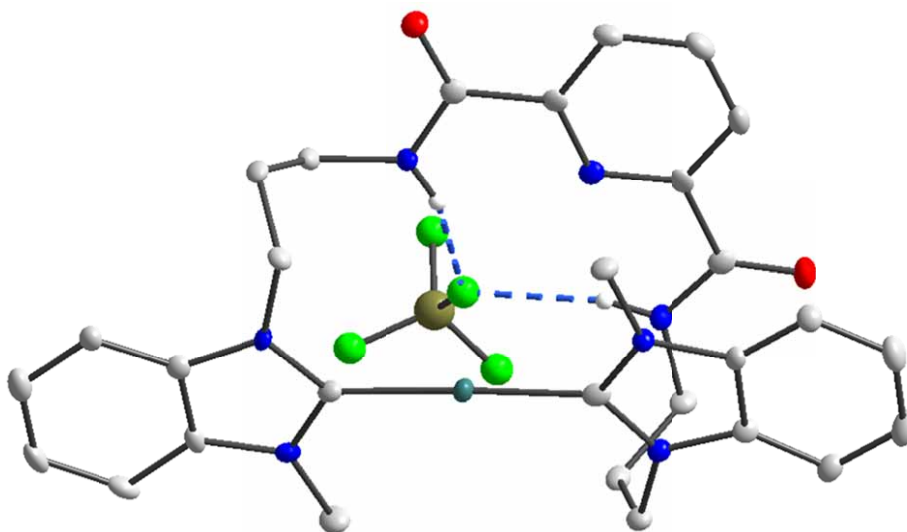
## Molecular structure of ligand precursor $\mathbf{B}_{\text{Bn}}$



**Figure S1.** Molecular structure and perspective view of  $\mathbf{B}_{\text{Bn}}$  showing 50% probability ellipsoids; solvent molecules and most hydrogen atoms are omitted for clarity.

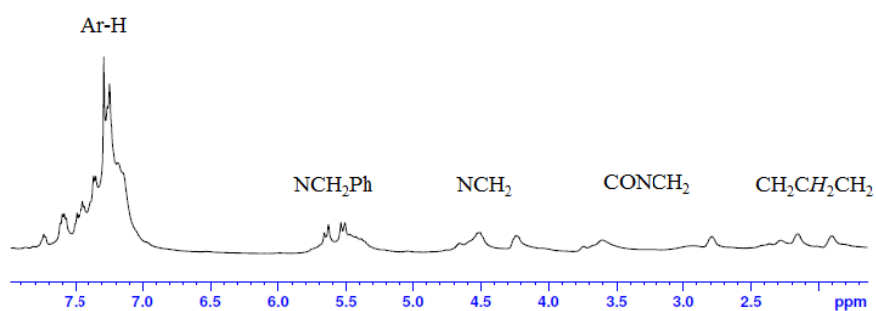
The amide protons (N3–H and N5–H), one of the NCHN protons (C28–H) and several aliphatic protons cooperatively form hydrogen bonds with one  $\text{BF}_4^-$  anion, embedding it inside a cationic cage-like structure (A). The molecular salts are arranged into an infinite chain via intermolecular hydrogen bonds between the  $\text{BF}_4^-$  anions and the various C–H protons (C). Besides, offset face-to-face  $\pi\cdots\pi$  interactions are noted between the two perfectly coplanar pyridine rings from the neighboring molecules with a separation of 3.293 Å (B).<sup>7</sup>

### Molecular structure of complex $2_{Me}$



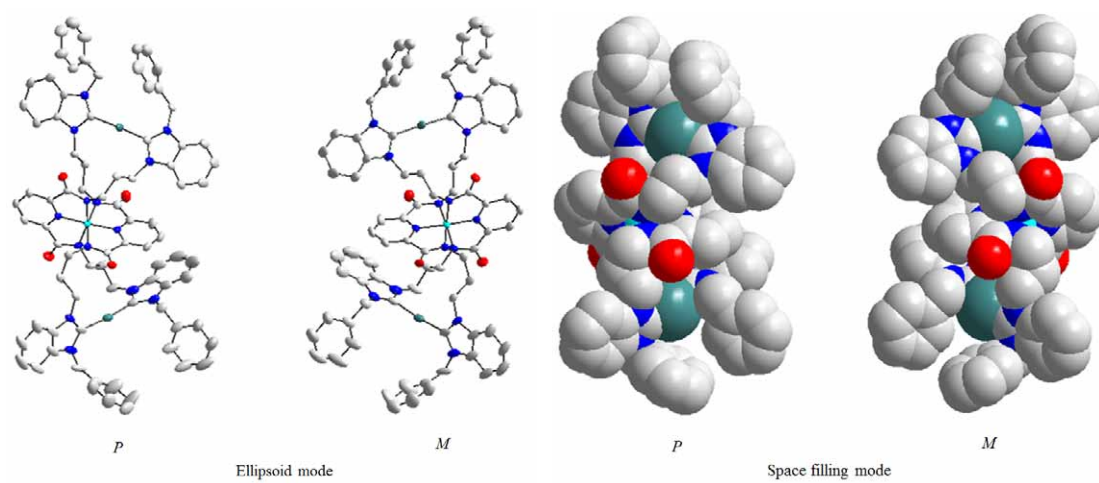
**Figure SII.** Molecular structure of  $2_{Me}$  showing 50% probability ellipsoids; most hydrogen atoms are omitted for clarity.

