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Bis(phenyl)dirhodium(III) Caprolactamate: A Dinuclear Paddlewheel Complex with No Metal−Metal Bond

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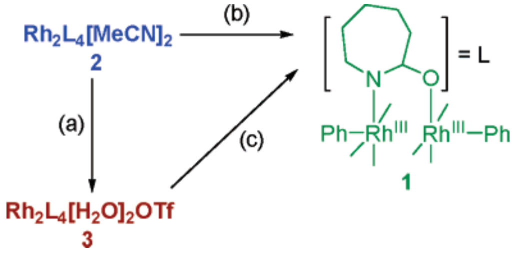
The preparation and electronic structure of dinuclear metal complexes with a metal−metal bond have been long-standing areas of interest.[1] Recent work has provided synthetic access to and/or elucidated the electronic structure of M_2^{6+} complexes (M = transition metal).[2] Despite the body of work, structurally well-defined Rh_2^{6+} complexes have remained an elusive target.[1] This manuscript reports the first unambiguous and fully characterized dirhodium(III) paddle-wheel complex, bis(phenyl)dirhodium(III) caprolactamate (**1**), and its synthesis by a novel oxidation of dirhodium(II) caprolactamate (**2**) (Scheme 1).[3] Isolating **1** allows a comparative analysis of the Rh_2^{n+} complexes ($n = 4$, 5, and 6) of dirhodium caprolactamate. This analysis demonstrates that **1** is a dinuclear paddlewheel complex without a formal metal−metal bond because of a ligand induced change in its electronic structure.[4] The formation of **1** under such mild oxidation conditions implies that similar species could play a role in the redox chemistry of dirhodium complexes.[5]

The aerobic oxidation of **2** with Cu(I)OTf (10 mol %) in the presence of $NaBPh_4$ (5 equiv) provided **1** in 77% yield after purification (Scheme 1b). The structure of **1** was first indicated by signals corresponding to two equivalent phenyl ligands in addition to the caprolactamate ligands observed in both the ^1H and ^{13}C NMR spectra. Aryl ring vibrations at 1583 and 1550 cm^{-1}, and the parent ion corresponding to **1** (M+H) by high-resolution mass spectroscopy (ESI) provided further evidence. The visible spectrum of **1** with λ_{max} (ϵ M^{-1} cm^{-1}) at 430 (4540) nm was consistent with previous reports of electrochemically generated Rh_2^{6+} complexes that were not isolated.[6] X-ray diffraction of a single-crystal grown in CH_2Cl_2 confirmed that **1** was indeed $[Rh_2(cap)_4](C_6H_5)_2$ (Figure 1). To complete the Rh_2^{n+} series, the Rh_2^{5+} complex, $[Rh_2(cap)_4](OTf){\cdot}2H_2O$ (**3**), was prepared by treating **2** with $Cu(II)[OTf]_2$ in wet ethyl acetate (Scheme 1a).[7] The visible spectrum of **3** in CH_2Cl_2 was typical of Rh_2^{5+} structures with λ_{max} (ϵ M^{-1} cm^{-1}) at 505 (4502) and 970 (1086) nm.[6] As an odd electron species, **3** exhibited severe line broadening in the ^1H NMR, but its structure was confirmed crystallographically to have the typical dirhodium core with axial aquo ligands and an outersphere triflate ion.[8]

In terms of the molecular geometry, **1** does not deviate from the general dirhodium(II) carboxamidate structure. The coordination sphere of **1**, however, is completed by two axial C_6H_5 anionic ligands with notable structural distortions. The Rh−Rh−C angles (155.4°, 156.2°) are significantly distorted from linearity toward the Rh−O bonds, and the Rh−Rh bond of **1** (2.519 Å) is lengthened compared to **2** (2.422 Å). Considering the general $\sigma^2\pi^4\delta^2\pi^{*4}\sigma^{*n}$ electronic structure of dinuclear paddlewheel complexes,[9] a shorter Rh−Rh bond is expected with increasing bond order upon oxidation from a Rh_2^{4+} ($n = 2$) to a Rh_2^{6+} complex ($n = 0$).[10] Consistent with this electronic structure, the Rh−Rh bond length shortens modestly as oxidation occurs from **2** ($n = 2$) to **3** ($n = 1$), 2.422 to 2.384 Å, respectively. However, the Rh−Rh bond length in **1** ($n = 0$) is approximately 0.1 Å *longer* than the corresponding bond length in **2**. The lengthening of the bond is an indication of a change in the electronic structure of the dirhodium core.[6,11]

Scheme 1. Oxidation of Rh_2L_4 = Dirhodium Caprolactamate[a]



[a] Conditions: (a) $Cu(II)[OTf]_2$ (1 equiv) in EtOAc; (b) Cu(I)OTf (10 mol %), $NaBPh_4$ (5 equiv), and O_2 in CH_2Cl_2/MeOH (9:1); (c) same as b.

