REVISED Electronic Supplementary Information (ESI)

Synthesis and structure of "16-electron" rhodium(III) catalysts for transfer hydrogenation of a cyclic imine: mechanistic implications

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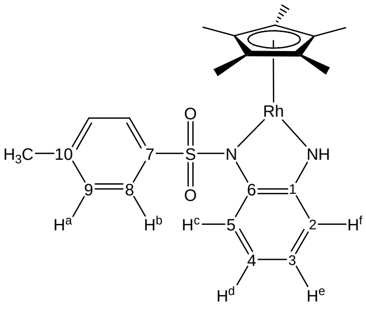
1. General synthetic procedures

Unless otherwise stated, synthetic work was carried out in air with untreated solvents. Commercially available reagents were obtained from the following sources: 6,7-dimethoxy-3,4-dihydroisoquinoline (donated by Piramal Healthcare); $RhCl_3.xH_2O$ (Precious Metals Online); pentamethylcyclopentadiene, *o*-phenylenediamine, triethylamine, formic acid, 5:2 formic acid / triethylamine (TEAF) (Aldrich); tosyl chloride (Alfa Aesar), Ar, N_2 and H_2 gases (BOC) and were used as received, without further purification. $[Cp^*RhCl_2]_2$ was made as previously reported.[1] When necessary dry solvents (Fisher Scientific AR or HPLC grade) were prepared by refluxing over Mg/I_2 (CH_3OH), CaH_2 (CH_3CN, CH_2Cl_2) or sodium/benzophenone (THF), were degassed and along with air- and moisture-sensitive materials, stored under a dry Ar atmosphere. Manipulations of these compounds were performed using standard Schlenk, high-vacuum, and glovebox techniques. Deuterated solvents (CD_3OH, CD_3CN, and CD_2Cl_2) (Aldrich) were dried using CaH_2 and degassed by three freeze-pump-thaw cycles. The chemical shift values are reported relative to the residual protons of the deuterated solvent, according to the standard Bruker list. ^1H-^{103}Rh HMQC spectra were run on a Bruker Avance II 700 MHz spectrometer calibrated against $[Cp^*RhCl_2]_2$ at δ 2303.[2] ESI mass spectra were recorded on a Thermo Electron LCQ Classic. Infrared spectra were recorded on a Unicam RS 10000E FTIR instrument. Microanalysis was carried out by Elemental Microanalysis Ltd., Okehampton, Devon.

2. Synthesis, spectroscopic and analytical data

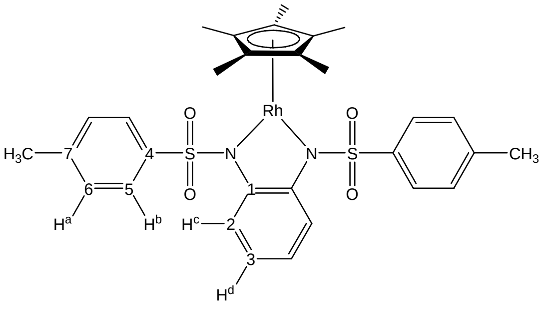
Cp*Rh(TsNC$_6$H$_4$NH) (1a)



(1a)

