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### **A chelating tetrapeptide rhodium complex comprised of a histidylidene residue: biochemical tailoring of a NHC-Rh hydrosilylation catalyst**

Angèle Monney and Martin Albrecht\*

#### **Experimental section**

##### ***General comments***

Boc-His\*-OMe,<sup>S1</sup> Boc-Met-Ala-Ala-OH,<sup>S2</sup> [NEt<sub>3</sub>Me]I,<sup>S3</sup> **3a**,<sup>S1</sup> and [Rh(cod)Cl]<sub>2</sub><sup>S4</sup> were prepared according to literature procedures. All other reagents are commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at room temperature on Varian spectrometers at the frequencies indicated. Chemical shifts ( $\delta$  in ppm, coupling constants  $J$  in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy and comparison with related compounds. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin (Ireland).

##### **Synthesis of Boc-Met-Ala-Ala-His\*-OMe**

A solution of hydrochloric acid (4 M in 1,4-dioxane, 23 mL, 92 mmol) was added to Boc-His\*-OMe (2.33 g, 5.47 mmol) at 0 °C and the reaction mixture was vigorously stirred at rt for 30 h. The volatiles were removed under reduced pressure in a well-ventilated fume hood. The residue was dissolved in a minimum amount of MeOH and precipitated with Et<sub>2</sub>O. After centrifugation, the supernatant was discarded. The brown oil was then dissolved in MeOH and passed through a small pad of ion-exchange resin (Dower<sup>®</sup> 1x4-200 ion-exchange resin) and eluted with MeOH. The solvent was removed under reduced pressure and the resulting colourless oil was purified three times by precipitation (MeOH/Et<sub>2</sub>O) and dried under high vacuum. Under N<sub>2</sub>, 266 mg of this residue was dissolved with Boc-Met-Ala-Ala-OH (386 mg, 0.99 mmol) and HATU (375 mg, 0.99 mmol) in dry THF (40 mL) at 0 °C. The mixture was

stirred at 0 °C for 20 min, then *i*-Pr<sub>2</sub>EtN (0.49 mL, 2.96 mmol) was added and the reaction mixture was stirring at rt overnight. The volatiles were removed under reduced pressure. The crude product was dissolved in a small amount of MeOH, precipitated with Et<sub>2</sub>O and separated by centrifugation (5 ×). The residue was then dissolved in MeOH and passed through a small pad of ion-exchange resin (Dower<sup>®</sup> 1x4-200 ion-exchange resin) and eluted with MeOH. The product was finally purified by gradient column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1 then 8:2) to give Boc-Met-Ala-Ala-His\*-OMe as a very hygroscopic off-white solid (272 mg, 45%).

<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 8.86 (s, 1H, C<sub>ε</sub>H), 7.40 (s, 1H, C<sub>δ</sub>H), 4.78-4.81 (m, 1H, C<sub>α</sub>H), 4.21-4.28 (m, 2H, 2 × CHCH<sub>3</sub>), 4.12 (dd, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz, 5.3 Hz, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 3.91 (s, 3H, NCH<sub>3</sub>), 3.88 (s, 3H, NCH<sub>3</sub>), 3.78 (s, 3H, COOCH<sub>3</sub>), 3.34-3.38 (m, 1H, C<sub>β</sub>H<sub>2</sub>), 3.17 (dd, <sup>2</sup>J<sub>HH</sub> = 15.8 Hz, <sup>3</sup>J<sub>HH</sub> = 10.2 Hz, 1H, C<sub>β</sub>H<sub>2</sub>), 2.49-2.62 (m, 2H, CH<sub>2</sub>S), 2.09 (s, 3H, SCH<sub>3</sub>), 1.98-2.05 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 1.86-1.95 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.37 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 6H, 2 × C<sub>Ala</sub>HCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}NMR (125 MHz, CD<sub>3</sub>OD) δ 175.1 (C=O), 175.0 (C=O), 174.6 (C=O), 171.7 (C=O), 158.1 (C=O), 138.2 (C<sub>ε</sub>H), 132.7 (C<sub>γ</sub>), 123.5 (C<sub>δ</sub>H), 80.9 (C(CH<sub>3</sub>)<sub>3</sub>), 55.6 (C<sub>Met</sub>HCH<sub>2</sub>), 53.3 (COOCH<sub>3</sub>), 51.6 (C<sub>α</sub>H), 50.8 (C<sub>Ala</sub>HCH<sub>3</sub>), 50.6 (C<sub>Ala</sub>HCH<sub>3</sub>), 36.6 (NCH<sub>3</sub>), 34.2 (NCH<sub>3</sub>), 32.5 (C<sub>Met</sub>HCH<sub>2</sub>), 31.1 (CH<sub>2</sub>S), 28.7 (C(CH<sub>3</sub>)<sub>3</sub>), 26.2 (C<sub>β</sub>H<sub>2</sub>), 17.7 (C<sub>Ala</sub>HCH<sub>3</sub>), 17.6 (C<sub>Ala</sub>HCH<sub>3</sub>), 15.3 (SCH<sub>3</sub>); *m/z* (HRMS, ESI<sup>+</sup>) found 571.2909 ([M - Cl]<sup>+</sup>), C<sub>25</sub>H<sub>43</sub>N<sub>6</sub>O<sub>7</sub>S requires 571.2914; [α]<sub>D</sub><sup>20</sup> = -37 (c = 1 in MeOH).

