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Novel redox active rhodium(III) complex with bis(arylimino)acenaphthene ligand: synthesis, structure and electrochemical studies

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EXPERIMENTAL SECTION

General Procedures. All the experiments were carried out in air. All commercially available reagents ($RhCl_3 \cdot 3H_2O$) were used as purchased. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) was prepared as reported [S1]. Organic solvents (MeOH, CH_2Cl_2, MeCN, Et_2O and hexane) were dried by standard methods before use.

Physical Measurements. Elemental C, H, N analyses were performed with a EuroEA3000 Eurovector analyzer. IR spectra were recorded in the 4000–300 cm^{-1} range with a Perkin–Elmer System 2000 FTIR spectrometer with samples in KBr pellets. ^1H NMR spectra were acquired on a Bruker Avance-500 spectrometer with a 5mm PABBO-PLUS probe. The chemical shifts were given in parts per million from $SiMe_4$. The cyclic voltammograms (CV) were recorded with a 797 VA Computrace system (Metrohm, Switzerland). All measurements were performed with a conventional three-electrode configuration consisting of glassy carbon working and platinum auxiliary electrodes and an Ag/AgCl/KCl reference electrode. The solvent used in all experiments was MeCN which was deoxygenated before use. Tetra-*n*-butylammonium hexafluorophosphate (0.1 *M* solution) was used as a supporting electrolyte. The concentration of the complex **1** was $1 \cdot 10^{-3}$ M. Redox potential values ($E_{1/2}$) were determined as $(E_a + E_c)/2$, where E_a and E_c are anodic and cathodic peak potentials, respectively. For experiments with carbon dioxide, the solution of **1** in CH_3CN was saturated with CO_2 by bubbling for 20 min.

Synthesis of $[Rh(dpp\text{-}bian)(H_2O)Cl_3] \cdot CH_2Cl_2$ ($1 \cdot CH_2Cl_2$)

Salt $RhCl_3 \cdot 3H_2O$ (70 mg, 0.308 mmol) and dpp-bian (154 mg, 0.308 mmol) were dissolved in MeOH (30 ml). The mixture was stirred at reflux for 12 hours. The resulting dark red solution was taken to dryness by rotary evaporation, and the solid residue was re-dissolved in dichloromethane (5 ml). The analytically pure product was obtained by adding a large excess of hexane to the solution in dichloromethane. Yield: 100 mg (40%). Crystals suitable for XRD were obtained by slow evaporation of the dichloromethane solution. Anal. Calc. for $C_{37}H_{44}N_2Cl_5ORh$: C, 54.6; H, 5.5; N, 3.5%. Found: C, 54.2; H, 5.6; N, 3.8%. IR (KBr, ν, cm^{-1}): 3347(w), 3176(m), 3058(w), 2970(s), 2928(s), 2865(m), 1659(w), 1619(w), 1597(m), 1570(m), 1487(w), 1463(m), 1434(m), 1417(m), 1383(m), 1361(m), 1324(w), 1293(m), 1273(m), 1221(w), 1181(w), 1148(w), 1085(w), 1058(w), 1042(w), 961(w), 938(w), 834(s), 799(s), 781(s), 758(s), 728(s), 698(m), 647(w), 624(w), 546(m), 481(w), 408(w). ^1H NMR (500 MHz, 298 K, DMSO-d_6): δ 0.57-0.73 (m, 12H, CH_3 (ipr)), 1.20-1.36 (m, 12H, CH_3 (ipr), 3.75-4.05 (m, 4H, CH (ipr)), 6.29-6.54 (m, 2H, H_3), 7.35-7.75 (m, 8H, $H_{4,10,11,12}$), 8.30-8.39 (m, 2H, H_5) ppm. UV/vis (DMF, λ_{max}, nm (ε)): 285 ($2.8 \cdot 10^4$), 359 sh ($7.0 \cdot 10^3$), 451 ($3.8 \cdot 10^4$).

Computational details. Geometry optimization of complex **1** and its oxidized (**1**$^{+}$) and reduced (**1**$^{-}$) species as well as double reduced Rh(I) complex, [Rh(bian)(H_2O)Cl], was performed in ADF2017 [S2,S3] program suit with BLYP [S4–S7] density functional, Grimme D3BJ [S8] dispersion correction and all-electron TZP [S9] basis set. Zero order regular approximation (ZORA) [S10] and Conductor like Screening Model (COSMO) [S11] were used to take into account scalar relativistic effects and acetonitrile environment, respectively. All geometries were optimized at C_1 symmetry and characterized by the absence of imaginary frequencies. Spin unrestricted method were used for **1**$^{+}$ and **1**$^{-}$ species. In order to analyze molecular orbitals, geometries optimized at BLYP+D3BJ/TZP level of theory were used for single point calculations with hybrid B3LYP [S12] density functional, Grimme D3BJ dispersion correction, all-electron TZP basis set, ZORA and COSMO.