Di-μ-chloro-dichlorobis(n^5-pentamethylcyclopentadienyl)dirhodium(III) (250 mg, 0.40 mmol) and *N*-tosyl-1,2-diaminobenzene (212 mg, 0.81 mmol) were added to a 250 mL round bottom flask and dissolved in 100 mL of dichloromethane at 0°C, using an ice-bath. The reaction mixture was stirred using a magnetic stirrer bar and triethylamine (225 μL, 1.62 mmol) was added dropwise. The solution turned from orange to dark purple on addition of base. The reaction mixture was stirred for a further 5 hours at room temperature before being washed with water three times and was then dried over magnesium sulfate. The solvent was removed under vacuum and the crude solid was crystallised from chloroform and hexane (or THF/hexane) to give dark purple 'needle-like' crystals (332 mg, 82%). A crystal suitable for X-ray diffraction analysis was grown by vapour diffusion of hexane into a solution of **1a** in methanol:toluene (1:1). ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.98 (15H, s, C_5Me_5), 2.35 (3H, s, CH_3), 6.61 (1H, t, $^{3}J_{HH}$ = 8, H^e), 6.68 (1H, t, $^{3}J_{HH}$ = 8, H^d), 6.82 (1H, d, $^{3}J_{HH}$ = 8, H^f), 7.20 (2H, d, $^{3}J_{HH}$ = 8.2, H^a), 7.35 (1H, d, $^{3}J_{HH}$ = 8, H^c), 7.64 (2H, d, $^{3}J_{HH}$ = 8.2, H^b), 8.25 (1H, br. s, N*H*). ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ 10.67 (s, $C_5\mathit{Me}_5$), 21.69 (s, CH_3), 94.88 (d, J_{RhC} = 8.3 Hz, C_5Me_5), 113.99 (s, C^2), 117.94 (s, C^4), 117.98 (s, C^5), 120.85 (s, C^3), 127.13 (s, C^8), 129.76 (s, C^9), 138.68 (s, C^6), 141.26 (s, C^7), 142.54 (s, C^{10}), 152.52 (s, C^1). ^{103}Rh-^{1}H HMQC (22.18 MHz, $CDCl_3$, 300 K): δ 2063.0. MS (FAB, m/z): 499 ($[MH]^+$). IR (KBr / cm^{-1}): 3316 (ν_{NH}). Anal. Calcd for $C_{25}H_{31}N_2O_{2.5}RhS$ (**1a**.0.5THF): C, 56.18; H, 5.85; N, 5.24. Found: C, 56.47; H, 5.99; N, 5.20.

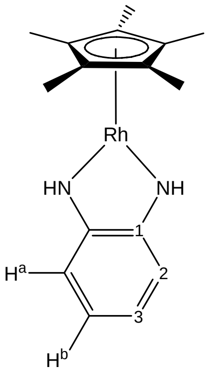
Cp*Rh($TsNC_6H_4NTs$) (1b)



(1b)

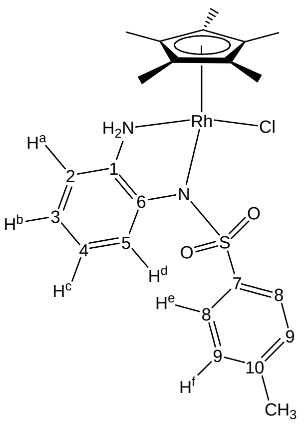
Di-μ-chloro-dichlorobis(n^{5}-pentamethylcyclopentadienyl)dirhodium(III) (250 mg, 0.40 mmol) and ditosyl-1,2-diaminobenzene (337 mg, 0.81 mmol) were added to a 250 mL round bottom flask and dissolved in 100 mL of dichloromethane at 0°C using an ice-bath. The reaction mixture was stirred using a magnetic stirrer bar and triethylamine (225 μL, 1.62 mmol) was added dropwise. The solution turned from orange to dark purple on addition of base. The reaction mixture was stirred for a further 5 hours at room temperature before being washed three times with water and then dried over magnesium sulfate. The solvent was removed under vacuum and the crude solid was crystallised from dichloromethane and methanol to give dark purple crystals of **1b**, which were suitable for X-ray diffraction (353 mg, 67%). ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.86 (15H, s, C_5Me_5), 2.33 (3H, s, CH_3), 6.41-6.45 (2H, m, H^d), 7.13 (4H, d, $^3J_{HH}$ = 8.0, H^a), 7.20-7.23 (2H, m, H^c), 7.50 (4H, d, $^3J_{HH}$ = 8.0, H^b). ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ 11.48 (s, $C_5\mathit{Me}_5$), 21.73 (s, CH_3), 99.34 (d, J_{RhC} = 8.9 Hz, C_5Me_5), 118.01 (s, C^2), 120.56 (s, C^3), 127.31 (s, C^5), 129.75 (s, C^6), 140.22 (s, C^4), 141.60 (s, C^1), 142.83 (s, C^7). ^{103}Rh-^{1}H HMQC (22.18 MHz, $CDCl_3$, 300 K): δ 1743.0. MS (ESI, m/z): 675.0848 ($[M+Na]^+$). IR (KBr / cm^{-1}): 1480, 1450, 1314, 1297, 1250, 1204, 1152, 1126, 1089, 1017, 943, 915, 857, 833, 822, 810, 754, 742, 708, 671, 661, 569, 562, 551. Anal. Calcd for $C_{30}H_{33}N_2O_4RhS_2$: C, 55.21; H, 5.10; N, 4.29. Found: C, 55.02; H, 4.96; N, 4.24.

