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

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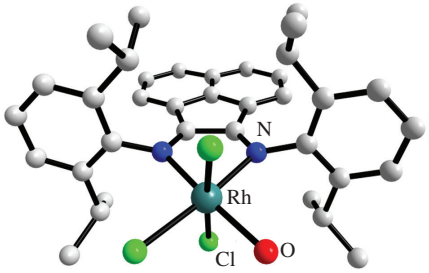
Rhodium trichloride reacts with 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene (dpp-bian) to afford new octahedral complex *mer*-[Rh(dpp-bian)(H_2O)Cl_3]·CH_2Cl_2. The CV of *mer*-[Rh(dpp-bian)(H_2O)Cl_3] in MeCN shows an irreversible reduction that corresponds to the Rh^{III}/Rh^{I} couple, followed by reversible or quasi-reversible cathodic waves assigned to reduction of the dpp-bian ligand. DFT calculations confirm the assignment of the redox processes and predict the elimination of two chloride ligands from axial positions upon two-electron reduction of *mer*-[Rh(dpp-bian)(H_2O)Cl_3] with the formation of a Rh^{I} square-planar complex [Rh^{I}(dpp-bian)(H_2O)Cl].



Keywords: rhodium, acenaphthene-1,2-diimines, crystal structure, cyclic voltammetry, DFT calculations, electrocatalyzed CO_2 reduction.

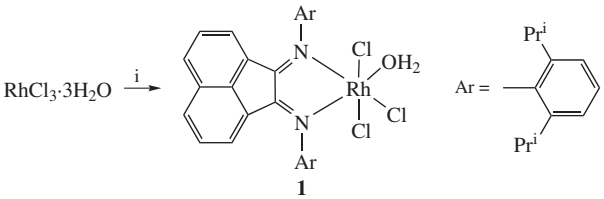
Rhodium(III) diimine complexes have gained considerable attention due to their relevance in catalysis[1–3] and photophysics.[4,5] Their ability to electrochemically activate CO_2 also has been assessed.[6–8] Bis(imino)acenaphthenes (BIANs) are well known redox active α-diimines that have been exploited widely as N,N-bidentate ligands in coordination chemistry and catalysis.[9–12] The key characteristic of BIANs as strong π-acceptor molecules is their ability to reversibly accept up to four electrons, and reversibly exchange electrons with the coordinated metal, which can trigger redox based chemical processes. The complexes with BIANs have been studied in olefin polymerization reactions as post-metallocene catalysts,[13,14] and have been shown to be catalytically active in many other organic transformations.[15,16] In addition, a reversible metal-to-ligand electron transfer (redox isomerism or valence tautomerism) has been established in such metal complexes.[12,17–19]

An important feature of the interaction between BIANs as redox active ligands and late transition metal ions is the energetic proximity of the metal *d* orbitals and the frontier ligand orbitals, which can lead to complicated, non-additive electronic properties of the resulting complexes. Indeterminacy in the assignment of metal and ligand oxidation states often originates here, prompting the description of BIANs as non-innocent ligands.[20] A number of late transition metal complexes (especially, those of 10 and 11 group metals) with BIANs have been prepared and thoroughly studied.[21–23] However, the 9 group metal complexes with BIANs, especially those of rhodium[24–26] and iridium[27–29] remain scarcely explored. In fact, there are only few reports on Rh-BIAN complexes.[24–26] Their first description included [Rh^{I}(CO)(dpp-bian)Cl] (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and its spectroscopic data.[25] Later, [Rh^{III}(Cp*)(Ph-bian)(Cl)]BF_4 was synthesized and its catalytic activity in reduction of terephthalaldehyde under aqueous aerobic conditions was studied.[24] Optoelectronic properties of some iridium complexes with BIAN ligands have been reported.[28]

We report here that the reaction of equimolar amounts of $RhCl_3·3H_2O$ with dpp-bian in methanol at 65 °C followed by recrystallization from CH_2Cl_2 yields new complex *mer*-[Rh(dpp-bian)(H_2O)Cl_3]·CH_2Cl_2 (**1**·CH_2Cl_2) (Scheme 1).