Single-crystal X-ray analysis

The diffraction data for **1**·CH_2Cl_2 were collected on a Bruker Apex Duo diffractometer with MoKα radiation (λ = 0.71073) by doing φ and ω scans of narrow (0.5°) frames at 150 K. Absorption correction was done empirically using SADABS [S13]. Crystallographic data and refinement details for **1**·CH_2Cl_2 are given in Table S1.

The structure was solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2017/1 [S14] in ShelXle program [S15]. Hydrogen atoms were refined in geometrically calculated positions.

In the crystal structure of **1**·CH_2Cl_2 there is a positional disordering of H_2O and Cl^- in two terminal sites of Rh. In the case of O1/Cl4 calculated occupancies are 0.8/0.2 which gives dividing of H_2O and Cl^- positions. In the case of O2/Cl3 calculated occupancies were found as 0.2/0.8 and positions of H_2O and Cl^- cannot be divided.

The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition code CCDC 1849307.

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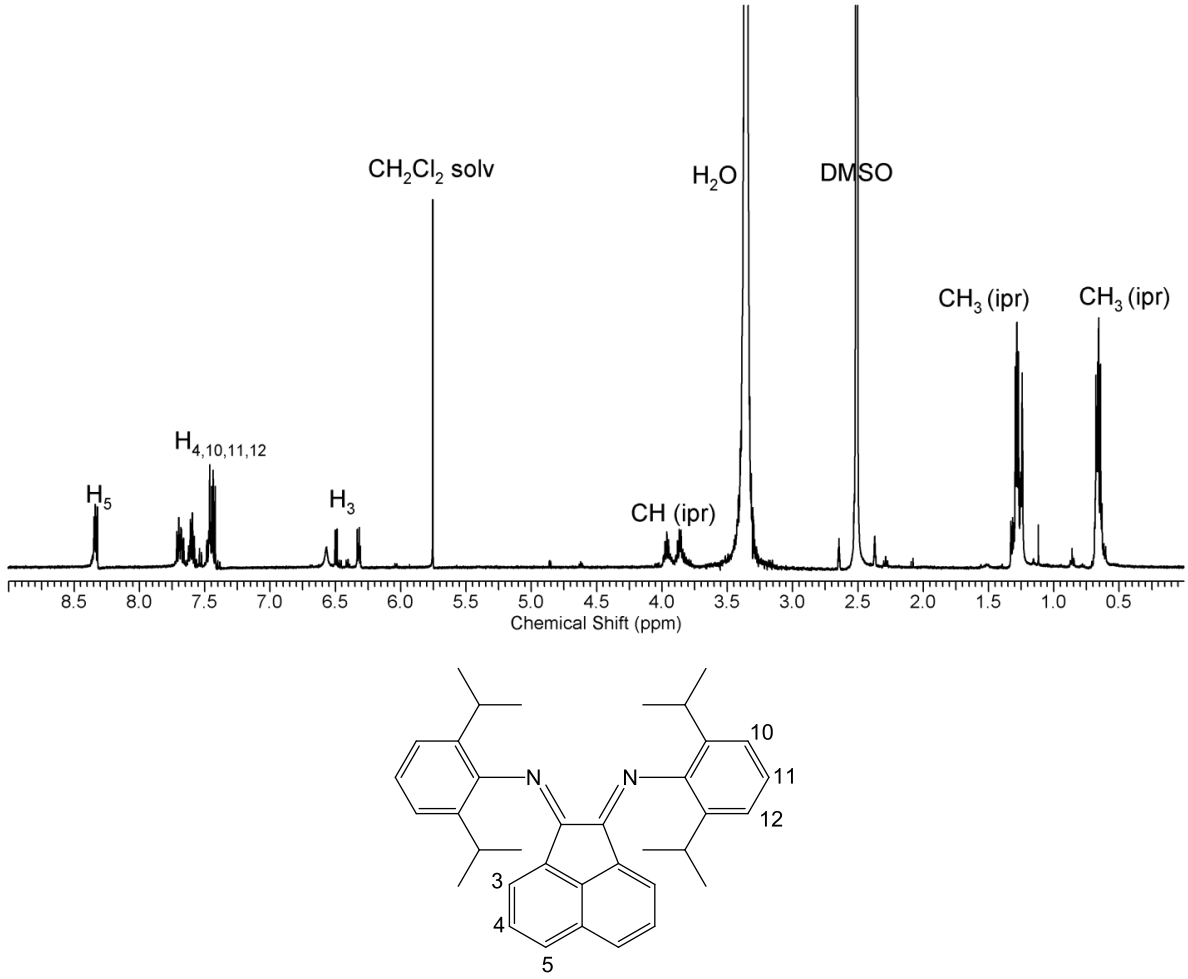

