

Synthesis and Catalytic Properties of Dirhodium Paddlewheel Complexes with Tethered, Axially Coordinating Thioether Ligands

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Supporting Information

ABSTRACT: Novel mixed-ligand rhodium(II) paddlewheel complexes incorporating tethered axial thioether ligands have been synthesized and characterized. The thioether moiety is essential for high yields and the suppression of byproducts in cyclopropanation reactions using an electron-deficient diazoacetate. Crystal structures, UV–vis analysis, and cyclic voltammetry experiments shed light on the catalytic performance of the complexes.

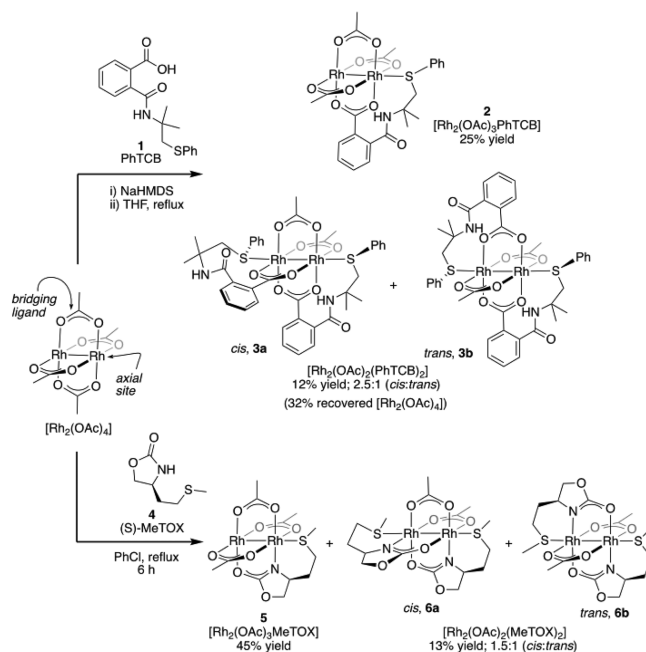
Rhodium(II) paddlewheel complexes [Rh(II)] are known for promoting effective transformations through the decomposition of α -diazocarbonyl compounds and in situ generation of rhodium carbenoids.^{1–8} These carbenes can undergo a variety of transformations such as cyclopropanation and C–H and X–H (X = O, N, S, Si) insertion reactions.^{9–13} Bridging ligands surrounding the bimetallic core of the Rh catalyst play an important role in the reactivity and selectivity of the complexes and are largely the focus of Rh(II) design.¹⁴ The axial sites of the complexes serve as sites of electrophilic reactivity and, as such, are often occupied by weakly coordinating solvent molecules that are easily displaced.¹⁴ Efforts to tune Rh(II) catalysis through axial coordination have been limited by the weaker interaction of axial ligands compared to the bridging ligands. Large excesses of the axial ligand¹⁵ or strong σ -donor ligands^{16,17} are required to observe significant effects, but this comes at a cost: when ligands block both axial sites, inert off-cycle complexes result.¹⁸ Also, coordination of a strong σ -donor ligand at one Rh axial site likely decreases the electrophilicity of the distal Rh axial site via electronic communication through the Rh–Rh bond, affecting the reactivity of the complex.^{18–22}

To combat this, our research focuses on tethering Lewis base moieties to the bridging ligand scaffold of Rh paddlewheel complexes in an effort to control and probe the beneficial aspects of their coordination. Described herein are new ligands incorporating chelated, axially coordinating thioether donor groups that can modulate the electron density about the Rh₂ core, enhancing the catalytic activity in cyclopropanation reactions with an electron-deficient diazoester. Similar ligand design strategies have been examined by Bera et al.²³ and Ball et

al.,²⁴ but hemilabile thioether ligands^{25,26} have not been explored and offer the potential for a reactive Rh(II) complex while providing an electron donor with the ability to remotely affect the reactivity of the transient rhodium carbene.