The IR spectrum of complex **1** shows that the ν(C=N) bands shift to lower wavenumbers, indicating the coordination of diimine nitrogen atoms of dpp-bian ligand to Rh^{III}. In the ^{1}H NMR spectrum, the protons associated with the aromatic moiety of dpp-bian are slightly downfield shifted as compared to uncoordinated dpp-bian.

The molecular structure of **1**·CH_2Cl_2 (Figure 1) was ultimately established by single-crystal X-ray diffraction at 150 K.† The coordination environment around rhodium is a distorted octahedron,



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Scheme 1 *Reagents and conditions*: dpp-bian, MeOH, 65 °C, 12 h.

† *Crystal data for* **1**. $C_{37}H_{44}C_{l5}N_2ORh$, M_r = 812.90, triclinic, space group $P\bar{1}$, a = 11.191(4), b = 12.066(4) and c = 14.055(5) Å, α = 76.987(11)°, β = 86.812(10)°, γ = 14.055(5)°, V = 1817.2(11) Å^3, Z = 2, crystal size 0.33×0.29×0.23 mm, μ = 0.87 mm^{-1}, the final R = 0.057, wR = 0.200 and S = 0.98 for 7277 observed reflections with $I > 2\sigma(I)$. The measurements were performed on a Bruker Apex Duo diffractometer with MoKα radiation (λ = 0.71073) using φ and ω scans of narrow (0.5°) frames at 150 K. Absorption correction was done empirically using SADABS. The structure was solved by direct method and refined by full-matrix least-squares treatment against

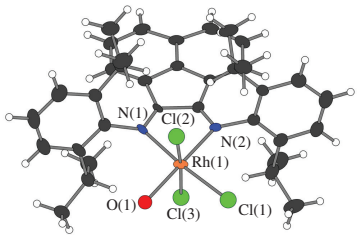


Figure 1 ORTEP representation of *mer*-[Rh(dpp-bian)(H_2O)Cl_3] **1** (50% probability ellipsoids).

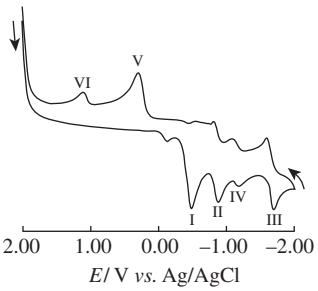
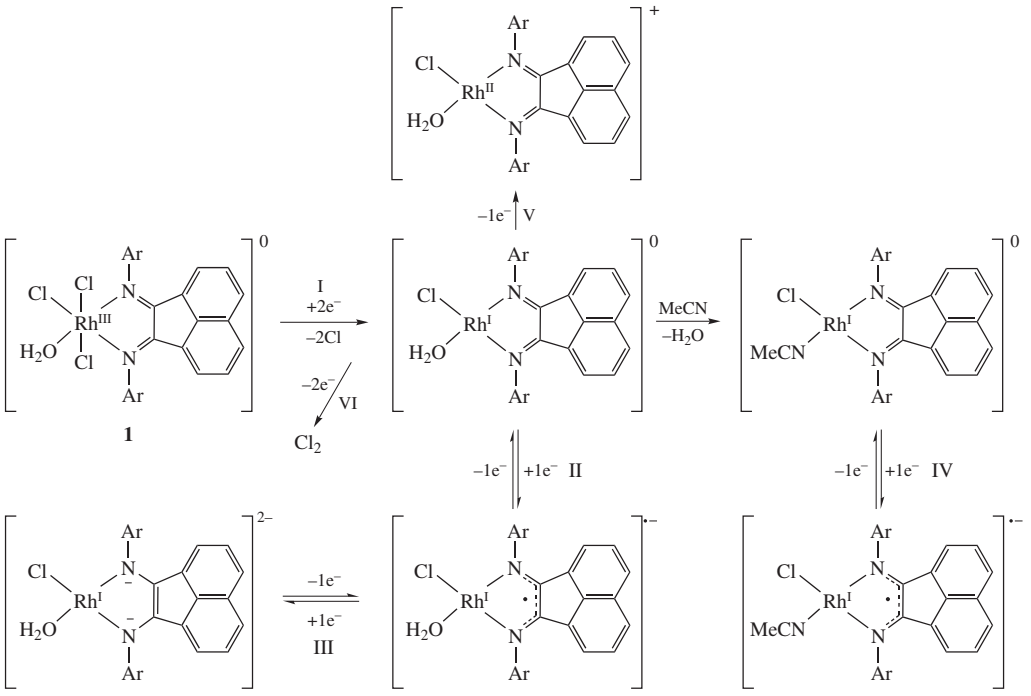