Figure S1. [1]H NMR spectrum of **1** in DMSO-d_6 and peak assignments

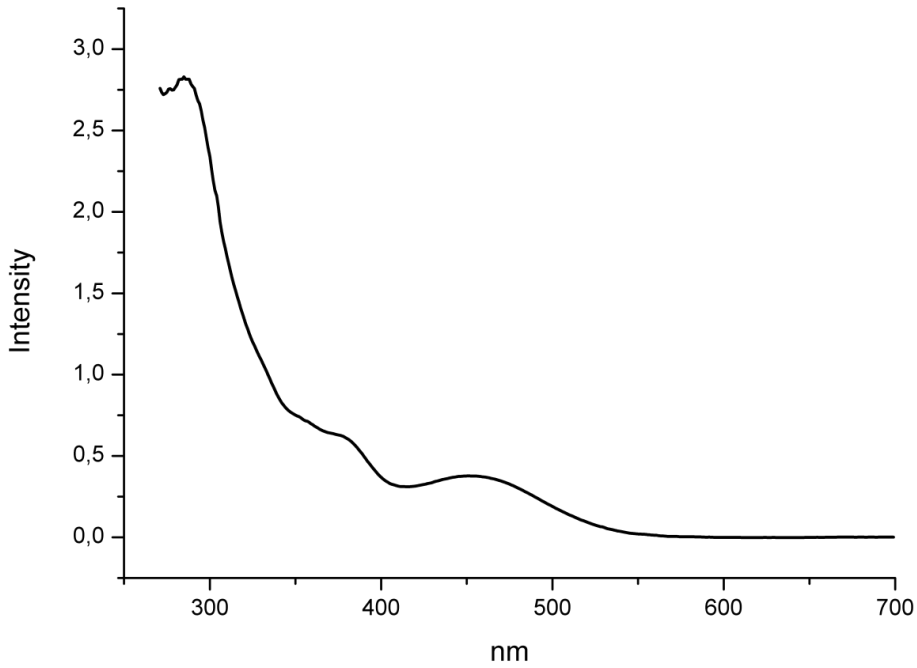

Figure S2. UV−vis spectrum of **1** in DMF

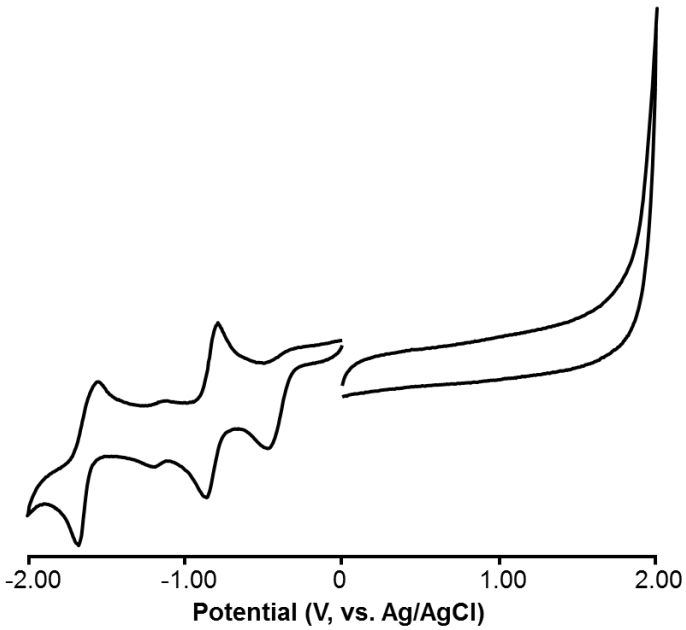

Figure S3. Cyclic voltammogram of 1 mM solution of **1** in CH_3CN in the ranges from 0 to 2.0 V and from 0 to -2.0 V with a scan rate of 100 mV/s