To demonstrate the applicability of this axial coordination method, both carboxylate- and carboxamidate-type²⁷ ligands bearing tethered donor groups were synthesized. Rh(II) compounds bearing phenylthiocarbamoyl benzoate ligand **1**^{28,29} (PhTCB, Scheme 1) and methylthiooxazolidinate ligand **4**³⁰ [(S)-MeTOX, Scheme 1] were synthesized from ligand-exchange reactions with Rh₂(OAc)₄. For ligand **1**, the acidity of the carboxylate ligand allowed Corey's base-promoted reaction in tetrahydrofuran to be employed (Scheme 1, top).³¹ A *gem*-dimethyl group was incorporated to enhance the chelate rigidity and promote axial coordination in PhTCB via the Thorpe–

Scheme 1. Ligand-Exchange Reactions



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Ingold effect.³² Soxhlet conditions³ were required to achieve ligand exchange with **4** (Scheme 1, bottom). Using 1 equiv of ligand, reactions predominantly formed monosubstituted Rh complexes (**2** and **5**, Scheme 1), with smaller amounts of cis and trans isomers of the disubstituted compounds (**3a**, **3b**, **6a**, and **6b**, Scheme 1). While ligand-exchange reactions have not been optimized, the axial tether prevented the formation of tri and tetrasubstituted Rh species in both instances, an issue that previously complicated the synthesis of mixed-ligand Rh(II) complexes.^{33,34}

Crystals of $\text{Rh}(\text{OAc})_3\text{MeTOX}$ (**5**) and *trans*- $\text{Rh}_2(\text{OAc})_2(\text{PhTCB})_2$ (**3b**) were obtained and analyzed by single-crystal X-ray diffraction, which confirmed axial coordination and chelation of the thioether donor groups (Figure 1). The crystal

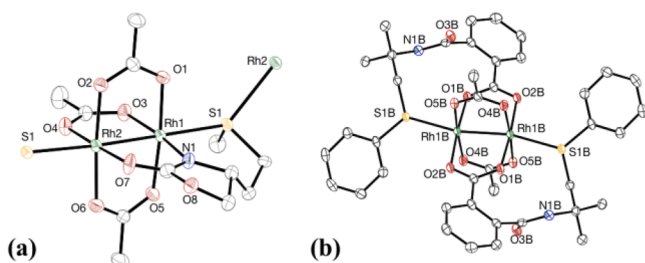


Figure 1. (a) Solid-state structure of $[\text{Rh}_2(\text{OAc})_3\text{MeTOX}] \cdot 2\text{MeCN}$, with 50% probability ellipsoids. Solvent molecules and H atoms omitted for clarity. Terminal S1 and Rh2 atoms denote the oligomeric nature of the structure. (b) Solid-state structure of *trans*- $[\text{Rh}_2(\text{OAc})_2(\text{PhTCB})_2]$, with 50% probability ellipsoids. Only one of the two molecules in the asymmetric unit is shown, with H atoms omitted for clarity.

structure of **5** adopts an oligomeric structure in the solid state, with the thiomethyl group binding both intra- and intermolecularly to the axial site of the Rh (Figure S1). This Rh–Rh–X–Rh–Rh motif has previously been observed with an O^{35,36} or halogen,^{37,38} spanning the Rh paddlewheel units. The Rh–S–Rh bond is asymmetric, with the intramolecular Rh–S bond shorter because of the chelate effect (2.484 vs 2.556 Å). By comparison, **3b** crystallizes as monomeric units, with both axial sites occupied by chelated thiophenyl units (Figure 1b). The average Rh–S bond length of **3b** (2.542 Å) is notably longer than that of **5** (2.484 Å) because of the stronger σ -donating ability of the thiomethyl group compared to the thiophenyl group. The favorable six-membered ring chelate in complex **5** also contributes to a stronger interaction at the axial site.

