ORGANOMETALLICS

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C–H Activation Induced by Oxidative Addition of N–O Bonds in Oxime Esters: Formation of Rhodacycles and Cycloaddition with Alkynes

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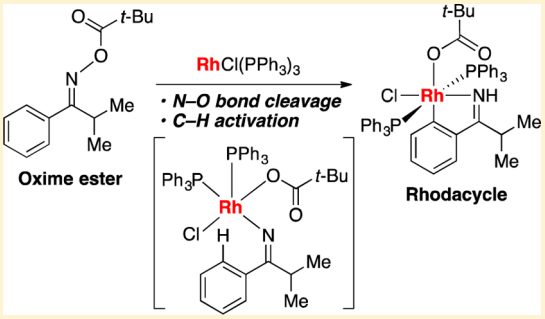
Supporting Information

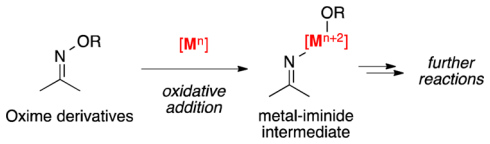
ABSTRACT: The reaction of oxime esters with a rhodium(I) precursor to form five-membered rhodacycles via N–O bond cleavage followed by C–H bond activation has been investigated by isolating these complexes. Kinetic studies on the formation of rhodacycles show that the reversible oxidative addition of the N–O bond in the oxime ester to $RhCl(PPh_3)_3$ occurs at room temperature. The *E*-isomer of the oxime ester was found to undergo rhodacycle formation faster than the *Z*-isomer, which suggests that the geometry of the oxime esters reflects the geometry of intermediates during C–H activation. The rhodacycle reacted with an alkyne to construct an isoquinoline ring in both stoichiometric and catalytic conditions, despite its basic stability in air, in moisture, and even during heating, which demonstrates the potential of the rhodacycle as an intermediate for further catalytic transformation of oxime esters.



INTRODUCTION

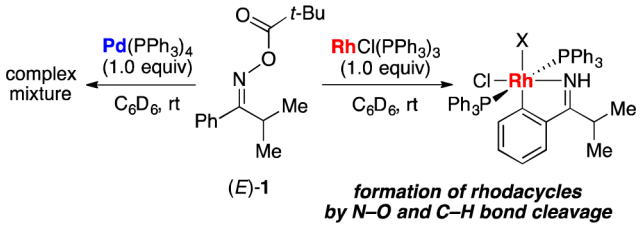
Recent progress in transition-metal-catalyzed transformation reactions of oximes and their derivatives has extended their synthetic utility in various nitrogen-containing organic compounds.[1] The key step for these reactions is the oxidative addition of their N–O bonds to low-valent metal species (Scheme 1). The stoichiometric oxidative addition of simple oximes to rhenium, osmium, and titanium was reported previously.[2] In 1999, Narasaka et al.[3] reported a palladium-catalyzed intramolecular amino-Heck reaction involving oxidative addition of oxime esters to palladium(0) species as a landmark study. Many transformation reactions using this concept have since been reported.[4,5] Recently, a few distinguished mechanistic studies have reported that the involvement of the oxidative addition of oxime esters to palladium(0) was confirmed by the isolation of oxidative adducts.[4b,g] Although other transition metals such as rhodium, copper, nickel, ruthenium, and iridium have also been studied in terms of their use as a catalyst in similar reactions,[6−8] there have been no reports on the isolation of the intermediate complexes of these transition metals.

Scheme 1. Oxidative Addition of N–O Bonds of Oxime Derivatives to Low-Valent Metal Species



We investigated the rhodium-mediated reaction of oxime esters, which involves the oxidative addition of oxime esters to rhodium(I), and found that the rhodacycle complexes were formed by the oxidative addition of oxime esters to rhodium(I) followed by C–H activation (Scheme 2).