Figure 2 Cyclic voltammogram of 1 mM solution of complex **1** in MeCN in the range from +2.0 to –2.0 V with a scan rate of 100 mV s^{-1}.

in which N(1), N(2), Cl(1) and O(2) atoms define the equatorial plane, the remaining coordination sites being occupied by two chlorine atoms [Cl(2) and Cl(3)] located in the axial positions (*mer*-isomer). The relatively long Rh–O(1) bond length of 2.048(5) Å indicates coordination of neutral H_2O molecule, rather than an OH^- anion. The Rh–N(1) and Rh–N(2) distances differ by 0.03 Å, being 2.067(4) and 2.033(4) Å, respectively. This difference can be explained by the fact that the N(1) atom is located *trans* to the Cl(1) atom, which exhibits stronger *trans* effect than the water molecule. A similar difference in Rh–N bond lengths has been observed in other Rh^{III} diimine complexes. In particular, in the closely related *mer*-[$RhCl_3$(bpy)(MeOH)] complex, the Rh–N bond length *trans* to Cl atom is 2.009 Å, whereas the Rh–N bond *trans* to the O atom of the MeOH molecule is 1.988 Å.[30] The C–N [1.307(6)–1.293(6) Å] and C–C distances [1.487(7) Å] are in a good agreement with those in free dpp-bian.[31,32]

Cyclic voltammetry (CV) of compound **1** was studied in acetonitrile with 0.1 M Bu_4NPF_6 as supporting electrolyte (Figure 2). The voltammogram shows a large irreversible reduction wave I centered at –0.47 V (*vs.* Ag/AgCl) followed by a reversible and a quasi-reversible redox couples II and III at $E_{1/2}$ = –0.85 V (ΔE = 0.06 V) and –1.64 V (ΔE = 0.10 V), respectively. By analogy to the reported electrochemical data for Rh^{III}-polypyridyl complexes, it appears that the first large cathodic peak is a composite wave corresponding to 2e reduction (Rh^{III}/Rh^{I}); the other redox couples at more negative potentials are ligand-based 1e processes.[33] Two consecutive reductions of the dpp-bian ligand to the monoanionic and dianionic forms, respectively, are very typical of the redox chemistry of metal complexes with bis(imino)acenaphthenes.[9,27,34]

Metal-centered 2e reduction was confirmed by DFT calculations which showed that the addition of two electrons to molecule **1** breaks two Rh–Cl bonds with the formation of a square-planar complex [Rh^{I}(dpp-bian)(H_2O)Cl]. The formation of a neutral Rh^{I} complex is also confirmed by the fact that an anodic peak V at E_a = +0.30 V corresponding to Rh(I) oxidation appears on the CV curve. A similar irreversible oxidation process at E_a = +0.9 V (*vs.* Ag/AgCl) was found for [Rh^{I}(dpp-bian)(CO)Cl].[25] It should be noted that no anodic peaks appear when scanning is restricted within the range from 0 to 2 V (Figure S3), thus confirming that all oxidation processes are related to products of the reduction of **1**. Thus, the subsequent 1e reduction processes II and III belong to reduction of [Rh^{I}(dpp-bian)(H_2O)Cl] (Scheme 2). The ligand-



Scheme 2

$|F|^2$ in anisotropic approximation with SHELX 2017/1 in ShelXle program. 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 O(1)/Cl(4), calculated occupancies are 0.8/0.2, which gives dividing of H_2O and Cl^- positions. For O(2)/Cl(3), calculated occupancies are 0.2/0.8 and positions of H_2O and Cl^- cannot be divided.