### Synthesis of 1a

Boc-Met-Ala-Ala-His\* -OMe (289 mg, 476 μmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (12 mL) in a Schlenk tube under N<sub>2</sub>. Solid [Et<sub>3</sub>MeN]I (116 mg, 476 μmol) was added, followed by freshly prepared Ag<sub>2</sub>O (57 mg, 0.25 mmol) and the mixture was stirred at rt in the dark for 1 h. [Rh(cod)Cl]<sub>2</sub> (117 mg, 238 μmol) was added and stirring was continued for 1 h. The crude reaction mixture was directly purified by gradient column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, then CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1). The second fraction was evaporated to dryness to give the desired complex as a yellow solid (244 mg, 63 %).

NMR spectroscopy showed two sets of signals in a ~1:0.7 integral ratio.

*Major isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43-6.94 (m, 3H, 2 × N<sub>Ala</sub>H + N<sub>His</sub>H), 6.69 (s, 1H, C<sub>δ</sub>H), 5.85 (br, 1H, N<sub>Met</sub>H), 4.95-4.88 (m, 2H, C<sub>cod</sub>H), 4.70-4.64 (m, 1H, C<sub>α</sub>H), 4.47-4.17 (m, 2H, 2 × CHCH<sub>3</sub>), 4.01 (s, 3H, NCH<sub>3</sub>), 3.92 (s, 3H, NCH<sub>3</sub>), 3.89-3.85 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 3.72 (s, 3H, COOCH<sub>3</sub>), 3.34-3.28 (m, 2H, C<sub>cod</sub>H), 3.12-2.93 (m, 2H, C<sub>β</sub>H<sub>2</sub>), 2.62-2.52 (m, 2H, CH<sub>2</sub>S), 2.42-2.31 (m, 4H, C<sub>cod</sub>H<sub>2</sub>), 2.09 (s, 3H, SCH<sub>3</sub>), 2.08-1.85 (m, 2H, C<sub>Met</sub>HCH<sub>2</sub>), 1.97-

1.88 (m, 4H, C<sub>cod</sub>H<sub>2</sub>), 1.43 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.42-1.30 (m, 6H, 2 × CHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}NMR (125 MHz, CDCl<sub>3</sub>) δ 181.8 (br, Rh-C<sub>e</sub>), 172.6 (C=O), 172.4 (C=O), 171.1 (C=O), 171.0 (C=O), 156.8 (NHCOO), 129.7 (C<sub>γ</sub>), 120.6 (C<sub>δ</sub>H), 98.4-98.0 (2 × C<sub>cod</sub>H), 81.0 (C(CH<sub>3</sub>)<sub>3</sub>), 68.9-68.5 (2 × C<sub>cod</sub>H), 54.9 (C<sub>Met</sub>HCH<sub>2</sub>), 52.8 (COOCH<sub>3</sub>), 50.43 (C<sub>α</sub>H), 50.38 (CHCH<sub>3</sub>), 49.1 (CHCH<sub>3</sub>), 37.6 (NCH<sub>3</sub>), 35.0 (NCH<sub>3</sub>), 33.1-32.8 (2 × C<sub>cod</sub>H<sub>2</sub>), 31.1-30.9 (CH<sub>2</sub>S), 30.6 C<sub>Met</sub>HCH<sub>2</sub>), 29.1-28.9 (2 × C<sub>cod</sub>H<sub>2</sub>), 28.4 (C(CH<sub>3</sub>)<sub>3</sub>), 26.9 (C<sub>β</sub>H<sub>2</sub>), 17.5-17.2 (2 × CHCH<sub>3</sub>), 15.90 (SCH<sub>3</sub>).

