

Synthesis, structure and DFT study of a pyrazolate stabilized mononuclear
Rh(II) complex

William J. McCarty, Richard A. Jones* and Xiaoping Yang

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX
78712.

Supplementary material:

General procedures

All reactions were performed under a dry, oxygen-free nitrogen atmosphere or under vacuum using standard Schlenk line and dry box techniques. All solvents were dried prior to use by distillation from sodium benzophenone ketyl under nitrogen. 3,5-bis(trifluoromethyl)pyrazole¹, was prepared according to literature procedures. Anhydrous RhCl₃ was prepared from RhCl₃·nH₂O and SOCl₂ in diethyl ether according to the literature procedure² and used immediately in the next step. ESIMS were collected on a Finnigan MAT TSQ 700 mass spectrometer. NMR spectra were recorded on a Varian 300 Unity Plus spectrometer 300 MHz at 298 K. Chemical shifts are referenced to the deuterated solvent. Infrared spectra were taken on a Nicolet IR 200 FTIR spectrometer between KBr plates.

Synthesis of [Li(THF)]₂ Rh(μ-3,5-(CF₃)₂Pz)₄ (1)

A solution of n-butyllithium (0.95 mL, 1.6 M) in hexane was added dropwise to a solution of 3,5-bis(trifluoromethyl)pyrazole (0.31 g, 1.51 mmol) in THF (25 ml) at -78 °C. This was allowed to warm to room temperature and was then stirred for 3 hours. This solution was added dropwise to a heterogeneous solution of anhydrous RhCl₃ (from 0.1 g RhCl₃ · nH₂O, 0.38mmol) in 10 mL diethyl ether. The resulting reaction mixture was stirred for 12 h at room temperature. During this time the color of the mixture changed from red to dark yellow. The mixture was then filtered. The filtrate was evaporated to dryness under vacuum and the residue was extracted with hexane (3 × 10mL). The extracts were combined and X-ray quality crystals were grown by slow evaporation of this yellow solution under N₂. Isolated: 0.18g, 44%; mp 126-127 °C. (dec.); ¹H-NMR (300 MHz, δ, CDCl₃): 6.59 (s, br, Pz-H), 3.46 (s, br, THF-CH₂O), 1.85 (s, br, THF-CH₂); ¹⁹F-NMR (CDCl₃): δ -60.7 (s, br), -61.2 (s, br); FT-IR (KBr, cm⁻¹):

1016 (s), 1128 (m), 1261 (w), 2964 (w), 1379 (m), 1450 (m); HRMS (chemical ionization) m/e 1005 [$M^+ - CF_3$], 859 [$M^+ - CF_3 - 2 THF$], 769 [$M^+ - 2CF_3 - 2 THF - Li$]. Calcd. for $C_{28}H_{20}F_{24}Li_2N_8O_2Rh$: C, 31.3; H, 1.9; N, 10.4, found C 30.8; H 1.8; N 10.0 %.

Single Crystal X-Ray Diffraction Analysis

Data was collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package. The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined.

X-Band EPR Studies of **1**

EPR data were collected on a Bruker EMX Pro with a liquid nitrogen cooled cryostat. Samples dissolved in dry, degassed toluene were transferred to a quartz EPR tube and quickly frozen and immediately used.

Electrochemical Studies of **1**

All electrochemical studies of complex **1** were performed in 0.1 M [TBA][PF₆] in methylene chloride or acetonitrile under a nitrogen atmosphere in a dry-box using a GPES system from Eco. Chemie B. V. Cyclic voltammograms were recorded against a ferrocene external standard with a Ag/AgNO₃ non-aqueous reference electrode, a Pt button working electrode (1.6 mm diameter), and a Pt wire coil counter electrode.

DFT Calculations of **1**

All calculations were performed with the Gaussian 03 suite of programs³. Initial atomic coordinates from the X-ray crystallographic data were input and the geometry was optimized using the B3LYP hybrid density functional method⁴ with the LANL2DZ basis set⁵. A single point energy calculation was performed at the same level of theory on the geometry optimized structures to produce graphical representations of molecular orbitals (all calculated with a 0.04 isovalue).

The singularly occupied molecular orbital (SOMO) of Complex **1** is shown with an isovalue of 0.04 in Figure S2. The tilted orientation of each pyrazolate ring with respect to the xy plane of the complex (121°) leads to efficient overlap of the ligand based π orbitals with the d_{xy} orbital on the metal, resulting in the formation of a bonding and anti-bonding pair of molecular orbitals. This orientation also diminishes the overlap with d_{xz} and d_{z^2} orbitals on the metal, rendering these predominantly non bonding. The result of this interaction is the placement of the unpaired electron in an $L_\pi + d_{xy}$ antibonding orbital of relatively high energy with substantial ligand and metal character. Optimized structural coordinates of **1** are listed in Table S1.

