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Rhodium(II) Dimers Without Metal-Metal Bonds

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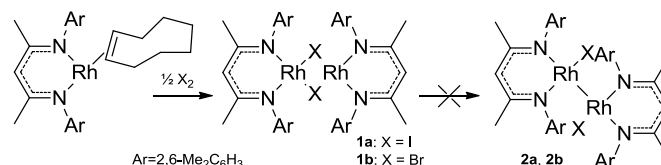
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Oxidation of $(^{\text{Me}}\text{BDI})\text{Rh}(\text{cyclooctene})$ ($^{\text{Me}}\text{BDI} = [2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NCMe}]_2\text{CH}$) with Br_2 or I_2 produces paramagnetic halide-bridged Rh^{II} dimers $[(^{\text{Me}}\text{BDI})\text{Rh}]_2(\mu\text{-X})_2$ without a direct Rh-Rh bond. Steric factors are proposed to play a key role in preventing formation of Rh-Rh bonded alternative structures.

Unlike the intensely studied diamagnetic complexes of Rh^{I} and Rh^{III} , complexes of Rh^{II} have received a rather limited amount of attention. True paramagnetic mononuclear complexes of Rh^{II} are relatively rare.¹⁻⁸ Much more common are metal-metal bonded dimers, where the designation of formal oxidation state +II is somewhat artificial and a consequence of the formal oxidation state counting rules. Well-known examples are quadruply carboxylate⁹ and amidinate¹⁰ bridged systems as well as A-frame complexes.¹¹⁻¹⁴ In the present paper, we report on what we believe are the first examples of paramagnetic, dimeric true Rh^{II} complexes which do not contain metal-metal bonds.

In earlier work, we^{15, 16} and others¹⁷⁻¹⁹ have reported on the oxidative addition of C-X, P-P, C-H, Si-H and Si-C bonds to the Rh atom of $(^{\text{R}}\text{BDI})\text{Rh}^{\text{I}}$ fragments, in which $^{\text{R}}\text{BDI}$ is the β -diiminate $[2,6\text{-R}_2\text{C}_6\text{H}_3\text{NCMe}]_2\text{CH}$ (R = Me, Et, ⁱPr). Such reactions invariably produced $(\text{BDI})\text{Rh}^{\text{III}}$ complexes as products or intermediates. However, elegant work by the group of Heyduk^{20, 21} demonstrated that for $(\text{BDI})\text{Rh}$ complexes also bearing a redox-active α -diimine (ADI) ligand, reaction with I_2 can get "blocked" at the end-on I_2 coordination stage, presumably due to non-innocent behaviour of the ADI ligand. Inspired by this, we decided to investigate the reaction of $(\text{BDI})\text{Rh}^{\text{I}}$ complexes with halogens in the absence of the complicating factor of a redox-active ligand.

Scheme 1. Reaction of $(^{\text{Me}}\text{BDI})\text{Rh}(\text{COE})$ with halogens.

We have commented recently on the analogy between Cp^* and BDI ligands.²² Since Cp^*RhX_2 complexes show interesting reactivity, such as tandem C-H bond activation of arenes or heteroarenes bearing directing groups and further cyclization with alkynes, as well as C-C and C-heteroatom bond-forming reactions,²³⁻²⁷ it was hoped that $(\text{BDI})\text{RhX}_2$ analogues would do the same. I_2 oxidation of $(\text{BDI})\text{Rh}(\text{COE})$ was expected to yield $(\text{BDI})\text{RhI}_2$ or more likely a halide-bridged dimer $[(\text{I})(\text{BDI})\text{Rh}]_2(\mu\text{-I})_2$ (c.f. $[(\text{I})(\text{Cp}^*)\text{Rh}]_2(\mu\text{-I})_2$ ²⁸). However, treatment of $(^{\text{Me}}\text{BDI})\text{Rh}(\text{COE})$ with 1 equivalent of I_2 invariably led to insoluble, ill-defined materials and free ligand $(^{\text{Me}}\text{BDI})\text{H}$. In contrast, use of only half an equivalent of I_2 produced intensely green solutions from which nearly black crystals of $[(^{\text{Me}}\text{BDI})\text{Rh}]_2(\mu\text{-I})_2$ (**1a**) could be obtained in 24% yield (Scheme 1).

