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# A new dirhodium tetraacetate carbenoid: Synthesis, crystal structure and catalytic application

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## Abstract

A new dirhodium tetraacetate **II** involving 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene **I** was synthesized and characterized by general spectroscopic tools in the solution state as well as single X-ray crystallographic analysis in the solid state. The catalytic activity of dirhodium tetraacetate carbenoid **II** was tested for the allylic oxidation, and the improved reactivity to the allylic oxidation was observed compared to that of Rh<sub>2</sub>(OAc)<sub>4</sub>. The different electrochemical properties of dirhodium tetraacetate carbenoid **II** and Rh<sub>2</sub>(OAc)<sub>4</sub> were compared *via* cyclic voltammetry.

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**Keywords:** Dirhodium tetraacetate; Carbene; Allylic oxidation; Electron donor

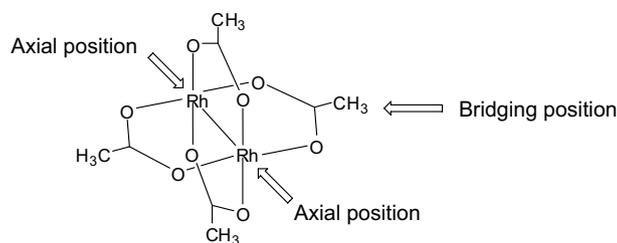
## 1. Introduction

Over the past years, various dirhodium complexes have been synthesized due to their powerful catalytic activity in organic reactions (e.g. cyclopropanation, C–H insertion reactions, oxidative amination, and cycloaddition [1]) as well as the biological activity as potential enzyme inhibitors [2] or therapeutic agents [3]. Therefore, considerable efforts have been directed to improving the catalytic reactivity and the biological activity of dirhodium complexes by the structural modification. Accordingly, a range of bridging ligands and axial ligands have been employed in the dirhodium complexes (Scheme 1) [4,5]. For example, it is demonstrated by Doyle that Rh<sub>2</sub>(cap)<sub>4</sub> (cap = caprolactamate) catalyzes the allylic oxidation effectively compared to Rh<sub>2</sub>(OAc)<sub>4</sub>. Caprolactamate ligands at the bridging position lower the oxidation potential of the dirhodium complex spawning oxidized rhodium species Rh<sub>2</sub><sup>5+</sup> from Rh<sub>2</sub><sup>4+</sup>. As a result, active Rh<sub>2</sub><sup>5+</sup> species catalyze the success-

ful catalytic allylic oxidation with highly improved yields [4f,6]. In addition to bridging ligands, axial ligands also play a significant role in inducing electronic, chemical, and structural changes and improving catalytic activities of dirhodium complexes. According to the results of X-ray crystallographic analysis of dirhodium complexes involving axial ligands, it is noteworthy that both axial positions are occupied by ligands in many dirhodium complexes [4]. On the other hand, few examples of mono axial position modified dirhodium complexes have been reported. As a mono axial position modified dirhodium complex, (1,3,4,5-tetramethylimidazol-2-ylidene) dirhodium tetracarboxylate was reported by Snyder and coworkers in 2001 and tested for the cyclopropanation reaction; however, Snyder's dirhodium carbenoid shows the same catalytic activity compared to the carbene free dirhodium tetracarboxylate complex [5r].

In this communication, we are pleased to report the synthesis of monoaxial position substituted dirhodium complex **II** containing a bulky carbene ligand. The significantly improved catalytic activity of dirhodium complex **II** in Rh(II)-catalyzed allylic oxidation will be presented.

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Scheme 1. The axial position and the bridging position of  $\text{Rh}_2(\text{OAc})_4$ .

## 2. Results and discussion

The dirhodium tetraacetate carbenoid,  $\text{Rh}_2(\text{OAc})_4$ -(NHC), **II** was obtained by the reaction of  $\text{Rh}_2(\text{OAc})_4$  and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (NHC) **I** in THF (Scheme 2). X-ray crystallography quality dirhodium complex **II** crystals were obtained *via* slow evaporation of diethyl ether solution containing dirhodium complex **II** at room temperature. The resulting crystals were analyzed by X-ray diffraction (Table 1). The structure of dirhodium complex **II** is depicted in Fig. 1.