UV–vis spectra of the complexes in dichloroethane (DCE) were obtained (Figure 2) to compare the ability of the axial thioether coordination to affect the electronic transitions within these Rh paddlewheel complexes and correlate the results to their reactivity. Axial ligands affect the electronic states of rhodium carboxylates and amides because of perturbation of the Rh–Rh π^* -to- σ^* HOMO–LUMO transition.³⁹ Shorter Rh–L_{ax} bonds from strong σ -donors increase the π^* -to- σ^* gap, leading to higher energy shifts in the UV–vis. In each case, the incorporation of a tethered axial thioether causes a shift of this band to higher energy. The disubstituted complexes caused a further blue shift from their respective monosubstituted complexes. When the (*S*)-MeTOX complexes (**5**, **6a**, and **6b**) are compared to the PhTCB complexes (**2**, **3a**, and **3b**), the data show that (*S*)-MeTOX has a stronger interaction at the axial site than PhTCB when incorporated into the Rh paddlewheel framework.

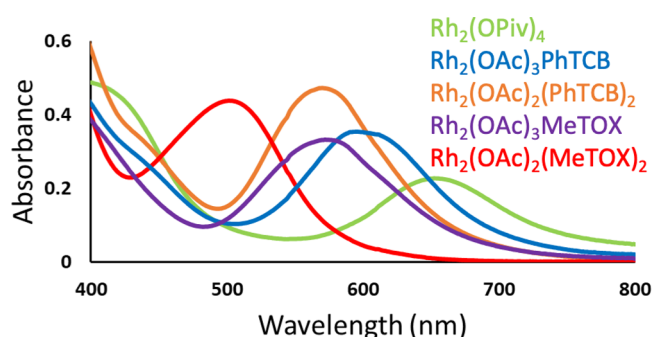


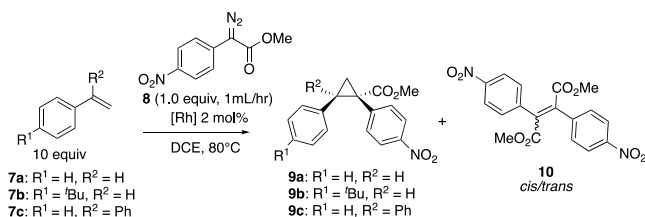
Figure 2. UV–vis spectra of Rh complexes recorded in DCE. $\text{Rh}_2(\text{OAc})_4$ was substituted with $\text{Rh}_2(\text{OPiv})_4$ because of solubility issues.

The electrochemical characteristics of Rh(II) complexes can be correlated with the reactivity and selectivity in diazo-mediated transformations,^{40,41} with electron-rich complexes having lower redox potentials, lower reactivities, and higher selectivities than electron-poor complexes. Electrochemical relationships for axially coordinating ligands have been limited to correlating the reactivity in Rh(II,III)-catalyzed oxidation reactions.⁴² Nevertheless, it is useful to compare these characteristics to approximate the electrophilicity of our complexes.

The cyclic voltammograms of all of the complexes showed reversible $\text{Rh}_2^{4+/5+}$ couples between 404 and 870 mV versus ferrocenium/ferrocene depending on the ligand architecture (Figure S2). Interestingly, the $\text{Rh}_2^{4+/5+}$ $E_{1/2}$ value of **2** was 36 mV higher than that of its monobenzoate control complex $\text{Rh}_2(\text{OAc})_3\text{OBz}$ (Figure S2; 870 mV compared to 834 mV), meaning that the presence of the axial tether in complex **2** should result in a more electrophilic catalyst compared to $\text{Rh}_2(\text{OAc})_3\text{OBz}$. Trends based on σ donation alone would have suggested a cathodic shift for complex **2**, implying that the tethered thioether ligand also has π -acceptor character.^{43,44} The more electron-rich axial thiomethyl donor for complex **5** reduces the redox potential to 603 mV (Figure S2), below that for complex **2**. Irreversible ligand-centered redox events linked to the number of axially coordinating ligands were observed in the cases of **2**, **3a**, and **3b**. The strength of the axial binding must also be a factor because **5**, **6a**, and **6b** do not follow this trend (Figure S2).