Scheme 2. Rhodium-Mediated Oxidative Cleavage of Oxime Esters to Form Rhodacycles



RESULTS AND DISCUSSION

As an initial attempt, a stoichiometric reaction of *O*-pivaloyl oxime ester (*E*)-**1** and $RhCl(PPh_3)_3$ in C_6D_6 at room temperature was traced with ^1H NMR (Figure 1). Immediately after mixing, a new doublet peak corresponding to the methyl protons of the isopropyl group was observed in the high-field

Received: April 18, 2016

DOI: 10.1021/acs.organomet.6b00311
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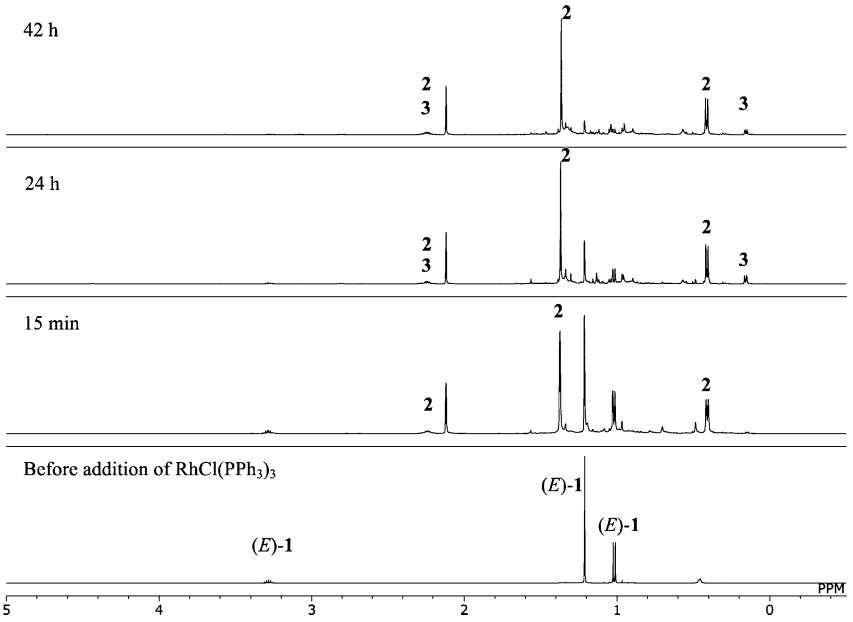
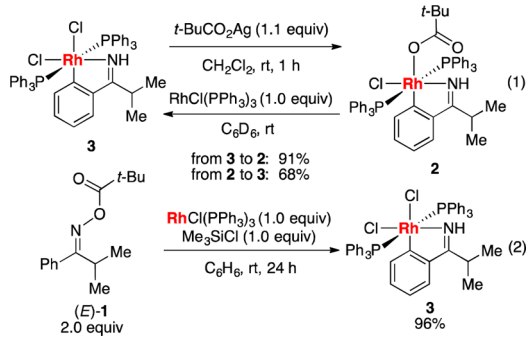


Figure 1. ^{1}H NMR spectra of time dependence of the reaction of (*E*)-**1** (0.02 mmol) with $RhCl(PPh_3)_3$ (0.02 mmol) in C_6D_6 at room temperature.

region, which was assigned to rhodacycle **2**. As the reaction proceeded, another doublet peak assigned to rhodacycle **3** was also observed in the high-field region. The yellow crystals of rhodacycle **3** precipitated after 24 h.[9] Complex **2**, bearing a pivalate ligand, was not isolated from this reaction mixture, but was successfully prepared in high yield from the isolated complex **3** by the treatment of silver pivalate (eq 1). In



addition, isolated complex **2** was also converted back to complex **3** by the treatment of $RhCl(PPh_3)_3$, which indicates that interconversion between two rhodacycles occurred in the reaction as shown in Figure 1. Finally, rhodacycle **3** was obtained almost quantitatively by adding Me_3SiCl as a chloride source after the completion of the reaction of oxime ester **1** and $RhCl(PPh_3)_3$ (eq 2).

Rhodacycles **2** and **3** were characterized by X-ray crystallographic analysis (Figures 2 and 3). Two PPh_3 ligands of both rhodacycle complexes **2** and **3** were located at the axial positions to a rhodacycle plane, and two chloride ligands were located on the rhodacycle plane. It is worth noting that the η^1-pivalate ligand of rhodacycle **2** is located at the *cis* position to an imine nitrogen whose proton forms the obvious hydrogen bond with the pivalate oxygen (the length of O···N = 2.82 Å).

