Supporting Information For

Recovery of rhodium with a novel soft donor ligand using solvent extraction techniques in chloride media

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Scheme S1. Synthesis of tridentate ligand and Rh complex.

1. Experimental and Characterization

General methods and materials

All reagents and organic solvents were of reagent grade or better and used as purchased from Aldrich, Acros, or Fluka without further purification. Rhodium starting material in the form of RhCl₃•xH₂O was purchased from Pressure Chemical. Standardized rhodium stock solution were made by dissolving RhCl₃•xH₂O in 18 MΩ H₂O. 2,6-bis(bromomethyl)pyridine was purchased from TCI and was also synthesized as previously described.^{1,2} 1-hexanethiol was used as purchased from Alfa Aesar. UV-Vis spectra were obtained using a Varian Cary 50 spectrophotometer (1 cm path-length). ¹H and ¹³C NMR spectra were recorded on a Varian 300 MHz instrument at 25 °C. Rh concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 3200 RL) and the instrument was calibrated with dilutions of a 1000 ppm Rh standard solution in 10% HCl (Acros Organics). Elemental analyses were performed by Atlantic Microlab, Inc (Norcross, GA). FT-IR spectra were obtained on a Thermo Nicolet 6700 FT-IR with an ATR cell and analyzed with OMNIC 7.1 software. Mass spectra were obtained on a Thermo-Finnigan LCQ Advantage ESI-MS.

2,6-((hexylthio)methyl)pyridine (SNS), 3.

1 (0.7906 g, 2.98 mmol) was dissolved in dry dimethylformamide (20 mL), K₂CO₃ (1.237 g, 8.95 mmol), and 2 (2.105 mL, 14.91 mmol) were added while stirring. The reaction was heated to 60 °C under N₂ for 3 h. H₂O (100 mL) was added to the reaction mixture and **3** was extracted with chloroform (3 x 50 mL). The combined organic layers were then washed with H₂O (5 x 100 mL), dried over MgSO₄, filtered and concentrated under vacuum. The resulting oil was purified by silica gel chromatography using hexanes:chloroform (0-100%) for elution. Concentration of the purified fractions under vacuum yielded **3** as a yellow oil (0.8685 g, 86%). ¹H NMR [δ (ppm), CDCl₃]: 7.59 (t, 1H, *J* = 7.7), 7.22 (d, 1H, *J* = 7.7), 3.79 (s, 4H), 2.46 (t, 4H, *J* = 7.3), 1.58-1.49 (m, 4H), 1.36-1.20 (m, 12H), 0.85 (t, 6H, *J* = 6.7). ¹³C NMR [δ (ppm), CDCl₃]:

158.57, 137.28, 121.05, 38.19, 31.80, 31.50, 29.32, 28.64, 22.63, 14.14. λ_{max}(CH₂Cl₂)/nm (ε/dm³ mol⁻¹ cm⁻¹): 273 (2,850). FT-IR (major absorbances, cm⁻¹): 2954.2, 2923.3, 2854.1, 1589.2, 1572.7, 1450.8, 747.8. *m/z* 340.2 (M+H⁺, 100%). Anal. Found: C, 67.29; H, 9.86; N, 4.18, Calcd for C₁₉H₃₃NS₂: C, 67.20; H, 9.80; N, 4.12.

mer-[RhCl₃(3)], 4.

3 (0.0641 g, 0.19 mmol) was dissolved in 4% v/v acetonitrile/EtOH (15 mL) and an aqueous solution of RhCl₃ (2.819 mL, 0.0703 ± 0.1 M, 0.20 mmol) was added drop-wise while stirring. The reaction was heated at 60 °C for 12 h. The mixture was then concentrated to dryness and the resulting oil was dissolved in dichloromethane (20 mL). The organic layer was washed with water (3 x 15 mL) and brine (1 x 15 mL) then dried over MgSO₄. Solution was filtered, and dried under vacuum overnight to yield an orange solid which was recrystallized by slow evaporation of EtOH to yield **4** as orange crystals (0.0986 g, 95%). ¹H NMR [δ (ppm), CDCl₃]: 7.78 (t, 1H, *J* = 7.8), 7.45 (d, 1H, *J* = 7.8), 4.87-4.60 (m, 4H), 3.54-3.06 (m, 4H), 1.99-1.78 (m, 4H), 1.57-1.48 (m, 5H), 1.36-1.25 (m, 7H), 0.91-0.86 (m, 6H). ¹³C NMR [δ (ppm), CDCl₃]: 13C NMR (75 MHz, CDCl3) δ 160.96, 138.69, 122.98, 47.54, 37.08, 31.36, 28.64, 27.32, 22.57, 14.11. λ_{max} (EtOH)/nm (ϵ /dm³ mol⁻¹ cm⁻¹): 240 (21,480); 370 (1,241). FT-IR (major absorbances, cm⁻¹): 2954.8, 2921.1, 2852.6, 1463.4, 1391.5, 787.2. *m*/*z* 548.0 (M⁻, 100%). Anal. Found: C, 41.33; H, 6.15; N, 2.59, Calcd for RhCl₃C₁₉H₃₃NS₂: C, 41.58; H, 6.06; N, 2.55.