CCDC 1849307 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

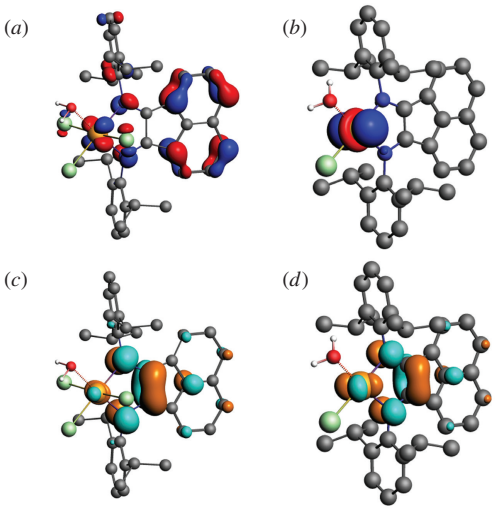


Figure 3 HOMO and LUMO for (*a*), (*c*) **1** and (*b*), (*d*) [Rh^{I}(dpp-bian)(H$_2$O)Cl] complexes, respectively.

centered nature of these processes is consistent with the mainly dpp-bian character of LUMO for [Rh^{I}(dpp-bian)(H$_2$O)Cl]. An observed satellite redox process IV at $E_{1/2} = -1.15$ V ($\Delta E = 0.06$ V) probably belongs to the reduction of [Rh^{I}(dpp-bian)(MeCN)Cl] formed from [Rh^{I}(dpp-bian)(H$_2$O)Cl] by solvent exchange. An irreversible redox event VI also occurred at +1.1 V which most likely corresponds to the oxidation of Cl$^-$ ions released in stage I.

DFT calculations were carried out in order to substantiate the interpretation of the redox processes observed on the cyclic voltammogram of complex **1**. Its HOMO and LUMO are mainly delocalized over the dpp-bian ligand with 76 and 92% contribution of C and N AOs, respectively (Figure 3). Contributions of Rh AOs to HOMO and LUMO are only 12 and 4%, respectively. Since the LUMO of **1** is anti-bonding relative to Rh–Cl interactions, its partial occupation leads to elongation of the Rh–Cl bonds (Table S3). Indeed, one-electron reduction of **1** elongates the Rh–Cl bond by 0.05 Å. Moreover, during optimization of the double reduced species the loss of two Cl$^-$ ions located in the axial position occurs to yield square-planar [Rh^{I}(dpp-bian)(H$_2$O)Cl] complex (Figure S7). The HOMO of [Rh^{I}(dpp-bian)(H$_2$O)Cl] mainly consists of Rh AOs (virtually 4d$_{z2}$, 83%), which is consistent with the metal-centered nature of the two-electron reduction of **1**. Contrary, the LUMO of [Rh^{I}(dpp-bian)(H$_2$O)Cl] has a predominantly dpp-bian centered character (77%), and this gives us the reason to believe that two subsequent reduction processes are ligand-centered.

Motivated by the relevance of metal polypyridine complexes and, in particular, Rh^{III}-polypyridyl complexes as electrocatalysts for reduction of carbon dioxide,[6–8] we recorded cyclic voltammogram of CO$_2$-saturated solution of **1** (Figure S4). A current enhancement in the CO$_2$-saturated solution relative to the blank experiment under argon was observed, which indicates the electrocatalyzed reduction of CO$_2$. This reduction occurs at –1.62 V, indicating strong catalytic effect, since the reduction of CO$_2$ in MeCN in the absence of catalysts is observed only at –2.1 V (*vs.* Ag/AgCl). The active species is most likely the Rh^{I} complex [Rh^{I}(dpp-bian)(H$_2$O)Cl] (or [Rh^{I}(dpp-bian)(MeCN)Cl]), which is formed in the first stage of the two-electron reduction of complex **1**.

In conclusion, we have prepared a new octahedral complex *mer*-[Rh(dpp-bian)(H$_2$O)Cl$_3$]·CH$_2$Cl$_2$ from RhCl$_3$·3H$_2$O and dpp-bian. This is the first example of a Rh^{III} complex containing bis(arylimino)acenaphthene ligand. The complex is redox active and undergoes an irreversible reduction process with elimination of two Cl$^-$ ions and formation of [Rh^{I}(dpp-bian)(H$_2$O)Cl], and subsequent reversible and quasi-reversible ligand-based reduction events. The saturation of MeCN solution of *mer*-[Rh(dpp-bian)(H$_2$O)Cl$_3$] with carbon dioxide results in appearance of an intense cathodic peak at –1.62 V on the CV curve, corresponding to the catalyzed reduction of CO$_2$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.027.

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