The crystal structure (Figure 1A) shows a halide-bridged dimer with a nearly square Rh_2I_2 core.²⁹ For comparison, Table 1 lists a number of representative examples of non-bonded ($\text{Rh}^{\text{I}}\text{-Rh}^{\text{I}}$ and $\text{Rh}^{\text{III}}\text{-Rh}^{\text{III}}$) as well as metal-metal bonded ($\text{Rh}^{\text{II}}\text{-Rh}^{\text{II}}$) distances.

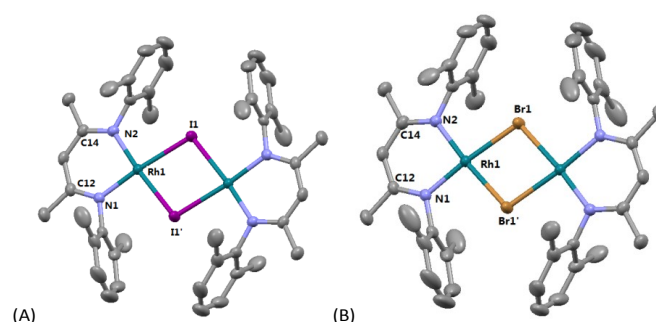


Figure 1. X-ray structures of (A) **1a** and (B) **1b** (one disordered toluene molecule and all hydrogen atoms omitted for clarity). Important bond lengths (Å) and angles (°): **1a**: Rh1-Rh1' 4.057(1), Rh1-I1 2.6420(11), Rh1-I1' 2.6449(9), Rh1-N1 2.003(4), Rh1-N2 2.008(4), I1-Rh1-I1' 79.756(19); **1b**: Rh1-Rh1' 3.819(2), Rh1-Br1 2.4921(9), Rh1-Br1' 2.4939(11), Rh1-N1 1.993(4), Rh1-N2 1.996(4), Br1-Rh1-Br1' 80.02(4).

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Table 1. Representative Rh-Rh distances.

Ox State	Compound	Rh-Rh (Å)	Ref
I	[(COD)Rh] ₂ (μ-Cl) ₂ (chloride-bridged non-bonded)	3.50(1)	30
I	[(COD)Rh] ₂ (μ-Br) ₂ (bromide-bridged non-bonded)	3.565(1)	31
I	[(CO) ₂ Rh] ₂ (μ-I) ₂ (iodide-bridged non-bonded)	3.637(2)	32
II	[(Cl)(^t BuNC)Rh] ₂ (μ-P ^t Bu ₂) ₂ (phosphide bridged)	2.7583(6)	33
II	[Cp*Rh] ₂ (μ-Cl) ₂ (chloride bridged)	2.617(1) 2.628(1)	34
II	[ClRh] ₂ [μ-CN(CH ₂) ₃ NC] ₄ ²⁺ (diisocyanide bridged)	2.837 (1)	35
II	[ClRh(CNCy) ₄] ₂ ²⁺ (unsupported Rh-Rh)	2.6944(3)	36
II	[(CO) ₂ RhCl ₂ Rh(κ ² -C(=O)Quin)] ₂ (unsupported Rh-Rh)	2.671(1)	37
II	Rh ₂ [μ-PhNC(Ph)NPh] ₄ (amidinate bridged)	2.389(1)	10
II	[(H ₂ O)Rh] ₂ (μ-MeCOO) ₄ (carboxylate bridged)	2.3855(5)	9
II	[^{Me} BDI)Rh] ₂ (μ-Br) ₂ (bromide-bridged non-bonded)	3.819(2)	this work
II	[^{Me} BDI)Rh] ₂ (μ-I) ₂ (iodide-bridged non-bonded)	4.057(1)	this work
III	[(Cl)(Cp*)Rh] ₂ (μ-Cl) ₂ (chloride-bridged non-bonded)	3.7191(6)	38
III	[(Br)(Cp*)Rh] ₂ (μ-Br) ₂ (bromide-bridged non-bonded)	3.854(1) 3.841(1)	39
III	[(I)(Cp*)Rh] ₂ (μ-I) ₂ (iodide-bridged non-bonded)	4.132(1)	28
III	[(Ph)(^{Me} BDI)Rh] ₂ (μ-Br) ₂ (bromide-bridged non-bonded)	3.827(1)	16

Typically, non-bonded distances of Rh₂(μ-X)₂ moieties tend to be > 3.5 Å, whereas metal-metal bonded situations have Rh-Rh < 3 Å. In the case of **1a**, the Rh-Rh distance of 4.057(1) Å is a clear indication of the absence of a direct metal-metal bond.

