Supplementary Material (ESI) for *Chemical Communications*

Supporting Information

Dioxygen activation by mixed-valent dirhodium complexes of redox non innocent azoaromatic ligands

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PART A: EXPERIMENTAL PART

Materials. $[Rh(COD)Cl]_2$ is an Aldrich reagent. The ligands L^a and L^b were prepared by following the reported procedure.[1] All other chemicals were of reagent grade and used as received. Solvents were purified and dried prior to use. Preparation and handling of air-sensitive materials were carried out under an inert atmosphere by using standard Schlenk techniques or a glove box.

Instrumentation. UV-vis-NIR absorption spectra were recorded on a Perkin-Elmer Lambda 950 UV-vis spectrophotometer and on a J&M TIDAS instrument. ^{1}H-NMR spectra were taken on a Bruker Advance DPX 300 spectrometer and $SiMe_4$ was used as the internal standard. Infrared spectra were obtained using a Perkin-Elmer 783 spectrophotometer. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263).

Syntheses

Complex 1a. 74 mg (0.4 mmol) of L^a, dissolved in dry dichloromeane, was added drop wise to a dichloromethane solution containing 100 mg (0.2 mmol) of $[Rh(COD)Cl]_2$ in a glove box with constant stirring. During this period the color of the solution changes from orange to dark red. Stirring was continued for 4 h. The crude mass, obtained by the evaporation of the solvent in vacuum, was purified by fractional crystallization from dichloromethane and ether solvent mixture. The precipitate was crystallized by the slow diffusion of a dichloromethane solution of the compound into methanol. Its yield and characterization data are as follows: Yield 91% ESI-MS, m/z: 751 $[MH]^+$ Anal. Calcd. for $C_{30}H_{30}Cl_2N_6Rh_2$: C, 47.96; H, 4.02; N, 11.19. Found: C, 47.92; H, 4.08; N, 11.21.

Complex 1b. This was synthesized following the same procedure as described for **1a**. Its yield and characterization data are as follows: Yield 93% ESI-MS, m/z: 820 $[MH]^+$ Anal. Calcd. for $C_{30}H_{28}Cl_4N_6Rh_2$: C, 43.93; H, 3.44; N, 10.25. Found: C, 43.89; H, 3.48; N, 10.27.

Complex 2a. 100 mg (0.13 mmol) of **1a** was dissolved in dichloromethane and to it dry oxygen (O_2) gas was purged for 6 hrs. During this period the color of the solution changes from dark red to brownish green. Upon addition of NaOTF (OTF^- = triflate anion) to the resultant mixture, a dark precipitate was obtained, which was purified by fractional crystallization using dichloromethane/hexane solvent mixture. X-ray quality crystals were obtained by the slow evaporation of a solution of **2a** in dichloromethane-methanol (1:1) solvent mixture. The yield and characterization data of the compound are as follows: Yield: 32% ESI-MS, m/z: 499$[M]^+$. Anal. Calcd. for $C_{23}H_{16}F_3N_6O_5RhS$: C, 42.61; H, 2.49; N, 12.96. Found: C, 42.58; H, 2.53; N, 12.99.

Complex 2b. The compound was synthesized following the same procedure as described for **2a**. Its yield and characterization data are as follows: Yield: 35% ESI-MS, m/z: 567$[M]^+$. Anal. Calcd. for $C_{23}H_{14}Cl_2F_3N_6O_5RhS$: C, 38.51; H, 1.97; N, 11.72. Found: C, 38.48; H, 2.01; N, 11.74.

Reaction of $[Rh(COD)Cl]_2$ with L^a in air. 148 mg (0.8 mmol) of L^a, dissolved in dry dichloromethane, was added drop wise to a dichloromethane solution containing 100 mg (0.2 mmol) of $[Rh(COD)Cl]_2$ in air. During this period the color of the solution changes from orange to greenish brown. Stirring was continued for 6 hrs. The crude mass, thus obtained by evaporation of the solvent, was dissolved in minimum volume of

dichloromethane and loaded on a preparative silica gel TLC plate for purification. Acetonitrile-chloroform (1:10) solvent mixture was used as the eluent. A green band was collected, and the solvent was evaporated under vacuum. The yield and characterization data of the compound, $[Rh^{III}(L^{a}O)(L^{a\bullet-})Cl]$ are as follows: Yield: 35% ESI-MS, m/z: 519 $[M]^{+}$. Anal. Calcd. for $C_{22}H_{17}ClN_6ORh$: C, 50.84; H, 3.30; N, 16.17. Found: C, 50.81; H, 3.34; N, 16.20.

Crystallography. Crystallographic data for the compounds **1b**, and **2b** are collected in Table S1. Suitable X-ray quality crystals of these are obtained as follows: **1b**, by slow diffusion of a dichloromethane solution of the compound into methanol and **2b**, by slow evaporation of dichloromethane/methanol solution of the compound.

All data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz-polarization effects. **1b**: A total of 36394 reflections were collected, of which 5539 were unique (R_{int} = 0.067), satisfying the ($I > 2\sigma(I)$) criterion, and were used in subsequent analysis. **2b**: A total of 8365 reflections were collected, of which 1758 were unique (R_{int} = 0.132).

The structures were solved by employing the SHELXS-97 program package[2] and were refined by full-matrix least-squares based on F^2 (SHELXL-97).[3] In the crystal structure of the complex, **2b** C1, C6, C11, C16, C17 and O2 atoms are refined isotropically. All hydrogen atoms were added in calculated positions. Data collected on several crystals of the complex **2b**, did not show diffraction beyond theta (max) = 17.5. Repeated attempts to obtain better quality crystals were not fruitful.

References:

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2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

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University of Göttingen; Göttingen, Germany, 1997.