The difference in reactivity between two stereoisomers of oxime ester **1** was examined with a reaction in diluted conditions where $RhCl(PPh_3)_3$ was dissolved sufficiently (eq 3). Oxime ester (*E*)- or (*Z*)-**1** was consumed within 2 h upon

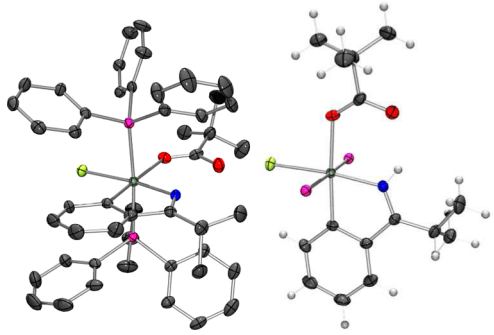


Figure 2. ORTEP illustrations of complex **2**. Left: Hydrogen atoms are omitted for clarity. Right: Phenyl groups on phosphorus atoms are omitted for clarity.

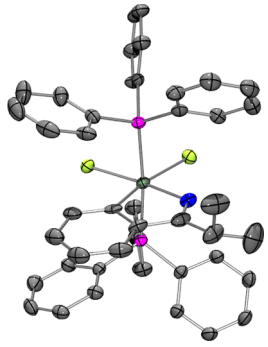


Figure 3. ORTEP illustration of complex **3**. Hydrogen atoms and solvent molecules are omitted for clarity.

mixing to afford the same rhodacycles **2** and **3** in each case. The reaction of (*E*)-**1** showed an obviously faster reaction rate than that of (*Z*)-**1** (Figure 4). The reaction rates of both isomers of oxime ester **1** (k_{obs}) were calculated using the inverse plot of a concentration of oxime ester **1** against time, which showed a linear relationship in the condition of an identical initial concentration of oxime ester **1** and $RhCl(PPh_3)_3$ (Figures S4 and S9, see Supporting Information). These results show the

DOI: 10.1021/acs.organomet.6b00311
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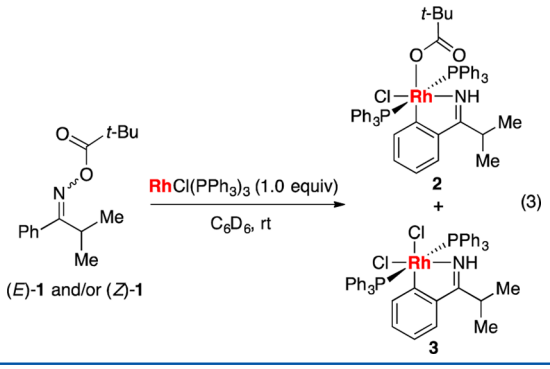


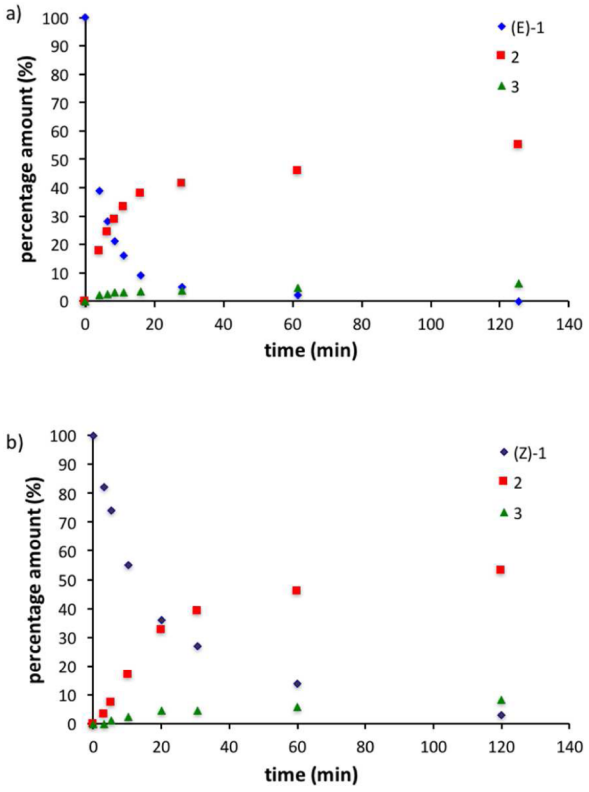
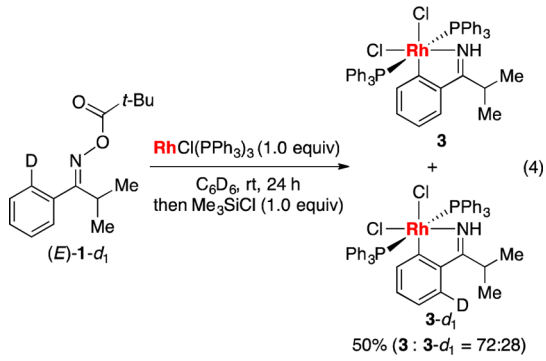