Cp*Rh(HNC_6H_4NH) (1c)



Complex **1c** was prepared using the procedure outlined by Maitlis.[1] Under argon, in a Schlenk tube, 1,2-diaminobenzene (87 mg, 0.8 mmol) was added slowly to a solution of di-μ-chloro-dichlorobis(n^5-pentamethylcyclopentadienyl)dirhodium(III) (250 mg, 0.40 mmol) in deoxygenated water (30 cm^3) with stirring. The solution changed colour rapidly from yellow to dark red and a very dark red solid precipitated. The reaction mixture was stirred for a further 5 hours and the precipitate was filtered off, washed with water (2 × 10 cm^3) and dried *in vacuo*. Crystals suitable for X-ray diffraction analysis were grown by layering a saturated solution of **1c** in toluene with *n*-pentane. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 2.07 (15H, s, C_5Me_5), 6.66-6.69 (2H, m, AA'XX', H^a), 6.85-6.88 (2H, m, AA'XX', H^b), 8.26 (2H, br. s, NH). ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ 10.81 (s, $C_5\mathit{Me}_5$), 91.54 (d, J_{RhC} = 7.3 Hz, C_5Me_5), 114.56 (s, C^3), 117.55 (s, C^2), 149.63 (s, C^1). IR (KBr / cm^{-1}): 3346 (A_1 stretch), 3322 (A_1 stretch), 2904, 1463, 1370, 1354, 1324, 1209, 1158, 1140, 1105, 1075, 1025, 948, 900, 727, 668, 655, 566, 549, 535, 454, 438.

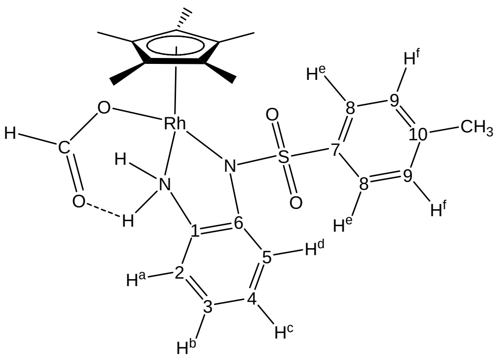
Cp*RhCl($HNC_6H_4NH_2$) (2a)



(2a)

$Cp^*Rh(TsNC_6H_4NH)$, **1a** (10.4 mg, 0.02 mmol) was added to a thoroughly cleaned and dried Young's tap NMR tube and dissolved in 0.5 mL of dry and degassed dichloromethane-d_2 on a high vacuum line. 1 mol equivalent of hydrochloric acid in ether solution (20 μL, 0.02 mmol) was added to the NMR tube, under argon at 193 K. The solution turned from purple/blue to orange. After confirming the 18-electron chloride product had been synthesised *in-situ* by NMR, the deuterated solvent and ether were removed *in-vacuo* and the crude product was dissolved in dichloromethane-d_2. Another NMR at room temperature confirmed the 18-electron chloride product was still present. Isolation of **2a** was achieved by layering approximately 1.5 mL of dry, degassed diethyl ether onto the solution containing the crude product in the NMR tube. The solvents were allowed to diffuse for 5 days and orange crystals of **2a** suitable for X-ray diffraction were obtained. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.68 (15H, s, C_5Me_5), 2.28 (3H, s, CH_3), 4.39 (1H, br. s, NH*H*), 5.27 (1H, br. s, N*H*H), 6.52 (1H, dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1 Hz, H^b), 6.84 (1H, dt, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1 Hz, H^c), 6.94 (1H, dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1 Hz, H^a), 7.09 (2H, d, $^3J_{HH}$ = 8.1, H^f), 7.41 (1H, dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1 Hz, H^d), 7.96 (2H, d, $^3J_{HH}$ = 8.1, H^e). ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ 9.80 (s, $C_5\mathit{Me}_5$), 21.64 (s, CH_3), 94.82 (d, J_{RhC} = 8.7 Hz, C_5Me_5), 118.96 (s, C^3), 120.07 (s, C^5), 123.13 (s, C^2), 127.76 (s, C^4), 129.11 (s, C^9), 129.13 (s, C^8), 133.81 (s, C^1), 140.38 (s, C^7), 141.74 (s, C^{10}), 146.77 (s, C^6).