Table S-1. Crystallographic Data of **1b** and **2b**

	1b	**2b**
empirical formula	$C_{30}H_{28}C_{l4}N_6Rh_2$, CH_4O, 0.92(O)	$C_{22}H_{14}Cl_2N_6O_2Rh$, CF_3O_3S, O
molecular mass	868.25	733.28
temperature (K)	150 (K)	150 (K)
crystal system	Monoclinic	Monoclinic
space group	P21/n	P21/c
a (Å)	9.3221(6)	10.220(11)
b (Å)	13.9691(9)	21.14(2)
c (Å)	25.3913(16)	13.429(14)
α (deg)	90	90
β (deg)	98.991(2)	106.99(3)
γ (deg)	90	90
V ($Å^3$)	3265.9(4)	2775(5)
Z	4	4
Dcalcd ($gmcm^{-3}$)	1.766	1.755
cryst. dimens. (mm)	0.13 x 0.15 x 0.17	0.07 x 0.17 x 0.20
θ range for data coll (deg)	1.6-24.7	1.9-17.5
GOF	1.08	1.11
reflns. collected	36394	8365
unique reflns.	5539	1758
largest diff. between peak and hole (e $Å^{-3}$)	0.01, 0.00	0.93, -0.48
final R indices [I > 2σ(I)	R1 = 0.0307, wR2 = 0.0664	R1 = 0.0754 wR2 = 0.2026

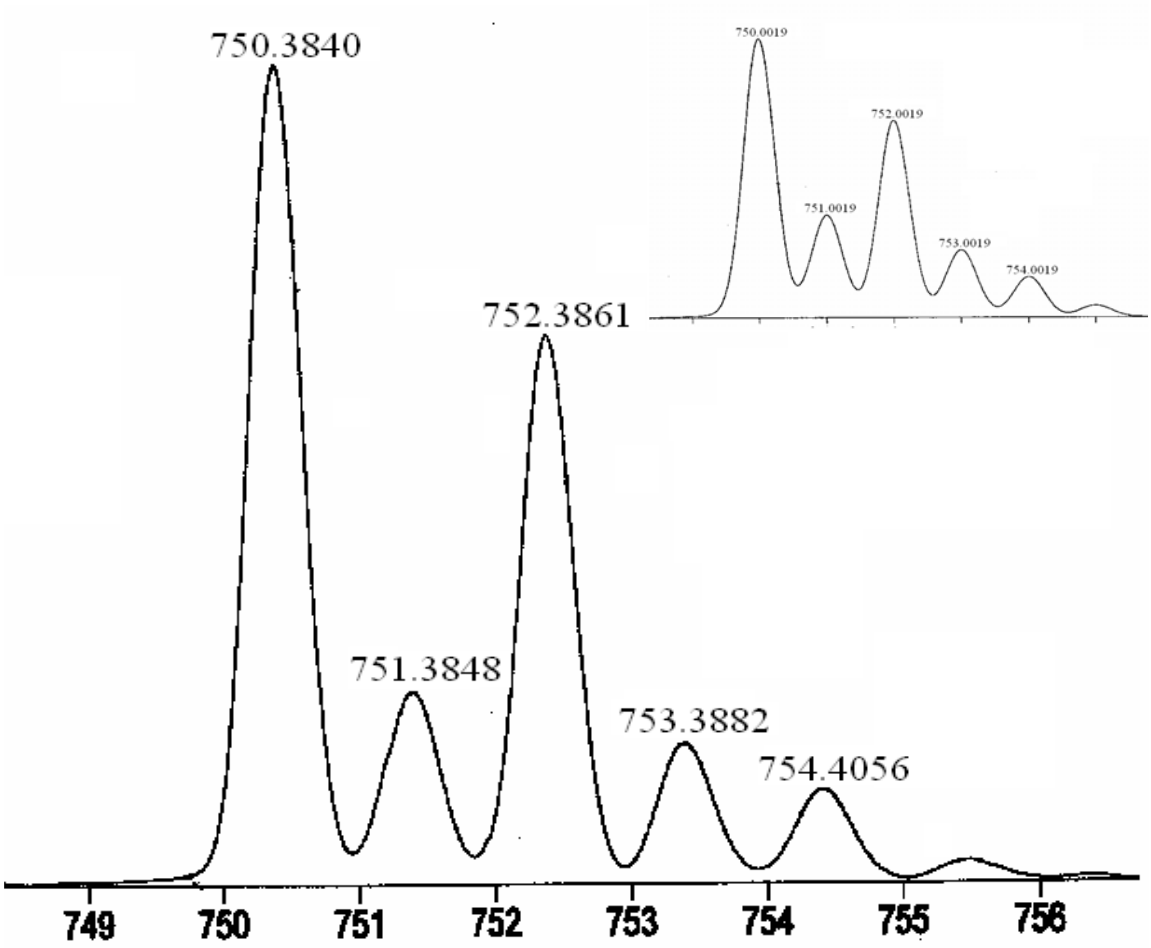

Figure S-1. ESI-MS spectrum of the compound, **1a**. Inset: simulated isotopic pattern.

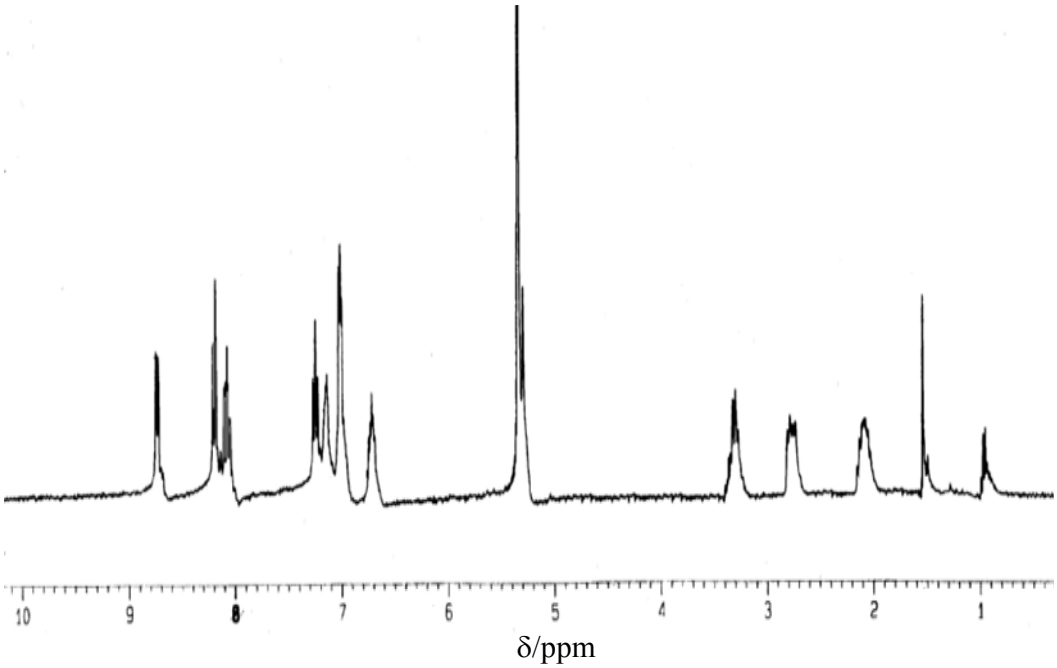

Figure S-2. ^{1}H NMR spectrum of the complex **1a** in CD_2Cl_2.