The extreme solution ¹H NMR chemical shifts (ranging from -153 to +24 ppm, see Figure S1) indicate that **1a** is paramagnetic, and solution measurements by the Evans method⁴⁰⁻⁴² indicate a magnetic moment of 2.2(2) μ_B per Rh. For comparison, Dunbar reported a μ_{eff} of 2.1 μ_B for mononuclear [(TMPP)₂Rh]²⁺ (TMPP = 2,4,6-(MeO)₃C₆H₂)₃P),⁸ while Bergman and Tilley obtained values of 1.87 and 1.98 μ_B for two [bis(oxazoline)pincer]₂Rh complexes.⁵ In the case of complex **1a**, we consider dissociation into three-coordinate mononuclear Rh^{II} fragments unlikely given the strength of the halide bridges and the similarity between ¹H NMR spectra recorded in different solvents. Therefore the observed magnetic moment is more likely to represent one of three possibilities: a triplet ground state for the dimer, a thermally populated mixture of singlet and triplet, or two effectively independent Rh-centred radicals.⁴³ Unfortunately, low-temperature EPR measurements were inconclusive (observation of integer-spin complexes by EPR is often problematic⁴⁴).

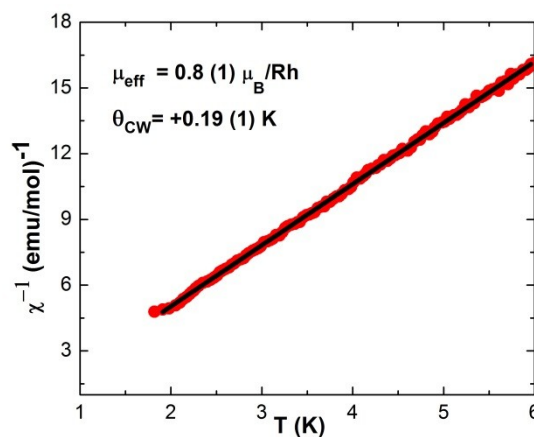


Figure 2. Temperature dependence of magnetic susceptibility.

The DC magnetic susceptibility was measured with an applied field of 0.1 T over the temperature range 1.8 K - 300 K. The magnetization data were fit to a Curie-Weiss law at low temperature (1.8 - 5 K, Figure 2), producing a moment of 0.8(1) μ_B per rhodium atom. The lower moment at low temperature might be due to significant zero-field splitting and/or a lower thermal population of the triplet state. Magnetic interactions are very weak, with θ_{CW} = 0.19(10) K, indicative of net ferromagnetic interactions between the clusters. No magnetic ordering was observed down to 1.8 K, which is consistent with the weak magnetism.

DFT calculations confirm the absence of a metal-metal bond and indicate that the energy difference between singlet and triplet states is close to zero. The spin density in the triplet state (Figure 3) is concentrated in Rh *d*_{xz} orbitals, which explains the weak interaction between the two Rh centres. Compared to any reasonable Rh^I reference structure (low spin, closed shell), this chemical oxidation has occurred predominantly at the metal centre (spin density 0.79) although a small contribution from the BDI ligand (spin density 0.18 e) is also evident.^{45, 46} Presumably, the presence of the bulky BDI ligand is a key factor in preventing shorter Rh-Rh distances or a rearrangement to the more "normal" metal-metal bonded isomer **2a** (Scheme 1) which is calculated to be 19.1 kcal/mol higher in energy (see also Tables S5-S7).

In the work of Heyduk mentioned above,^{20, 21} oxidation of (BDI)Rh(ADI) by bromine (instead of iodine) did proceed to the expected Rh^{III} complex. We also explored bromine oxidation, but again only obtained poorly defined products when aiming for Rh^{III}. However, with 0.5 equiv of Br₂, deep green [(^{Me}BDI)Rh]₂(μ-Br)₂ (**1b**) was obtained in fair yield and purity; the X-ray structure, shown in Figure 1B, is rather similar to that of **1a**, and again indicates the absence of a metal-metal bond (Rh-Rh = 3.819 Å).