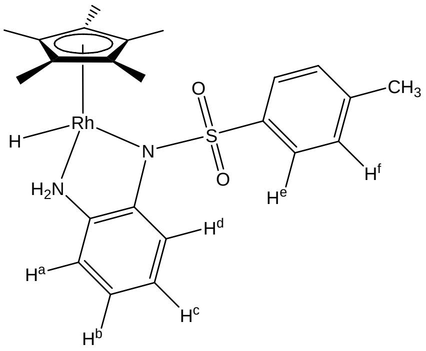
Cp*Rh(OCHO)($TsNC_6H_4NH_2$) (3a)



(3a)

Cp*Rh($TsNC_6H_4NH$), **1a** (10.1 mg, 0.02 mmol) was added to a Young's tap NMR tube and dissolved in 0.5 mL of dry and degassed dichloromethane-d_2. A dry and degassed solution of formic acid (0.02 mmol) in dichloromethane-d_2 was added to the NMR tube under argon at 193 K and shaken vigorously. The solution turned from purple/blue to orange immediately. The 18-electron product was analysed by ^{1}H, ^{13}C, HSQC, HMBC, COSY and NOESY NMR experiments. ^{1}H NMR (500 MHz, CD_2Cl_2, 213 K): δ 1.57 (15H, s, C_5Me_5), 2.23 (3H, s, CH_3) 4.92 (1H, br. d, $^2J_{HH}$ = 9, N*H*H…O), 6.50 (1H, t, $^3J_{HH}$ = 7.5, H^b/H^c), 6.77 (1H, t, $^3J_{HH}$ = 7.5, H^b/H^c), 6.96 (1H, d, $^3J_{HH}$ = 7.5, H^a/H^d), 7.08 (2H, d, $^3J_{HH}$ = 8, H^f), 7.20 (1H, d, $^3J_{HH}$ = 7.5, H^a/H^d), 7.66 (2H, d, $^3J_{HH}$ = 8, H^e), 8.35 (1H, br. d, $^2J_{HH}$ = 9, NH*H*…O), 8.70 (1H, s, COO*H*).

$Cp^*Rh(H)(TsNC_6H_4NH_2)$ (4a)



The sample was prepared as for **3a** but in THF-d_8. It was brought to 233 K and inserted into the NMR spectrometer at that temperature. Molecular connectivity was established by ^1H-^{103}Rh correlation and by ^1H COSY spectroscopy. ^1H NMR (700 MHz, THF-d_8, 233 K) δ -9.51 (1H, d J_{RhH} 22 Hz) hydride, 1.96 (15H, s, $C_5(CH_3)_5$), 2.42 (3H, s, CH_3), 5.46 (1H, d br, $^2J_{HH}$ 12 Hz NH), 6.05 (1H, d br, NH, $^2J_{HH}$ 12 Hz), 6.45 (1H, H^a,H^b,H^c,H^d), 6.69 (1H, H^a,H^b,H^c,H^d), 6.78 (1H, H^a,H^b,H^c,H^d), 6.85 (1H, H^a,H^b,H^c,H^d) 7.03 (2H, d, $^3J_{HH}$ 8.0 Hz, H^f), 7.69 (2H, d, $^3J_{HH}$ 8.0 Hz, H^e). ^{103}Rh-^1H HMQC (22.18 MHz, THF-d_8, 233K) δ 1472

3. Catalytic experiments

Catalytic hydrogenation of a secondary imine with 16-electron catalyst (1a) and TEAF solution in methanol-d_4 and dichloromethane-d_2

A stock solution of imine was prepared by dissolving 3,4-dihydro-6,7-dimethoxy-1-methylisoquinoline (121.0 mg, 0.5 mmol) in methanol-d_4 and making up to 5 mL in a volumetric flask. The 16-electron catalyst stock solution was prepared using **1a** (10.0 mg, 0.02 mmol) in methanol-d_4 and making up to 2 mL in a volumetric flask. For catalytic runs of **1b** and **1c** in dichloromethane-d_2, the stock solutions were (13.1 mg, 0.02 mmol) and (6.9 mg, 0.02 mmol) in 2 mL of dichloromethane-d_2, respectively.