X-Ray Crystallography

Crystals of compound 4 were analyzed at 173(2) K on a Bruker CCD diffractometer using Mo K_{α} irradiation ($\lambda = 0.71073$ Å) in a series of omega scans. Data collection, cell refinement and data reduction were performed using *APEX II³ and SAINT⁴*. The crystal structures were solved by direct methods and refined by least squares method on F^2 using SHELXS-97 and SHELXL-97,

respectively.⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and included in the refinement using a riding model with isotropic thermal parameters calculated from that of the attached atom. Crystallographic data of the investigated compound is available in the cif file and as a footnote in the communication. All bond distances (Å) and angles (°) are listed in Table S3.

Kinetic Studies of the reaction between 2,6-((hexylthio)methyl)pyridine (SNS), 3, and RhCl₃ in EtOH.

Kinetic data were collected on a Varian 50 UV-Vis spectrometer fitted with a Quantum Northwest temperature control system with a water bath, and reactions were done inside a sealable 10 mm quartz cuvette (Starna, Inc) with 5x2 mm micro stir bars (Fisher). Reaction progress was monitored by examining the absorbance change at 370 nm with an averaging time of 0.10 sec for 17-24 h utilizing a four stage progression as follows: Stage 1: 0.17 min for 10 min; Stage 2: 1 min for 120 min; Stage 3: 5 min for 360 min; Stage 4: 10 min for remaining time (Cary WinUV-Kinetics). The data all involved pseudo-first-order conditions with the rhodium concentration constant at 1.3×10^{-4} M and the ligand concentrations in large excess (1.3×10^{-3} to 1.3×10^{-2} M). Studies were carried out at 40, 45, 50, 55, and 60 °C and initial reaction solutions were allowed to come to temperature for 10 min before addition of ligand and reaction monitoring took place. All data were fit to a sum of two exponentials using nonlinear leastsquares analysis in OriginPro 9.1.

Extraction studies

Liquid-liquid extraction experiments were performed in quadruplicate at specified temperatures with ligand concentrations of 0.005-0.01 M in 1-pentanol (1 mL) and standardized rhodium stocks diluted to 0.0005 M Rh in 18 M Ω H₂O in sealed polypropylene tubes or glass vials with PTFE lids. In all cases, controls were run to verify the Rh did not adsorb to the reaction vessel. Room temperature extractions were rotated at 55 rpm for the specified times. Heated extractions were mixed with magnetic stirrers in a temperature controlled oil bath for 7 d. The concentration of Rh in the aqueous phase was measured using ICP-OES. The distribution value, D, was calculated using the equations

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{S1}$$

 $[M]_{org} = [M]_{aq, i} - [M]_{aq}$ (S2)

where $[M]_{aq,i}$ and $[M]_{aq}$ are the initial and final concentrations of metals ions, respectively, in the aqueous phase.⁶

2. Figures and Tables

Figure S1. UV-Vis absorbance vs time for the formation of 4 in EtOH.





Figure S2. Eyring plot of the formation of 4.



Figure S3. Slope analysis of extraction of Rh at 70 °C after 7 d.

Table S1. Distribution values (D) calculated using equations S1 and S2 for 24 h and 7 d at room temperature.

[3] M	D 24 h	D 7 d
0.0005	0.21 ± 0.02	0.26 ± 0.03
0.005	0.22 ± 0.01	0.27 ± 0.02
0.05	0.22 ± 0.02	0.29 ± 0.02
0.1	0.25 ± 0.02	0.36 ± 0.03

Table S2. Distribution values D calculated using equations S1 and S2 for 7 d at 70 °C.

[3] M	D 7 d	
0.005418	0.76 ± 0.04	
0.01354	1.31 ± 0.18	
0.03863	2.21 ± 0.42	
0.05241	2.21 ± 0.16	

formula	$C_{19}H_{33}Cl_3NRhS_2$	<i>T</i> (K)	173(2)
M _r	548.84	λ (Å)	0.71073
cryst syst	orthorhombic	cryst size, mm	$0.35 \times 0.25 \times 0.10$
space group	P212121	range of indices	$-10 \le h \le 10, -16 \le k \le 16, -29 \le l \le 29$
<i>a</i> , Å	8.2408(13)	no. of reflns collected	28087
b, Å	12.5927(19)	no. of unique reflns	5486
с, Å	23.083(4)	<i>R</i> _{int}	0.0320
α, °	90	no. of reflns with $I > 2\sigma(I)$	5486
β, °	90	no. of parameters	256
γ, °	90	$R(F), F > 2\sigma(F)$	0.0245
V (Å-3)	2395.4(6)	wR(F ²), F > $2\sigma(F)$	0.0567
Ζ	4	R(F), all data	0.0268
$ ho_{ m calc}$ (g cm ⁻³)	1.522	wR(F ²), all data	0.0578
<i>F</i> (000)	1128	$\Delta_{\rm r}$ (min, max) eÅ ⁻³	-0.342-0.585