*Minor isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43-6.94 (m, 3H, 2 × N<sub>Ala</sub>H + N<sub>His</sub>H), 6.67 (s, 1H, C<sub>δ</sub>H), 5.69 (br, 1H, N<sub>Met</sub>H), 4.95-4.88 (m, 2H, C<sub>cod</sub>H), 4.61-4.57 (m, 1H, C<sub>α</sub>H), 4.47-4.17 (m, 2H, 2 × CHCH<sub>3</sub>), 4.13-4.09 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 3.97 (s, 3H, NCH<sub>3</sub>), 3.96 (s, 3H, NCH<sub>3</sub>), 3.69 (s, 3H, COOCH<sub>3</sub>), 3.34-3.28 (m, 2H, C<sub>cod</sub>H), 3.12-2.93 (m, 2H, C<sub>β</sub>H<sub>2</sub>), 2.62-2.52 (m, 2H, CH<sub>2</sub>S), 2.42-2.31 (m, 4H, C<sub>cod</sub>H<sub>2</sub>), 2.10 (s, 3H, SCH<sub>3</sub>), 2.08-1.85 (m, 2H, C<sub>Met</sub>HCH<sub>2</sub>), 1.97-1.88 (m, 4H, C<sub>cod</sub>H<sub>2</sub>), 1.41 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.42-1.30 (m, 6H, 2 × CHCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H}NMR (125 MHz, CDCl<sub>3</sub>) δ 181.8 (br, Rh-C<sub>e</sub>), 172.6 (C=O), 172.4 (C=O), 171.1 (C=O), 171.0 (C=O), 156.8 (NHCOO), 129.3 (C<sub>γ</sub>), 120.8 (C<sub>δ</sub>H), 98.4-98.0 (2 × C<sub>cod</sub>H), 80.7 (C(CH<sub>3</sub>)<sub>3</sub>), 68.9-68.5 (2 × C<sub>cod</sub>H), 55.7 (C<sub>Met</sub>HCH<sub>2</sub>), 52.7 (COOCH<sub>3</sub>), 51.2 (C<sub>α</sub>H), 50.38 (CHCH<sub>3</sub>), 49.2 (CHCH<sub>3</sub>), 37.7 (NCH<sub>3</sub>), 35.1 (NCH<sub>3</sub>), 33.1-32.8 (2 × C<sub>cod</sub>H<sub>2</sub>), 31.1-30.9 (CH<sub>2</sub>S), 29.8 (C<sub>Met</sub>HCH<sub>2</sub>), 29.1-28.9 (2 × C<sub>cod</sub>H<sub>2</sub>), 28.4 (C(CH<sub>3</sub>)<sub>3</sub>), 26.2 (C<sub>β</sub>H<sub>2</sub>), 17.5-17.2 (2 × CHCH<sub>3</sub>), 15.86 (SCH<sub>3</sub>).

*m/z* (HRMS, ESI<sup>+</sup>) found 781.2845 ([M - Cl]<sup>+</sup>), C<sub>33</sub>H<sub>54</sub>N<sub>6</sub>O<sub>7</sub>SRh requires 781.2830; [α]<sub>D</sub><sup>20</sup> = -8° (c = 1 in CHCl<sub>3</sub>).