NMR samples were prepared by combining the imine stock solution (0.5 mL) and catalyst stock solution (50 μL for 1 mol %) and shaking the tube to afford complete mixing. A single scan ^{1}H NMR spectrum was recorded (t = 0), the sample was removed from the magnet and TEAF (21 μL) was added to the tube (which was vigorously shaken) and it was returned to the spectrometer. Single scan spectra were recorded every 2 minutes until the reaction was complete. Results are reported as the average of 2 runs.

4. Crystallographic data

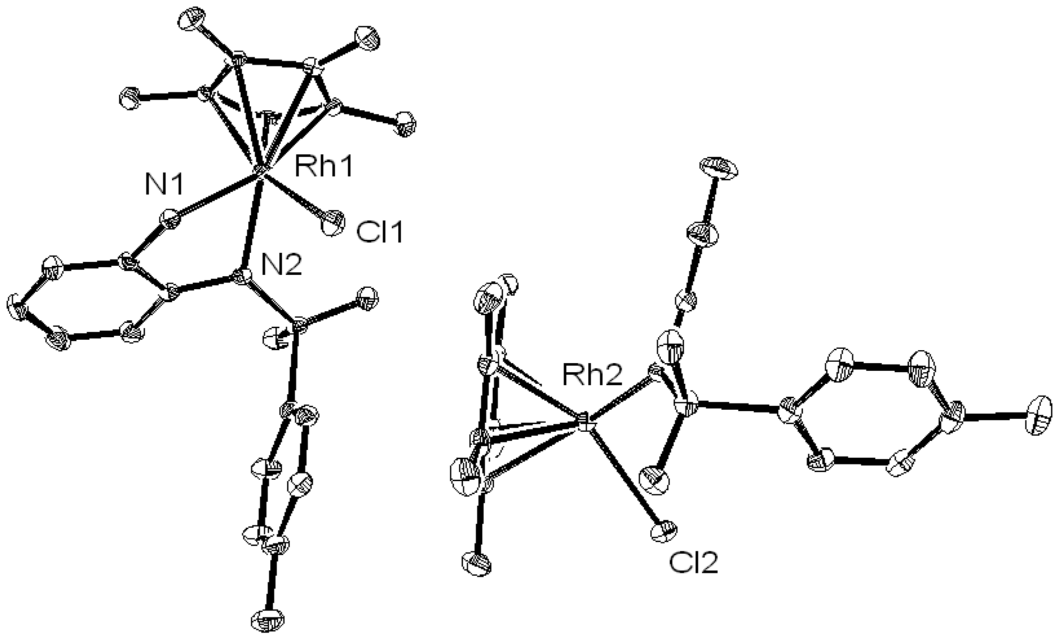


Figure S1: Molecular structure of Cp*Rh(Cl)($TsNC_6H_4NH_2$), **2a** (two molecules in asymmetric unit), hydrogens omitted except NH_2.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for free ligands[a]

	complex		
bond	**$H_2NC_6H_4NH_2$**	**$TsNHC_6H_4NH_2$**	**$TsNHC_6H_4NHTs$**
N(1)-C(11)	1.406	1.368(4)	1.417(4)
N(2)-C(16)	1.408	1.439(4)	1.431(4)
C(11)-C(16)[b]	1.406	1.397(4)	1.388(4)

[a] C. Stalhandske, *Cryst. Struct. Commun.*, 1981, **10**, 1081; (b) C. Squires, C. W. Baxter, J. Campbell, L. F. Lindoy, H. McNab, A. Parkin, S. Parsons, P. A. Tasker, G. Wei, D. J. White, *J. Chem. Soc., Dalton Trans.*, 2006, 2026-2034; (c) T. Kato, H. Masu, H. Takayanagi, E. Kaji, K. Katagiri, M. Tominaga, I. Azumaya, *Tetrahedron*, 2006, **62**, 8458-8462.
[b] C-C is the distance between the carbon atoms on the phenylenediamine ligand that are attached directly to nitrogen atoms.