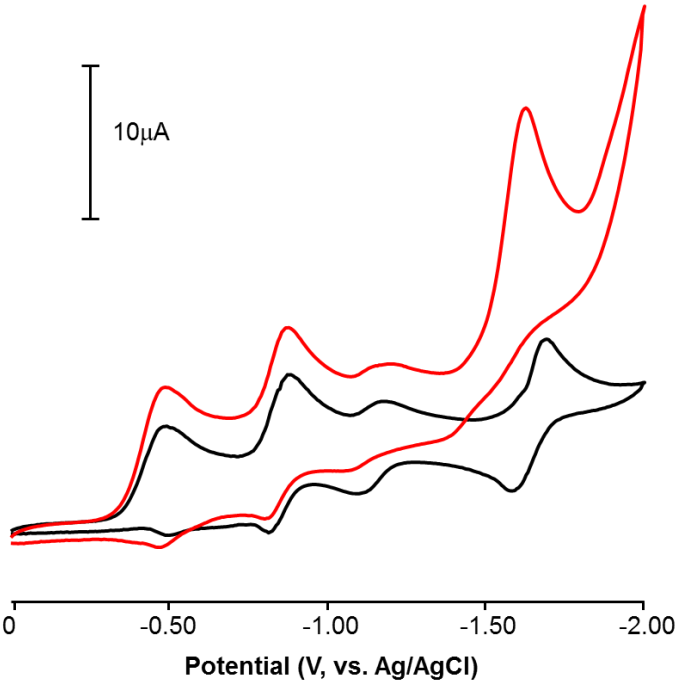

Figure S4. Cyclic voltammograms of 1 mM solution of **1** in CH_3CN recorded in Ar (black line), and in the presence of CO_2 (red line), scan rate 100 mV/s. No peaks were found in the cyclic voltammogram of a saturated solution of CO_2 in CH_3CN without **1** in the range from 0 to -2 V

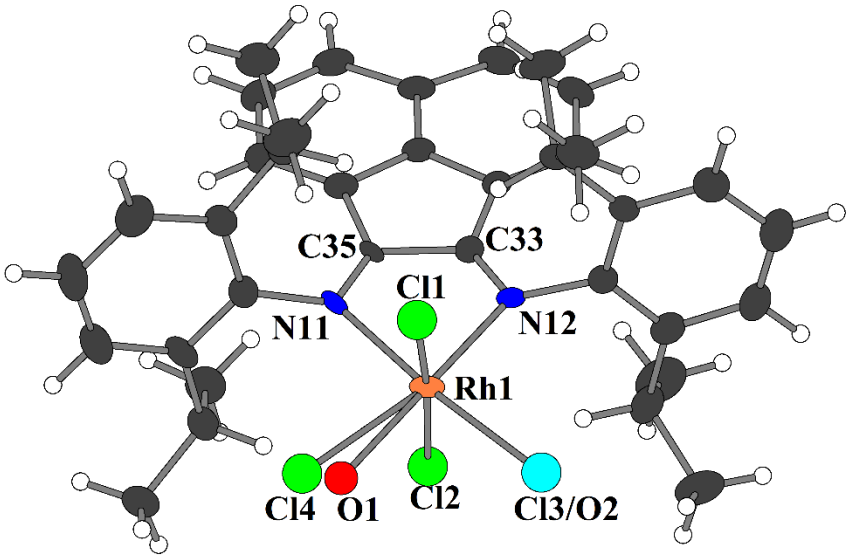

Figure S5. Molecular structure of **1** showing a positional disordering of H_2O and Cl^- in two terminal sites of Rh.