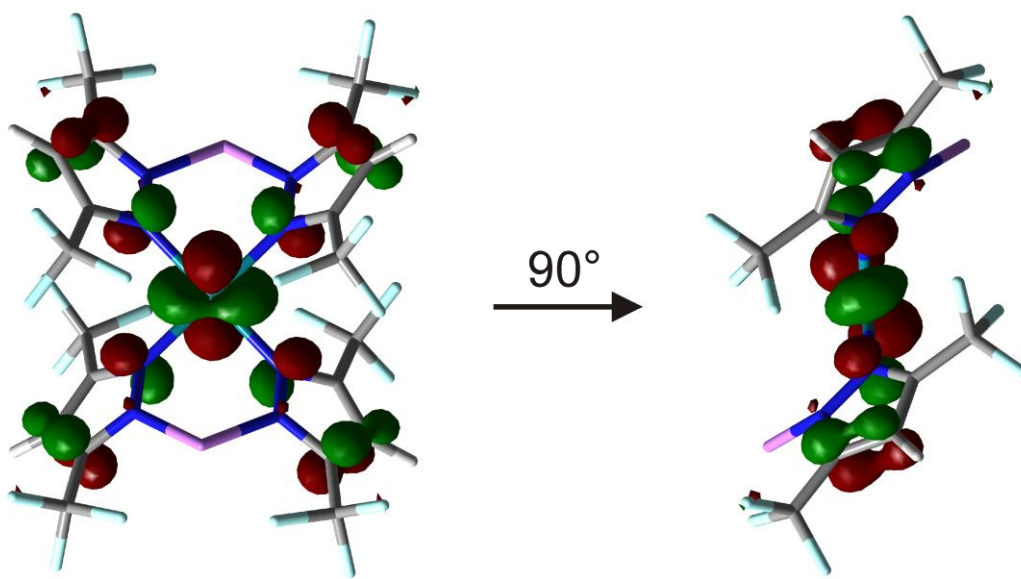


Figure S1. Top and side view of the SOMO of Complex **1**.

Table S1. B3LYP/LANL2DZ optimized structural coordinates for Complex 1.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	45	0	0.000000	0.000000	0.000000
2	9	0	1.756130	3.574230	0.762926
3	9	0	2.673725	1.538857	0.501905
4	6	0	-1.443454	-3.149242	2.586713
5	1	0	-2.050781	-3.991637	2.877453
6	9	0	2.625508	-1.600640	0.566234
7	6	0	2.259597	-2.792998	-0.092669
8	9	0	-3.538944	-3.327943	0.571613
9	6	0	-1.352681	3.282355	2.467944
10	1	0	-1.934987	4.152420	2.726619
11	6	0	1.443454	3.149242	-2.586713
12	1	0	2.050781	3.991637	-2.877453
13	9	0	0.757285	-1.494172	5.120426
14	7	0	-0.513206	1.491115	1.341961
15	7	0	-0.065361	1.433796	-2.607651
16	6	0	-0.460464	-2.471726	3.326647
17	6	0	2.339262	2.718755	-0.195482
18	7	0	0.104928	1.525279	2.553515
19	6	0	-1.469960	-2.450391	1.367982
20	9	0	0.966034	-3.723150	4.844589
21	9	0	0.800409	1.657494	5.061836
22	7	0	0.553067	1.425812	-1.395878
23	7	0	0.065361	-1.433796	2.607651
24	9	0	1.071131	3.868481	4.706378
25	6	0	1.352681	-3.282355	-2.467944
26	1	0	1.934987	-4.152420	-2.726619
27	6	0	1.399511	-2.540434	-1.275501
28	6	0	-2.339262	-2.718755	0.195482
29	6	0	0.051397	-2.677330	4.702459
30	6	0	-0.390234	2.603745	3.233423
31	6	0	0.127530	2.844136	4.601392
32	7	0	-0.553067	-1.425812	1.395878
33	6	0	0.460464	2.471726	-3.326647
34	6	0	1.469960	2.450391	-1.367982
35	9	0	-0.865076	3.122967	5.539436
36	9	0	1.651751	-3.600367	0.891963
37	9	0	-2.673725	-1.538857	-0.501905
38	9	0	3.538944	3.327943	-0.571613
39	9	0	-1.756130	-3.574230	-0.762926
40	7	0	-0.104928	-1.525279	-2.553515
41	7	0	0.513206	-1.491115	-1.341961
42	6	0	0.390234	-2.603745	-3.233423
43	9	0	-0.948245	-2.894511	5.649336
44	9	0	3.442582	-3.447154	-0.445767
45	3	0	-0.956356	-0.051620	-3.550970
46	3	0	0.956356	0.051620	3.550970
47	9	0	-2.625508	1.600640	-0.566234
48	9	0	-0.966034	3.723150	-4.844589
49	9	0	-3.442582	3.447154	0.445767

50	9	0	-0.757285	1.494172	-5.120426
51	9	0	-1.651751	3.600367	-0.891963
52	9	0	-1.071131	-3.868481	-4.706378
53	6	0	-1.399511	2.540434	1.275501
54	9	0	-0.800409	-1.657494	-5.061836
55	6	0	-2.259597	2.792998	0.092669
56	6	0	-0.051397	2.677330	-4.702459
57	6	0	-0.127530	-2.844136	-4.601392
58	9	0	0.865076	-3.122967	-5.539436
59	9	0	0.948245	2.894511	-5.649336

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