Table S2. Crystallographic data for 1a, 1b, 1c and 2

	1a·½toluene	**1b**	**1c**	**2a**
Formula	$C_{26.5}H_{31}N_2O_2RhS$	$C_{30}H_{33}N_2O_4RhS_2$	$C_{16}H_{21}N_2Rh$	$C_{23}H_{28}ClN_2O_2RhS$
M / g mol^{-1}	544.50	652.61	344.26	534.89
a / Å	24.313(2)	8.6640(8)	20.8896(6)	11.0617(11)
b / Å	13.1324(13)	12.2229(11)	13.4599(4)	15.1303(15)
c / Å	15.5915(15)	14.2366(13)	21.1659(6)	16.2600(17)
α / deg	90	76.388(2)	90	117.247(2)
β / deg	101.223(2)	84.315(2)	95.4840(10)	104.377(2)
γ / deg	90	75.726(2)	90	92.805(2)
V / Å^3	4883.1(8)	1418.7(2)	5924.0(3)	2301.5(4)
T / K	110(2)	110(2)	110(2)	110(2)
space group	C2/c	*P*-1	P2(1)/c	*P*-1
Z	8	2	16	4
μ(Mo Kα) / mm^{-1}	0.811	0.788	1.141	0.971
reflns measd	26956	14287	66450	31550
reflns indep	7031	6939	17170	11375
R_{int}	0.0321	0.0250	0.0251	0.0213
final $R[I > 2\sigma(I)]$	$R_1 = 0.0298$	$R_1 = 0.0330$	$R_1 = 0.0328$	$R_1 = 0.0232$
	$wR_2 = 0.0714$	$wR_2 = 0.0824$	$wR_2 = 0.0790$	$wR_2 = 0.0573$
final R (all data)	$R_1 = 0.0380$	$R_1 = 0.0419$	$R_1 = 0.0461$	$R_1 = 0.0282$
	$wR_2 = 0.0750$	$wR_2 = 0.0867$	$wR_2 = 0.0883$	$wR_2 = 0.0591$
CCDC number	729047	729048	729049	729050

Table S3. Selected bond lengths (Å) and angles (degrees) for 1a, 1b, 1c and 2a

	Complex							
Bond	**(1a·½toluene)**	**(1b)**	**(1c) mol 1**	**(1c) mol 2**	**(1c) mol 3**	**(1c) mol 4**	**(2a) mol 1**	**(2a) mol 2**
M–N(1)	1.9372(15)	2.0403(19)	1.9824 (18)	1.9831(18)	1.9842(18)	1.9833(18)	2.1535(14)	2.1377(15)
M–N(2)	2.0796(14)	2.0435(19)	1.9745(19)	1.9701(19)	1.9724(19)	1.9716(19)	2.1528(14)	2.1502(14)
Δr(M–N)[a]	0.1424(10)	0.0032(13)	0.0079(13)	0.0130(13)	0.0118(13)	0.0117(13)	0.0007(10)	0.0125(10)
N(1)–C(11)	1.369(2)	1.421(3)	1.360(3)	1.362(3)	1.363(3)	1.360(3)	1.446(2)	1.450(2)
N(2)–C(16)	1.413(2)	1.422(3)	1.368(3)	1.363(3)	1.361(3)	1.364(3)	1.409(2)	1.414(2)
C(11)–C(16)[b]	1.416(2)	1.404(3)	1.420(3)	1.421(3)	1.424(3)	1.425(3)	1.407(2)	1.402(2)
θ_{oop}[c]	0.03°	8.40°	0.73°	1.09°	0.92°	1.99°	37.64°	38.07°
θ_{tilt}[d]	0.82°	20.98°	2.72°	0.98°	0.60°	4.44°	36.94°	41.26°

5. Computational Details

All calculations were performed with the Gaussian03 package[3] of programs with the hybrid B3PW91 functional.[4,5] The Rh atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set,[6] augmented by an *f* polarization function.[7] The remaining atoms (C, H, N, O) were represented by a 6-31G(*d,p*) basis set.[8] The sulfur atom was represented by RECP from the Stuttgart group and the associated basis set,[9] augmented by a *d* polarization function.[10] Full optimization of geometry was performed without any constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima. Natural bonding orbital analysis[11] was performed with the NBO 5.0 version implemented in Gaussian03.