In the solid state, dirhodium complex **II** has the typical lantern structure where four acetate ligands surround the central rhodium ions, and carbene (NHC) **I** is placed at one of axial positions. Like other dirhodium tetracarboxylate complexes, in dirhodium complex **II**, two  $\text{Rh}(\text{O})_4$  planes are parallel to each other and perpendicular to the

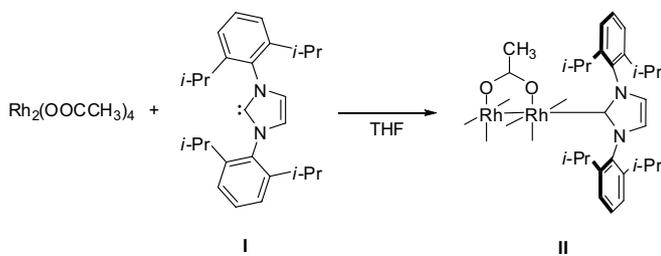
Scheme 2. Synthesis of complex **II**.

Table 1  
Selected crystallographic data for dirhodium complex **II**

Empirical formula	$\text{C}_{35}\text{H}_{48}\text{N}_2\text{O}_8\text{Rh}_2$
Formula weight	830.57
Crystal system, space group	Monoclinic, $P21/c$
Unit cell dimensions	
$a$ (Å)	11.1108(2)
$b$ (Å)	22.4905(6)
$c$ (Å)	17.2037(5)
$\alpha$ (°)	90
$\beta$ (°)	106.6750(10)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	4118.21(18)
$Z$	4
Calculated density (mg/m <sup>3</sup> )	1.340
Crystal size (mm)	$0.30 \times 0.23 \times 0.16$
Goodness-of-fit on $F^2$	1.067
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0479$ , $wR_2 = 0.1565$
$R$ indices (all data)	$R_1 = 0.0759$ , $wR_2 = 0.1764$

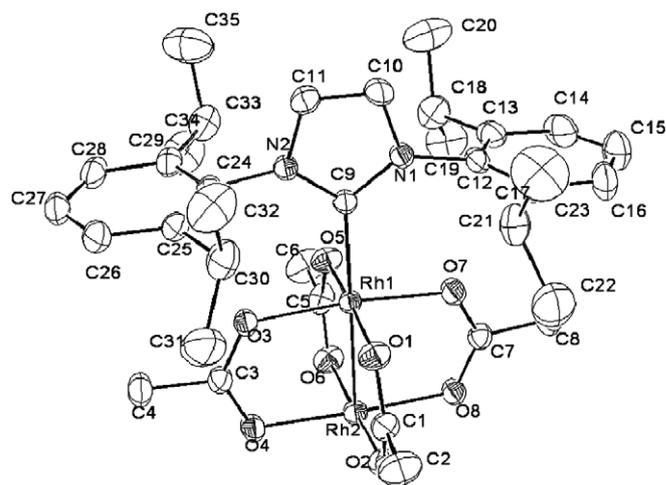


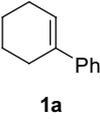
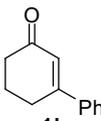
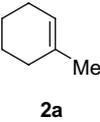
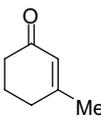
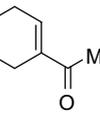
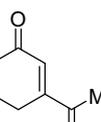
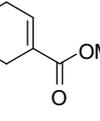
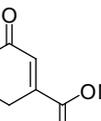
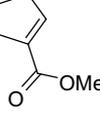
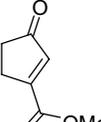
Fig. 1. ORTEP of complex **II**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Rh1–Rh2, 2.4279(5); Rh1–C9, 2.121(4); Rh1–O1, 2.025(4); C9–N1, 1.362(6). Selected bond angles (°): O1–Rh1–O5, 175.43(15); O3–Rh1–O1, 89.27(16); C9–Rh1–O7, 94.25(16); C10–N1–C12, 118.6(4); C20–C18–C13, 109.6(6); N1–C9–Rh1, 128.2(3).

Rh–Rh axis. The most distinctive feature of dirhodium complex **II** is that the Rh–Rh distance of 2.428 Å is slightly longer than the corresponding distance in  $\text{Rh}_2(\text{OAc})_4$ -( $\text{H}_2\text{O}$ )<sub>2</sub> (2.386 Å) [5c]. This elongated Rh–Rh distance of X-ray crystallography results strongly supports the notion that the carbene ligand acts as a good electron donor to rhodium rendering longer Rh–Rh distance [7]. This hypothesis was also supported by previously reported X-ray crystal data of dirhodium complexes possessing axial ligands, e.g. pyridine, amines, water, aromatic rings [5a–5q, 5s, 5v–5x] and self-ligating chains [8]. Furthermore, in Snyder's recent publication, 1,3,4,5-tetramethylimidazol-2-ylidene dirhodium tetracarboxylate close cogent with dirhodium complex **II** shows the similar distance between two rhodium ions 2.424 Å [5q, 5r].