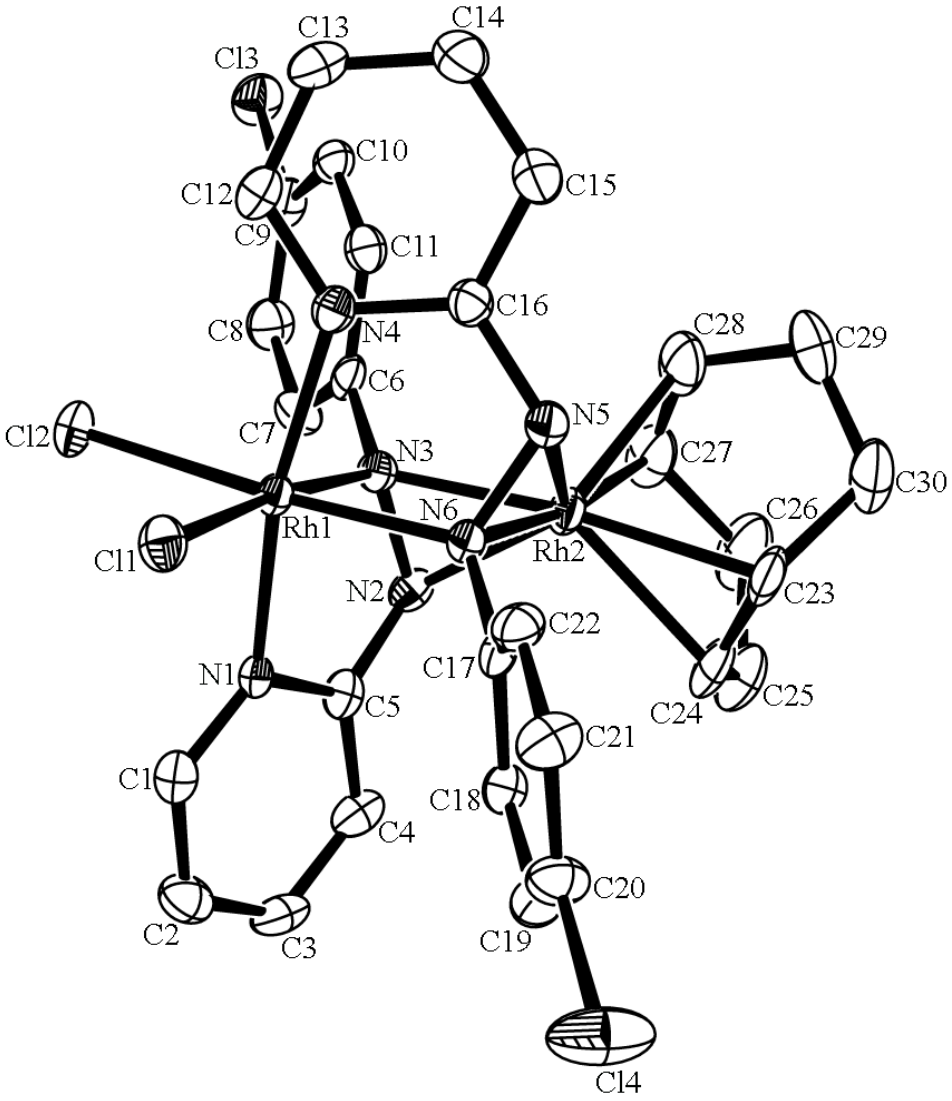

Figure S-3. ORTEP representation and atom numbering scheme for the complex **1b**. Hydrogen atoms are not shown for clarity.

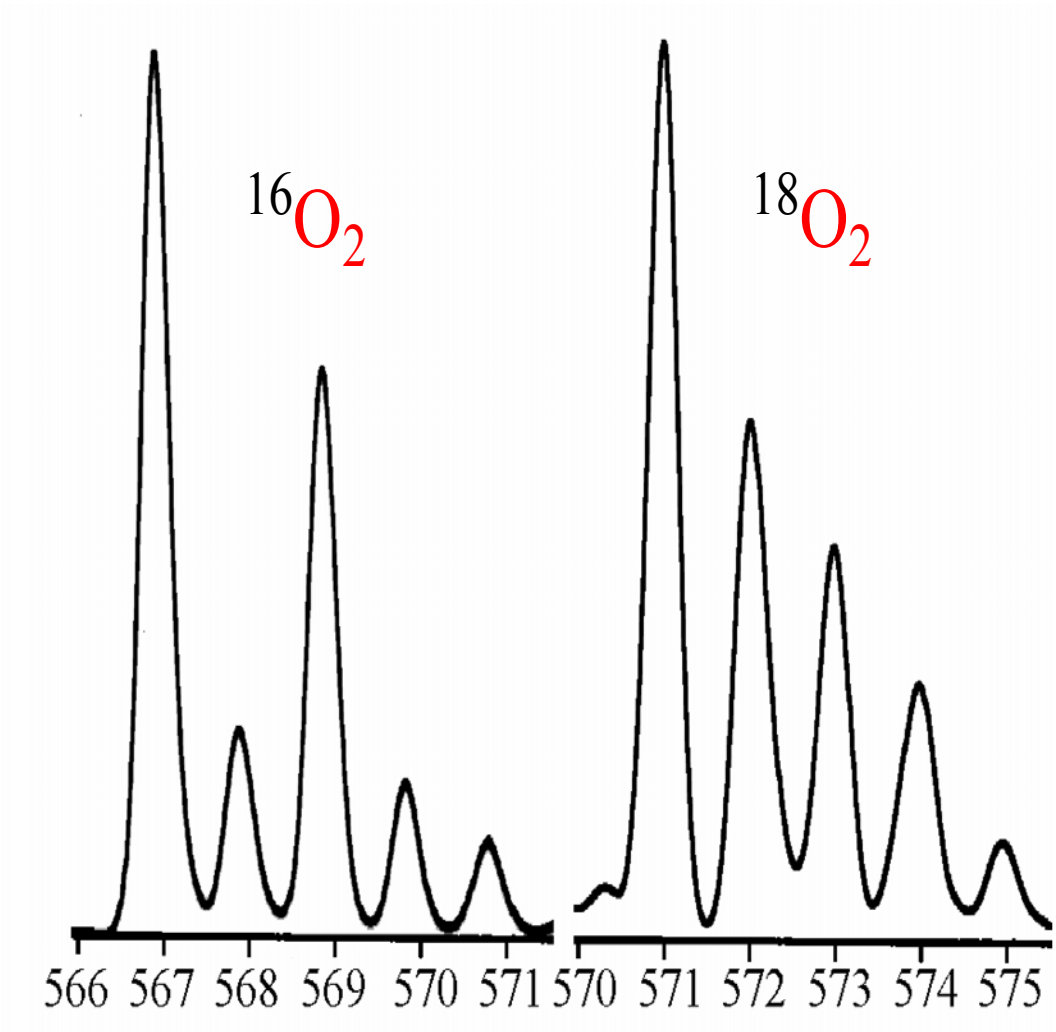

Figure S-4. ESI-MS spectra of the compound, **2b**. (^{16}O and ^{18}O labeled).