### $^1\text{H}$ NMR spectrum of complex **5**



**Figure SIII.**  $^1\text{H}$  NMR spectrum of complex **5**.

## Molecular structure of complex 5



**Figure SIV.** Molecular structures of *P*- and *M*-helicates of racemic complex **5** in ellipsoid and space filling modes;  $\text{BF}_4^-$  anion and hydrogen atoms are omitted for clarity.



**Table S1.** Selected X-ray crystallographic data for **B<sub>Bn</sub>**·(CH<sub>3</sub>)<sub>2</sub>CO, **2<sub>Me</sub>**, **3<sub>Bn</sub>**·0.5H<sub>2</sub>O and **5**·0.25CH<sub>2</sub>Cl<sub>2</sub>

|  | <b>B<sub>Bn</sub></b> ·(CH <sub>3</sub> ) <sub>2</sub> CO   | <b>2<sub>Me</sub></b>   | <b>3<sub>Bn</sub></b> ·0.5H <sub>2</sub> O  | <b>5</b> ·0.25CH <sub>2</sub> Cl <sub>2</sub>   |
|--|---|---|---|---|
| formula                                    | C <sub>41</sub> H <sub>41</sub> B <sub>2</sub> F <sub>8</sub> N <sub>7</sub> O <sub>2</sub> ·(CH <sub>3</sub> ) <sub>2</sub> CO | C <sub>29</sub> H <sub>31</sub> AuBF <sub>4</sub> N <sub>7</sub> O <sub>2</sub> | C <sub>82</sub> H <sub>78</sub> Au <sub>2</sub> B <sub>2</sub> F <sub>8</sub> N <sub>14</sub> O <sub>4</sub> ·0.5H <sub>2</sub> O | C <sub>82</sub> H <sub>74</sub> Au <sub>2</sub> BCoF <sub>4</sub> N <sub>14</sub> O <sub>4</sub> ·0.25CH <sub>2</sub> Cl <sub>2</sub> |
| fw   | 895.51  | 793.38  | 1908.14   | 1883.45   |
| color, habit                               | colourless, block   | colourless, plate   | colourless, needle  | yellow, block   |
| cryst size [mm]                            | 0.34×0.24×0.15  | 0.36×0.26×0.10  | 0.13×0.10×0.06  | 0.36×0.26×0.10  |
| temp [K]                                   | 100(2)  | 100(2)  | 100(2)  | 100(2)  |
| crystalsyst                                | triclinic   | monoclinic  | monoclinic  | triclinic   |
| space group                                | <i>P</i> -1   | <i>P</i> 2(1)/n   | <i>P</i> 21/c   | <i>P</i> -1   |
| <i>a</i> [Å]                               | 8.6769(11)  | 13.924(7)   | 23.2600(14)   | 15.0076(16)   |
| <i>b</i> [Å]                               | 15.920(2)   | 15.956(8)   | 20.2750(11)   | 16.2066(16)   |
| <i>c</i> [Å]                               | 17.935(3)   | 14.787(8)   | 8.2071(4)   | 17.9512(19)   |
| <i>α</i> [deg]                             | 115.794(4)  | 90.00   | 90.00   | 63.780(3)   |
| <i>β</i> [deg]                             | 103.951(3)  | 116.941(9)  | 94.156(4)   | 82.005(3)   |
| <i>γ</i> [deg]                             | 90.302(3)   | 90.00   | 90.00   | 79.629(3)   |
| <i>V</i> [Å <sup>3</sup> ]                 | 2147.5(5)   | 2929(3)   | 3860.3(4)   | 3844.1(7)   |
| <i>Z</i>                                   | 2   | 4   | 2   | 2   |
| <i>D<sub>c</sub></i> [g cm <sup>-3</sup> ] | 1.385   | 1.799   | 1.642   | 1.627   |
| radiation used                             | Mo Kα   | Mo Kα   | Cu Kα   | Mo Kα   |
| <i>μ</i> [mm <sup>-1</sup> ]               | 0.111   | 5.090   | 7.732   | 4.108   |
| <i>θ</i> range [deg]                       | 1.44–27.49  | 1.67–27.50  | 2.894–66.595  | 2.105–27.499  |
| no. of unique data                         | 28066   | 20375   | 27316   | 158525  |
| max., min. transmn                         | 0.9835, 0.9631  | 0.7898, 0.5489  | 0.7528, 0.6022  | 0.7457, 0.5929  |
| final R indices                            | R1 = 0.0720,  | R <sub>1</sub> = 0.0315,  | R1 = 0.0794,  | R <sub>1</sub> = 0.0563,  |
| [ <i>I</i> > 2σ( <i>I</i> )]               | wR2 = 0.1545  | wR <sub>2</sub> = 0.0685  | wR2 = 0.1700  | wR <sub>2</sub> = 0.1493  |
| R indices (all data)                       | R1 = 0.1026,  | R <sub>1</sub> = 0.0445,  | R1 = 0.1296,  | R <sub>1</sub> = 0.0767,  |
|  | wR2 = 0.1672  | wR <sub>2</sub> = 0.0735  | wR2 = 0.1936  | wR <sub>2</sub> = 0.1603  |
| goodness-of-fit                            | 1.090   | 1.027   | 1.072   | 1.071   |
| peak/hole [e Å <sup>-3</sup> ]             | 0.602/−0.315  | 1.624/−0.829  | 1.785/−1.091  | 6.166/−2.353  |

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