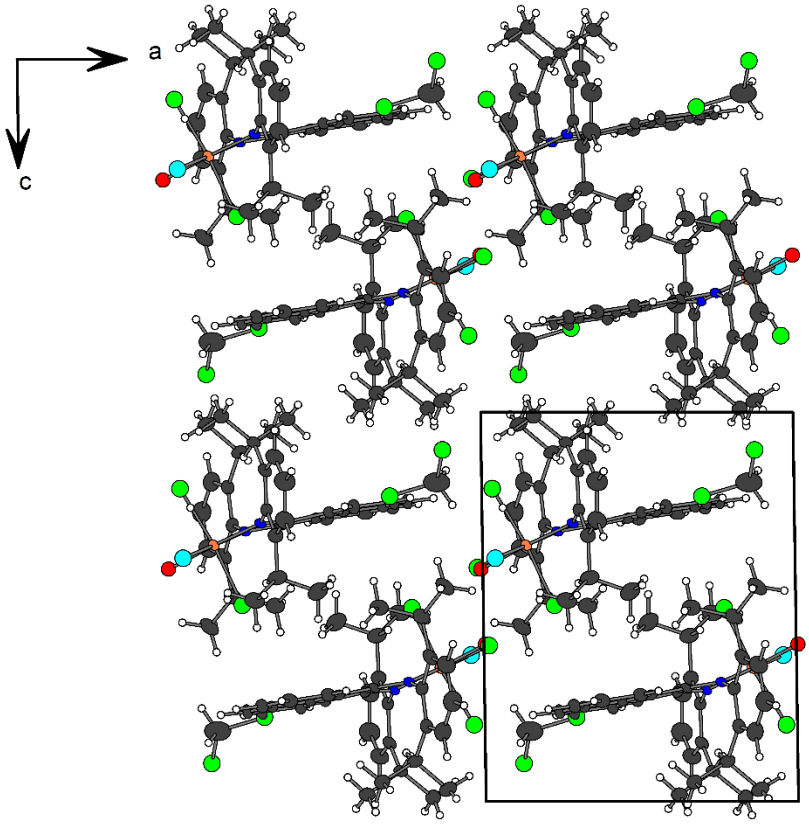

Figure S6. Crystal packing for **1**·CH_2Cl_2

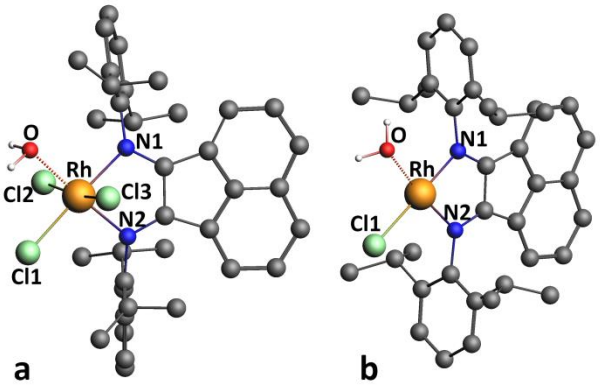

Figure S7. Optimized structure of $\mathbf{1}^0$ and [Rh^I(dpp-bian)(H_2O)Cl] complexes

Table S1. Summary of crystal data for **1**·CH_2Cl_2.

	1·CH_2Cl_2
Empirical formula	$C_{37}H_{44}Cl_5N_2ORh$
M_r	812.90
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, *b*, *c* (Å)	11.191 (4), 12.066 (4), 14.055 (5)
α, β, γ (°)	76.987 (11), 86.812 (10), 79.358 (11)
V (Å^3)	1817.2 (11)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	0.87
Crystal size (mm)	0.33 × 0.29 × 0.23
Diffractometer	Bruker Apex Duo
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.670, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14696, 7277, 5146
R_{int}	0.037
θ values (°)	θ_{max} = 27.1, θ_{min} = 1.8
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642
Range of *h*, *k*, *l*	$-14 \le h \le 13$, $-15 \le k \le 15$, $-17 \le l \le 17$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.057, 0.200, 0.98
No. of reflections, parameters, restraints	7277, 409, 0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.17, -1.76

Table S2. Selected geometric parameters (Å) for **1**·CH_2Cl_2.

Rh1—O1	2.048 (5)	Cl2—Rh1	2.3423 (13)
N11—Rh1	2.067 (4)	Cl3/O2—Rh1	2.3362 (16)
N12—Rh1	2.033 (4)	Cl4—Rh1	2.452 (10)
Cl1—Rh1	2.3176 (13)	C33–N12	1.307(6)
C33–C35	1.487(7)	C35–N11	1.293(6)

Table S3. Selected interatomic distances (*d*, Å) calculated at BLYP+D3BJ/TZP for $\mathbf{1}^n$ (n = 0, -1, +1) and [Rh^I(dpp-bian)(H_2O)Cl].

	$\mathbf{1}^0$	$\mathbf{1}^-$	$\mathbf{1}^+$	[Rh^I(dpp-bian)(H_2O)Cl]
Rh-N1	2.10	2.10	2.13	2.01
Rh-N2	2.05	2.06	2.06	2.0
Rh-Cl1	2.41	2.46	2.37	2.40
Rh-Cl2	2.40	2.41	2.37	-
Rh-Cl3	2.41	2.43	2.37	-
Rh-O	2.17	2.21	2.17	2.18