Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2019

Supplemental Information

Robust Bis-rhodium(I) complex of π -extended planar, anti-aromatic hexaphyrin[1.0.1.0.1.0]

Srinivas Samala,^a Ranjan Dutta,^a Qing He,^b Yeonju Park,^a Brijesh Chandra.^a Vincent M. Lynch,^c Young Mee Jung^a Jonathan L. Sessler^{*,c}, and Chang Hee Lee^{*,a}

^aDepartment of Chemistry, Kangwon National University, Chun Cheon Korea 24341. ^b State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China. ^cDepartment of Chemistry, The University of Texas at Austin, Austin TX, 78712-1224 USA.

2

4

Table of Contents:	
Materials and methods	S2
Synthetic experimental	S2- S3
NMR (¹ H & ¹³ C) and MALDI-TOF spectra	S4- S5
NMR & IR spectral data	S6- S11
Photophysical data	S11- S12
Crystallographic data	S13- S14
References	S15

Materials and methods:

All reagents and compounds were purchased commercially and used as received without further purification. All solvents were dried and distilled before going to use. All reactions considered sensitive to moisture or oxygen were performed under a nitrogen atmosphere. Thin layer chromatography (TLC) was performed on aluminum backed silica gel 60 F254 (Merck) or neutral alumina F254 (Sigma-Aldrich) plates. Product purification was performed by column chromatography on silica gel (230–400 mesh, MN) or neutral aluminum oxide 90 (70–230 mesh, Merck).

The identity and purity of all newly synthesized compounds was confirmed using 400/ 600 NMR spectroscopy. A Jeol 400 MHz instrument was used for the various ¹H NMR spectral studies, including the TFA titrations. For the ¹³C NMR & 2D-NMR (COSY, ¹H-¹³C HSQC) spectroscopic analyses, a Bruker 600 MHz instrument was used. A Bruker 850 MHz instrument was used to perform the ¹H-¹⁵N HSQC analysis. Mass spectrometric data were obtained using either a Voyager DE-STR MALDI-TOF or a JEOL JMS-700 GC instrument. Absorption spectra were recorded using a Varian CARY 100 Conc spectrometer. The single crystal X-ray crystallographic analysis was carried out on an Agilent Technologies SuperNova Dual Source diffractometer using a μ -focused Cu K α radiation source ($\lambda = 1.5418$ Å) with collimating mirror monochromators. Further details of the structure and its refinement are provided in a later section.

Electrochemical studies:

Cyclic voltammograms (CVs) were recorded on CH instruments. Three-electrode cells were used that consisted of a platinum disk electrode as the working electrode, a platinum wire as the counter electrode, and a platinum wire as the reference electrode. The reference potential was calibrated to the ferrocene/ferrocenium (Fc/Fc⁺) couple. The electrolyte solution consisted of dichloromethane (DCM) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆), which was bubbled with N₂ gas prior to use in the electrochemical studies.

Synthetic experimental:

Synthesis of Rh-Rosarin (3):

A flame dry 50 ml RBF was closed with septa and flushed with nitrogen twice. Free base rosarin **2** (0.04 g, 1 equiv.) was then added to the flask under nitrogen, followed by the addition of 10 ml of DCM. After stirring for 5 min, 25 equiv. of NaOAc was added to the reaction mixture portion-wise. Stirring was continued for and additional 10 min. In a separate 10 ml vial, 6 molar equivalents of [Rh(CO)₂Cl]₂ were added to 1 ml of DCM and the resulting solution purged with N₂ for 2 min. This solution was then added to the original reaction mixture under nitrogen without further delay. The resulting mixture was then stirred for 24 h allowing the starting material to be consumed. The crude product obtained in this way was further purified by flash column chromatography over silica gel (eluent 5% ethyl acetate (EA) in hexanes) to yield the bis-rhodium rosarin complex **3** as a green-dark solid in 60% (0.031 gr.). ¹H NMR (CDCl₃, 400 MHz): δ 33.07 (s, 1H), 6.98 – 6.95 (m, 6H), 6.76 – 6.73 (m, 6H), 4.08 (s, 2H), 4.02 (s, 2H), 3.93 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 196.0 (d, ¹*J*_{Rh-C} = 67.9 Hz, CO), 195.1 (d, ¹*J*_{Rh-C} = 65.4 Hz, CO), 158.5, 156.8, 153.7, 152.3, 150.6, 150.1, 132.7, 131.9, 131.7, 130.8, 128.8, 126.5, 126.1, 126.0, 122.9, 122.7, 122.5, 121.9, 121.7, 120.9, 120.8, 119.8, 116.8. MS (MALDI-TOF) calcd. for C₆₇H₁₉F₁₅N₆O₄Rh₂ ([M-4(CO)]⁺): m/z 1349.954 and found: 1349.981.