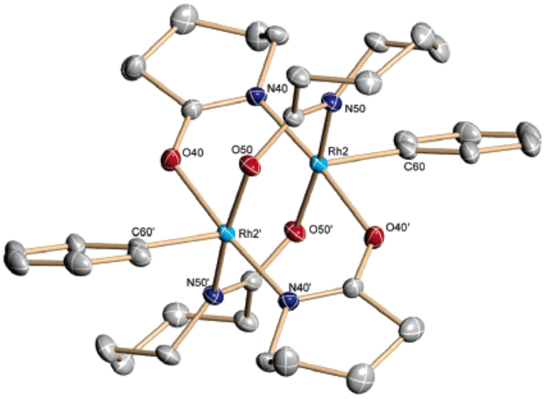


Figure 1. ORTEP drawing of one of two crystallographically independent molecules of **1**, $C_{36}H_{50}N_4O_4Rh_2$, R_1 = 3.00%. Selected bondlengths (Å) and angles (deg): Rh2−Rh2′ (2.519); Rh2−C60 (2.000), Rh2′−O40′ (2.085); Rh2′−O50 (2.083); Rh2−N40 (2.011); Rh2−N50 (2.014); Rh2−Rh2′−C60 (155.4); Rh2′−Rh2−N40 (96.4); Rh2′−Rh2−N50 (94.0); Rh2−Rh2′−O40 (77.4); Rh2−Rh2′−O50 (79.8). Ellipsoids are shown at a 30% probability level. Solvent and hydrogens are omitted for clarity.

The formation of two new Rh−C bonds can be expected to change the hybridization of the Rh-centered orbitals from **2** (dsp^2) to **1** (d^2sp^3).[12] An alternative electronic configuration of **1** would then be $\pi^4\delta^2\pi^{*4}\delta^{*2}$ for a d^2sp^3 dimer resulting in the formal cleavage of the Rh−Rh bond.[13] X-ray photoelectron spectroscopy (XPS) of compounds **1**−**3** indicates that a fundamental change in the metal-centered orbitals indeed occurs when **2** is oxidized to **1**. The electron binding energy (E_b) for the rhodium 3d-orbitals (Rh $3d_{5/2}$) increased from 308.08 to 309.09 eV upon oxidation from **2** to **3**. The ~1 eV increase in E_b from Rh_2^{4+} to Rh_2^{5+} is consistent with other dirhodium(II) complexes.[14] However, upon oxidation from Rh_2^{5+} to Rh_2^{6+} (**3** to **1**), E_b(Rh $3d_{5/2}$) remained virtually unchanged

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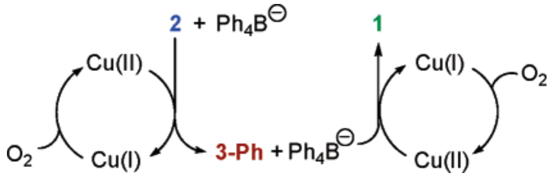
Scheme 2. Proposed Mechanism of Formation of **1** from **2**.



at 309.11 eV. The binding energy of **1** suggests that the complex does not retain the $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*n}$ electronic structure with $n = 0$. However, E_b(Rh $3d_{5/2}$) is consistent with monomeric d^2sp^3 hybridized Rh(III) complexes and a $\pi^4\delta^2\pi^{*4}\delta^{*2}$ electron configuration.[15] The presence of ^{1}H and ^{13}C NMR signals, the lack of a measurable magnetic susceptibility for **1**, and the disappearance of the $\delta-\delta^*$ transition at 970 nm in the visible spectrum of **1** indicate that the δ^* orbital is occupied and **1** is diamagnetic, consistent with the configuration assignment.

In addition to the structural features of **1**, its formation from **2** was surprising. How does the oxidation of **2** occur in the presence of Cu(II) and $NaBPh_4$? The instability of $NaBPh_4$ toward metal cations has been well documented, including aryl transfer processes,[16] but the oxidation of a metal center by a tetraarylborate salt is unlikely.[17] The more likely oxidant is a Cu(II) salt catalytically regenerated in the presence of oxygen. The preparation of **3** from **2** with Cu(II)$[OTf]_2$ demonstrated clearly that the first oxidation was possible. Submitting **3** to the original reaction conditions gave **1** in 73% yield after purification (Scheme 1c). This indicated that the key transformation occurs from the Rh_2^{5+} redox state.

A series of experiments helped determine the role of copper salts and $NaBPh_4$ in the reaction. Complex **3** was diluted in ethyl acetate, washed repeatedly with water, and concentrated to dryness to minimize the amount of residual copper salts from its preparation. The oxidation of **3** to **1** was observed over 60 min via spectral changes at the λ_{max} of **1** (430 nm). Under the reaction conditions, there was no reaction between **3** and $NaBPh_4$ (5 equiv) or **3** and excess Cu(II)$[OTf]_2$. Very little conversion of **3** to **1** occurred under nitrogen while the aerobic reaction in the presence of a catalytic amount of Cu(I)OTf (10 mol %) rapidly generated **1** in almost complete conversion. A simple model can be proposed for the oxidation of **2** to **1** on the basis of these data (Scheme 2). A Cu(II)/Cu(I) couple with oxygen as a terminal oxidant oxidizes **2** to **3**. An aryl-transfer from $NaBPh_4$ to **3** gives a transient **3**-Ph species whose oxidation potential is low enough[18] for Cu(II)/Cu(I) couple to oxidize it to **3**-Ph^+.[19] Phenyl transfer from an additional equivalent of $NaBPh_4$ completes the process and generates **1**.

The isolation of **1** provides the first unequivocal example of a dirhodium(III) complex. A copper catalyzed aerobic oxidation with $NaBPh_4$ as a phenyl transfer agent provides entry into this novel Rh_2^{6+} species. Structural and spectroscopic data indicate a cleavage of the Rh−Rh bond resulting from a change in the electronic structure of the complex. Preliminary data suggest that this synthetic approach can be employed with other dirhodium(II) carboxamidates, and work is underway to explore the structural scope and applications of dirhodium(III) complexes.

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Supporting Information Available: Experimental procedures, CIF files, XPS data, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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