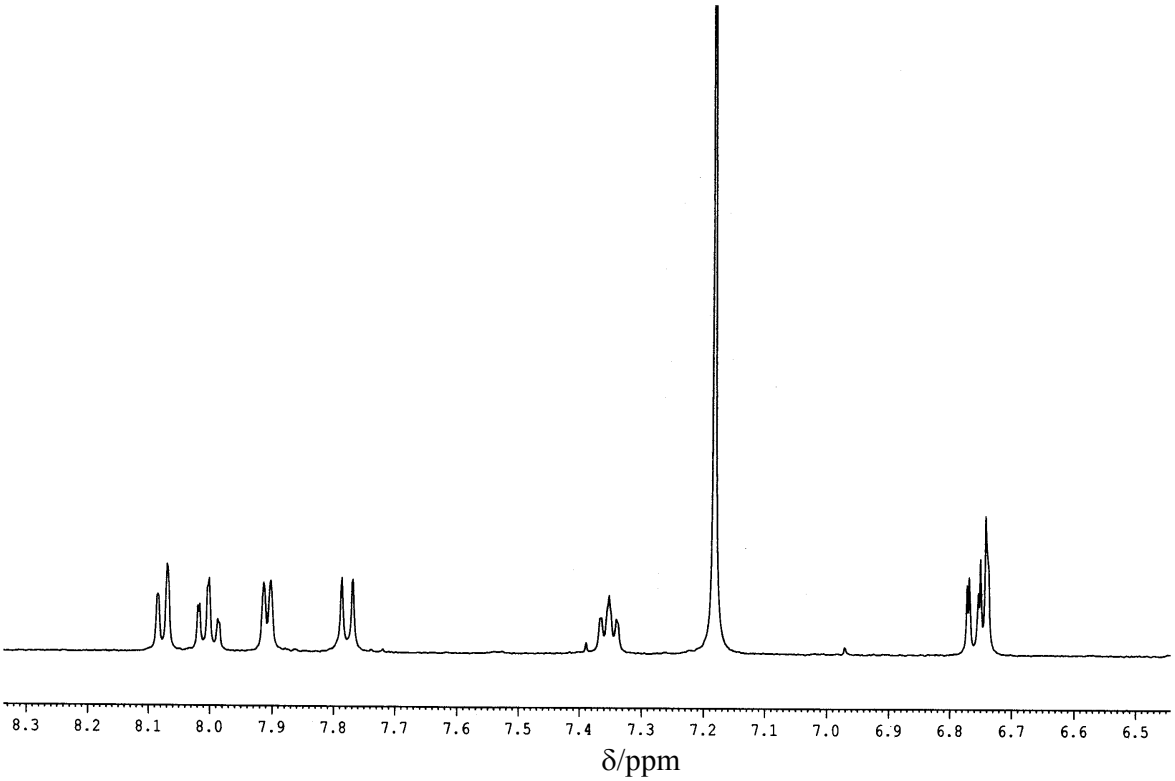

Figure S-5: ^{1}H NMR spectrum of the complex **2b** in $CDCl_3$.

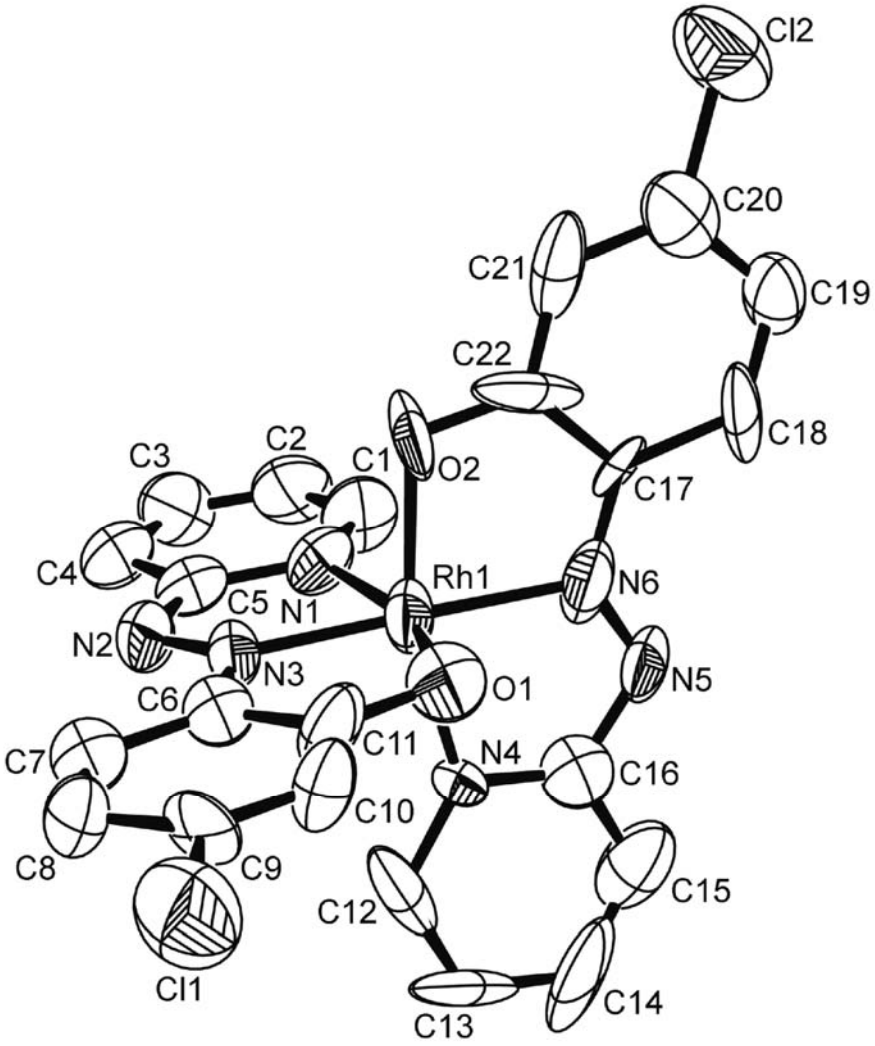

Figure S-6. ORTEP representation and atom numbering scheme for the complex **2b**. Hydrogen atoms and $CF_3SO_3^-$ are not shown for clarity.