With dirhodium complex **II** in hand, we examined the catalytic activity of dirhodium complex **II** for the allylic oxidation (Table 2). Slow addition of *tert*-butyl hydroperoxide (TBHP, 100 mol%) to a solution of dirhodium complex **II** (1 mol%), 1-phenylcyclohexene, **1a** (100 mol%) and  $\text{K}_2\text{CO}_3$  (50 mol%) in  $\text{CH}_2\text{Cl}_2$  provided desired oxidized product **1b** in 57% yield. In comparison to dirhodium complex **II**,  $\text{Rh}_2(\text{OAc})_4$ -catalyzed reaction afforded the allylic oxidation products in only 9% yield (entry 1, Table 2). To optimize the reaction conditions, the various amounts of dirhodium complex **II**, TBHP, and  $\text{K}_2\text{CO}_3$  were tested, yet improved results were not observed. Thus, the reaction conditions involving 1 mol% dirhodium complex **II**, 50 mol%  $\text{K}_2\text{CO}_3$  and 100 mol% of TBHP were chosen as the standard conditions. Under the standard conditions, regular cyclic olefin **2a** and electron deficient cyclic olefins **3a**, **4a**, **5a** underwent the allylic oxidation in moderate yield [9].

With regard to the effect of the carbene ligand, significantly improved yield of the dirhodium complex **II**-catalyzed allylic oxidation reaction might be attributed to the

Table 2  
Dirhodium complex **II**-catalyzed allylic oxidations

Entry	Substrate	Product	Yield (%)
$\text{R}_1\text{CH}=\text{CH}-\text{CH}(\text{R}_2)\text{R}_3 \xrightarrow[\text{r.t.}]{\text{Complex II (1 mol\%)} \text{ TBHP (100 mol\%)} \text{ CH}_2\text{Cl}_2 (0.48 \text{ M})}$ $\text{R}_1\text{C}(=\text{O})\text{CH}=\text{CH}-\text{CH}(\text{R}_2)\text{R}_3$			
1			57, (9) <sup>a</sup>
2			47
3			39
4			45
5			18

To obtain the product, complex **II** (1 mol%),  $\text{K}_2\text{CO}_3$  (50 mol%), and substrates (1.20 mmol, 100 mol%) were mixed in  $\text{CH}_2\text{Cl}_2$  at ambient temperature. Then, TBHP (100 mol%) was added into this mixture. The reaction was run until substrates were consumed.

<sup>a</sup> The reaction was catalyzed by 1 mol% of  $\text{Rh}_2(\text{OAc})_4$ .

electronic effect of the carbene ligand. To evaluate the NHC ligand effect in dirhodium complex **II**, electrochemical studies were performed on  $\text{Rh}_2(\text{OAc})_4$  and dirhodium complex **II** ( $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ ) in THF (0.1 M tetrabutylammonium perchlorate as an electrolyte). As shown in Fig. 2, dirhodium complex **II** ( $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ ) exhibits the quasi-reversible oxidation/reduction wave corresponding to the  $\text{Rh}_2^{4+}/\text{Rh}_2^{5+}$  redox couple with ca. 120 mV of the peak separation. In contrast,  $\text{Rh}_2(\text{OAc})_4$  undergoes irreversible one-electron oxidation/reduction with higher

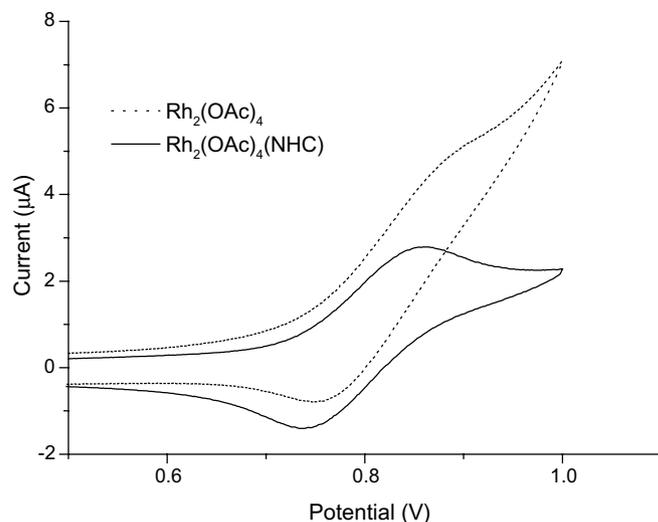


Fig. 2. Cyclic voltammograms of  $\text{Rh}_2(\text{OAc})_4$  and dirhodium complex **II** ( $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ ) in THF solution at 100 mV/s scan rate.