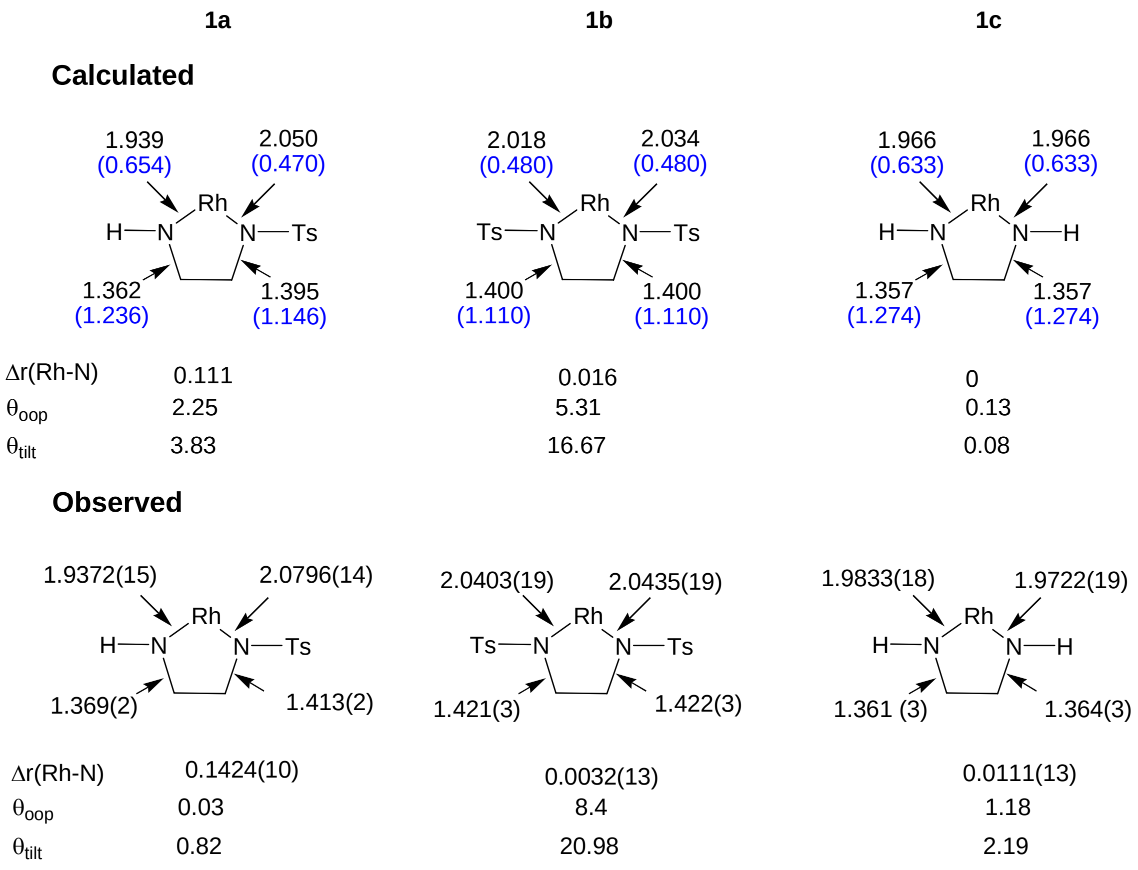
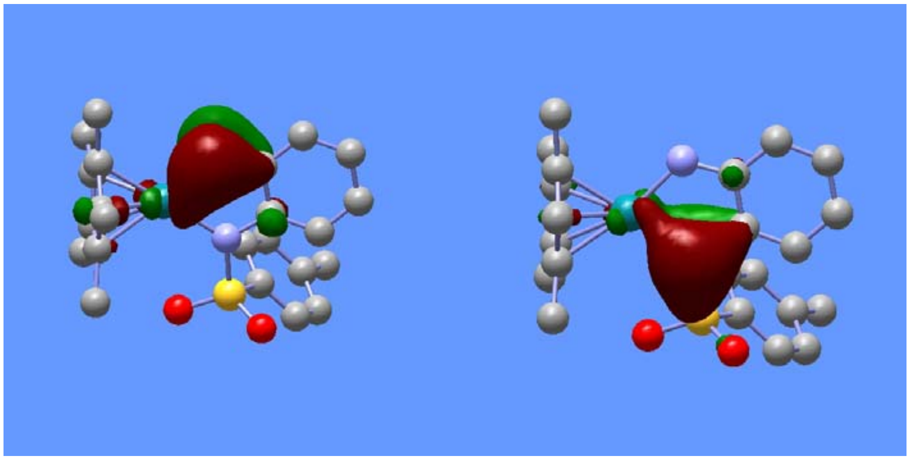