PART B: COMPUTATIONAL PART

(a) Computational methodology:

All calculations described in this paper were performed using density functional theory as implemented in the Gaussian 03 package.[4] Full geometry optimisations were performed without symmetry constraints, and stationary points were confirmed to be minima (no imaginary frequency) by vibrational analysis. The hybrid B3LYP exchange-correlation functional[5] was used in conjunction with the SDD basis set (Stuttgart/Dresden ECP with D95) on Rh,[6] and Ahlrich's triple-ζ valence basis set extended by one polarization function (TZVP) on all coordinating atoms (N(1)-N(6), Cl(3), Cl(4), C(22), C(23), C(24), C(26)).[7] The remaining atoms were described by slightly smaller basis sets (SVP) that are of double-ζ quality in the valence region and contain one polarization function.[8] The topological properties of electron densities, calculated with B3LYP in conjunction with the DGDZVP basis set on Rh,[9] and TZVP and SVP as defined above, were characterized by using the Atoms In Molecules (AIM) theory of Bader[10] with the AIM2000 program package.[11]

(b) Summary:

Structural optimizations:

In the text we describe a series of calculations performed using the B3LYP functional which suggest that a triplet diradical state (^{3}**1b**) lies considerably higher than a closedshell singlet (^{1}**1b**) that we formulate as a Rh(III)Rh(-1) dimer. Optimized structures of the two states are shown in Figures S-7 and S-8, key bond lengths and angle are compared to experiment in Table S-2 and optimized Cartesian coordinates are collected

in Table S-3. We note in the text that we were unable to locate a broken-symmetry singlet state corresponding to the diradical limit, because all attempts converged instead to the closedshell alternative. We anticipate that functionals with greater HF exchange will stabilize the radical forms relative to their closed-shell alternatives, and indeed with BH and HLYP we have been able to locate the broken-symmetry singlet (Figure S-9) 1.3 kcal/mol below the triplet, and with very similar structure. However, the broken-symmetry state remains 7.8 kcal/mol above its closed-shell analogue, and the fact that the diradical state remains relatively unstable even with the most 'forcing' of functionals offers convincing evidence that the Rh(III)Rh(-I) formulation is more reasonable in this case.

Analysis of the topology of the computed electron density in ^{1}1b:

The closed-shell singlet ground state of complex ^{1}**1b** is in principle consistent with a Rh(II)-Rh(0) formulation with a dative metal-metal bond formation. We noted in the text that this appears inconsistent with the Rh-Rh separation of 3.21 Å, and an analysis of the topology of the electron density using Bader's Atoms In Molecules (AIM) theory confirms that no bond critical point (BCP) is present between the Rh centres. Instead, a ring critical point is located at the centre of the Rh_2N_2 diamond (Figure S-10), and the negligible density at this point (ρ = 0.04 e / au^3) confirms the absence of direct overlap between the two Rhodium atomic basins. In contrast, BCPs were located between each of the nitrogen atoms in the azo groups and the rhodate centre (Figure S-11), along with ring critical points at the centre of both N-N-Rh triangles, a situation characteristic of strong Rh-(N=N) back-bonding.

References:

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Table S-2. Summary of selected experimental and calculated bond lengths (Å) and angles (°) of complex **1b**.

Parameter	Exp.	^{1}**1b**	^{3}**1b**	^{BS}**1b**
Rh(1)−Rh(2)	3.15	3.21	3.23	3.21
Rh(1)−Cl(1)	2.36	2.38	2.39	2.37
Rh(1)−Cl(2)	2.35	2.38	2.39	2.37
Rh(1)−N(1)	2.00	2.04	2.05	2.04
Rh(1)−N(4)	2.01	2.04	2.05	2.04
Rh(1)−N(3)	2.04	2.11	2.14	2.11
Rh(1)−N(6)	2.04	2.11	2.14	2.11
Rh(2)−N(3)	2.07	2.10	2.29	2.24
Rh(2)−N(6)	2.08	2.10	2.29	2.24
Rh(2)−N(2)	2.16	2.22	2.95	2.89
Rh(2)−N(5)	2.18	2.22	2.95	2.89
Rh(2)−C(23)	2.19	2.26	2.18	2.21
Rh(2)−C(24)	2.20	2.24	2.18	2.21
Rh(2)−C(27)	2.20	2.26	2.18	2.21
Rh(2)−C(28)	2.19	2.24	2.18	2.21
N(2)−N(3)	1.41	1.39	1.36	1.35
N(5)−N(6)	1.40	1.39	1.36	1.35
C(20)−Cl(4)	1.75	1.75	1.75	1.74
C(9)−Cl(3)	1.74	1.75	1.75	1.74
N(1)-Rh(1)-N(4)	168.6	171.0	176.8	175.7
Cl(1)-Rh(1)-Cl(2)	91.8	92.3	92.3	92.8
N(3)-Rh(1)-N(6)	81.2	80.5	89.7	88.2
N(3)-Rh(2)-N(6)	79.6	81.0	82.5	82.0
Rh(1)-N(3)-Rh(2)	99.7	99.3	93.9	94.9
C(3)-N(3)-N(2)	112.8	113.3	111.9	111.5
C(12)-N(2)-N(3)	113.0	114.4	115.4	115.8

Table S-3. Cartesian coordinates of optimised structures.

[Rh2(p-Clpap)2(COD)Cl2] (^{1}1b) / *S* = 0 (B3LYP)