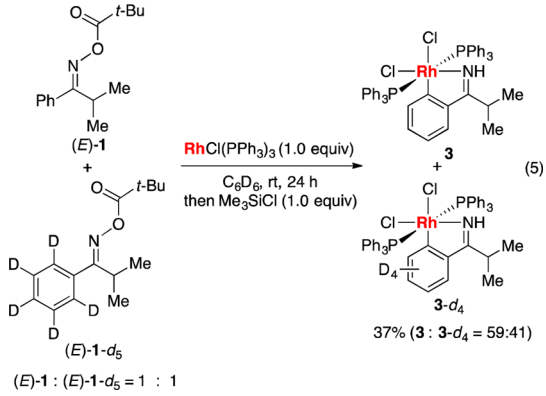
Figure 4. Time dependence of percentage amounts of each species in the reaction of (*E*)-**1** (a) or (*Z*)-**1** (b) (8.1 μmol) with $RhCl(PPh_3)_3$ (8.1 μmol) in C_6D_6 (0.8 mL) at room temperature. The percentage amounts were determined by ^1H NMR using hexamethylbenzene as an internal standard.

first-order dependence of these reactions on both **1** and $RhCl(PPh_3)_3$. Moreover, the activation parameters were calculated from Arrhenius and Eyring plots with the traces of the reactions at various temperatures (range 10−55 °C) (Figures S12 and S13, see Supporting Information). The calculated values of activation energies were 19.9 kcal/mol for (*E*)-**1** and 22.8 kcal/mol for (*Z*)-**1**, which are consistent with the result that the reactions proceeded smoothly at room temperature. The calculated values for activation enthalpy were 19.3 kcal/mol for (*E*)-**1** and 22.2 kcal/mol for (*Z*)-**1**, and those for activation entropy were -4.48×10^{-3} kcal/mol·K for (*E*)-**1** and 2.64×10^{-3} kcal/mol·K for (*Z*)-**1**. The activation entropies in the rhodacycle formation did not affect the total energy difference significantly.

Competitive experiments using oxime esters labeled with deuterium have been performed to observe kinetic isotope effects (KIEs) in the rhodacycle formation. Substrate (*E*)-**1**-*d*, in which one of the two reactive hydrogens is deuterated, reacted with $RhCl(PPh_3)_3$ to give a mixture of **3**-d_1 and **3** totally in 50% yield with a 72:28 ratio (eq 4; KIE value = 2.57).

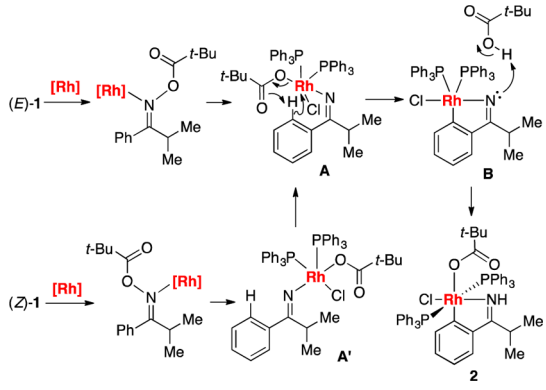


In contrast to the intramolecular control experiment, an intermolecular competitive experiment using (*E*)-**1** and (*E*)-**1**-d_5 resulted in a less significant KIE value (eq 5; KIE value = 1.44).



A proposed mechanism for the formation of rhodacycle complexes is shown in Scheme 3. The oxidative addition of the

Scheme 3. Proposed Mechanism for Generation of Rhodacycles from Oxime Ester 1



N−O bond of oxime ester (*E*)- or (*Z*)-**1** is likely to be initiated by the dissociation of one PPh_3 and the following η^1-coordination of the oxime nitrogen atom to rhodium(I) species (coordination of the carbonyl oxygen may also participate in this step)[10] and then forms intermediate **A** or **A′**, depending on the geometry of the starting oxime esters.[11] Considering the distance between the rhodium center and the C−H bond at the