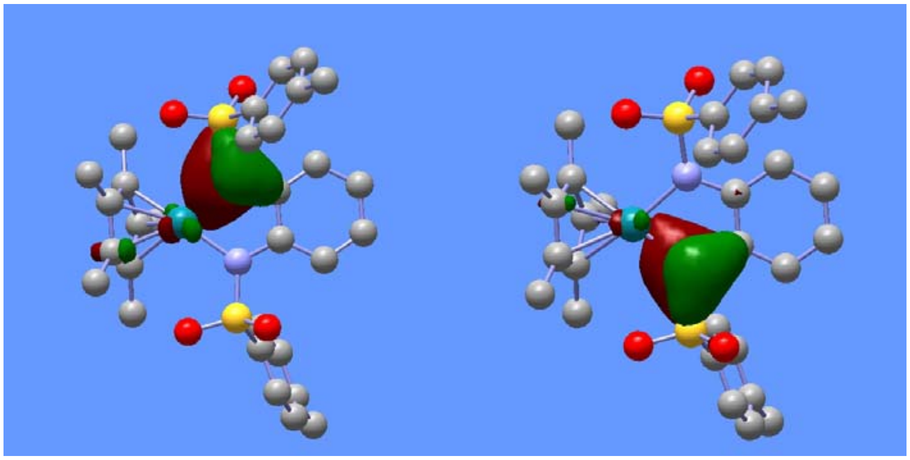
Figure S2 Comparison of calculated and observed bond lengths (Å) for **1a**, **1b** and **1c**. Wiberg indices are shown in brackets (blue).The difference between the Rh-N bond lengths is shown as Δr. Calculated and observed interplane angles θ_{oop} and θ_{tilt} also shown in degrees. (Definitions in main text.) The calculations do not impose any symmetry.

Table S4. Composition of nitrogen NLMOs (%). (The values are averaged for the two nitrogen atoms of **1b** and for the two nitrogen atoms of **1c**)

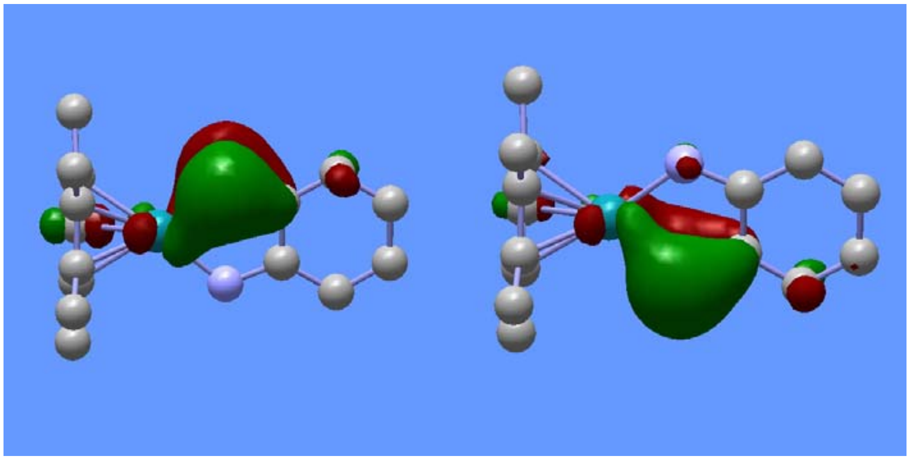
	N	**Rh**	**Directly bound C**	**S**
1a (NH)	73.4	8.5	5.8	-
1a (NTs)	80.1	3.8	4.0	2.3
1b	80.8	5.4	3.0	1.9
1c	73.9	6.8	6.8	-



1a



1b



1c

Figure S3. NLMOs for each of the nitrogen lone pairs of **1a** (above), **1b** (centre) and **1c** (bottom) displayed with RhN(1)N(2) close to the plane of the paper. Rh cyan, S yellow, O red, N lilac.

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