oxidation current ( $i_a$ ) than that of dirhodium complex **II** ( $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ ) under the same conditions. In light of CV results, it can be speculated that the reversible one-electron oxidation/reduction behavior of dirhodium complex **II** is related to the formation of catalytically competent  $\text{Rh}_2^{5+}$  species and the regeneration of  $\text{Rh}_2^{4+}$  species to complete the catalytic cycle of the allylic oxidation. In contrast, the irreversible oxidation/reduction pattern with significantly high  $i_a$  of  $\text{Rh}_2(\text{OAc})_4$  might indicate the structural change of  $\text{Rh}_2(\text{OAc})_4$  during the oxidation resulting in the poor catalytic activity toward the allylic oxidation. Regarding the oxidation potential shift, the remarkable oxidation potential change by inserting the NHC ligand at the axial position of  $\text{Rh}_2(\text{OAc})_4$  was not observed in contrary to what was shown in the cyclic voltammetric data of  $\text{Rh}_2(\text{cap})_4$  (cap = caprolactamate) [4f].

In conclusion, new dirhodium tetraacetate carbenoid **II** has been synthesized. On the basis of X-ray crystallography, the structure of dirhodium complex **II** is illustrated where only one carbene ligand is coordinated at the axial position. The quasi-reversible cyclic voltammetric data of dirhodium complex **II** appears to be related to the excellent catalytic activity of dirhodium complex **II** in the allylic oxidation. Currently, the mechanistic studies are being carried out to improve the catalytic activity of this system.

### 3. Experimental

All manipulations and reactions were performed under an inert atmosphere using standard glove box and Schlenk techniques. Anhydrous solvents were transferred by an oven dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. THF was distilled from benzophenone ketyl. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, part per million (ppm) downfield from tri-

methylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, part per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. Elemental analysis was carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Electrochemical data were recorded on a potentiostat/galvanostat (PARC (Princeton Applied Research), model 263) with Electrochemistry Power Suite Module and Cyclic voltammetry software. The three-electrode cell consisting of Pt disc (the working electrode), Ag wire (the reference electrode), and Pt wire (the auxiliary electrode) was employed. Dirhodium complexes ( $5 \times 10^{-4}$  M) were dissolved in THF solution containing 0.1 M tetrabutylammonium perchlorate. The resulting solutions were subject to cyclic voltammetry experiments at a scan rate of 100 mV/s.

### 3.1. Synthesis of $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ (**II**)

The reaction of  $\text{Rh}_2(\text{OAc})_4$  (150 mg, 0.34 mmol) and carbene ligand (NHC) **I**, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, (270 mg, 0.69 mmol) was performed in THF (5 ml) for 5 h at ambient temperature under an atmosphere of nitrogen. Color change was observed immediately from blue to red. Upon the removal of THF, the residual mixture was purified *via* column chromatography using hexane:ethyl acetate 2:1 to afford analytical pure purple crystals (272 mg) in 93% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.35 (t,  $J = 8.8$  Hz, 2H), 7.19 (d,  $J = 8.8$  Hz, 4H), 7.17 (s, 2H), 3.24 (sep,  $J = 7.6$  Hz, 4H), 1.43 (br, 12H), 1.28 (d,  $J = 7.6$  Hz, 12H), 1.07 (d,  $J = 7.6$  Hz, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  22.99, 25.43, 28.33, 122.85, 124.56, 128.73, 137.82, 145.59, 189.04. Anal. Calc. ( $\text{C}_{35}\text{H}_{48}\text{N}_2\text{O}_8\text{Rh}_2$ ): C, 50.06; H, 5.84; N, 3.37. Found: C, 50.10; H, 5.86; N, 3.34%.

### 3.2. Representative procedure for the allylic oxidation

To a stirred mixture of  $\text{Rh}_2(\text{OAc})_4(\text{NHC})$ , **II** (10 mg, 0.012 mmol), crashed potassium carbonate (83 mg, 0.60 mmol) and 1-phenyl cyclohexene (190 mg, 1.20 mmol) in dichloromethane (2.5 ml) was added a solution of TBHP (176 mg, 5.0–6.0 M in decane solution) slowly at room temperature. The resulting mixture was stirred overnight. The solvent was removed with a rotary evaporator to produce a residue which was purified by column chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 10:1).

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