45	0.000016000	-1.695911000	0.000022000
45	-0.000019000	1.516710000	-0.000014000
17	1.601180000	-3.343859000	0.616311000
17	-1.601113000	-3.343907000	-0.616231000
17	-7.167142000	0.007934000	-0.388125000
17	7.167137000	0.008104000	0.388122000
6	4.668435000	-0.020840000	-0.702934000
1	5.172752000	-0.021494000	-1.670395000
6	3.276835000	-0.033802000	-0.632662000
1	2.699656000	-0.041700000	-1.555183000
6	2.622976000	-0.032878000	0.609009000
6	3.391697000	-0.030922000	1.782754000
1	2.891621000	-0.053095000	2.749970000
6	4.785447000	-0.016352000	1.718498000
1	5.380300000	-0.022509000	2.633258000
6	5.421593000	-0.009424000	0.475307000
7	0.604164000	-1.535381000	-1.940487000
6	0.225025000	-0.353599000	-2.495879000
6	1.356590000	-2.409415000	-2.628805000
1	1.592997000	-3.334590000	-2.100706000
6	1.827461000	-2.119111000	-3.903062000
1	2.443371000	-2.847582000	-4.431524000
6	1.496211000	-0.880673000	-4.476992000
1	1.854110000	-0.622551000	-5.476750000
6	0.689366000	0.006688000	-3.779289000
1	0.371163000	0.959602000	-4.202836000
7	-0.604135000	-1.535350000	1.940528000
6	-0.225021000	-0.353547000	2.495892000
6	-0.689368000	0.006759000	3.779295000
1	-0.371184000	0.959689000	4.202820000
6	-1.356542000	-2.409384000	2.628866000
1	-1.592929000	-3.334577000	2.100789000
6	-1.827418000	-2.119061000	3.903117000
1	-2.443310000	-2.847533000	4.431596000
6	-1.496193000	-0.880604000	4.477019000
1	-1.854096000	-0.622466000	5.476772000
6	-4.668441000	-0.020944000	0.702934000
1	-5.172759000	-0.021601000	1.670394000
6	-3.391700000	-0.031022000	-1.782752000
1	-2.891622000	-0.053194000	-2.749967000
6	-2.622980000	-0.032949000	-0.609007000
6	-3.276841000	-0.033876000	0.632663000

1	-2.699663000	-0.041755000	1.555186000
6	-4.785451000	-0.016483000	-1.718498000
1	-5.380302000	-0.022662000	-2.633259000
6	1.415569000	3.163122000	0.612052000
1	2.176930000	2.630657000	1.175436000
6	1.459340000	3.031199000	-0.766382000
1	2.273613000	2.434887000	-1.174765000
6	-1.415642000	3.163083000	-0.612107000
1	-2.176990000	2.630593000	-1.175484000
6	0.743701000	3.908299000	-1.769858000
1	0.726893000	3.371763000	-2.730259000
1	1.336853000	4.825810000	-1.947378000
6	-1.459411000	3.031178000	0.766329000
1	-2.273671000	2.434855000	1.174721000
6	0.699640000	4.273343000	1.365886000
1	0.709938000	5.193336000	0.763300000
1	1.275994000	4.505462000	2.274175000
6	-0.699737000	4.273310000	-1.365955000
1	-0.710053000	5.193310000	-0.763380000
1	-1.276097000	4.505406000	-2.274246000
6	-0.743791000	3.908308000	1.769793000
1	-0.726972000	3.371786000	2.730201000
1	-1.336962000	4.825809000	1.947299000
6	-5.421598000	-0.009556000	-0.475308000
7	1.189088000	-0.083218000	0.671902000
7	-1.189091000	-0.083259000	-0.671896000
7	0.672251000	0.459624000	1.836927000
7	-0.672263000	0.459568000	-1.836933000

[Rh2(p-Clpap)2(COD)Cl2] (^{3}1b) / *S* = 1 (B3LYP)

45	0.000018000	-1.574424000	- 0.000004000
45	-0.000007000	1.657400000	0.000002000
17	1.553274000	-3.228880000	0.744520000
17	-1.553216000	-3.228901000	-0.744533000
17	-6.979853000	0.267525000	0.781829000
17	6.979869000	0.267608000	-0.781763000
6	4.295863000	0.489926000	-1.211189000
1	4.559161000	0.799461000	-2.223794000
6	2.960961000	0.413283000	-0.819254000
1	2.179672000	0.682721000	-1.530058000
6	2.611759000	0.022526000	0.485014000
6	3.637179000	-0.304883000	1.388788000
1	3.375298000	-0.635917000	2.392239000
6	4.975212000	-0.226447000	1.004026000
1	5.766797000	-0.489168000	1.707627000

6	5.303473000	0.171601000	-0.294603000
7	0.684475000	-1.517190000	-1.929963000
6	-0.033861000	-0.661056000	-2.725015000
6	1.660734000	-2.265317000	-2.453629000
1	2.158062000	-2.938030000	-1.751915000
6	2.011136000	-2.186246000	-3.801179000
1	2.814584000	-2.816124000	-4.184787000
6	1.309898000	-1.298723000	-4.633303000
1	1.561544000	-1.218545000	-5.693536000
6	0.284205000	-0.534165000	-4.101524000
1	-0.308264000	0.151967000	-4.707223000
7	-0.684487000	-1.517203000	1.929936000
6	0.033827000	-0.661056000	2.724999000
6	-0.284269000	-0.534163000	4.101501000
1	0.308180000	0.151978000	4.707210000
6	-1.660747000	-2.265340000	2.453584000
1	-2.158054000	-2.938062000	1.751865000
6	-2.011178000	-2.186265000	3.801127000
1	-2.814626000	-2.816150000	4.184722000
6	-1.309965000	-1.298731000	4.633262000
1	-1.561635000	-1.218550000	5.693490000
6	-4.295847000	0.489898000	1.211221000
1	-4.559139000	0.799447000	2.223824000
6	-3.637178000	-0.304948000	-1.388749000
1	-3.375302000	-0.635997000	-2.392196000
6	-2.611753000	0.022498000	-0.484992000
6	-2.960948000	0.413272000	0.819272000
1	-2.179655000	0.682738000	1.530062000
6	-4.975208000	-0.226528000	-1.003973000
1	-5.766796000	-0.489277000	-1.707560000
6	0.463082000	3.213402000	1.447548000
1	0.570843000	2.673436000	2.387206000
6	1.530361000	3.103175000	0.553103000
1	2.387457000	2.526588000	0.891543000
6	-0.463107000	3.213383000	-1.447561000
1	-0.570863000	2.673405000	-2.387214000
6	1.811027000	4.018491000	-0.614540000
1	2.551703000	3.515684000	-1.255335000
1	2.300042000	4.946607000	-0.261766000
6	-1.530386000	3.103156000	-0.553116000
1	-2.387477000	2.526558000	-0.891550000
6	-0.552656000	4.347672000	1.442440000
1	-0.072814000	5.264395000	1.067551000
1	-0.845745000	4.565388000	2.480777000
6	0.552622000	4.347661000	-1.442467000
1	0.072772000	5.264385000	-1.067587000

1	0.845709000	4.565368000	-2.480806000
6	-1.811060000	4.018484000	0.614517000
1	-2.551732000	3.515678000	1.255317000
1	-2.300081000	4.946592000	0.261732000
6	-5.303461000	0.171539000	0.294652000
7	1.233912000	-0.060781000	0.864114000
7	-1.233909000	-0.060792000	-0.864109000
7	1.070976000	0.035267000	2.215533000
7	-1.071003000	0.035254000	-2.215530000

[Rh2(p-Clpap)2(COD)Cl2] (^{BS}1b) / *S* = 0 (BH and HLYP)