## Synthesis of 2a

To a solution of **1a** (63.0 mg, 77 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added a solution of KPF<sub>6</sub> (142 mg, 0.77 mmol) in H<sub>2</sub>O (3 mL). The biphasic mixture was vigorously shaken, the organic layer was collected and the aqueous layer was further extracted with CH<sub>2</sub>Cl<sub>2</sub> until colourless. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by precipitation (3 × CH<sub>2</sub>Cl<sub>2</sub>/pentane), followed by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 9:1) and the resulting yellow solid (53 mg, 74 %) was dried under high vacuum.

<sup>1</sup>H and <sup>13</sup>C NMR spectra are only poorly resolved. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.4-7.2 (N<sub>His</sub>H), 7.2-6.9 (N<sub>Ala</sub>H), 6.9-6.7 (N<sub>Ala</sub>H), 6.7-6.6 (C<sub>δ</sub>H), 6.0-5.6 (N<sub>Met</sub>H), 4.8-4.5 (C<sub>α</sub>H + 2 × C<sub>cod</sub>H), 4.5-4.3 (CHCH<sub>3</sub>), 4.2-3.6 (CHCH<sub>3</sub> + C<sub>Met</sub>HCH<sub>2</sub> + 2 × NCH<sub>3</sub> + COOCH<sub>3</sub> + 2 × C<sub>cod</sub>H), 3.3-2.9 (C<sub>β</sub>H<sub>2</sub>), 2.8-2.3 (CH<sub>2</sub>S + 2 × C<sub>cod</sub>H<sub>2</sub>), 2.3-1.8 (C<sub>Met</sub>HCH<sub>2</sub> + SCH<sub>3</sub> + 2 × C<sub>cod</sub>H<sub>2</sub>), 1.5-

1.3 ( $2 \times \text{CHCH}_3 + \text{C}(\text{CH}_3)_3$ );  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -144.34 (septet,  $^1J_{\text{PF}} = 714$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -71.69 (d,  $^1J_{\text{PF}} = 714$  Hz);  $m/z$  (HRMS,  $\text{ESI}^+$ ) found 781.2859 ( $[\text{M} - \text{PF}_6^-]^+$ ),  $\text{C}_{33}\text{H}_{54}\text{N}_6\text{O}_7\text{SRh}$  requires 781.2830;  $[\alpha]_{\text{D}}^{20} = -3^\circ$  ( $c = 1$  in  $\text{CHCl}_3$ ).

### Synthesis of 4a

Complex **3a** (75 mg, 0.138 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (4 mL). Dimethylsulfide (11.1  $\mu\text{L}$ , 0.152 mmol) was added, followed by a solution of  $\text{KPF}_6$  (254 mg, 1.38 mmol) in  $\text{H}_2\text{O}$  (3 mL). The biphasic mixture was vigorously shaken, the organic layer was collected and the aqueous layer was further extracted with  $\text{CH}_2\text{Cl}_2$  until colourless. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by precipitation ( $3 \times \text{CH}_2\text{Cl}_2/\text{pentane}$ ), followed by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 9:1) and the resulting yellow solid (99 mg, quant.) was dried under high vacuum.

NMR spectroscopy showed two sets of signals in a 1:0.8 integral ratio.