Figure S1. ¹H NMR spectrum of the bis-rhodium rosarin complex $\mathbf{3}$



Figure S2. ¹³C NMR spectrum of the bis-rhodium rosarin complex **3** (inset: expanded region showing CO resonances)



Figure S3. MALDI-TOF MS spectra of compound 3 (Rh-Rosarin)





Figure S4. Expanded MALDI-TOF MS spectrum of the bis-rhodium rosarin complex 3

Figure S5. Deuterium exchange studies of complex 3 monitored by ¹H NMR spectroscopy



Figure S6. ¹H-¹H COSY NMR spectrum of complex **3**



Figure S8. Expansion of ¹H-¹³C HSQC NMR spectrum of complex **3**



Figure S9. ¹H-¹⁵N HSQC NMR spectrum of complex **3**





Figure S10. ¹H-¹⁵N HMBC NMR spectrum of complex **3**

Figure S11. Variable temperature ¹H NMR spectra of complex **3**



^{33.26 33.24 33.22 33.20 33.18 33.16 33.14 33.12 33.10 33.08 33.06 33.04 33.02 33.00 32.98 32.96 32.94 32.92 32.90 32.86} f1 (ppm)





Figure S13. ¹H NMR spectral changes observed when complex **3** (6.83×10^{-3} M) is treated with TFA in CDCl₃ at room temperature.



Figure S14. ¹H NMR spectra of **3** recorded after adding excess TEA to the complex **3** (6.83×10^{-3} M) pretreated with 50 equiv TFA in CDCl₃ at room temperature.



Figure S15. FTIR spectra of complex 3



Figure S16. UV-vis spectrum of complex 3 (6.83×10^{-6} M) (red line) and free base 2 (6.83×10^{-6} M) (black line) in CH₂Cl₂.



Figure S17. Absorption spectral changes of **3** (6.83×10^{-6} M) recorded in the presences of TFA in CH₂Cl₂ at 25 °C.



Figure S18. Absorption spectral changes of **3** (6.83×10^{-6} M) after the addition of excess HClO₄ and MSA in CH₂Cl₂ at 25 °C.

Crystallographic data:

Single crystals of the Rh complex **3** were obtained as dark brown blocks via the slow evaporation of a DCM/hexanes solution of **3**. A suitable crystal was selected and the data were collected on an Agilent Technologies Super Nova Dual Source diffractometer using a μ -focus Cu K α radiation source ($\lambda = 1.5418$ Å) with collimating mirror monochromators. The crystal was kept at 100.15 K during data collection. Using Olex2,¹ the structure was solved with the ShelXT² structure solution program using Direct Methods and refined with the ShelXL³ refinement package using Least Squares minimization. Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are in the CIF file. CCDC deposition number: 1947660.



Figure S21. View of complex **3**. Displacement ellipsoids are scaled to the 50% probability level.

Table 1 Crystal data and structure refinement for complex 3	
Identification code	BiRhcomplex 3
Empirical formula	$C_{67}H_{18}F_{15}N_6O_4Rh_2$
Formula weight	1461.69
Temperature/K	99.9(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.5064(2)
b/Å	13.7489(2)
c/Å	36.4349(8)
α/°	90
β/°	97.870(2)
γ/°	90
Volume/Å ³	5213.50(17)
Ζ	4
$\rho_{calc}g/cm^3$	1.862
μ/mm^{-1}	6.165
F(000)	2876.0
Crystal size/mm ³	$0.088\times0.056\times0.054$
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
2Θ range for data collection/°	6.88 to 151.174
Index ranges	$-12 \le h \le 12, -17 \le k \le 17, -35 \le l \le 44$
Reflections collected	37729
Independent reflections	10637 [$R_{int} = 0.0599, R_{sigma} = 0.0538$]
Data/restraints/parameters	10637/1142/1036
Goodness-of-fit on F ²	1.153
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0929, wR_2 = 0.2224$
Final R indexes [all data]	$R_1 = 0.1035, wR_2 = 0.2295$
Largest diff. peak/hole / e Å ⁻³	2.29/-1.31
CCDC number	1947660

References:

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. J. Appl. Cryst. 2009, **42**, 339-341.

- 2. Sheldrick, G.M. Acta Cryst. 2015, A71, 3-8.
- 3. Sheldrick, G.M. Acta Cryst. 2015, C71, 3-8.