DOI: 10.1021/acs.organomet.6b00311
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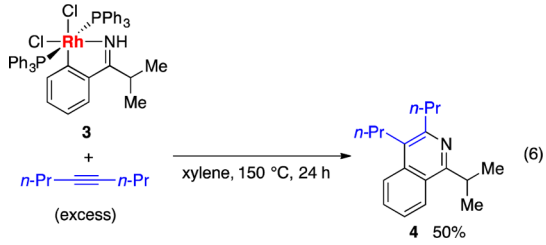
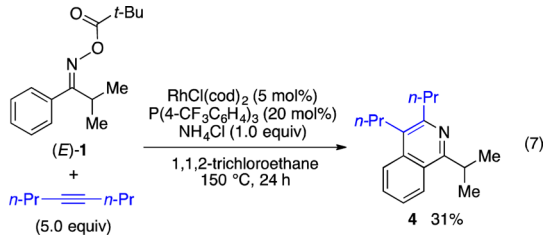
ortho position of the phenyl group, C−H activation in complex **A** is much preferred than in complex **A′**. Complex **A′** needs to isomerize into complex **A** prior to C−H activation, which may become a major factor for decreasing the reaction rate from oxime ester (*Z*)-**1**. This explanation agrees with the apparent difference in activation parameters between both stereoisomers of oxime ester **1**. After the oxidative addition step, activation of *ortho* C−H bonds is considered to proceed in a concerted metalation−deprotonation mechanism[12] induced by the η^1-pivalate ligand to afford five-membered rhodacycle **B**. Rhodacycle **B** is readily protonated at the iminide nitrogen by the pivalic acid to give pivalate-coordinated complex **2**. The ligand exchange between chloride and pivalate on complex **2** affords dichloride complex **3**, as described previously. The large KIE value observed in the intramolecular comparison using (*E*)-**1**-*d* indicates that the N−O bond cleavage would be a rate-determining step because it occurs before the C−H activation step.[13,14] The small KIE value observed in the intermolecular comparison may indicate the reversibility of N−O bond cleavage that occurs before the C−H activation.[15]

The reactivity of rhodacycle complex **3** with an excess amount of 4-octyne was examined. Isoquinoline **4** as a cycloaddition product was obtained in 50% yield by the reaction of complex **3** with 20 equiv of 4-octyne in xylene at 150 °C (eq 6). Moreover, a rhodium-catalyzed reaction of



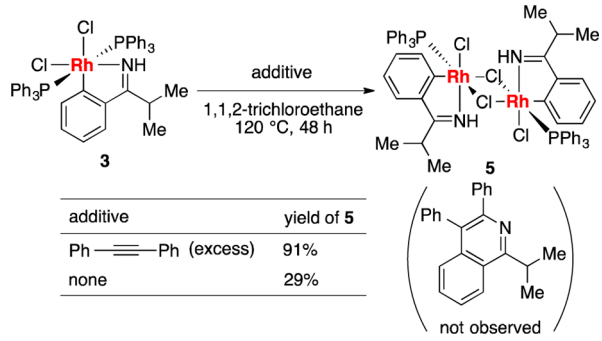
oxime ester (*E*)-**1** with 4-octyne also proceeded to afford isoquinoline **4** in 31% yield (eq 7).[16] As a remarkable result, the



reaction of complex **3** with diphenylacetylene formed no insertion products, but formed chloro-bridged dimer complex **5** in high yield (Scheme 4). The ORTEP drawing of **5** is shown in Figure 5. The simple heating of complex **3** in the absence of diphenylacetylene also gave only the dimer complex **5** in 29% yield, which indicates that the alkyne promotes the dissociation of PPh_3, leading to the formation of dimer complex **5**.

On the basis of the observation of the stoichiometric and catalytic reactions with alkynes involving rhodacycles, we propose a reaction mechanism for the formation of isoquinoline **4** (Scheme 5). Considering the formation of dimer complex **5**, the reaction with 4-octyne would be initiated by the ligand exchange between PPh_3 and 4-octyne. When the alkyne dissociates from the resulting intermediate **C**, a thermally more stable chloro-bridged dimer **5** is formed. When intermediate **C** undergoes alkyne insertion into a carbon−