*Major isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 50  $^\circ\text{C}$ )  $\delta$  6.86 (s, 1H,  $\text{C}_\delta\text{H}$ ), 5.23 (br, 1H, NH), 4.69 (br, 2H,  $\text{C}_{\text{cod}}\text{H}$ ), 4.48-4.38 (m, 1H,  $\text{C}_\alpha\text{H}$ ), 4.08-4.02 (m, 2H,  $\text{C}_{\text{cod}}\text{H}$ ), 3.99 (s, 3H,  $\text{NCH}_3$ ), 3.91 (s, 3H,  $\text{NCH}_3$ ), 3.75 (s, 3H,  $\text{COOCH}_3$ ), 3.14-3.09 (m, 1H,  $\text{C}_\beta\text{H}_2$ ), 2.94-2.87 (m, 1H,  $\text{C}_\beta\text{H}_2$ ), 2.50-2.42 (m, 4H,  $\text{C}_{\text{cod}}\text{H}_2$ ), 2.17-2.11 (m, 4H,  $\text{C}_{\text{cod}}\text{H}_2$ ), 2.05 (s, 6H,  $\text{S}(\text{CH}_3)_2$ ), 1.39 (s, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 50  $^\circ\text{C}$ )  $\delta$  176.9 ( $^1J_{\text{RhC}} = 50.0$  Hz,  $\text{C}_\epsilon\text{-Rh}$ ), 171.3 ( $\text{COOCH}_3$ ), 155.4 (NHCOO), 131.3 ( $\text{C}_\gamma$ ), 122.3 ( $\text{C}_\delta\text{H}$ ), 95.3 ( $2 \times \text{C}_{\text{cod}}\text{H}$ ), 83.4 ( $2 \times \text{C}_{\text{cod}}\text{H}$ ), 80.3 ( $\text{C}(\text{CH}_3)_3$ ), 52.9 ( $\text{COOCH}_3$ ), 52.4 ( $\text{C}_\alpha\text{H}$ ), 37.57 ( $\text{NCH}_3$ ), 35.0 ( $\text{NCH}_3$ ), 31.9-31.6 ( $2 \times \text{C}_{\text{cod}}\text{H}_2$ ), 29.8-29.6 ( $2 \times \text{C}_{\text{cod}}\text{H}_2$ ), 28.3 ( $\text{C}(\text{CH}_3)_3$ ), 27.8 ( $\text{C}_\beta\text{H}_2$ ), 21.5 ( $\text{S}(\text{CH}_3)_2$ );

*Minor isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 50  $^\circ\text{C}$ )  $\delta$  6.87 (s, 1H,  $\text{C}_\delta\text{H}$ ), 5.23 (br, 1H, NH), 4.69 (br, 2H,  $\text{C}_{\text{cod}}\text{H}$ ), 4.48-4.38 (m, 1H,  $\text{C}_\alpha\text{H}$ ), 4.15-4.11 (m, 2H,  $\text{C}_{\text{cod}}\text{H}$ ), 3.96 (s, 3H,  $\text{NCH}_3$ ), 3.93 (s, 3H,  $\text{NCH}_3$ ), 3.74 (s, 3H,  $\text{COOCH}_3$ ), 3.14-3.09 (m, 1H,  $\text{C}_\beta\text{H}_2$ ), 2.94-2.87 (m, 1H,  $\text{C}_\beta\text{H}_2$ ), 2.50-2.42 (m, 4H,  $\text{C}_{\text{cod}}\text{H}_2$ ), 2.17-2.11 (m, 4H,  $\text{C}_{\text{cod}}\text{H}_2$ ), 2.05 (s, 6H,  $\text{S}(\text{CH}_3)_2$ ), 1.36 (s, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 50  $^\circ\text{C}$ )  $\delta$  176.9 ( $^1J_{\text{RhC}} = 50.0$  Hz,  $\text{C}_\epsilon\text{-Rh}$ ), 171.3 ( $\text{COOCH}_3$ ), 155.4 (NHCOO), 131.5 ( $\text{C}_\gamma$ ), 122.2 ( $\text{C}_\delta\text{H}$ ), 95.3 ( $2 \times \text{C}_{\text{cod}}\text{H}$ ), 83.4 ( $2 \times \text{C}_{\text{cod}}\text{H}$ ), 80.5 ( $\text{C}(\text{CH}_3)_3$ ), 52.9 ( $\text{COOCH}_3$ ), 52.7 ( $\text{C}_\alpha\text{H}$ ), 37.62 ( $\text{NCH}_3$ ), 35.0 ( $\text{NCH}_3$ ), 31.9-31.6 ( $2 \times \text{C}_{\text{cod}}\text{H}_2$ ), 29.8-29.6 ( $2 \times \text{C}_{\text{cod}}\text{H}_2$ ), 28.3 ( $\text{C}(\text{CH}_3)_3$ ), 27.7 ( $\text{C}_\beta\text{H}_2$ ), 21.5 ( $\text{S}(\text{CH}_3)_2$ );

$^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ , 50  $^\circ\text{C}$ )  $\delta$  -144.32 (septet,  $^1J_{\text{PF}} = 712$  Hz);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ , 30  $^\circ\text{C}$ )  $\delta$  -72.81 (d,  $^1J_{\text{PF}} = 712$  Hz);  $m/z$  (HRMS,  $\text{ESI}^+$ ) found 508.1666 ( $[\text{M} - \text{S}(\text{CH}_3)_2 - \text{PF}_6^-]^+$ ),  $\text{C}_{22}\text{H}_{35}\text{N}_3\text{O}_4\text{Rh}$  requires 508.1683;  $[\alpha]_{\text{D}}^{20} = -5^\circ$  ( $c = 1$  in  $\text{CHCl}_3$ ).