45	0.000082000	-1.582757000	-0.000011000
45	-0.000022000	1.628512000	-0.000030000
17	1.539295000	-3.214275000	0.753454000
17	-1.539105000	-3.214343000	-0.753468000
17	-6.938297000	0.233770000	0.731219000
17	6.938389000	0.233925000	-0.730928000
6	4.280505000	0.472795000	-1.184721000
1	4.554510000	0.784301000	-2.185051000
6	2.949812000	0.403908000	-0.810012000
1	2.185346000	0.680708000	-1.523870000
6	2.585578000	0.010471000	0.477305000
6	3.590407000	-0.328459000	1.381205000
1	3.320043000	-0.665054000	2.371428000
6	4.924933000	-0.255467000	1.014615000
1	5.700465000	-0.525233000	1.720657000
6	5.268435000	0.145524000	-0.266699000
7	0.697954000	-1.506613000	-1.915360000
6	0.001005000	-0.642939000	-2.688579000
6	1.667114000	-2.244160000	-2.435364000
1	2.153227000	-2.926531000	-1.748696000
6	2.030552000	-2.140514000	-3.768849000
1	2.830603000	-2.759018000	-4.154275000
6	1.344464000	-1.241221000	-4.582270000
1	1.604070000	-1.141474000	-5.630329000
6	0.321489000	-0.488489000	-4.048102000
1	-0.260484000	0.204758000	-4.640550000
7	-0.697931000	-1.506597000	1.915283000
6	-0.001038000	-0.642900000	2.688535000
6	-0.321624000	-0.488395000	4.048026000
1	0.260300000	0.204880000	4.640490000
6	-1.667131000	-2.244118000	2.435245000
1	-2.153194000	-2.926512000	1.748565000
6	-2.030665000	-2.140424000	3.768702000
1	-2.830750000	-2.758912000	4.154085000

6	-1.344639000	-1.241110000	4.582146000
1	-1.604326000	-1.141327000	5.630181000
6	-4.280396000	0.472736000	1.184851000
1	-4.554355000	0.784280000	2.185182000
6	-3.590415000	-0.328649000	-1.381061000
1	-3.320099000	-0.665316000	-2.371271000
6	-2.585544000	0.010380000	-0.477240000
6	-2.949721000	0.403866000	0.810077000
1	-2.185226000	0.680705000	1.523891000
6	-4.924926000	-0.255667000	-1.014408000
1	-5.700484000	-0.525507000	-1.720393000
6	0.562578000	3.228469000	1.421467000
1	0.702500000	2.682954000	2.343185000
6	1.561644000	3.112177000	0.490380000
1	2.418740000	2.520803000	0.770070000
6	-0.562622000	3.228472000	-1.421537000
1	-0.702548000	2.682956000	-2.343255000
6	1.765056000	3.983122000	-0.717066000
1	2.431924000	3.444867000	-1.394651000
1	2.302565000	4.897105000	-0.432803000
6	-1.561689000	3.112179000	-0.490453000
1	-2.418789000	2.520807000	-0.770147000
6	-0.469055000	4.335052000	1.451862000
1	-0.030176000	5.245606000	1.040454000
1	-0.700892000	4.563134000	2.494714000
6	0.469017000	4.335050000	-1.451939000
1	0.030131000	5.245612000	-1.040554000
1	0.700862000	4.563111000	-2.494793000
6	-1.765098000	3.983103000	0.717009000
1	-2.431938000	3.444821000	1.394601000
1	-2.302639000	4.897076000	0.432772000
6	-5.268370000	0.145394000	0.266898000
7	1.208639000	-0.064234000	0.838617000
7	-1.208623000	-0.064334000	-0.838612000
7	1.040339000	0.040388000	2.173293000
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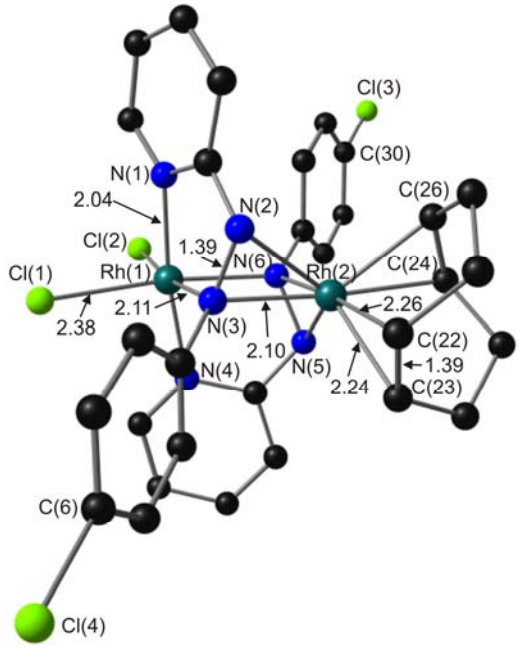

Figure S-7. Optimized (B3LYP) molecular structure (incl. selected bond lengths) of complex ^{1}**1b** in the closed-shell singlet ground state (S = 0). Hydrogen atoms have been omitted for clarity.

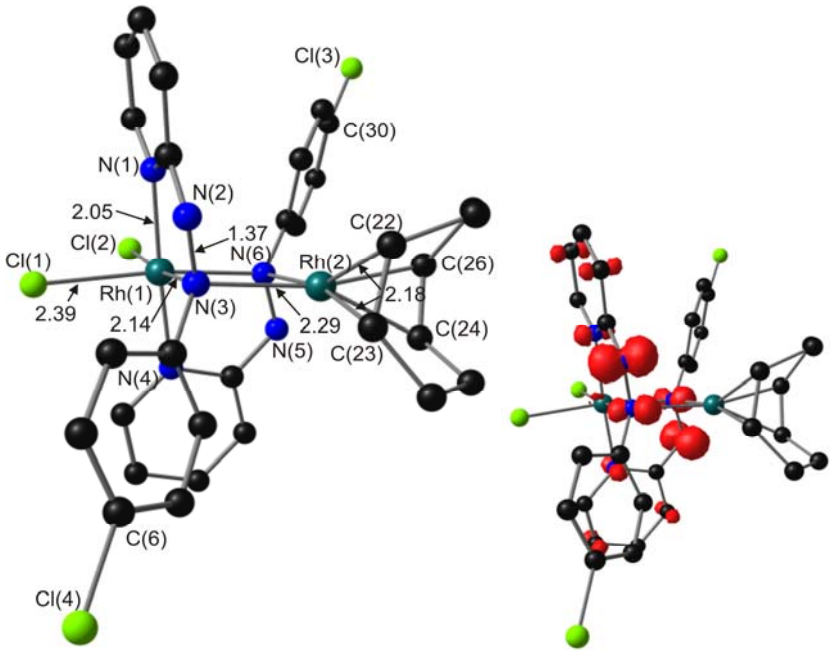

Figure S-8. Left: optimized (B3LYP) molecular structure (incl. selected bond lengths) of complex ^{3}**1b** corresponding to the triplet electronic state (S = 1). Right: plot of the Mulliken spin density. Hydrogen atoms have been omitted for clarity.