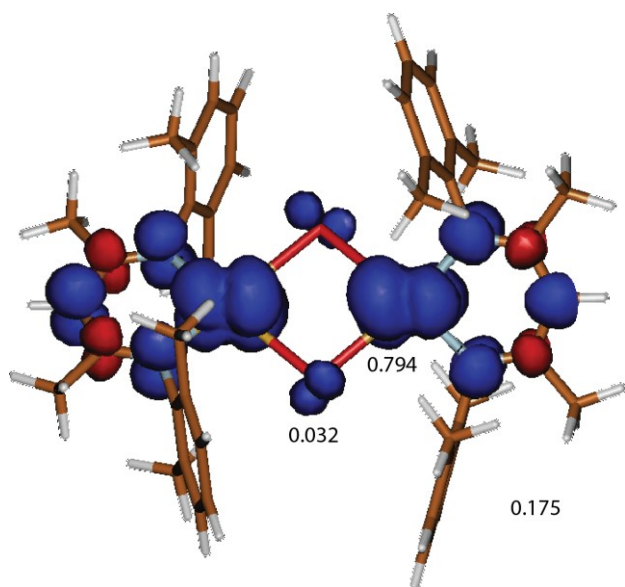
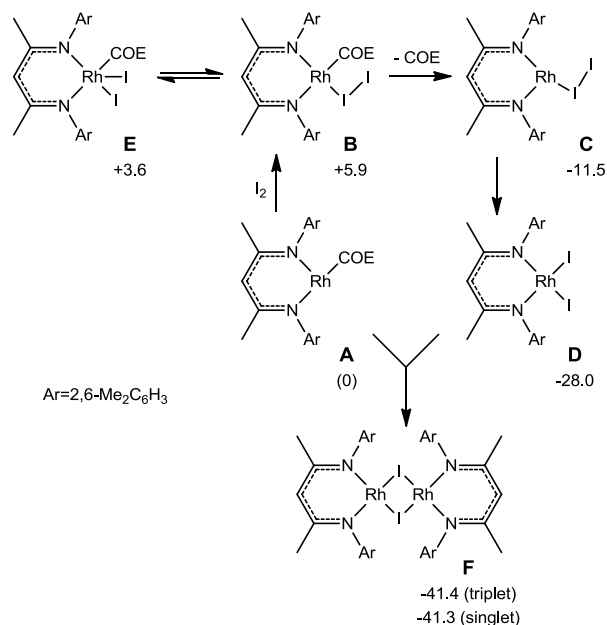


Figure 3. Calculated (Turbomole: b3-lyp/TZVP) spin density plot (Molden⁴⁷) for triplet state of **1a**, with spin density values for each Rh and I atom and ^{Me}BDI ligand.

In order to understand the reason why the reaction of (BDI)Rh(COE) with iodine leads only to [(BDI)Rh]₂(μ-I)₂ instead of (BDI)RhI₂ or its dimer, DFT calculation were further used to explore possible reaction paths. Several trials produced a mechanism which seems reasonable (Scheme 2; see also Tables S8 and S9). The added iodine first coordinates end-on to starting material **A** to form complex **B**, which easily releases COE to generate complex **C**. From there, further intramolecular oxidation to form **D** is quite favourable. Attempts to locate a transition state for this step were unsuccessful: the barrier appears to be extremely low (in contrast, Renz et al found a substantial barrier for the Br-Br bond breaking step in the reaction of Ni(Ar)(Br)(picoline) with Br₂⁴⁸). Since **D** was never observed, we propose that it reacts quickly with **A** remaining in solution to form the observed final product **F**. It is still not entirely clear why treatment of this complex with another half equivalent of I₂ leads to decomposition rather than to the expected Rh^{III} complex **E**.

In summary, the coordinatively unsaturated complex (BDI)Rh(COE) reacts with halogens (I₂ or Br₂) to generate paramagnetic halide-bridged Rh^{II} dimers, characterized by X-ray diffraction, NMR and magnetic measurements. DFT calculations support the surprising absence of metal-metal bonding, leading to the expectation that related complexes with less steric protection might exhibit interesting biradical chemistry.

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Scheme 2. Possible mechanism for the generation of [(^{Me}BDI)Rh]₂(μ-I)₂. Free energies (Turbomole: b3-lyp/TZVP, 298K) in kcal/mol.

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