## General Procedure for the Cyclooctadiene Displacement by Carbon Monoxide

The rhodium complex was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and gaseous CO was bubbled through the solution for 10 min. The mixture was then stirred overnight at rt under an atmosphere of CO. The solvent was removed under reduced pressure in a well-ventilated fumehood and the dark yellow solid was dried under high vacuum. The crude product was used for <sup>13</sup>C-NMR and IR spectroscopic measurements. Key spectroscopic data are compiled in Table S1. The <sup>1</sup>H NMR spectrum of **2b** is very poorly resolved and features broad signals.

**Table S1** Relevant <sup>13</sup>C{<sup>1</sup>H} NMR and IR data for the di(carbonyl) rhodium complexes.

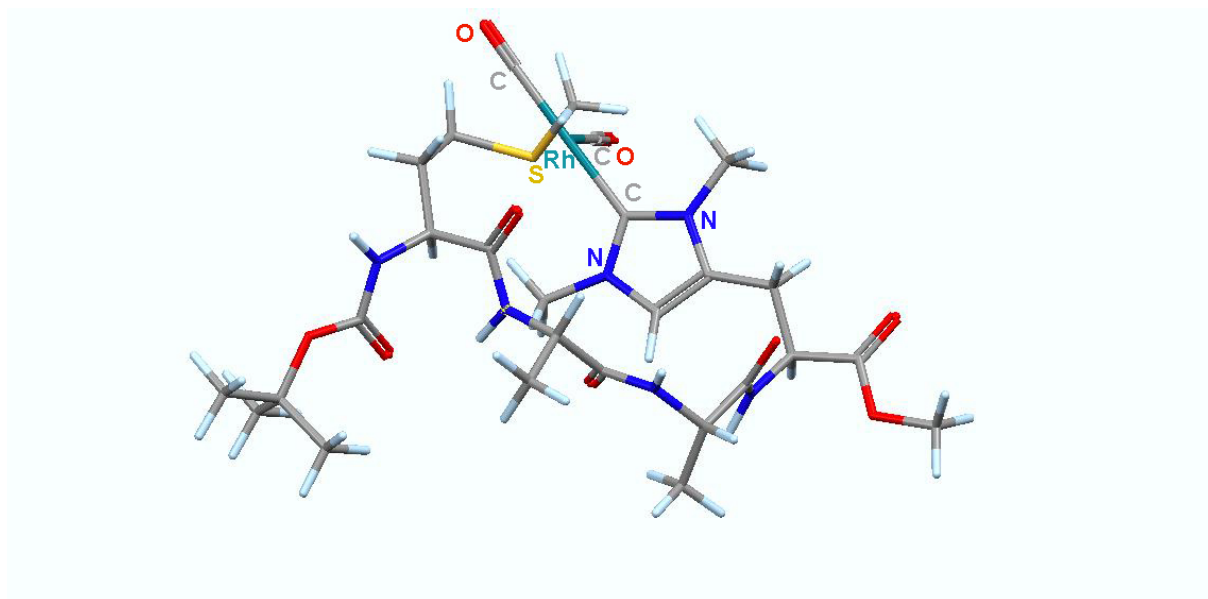
entry	complex	chemical shift $\delta_C$ , $^1J_{RhC}$ ( $^2J_{CC}$ ) <sup>a</sup>		$\nu_{asym}$ , $\nu_{sym}$ <sup>b</sup>
1	<b>1b</b>	187.2 ppm, 53 Hz (5 Hz)	183.8 ppm, 75 Hz (5 Hz)	2088 cm <sup>-1</sup> , 1965 cm <sup>-1</sup>
2	<b>2b</b>	188.8 ppm, 84 Hz	187.5 ppm, 79 Hz	2088 cm <sup>-1</sup> , 1989 cm <sup>-1</sup>
3	<b>3b</b>	187.2 ppm, 53 Hz	183.7 ppm, 75 Hz	2088 cm <sup>-1</sup> , 2006 cm <sup>-1</sup>
4	<b>4b</b>	<i>n/a</i>	<i>n/a</i>	2088 cm <sup>-1</sup> , 2039 cm <sup>-1</sup>