 Table S3. Crystallographic data and experimental details for *mer*-[RhCl₃(3)], 4.

Rh(1)-N(1)	2.011(2)	C(16)-C(17)	1.504(5)	C(2)-N(1)-C(6)	120.3(2)
Rh(1)-S(2)	2.3176(7)	C(17)-C(18)	1.506(6)	C(2)-N(1)-Rh(1)	120.35(18)
Rh(1)-S(1)	2.3283(7)	C(18)-C(19)	1.526(7)	C(6)-N(1)-Rh(1)	119.22(17)
Rh(1)-Cl(2)	2.3439(7)			C(2)-C(1)-S(1)	114.0(2)
Rh(1)-Cl(3)	2.3497(7)	N(1)-Rh(1)-S(2)	86.01(7)	N(1)-C(2)-C(3)	120.7(3)
Rh(1)-Cl(1)	2.3568(7)	N(1)-Rh(1)-S(1)	85.68(7)	N(1)-C(2)-C(1)	118.3(2)
S(1)-C(8)	1.819(3)	S(2)-Rh(1)-S(1)	171.63(3)	C(3)-C(2)-C(1)	120.9(3)
S(1)-C(1)	1.826(3)	N(1)-Rh(1)-Cl(2)	89.72(7)	C(4)-C(3)-C(2)	119.4(3)
S(2)-C(7)	1.807(3)	S(2)-Rh(1)-Cl(2)	82.52(3)	C(3)-C(4)-C(5)	119.4(3)
S(2)-C(14)	1.814(3)	S(1)-Rh(1)-Cl(2)	96.52(3)	C(6)-C(5)-C(4)	119.6(3)
N(1)-C(2)	1.349(3)	N(1)-Rh(1)-Cl(3)	87.77(7)	N(1)-C(6)-C(5)	120.5(3)
N(1)-C(6)	1.357(3)	S(2)-Rh(1)-Cl(3)	97.28(3)	N(1)-C(6)-C(7)	117.4(2)
C(1)-C(2)	1.504(4)	S(1)-Rh(1)-Cl(3)	83.32(3)	C(5)-C(6)-C(7)	122.1(2)
C(2)-C(3)	1.389(4)	Cl(2)-Rh(1)-Cl(3)	177.50(3)	C(6)-C(7)-S(2)	113.80(19)
C(3)-C(4)	1.374(4)	N(1)-Rh(1)-Cl(1)	179.12(8)	C(9)-C(8)-S(1)	108.5(3)
C(4)-C(5)	1.385(4)	S(2)-Rh(1)-Cl(1)	93.54(3)	C(10)-C(9)-C(8)	112.6(6)
C(5)-C(6)	1.380(4)	S(1)-Rh(1)-Cl(1)	94.78(3)	C(9)-C(10)-C(11)	108.0(5)
C(6)-C(7)	1.487(4)	Cl(2)-Rh(1)-Cl(1)	90.96(3)	C(12)-C(11)-C(10)	125.6(4)
C(8)-C(9)	1.568(7)	Cl(3)-Rh(1)-Cl(1)	91.54(3)	C(11)-C(12)-C(13)	113.9(4)
C(9)-C(10)	1.511(9)	C(8)-S(1)-C(1)	101.80(17)	C(15)-C(14)-S(2)	111.8(2)
C(10)-C(11)	1.548(8)	C(8)-S(1)-Rh(1)	110.95(13)	C(14)-C(15)-C(16)	112.2(3)
C(11)-C(12)	1.469(6)	C(1)-S(1)-Rh(1)	96.03(10)	C(17)-C(16)-C(15)	111.4(3)
C(12)-C(13)	1.517(6)	C(7)-S(2)-C(14)	99.31(14)	C(16)-C(17)-C(18)	113.0(4)
C(14)-C(15)	1.496(4)	C(7)-S(2)-Rh(1)	95.25(10)	C(17)-C(18)-C(19)	111.8(4)
C(15)-C(16)	1.575(5)	C(14)-S(2)-Rh(1)	112.53(11)		

 Table S4. All bond lengths (Å), and bond angles (°) for *mer*-[RhCl₃(3)], 4.

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