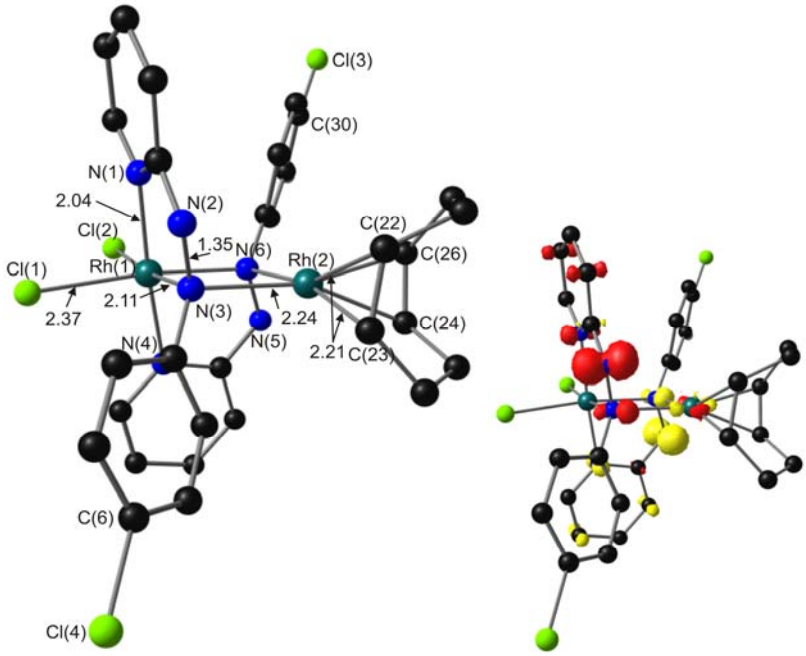

Figure S-9. Left: optimized (BH and HLYP) molecular structure (incl. selected bond lengths) of complex ^{BS}**1b** corresponding to the broken symmetry singlet state (M_s = 0). Right: plot of the Mulliken spin density. Hydrogen atoms have been omitted for clarity.

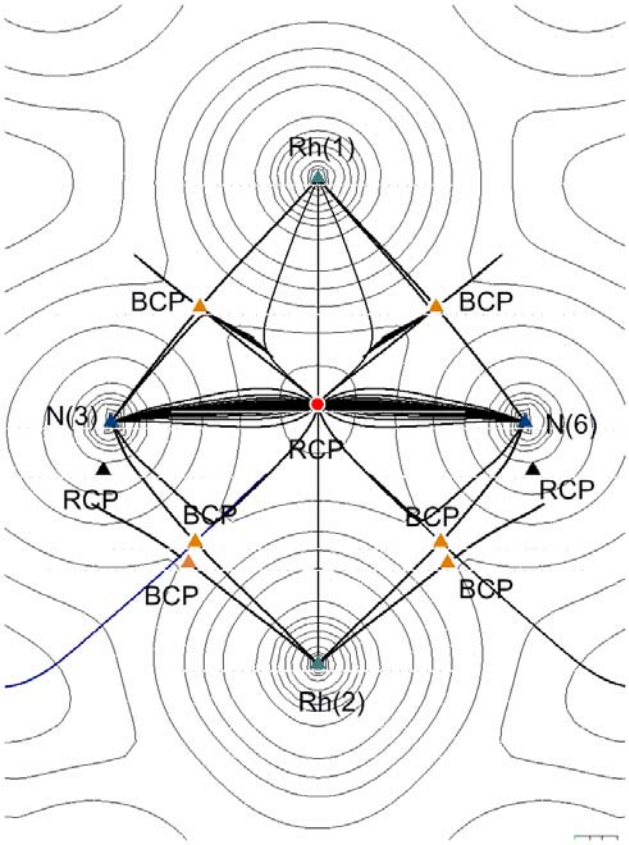

Figure S-10. Contour plot of the electron density ρ of complex **[1]1b** in the Rh(1)-N(3)-N(6)-Rh(2) plane, including ring critical points (RCP) and bond critical points (BCP). Note that the 4 atoms, the central RCP (●) as well as the 4 BCP connecting Rh(1), N(3), Rh(2) and N(6) lie in the same plane, whereas the remaining RCPs and BCPs lie above or below the plane in 3-D and are projected onto it in this representation.

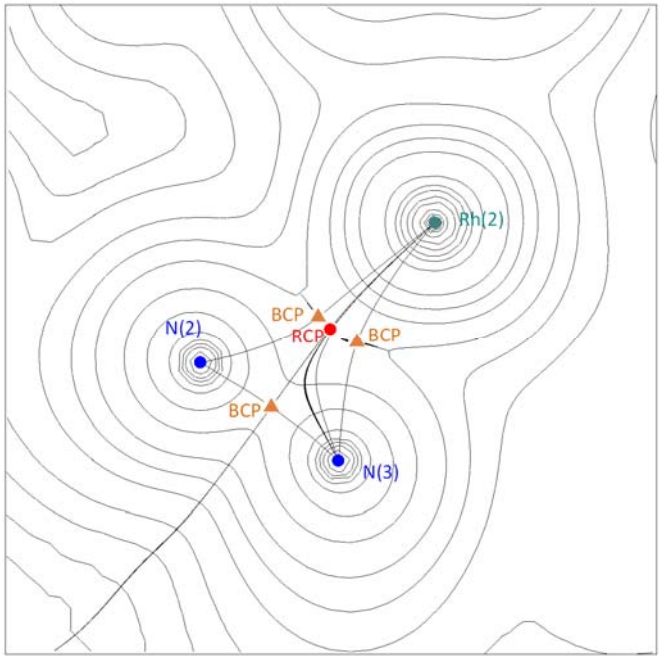

Figure S-11. Contour plot of the electron density ρ of complex **[1]1b** in the Rh(2)-N(2)-N(3) plane, including ring critical points (RCP) and bond critical points (BCP). Note the presence of BCPs between Rh and both nitrogen atoms, consistent with a 'metallacycle' formulation for the $Rh(N_2)$ unit.