To assess the axial tether concept in catalysis, complexes were screened for their ability to catalyze the cyclopropanation of alkene substrates with methyl-*p*-nitrophenyldiazoacetate (**8**). Compound **8** is a diazoacetate that has been previously reported to give low yields of cyclopropanes in Rh(II)-catalyzed cyclopropanation reactions,^{45,46} giving mostly undesired homo-coupled side product **10**, unless bulky catalysts are used.⁴⁷ Under optimal conditions (see Table S1), **2** was found to be the best catalyst for the transformation, while reactions carried out with **5** were less successful in yield for cyclopropane **9a**, giving yields comparable to those for $\text{Rh}_2(\text{OAc})_4$ (Table 1, entries 1–3). Disubstituted complexes **3a** and **3b** were also tested and, despite having sulfur coordinated at both axial sites, outperformed $\text{Rh}_2(\text{OAc})_4$ in yield and product ratio (in the case of **3b**) for cyclopropane **9a** (entries 4 and 5). Complexes **6a** and **6b** performed poorly, giving 17% yield of cyclopropane. As a control, the monobenzoate complex $\text{Rh}_2(\text{OAc})_3(\text{OBz})$ was tested (entry 7) and displayed poorer yield and similar product ratios compared to those of **2**, demonstrating that the axial tether

Table 1. Cyclopropanation of Alkene Substrates



entry	product	[Rh]	yield (%) ^a	9/10 ^b
1	9a	[Rh ₂ (OAc) ₄]	49	5.4:1
2	9a	2	74	>20:1 ^c
3	9a	5	46	5.0:1
4	9a	3a	48	9.3:1
5	9a	3b	59	16:1
6	9a	6a and 6b	17	4.5:1
7	9a	[Rh ₂ (OAc) ₃ OBz]	52	17:1
8	9b	[Rh ₂ (OAc) ₄]	57	12:1
9	9b	2	78	>20:1 ^c
10	9c	[Rh ₂ (OAc) ₄]	8	1:1
11	9c	2	28	9:1

^aYields are averaged over two runs. Determined by ¹H NMR using mesitylene as an internal standard. ^bRatio determined by ¹H NMR. ^cThe ratio calculated was beyond the standard NMR detection limits.

leads to increased yields. While results for the sterically congested 9c were modest with 2, they were a significant improvement in yield and 9c/10 ratio over those of Rh₂(OAc)₄ (entries 10 and 11), further demonstrating the potential of the ligand to enhance existing Rh paddlewheel complexes.

Some conclusions can be drawn from the data presented. Yields for cyclopropane 9a are better for complexes incorporating ligand 1 than the respective complexes from ligand 4, suggesting that weaker interaction of the axial donor group is important for optimal performance. The six-membered chelate coordination of the thioether donor group in 4 means that the thiomethyl is more tightly bound to the Rh atom, decreasing the Lewis acidity of the Rh center compared to that of 1. The electrochemistry data suggest, though, that the presence of a tethered axially coordinating thioether in carboxylate complexes results in a more electrophilic catalyst (compare the *E*_{1/2} values and yields for complex 2 and Rh₂(OAc)₃OBz). A representative control for complex 5 is needed to extend this trend to mixed oxazolidinate/carboxylate complexes.⁴⁸

In conclusion, new heteroleptic Rh complexes incorporating tethered thioether axial coordination have been synthesized and characterized. Their catalytic properties were probed in a cyclopropanation reaction with a diazo compound that is known for difficult reactivity and poor selectivity with regard to the suppression of diazo coupling. Our modified rhodium carboxylates successfully improved the reaction yield and decreased olefin formation. The modular nature of our design allows for experimentation with a variety of donor groups and equatorial ligands, with the goal of designing a new generation of Rh catalysts that incorporate axial coordination. Exploration into the scope of the effects of ligands is currently under investigation in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02627.

Experimental details, optimization table, X-ray crystal data, cyclic voltammetry, and NMR spectra (PDF)

Accession Codes

CCDC 1861873–1861874 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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