<sup>a</sup> measured at room temperature in CD<sub>3</sub>OD, data for complexes **1b** and **2b** obtained from reaction with isotopically labelled <sup>13</sup>CO, *n/a* = not available; <sup>b</sup> measured at room temperature in CHCl<sub>3</sub>

<sup>1</sup>H NMR spectroscopic data for **1b**; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.27–6.62 (m, 3H, 2 × N<sub>Ala</sub>H + N<sub>His</sub>H), 6.77 (s, 1H, C <sub>$\delta$</sub> H), 4.62–4.57 (m, 1H, C <sub>$\alpha$</sub> H), 4.34–4.28 (m, 1H, CHCH<sub>3</sub>), 4.21–3.96 (m, 2H, CHCH<sub>3</sub> + C<sub>Met</sub>HCH<sub>2</sub>), 3.74, 3.71, 3.66 (3 × s, 9H, 2 × NCH<sub>3</sub> + COOCH<sub>3</sub>), 3.10–3.00 (m, 2H, C <sub>$\beta$</sub> H<sub>2</sub>), 2.66–2.60 (m, 2H, CH<sub>2</sub>S), 2.14 (s, 3H, SCH<sub>3</sub>), 2.05–1.98 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 1.93–1.86 (m, 1H, C<sub>Met</sub>HCH<sub>2</sub>), 1.37 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.34–1.28 (m, 6H, 2 × CHCH<sub>3</sub>).

The <sup>1</sup>H NMR spectroscopic data for **2b** are complicated as most signals are broad at RT, except those attributed to the methyl groups of the SMe, NMe COOMe and Boc groups, which are better resolved but appear as multiple singlets. This is in agreement with the presence of different conformers. Due to the low resolution, 2-dimensional NMR spectroscopy provides little information and assignment of signals is tentative: <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.4–6.7 (m, 2 × N<sub>Ala</sub>H + N<sub>His</sub>H), 6.6–6.4 (br, C <sub>$\delta$</sub> H), 4.6–4.5 (m, C <sub>$\alpha$</sub> H), 4.3–4.0 (m, 2 × C <sub>$\alpha$</sub> (Ala)H + C <sub>$\alpha$</sub> (Met)H), 3.05, 3.90, 3.87, 3.82, 3.67, 3.62 (6 s, NCH<sub>3</sub> + COOCH<sub>3</sub>), 3.3–3.1 (m, C <sub>$\beta$</sub> H<sub>2</sub>), 2.7–2.5 (m, CH<sub>2</sub>S), 2.13, 2.11, 2.06, 2.05 (4 s, SCH<sub>3</sub>), 2.1–1.9 (m, C<sub>Met</sub>HCH<sub>2</sub>), 1.46, 1.43, 1.42, 1.40 (4 s, C(CH<sub>3</sub>)<sub>3</sub>), 1.35–1.2 (m, CHCH<sub>3</sub>).

## Molecular Mechanics (mm2) Geometry Optimization of 2b



### General Procedure for the Catalytic Hydrosilylation

The catalyst (10  $\mu\text{mol}$ ) and 4'-fluoroacetophenone (0.12 mL, 1.0 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$  (1 mL). Diphenylsilane (0.37 mL, 2.0 mmol) was added and the mixture was placed in an NMR tube. Conversions were determined by  $^1\text{H}$  and/or  $^{19}\text{F}$  NMR spectroscopy. Hydrolysis was performed by addition of TFA in MeOH (1%, 0.5 mL). The solution was stirred for 10 min and then filtered through a small pad of  $\text{SiO}_2$ , eluting with pentane/ $\text{Et}_2\text{O}$  (3:1). The enantiomeric excess was determined by chiral HPLC (IA or OBH column, heptane/ $\text{EtOH}$  99:1, 1 mL/min).

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