Scheme 4. Formation of Chloro-Bridged Dimer 5 in the Presence of Diphenylacetylene



additive	yield of **5**
Ph—≡—Ph (excess)	91%
none	29%

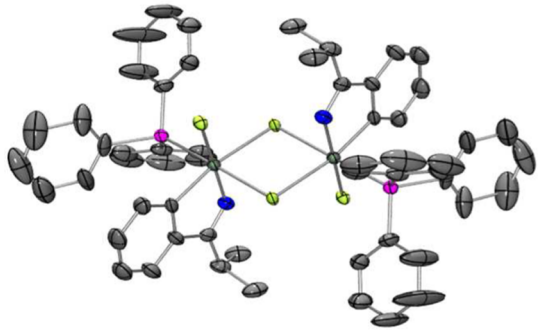
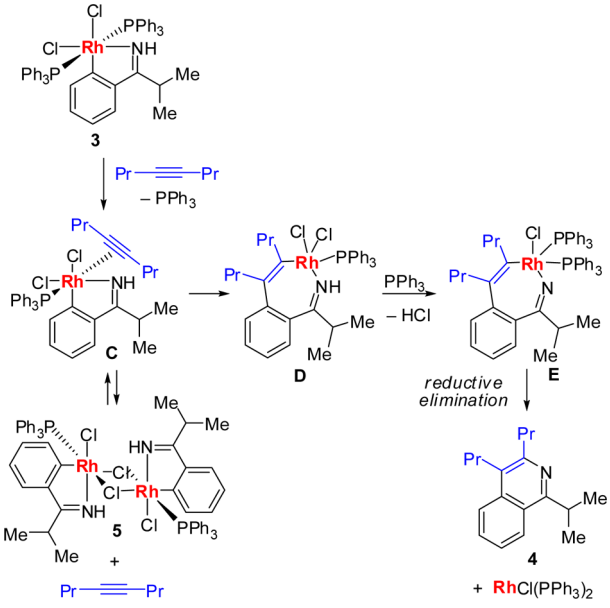


Figure 5. ORTEP illustration of rhodacycle dimer **5**. Hydrogen atoms are omitted for clarity.

Scheme 5. Proposed Mechanism for Alkyne Insertion Giving Isoquinoline 4



rhodium σ-bond, a seven-membered rhodacycle **D** is formed. Under high-temperature conditions, intermediate **D** is considered to be in an equilibrium with dehydrochlorinated rhodacycle **E**, which undergoes reductive elimination to give isoquinoline **4** as a product as well as the regeneration of rhodium(I) catalyst.[17,18] This stoichiometric reaction of complex **3** strongly supports the intermediacy of a five-membered rhodacycle.

DOI: 10.1021/acs.organomet.6b00311
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CONCLUSION

In summary, we have achieved isolation and identification of the rhodacycle complexes by the reaction of a rhodium precursor and aromatic oxime esters. The oxidative addition of the N−O bonds in the oxime esters plays two characteristic roles in the rhodacycle formation: (1) the rhodium center is strongly attached to the nitrogen atom with the covalent bond; therefore, it is close to the aromatic C−H bond; (2) the valency of the rhodium center was changed into the higher oxidation state; therefore, it reduces the barrier to C−H activation. Moreover, the potential of the rhodacycles as an intermediate for the cycloaddition of alkynes with oxime esters has also been demonstrated. Further investigations for the effective catalytic transformation of oxime esters are currently under way 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.organomet.6b00311.

Experimental procedures for preparation of oxime esters and rhodacycle complexes; procedures for stoichiometric and catalytic reactions; and NMR spectroscopic data (PDF)

X-ray crystallographic data for the oxime and rhodium complexes **2**, **3**, and **5** (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study has been financially supported by JSPS KAKENHI (Grant-in-Aid for Young Scientists (B); Grant No. 24750085). The authors thank Prof. Tetsuaki Fujihara (Kyoto University) for his support with NMR measurements and X-ray crystallographic analyses. Helpful and suggestive comments from the reviewers are gratefully appreciated.

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(9) Similar imine-containing five-membered rhodacycles bearing two phosphine ligands at axial positions were reported. See: (a) Huang, L.-Y.; Aulwurm, U. R.; Heinemann, F. W.; Knoch, F.; Kisch, H. *Chem. - Eur. J.* **1998**, *4*, 1641−1646. (b) Marcazzan, P.; Patrick, B. O.; James, B. R. *Organometallics* **2005**, *24*, 1445−1451. (c) Ezhova, M. B.; Patrick, B. O.; James, B. R. *Organometallics* **2005**, *24*, 3753−3757.

(10) One might think about the possibility of another mechanism in which the C−H activation occurs first and then the oxidative addition of N−O bonds follows (see also ref 6b). However, in the case of rhodium(I) complexes, such a mechanism can be excluded by the result that other oxime derivatives such as oxime ethers (no N−O bond cleavage occurs) did not give any C−H activation products under similar conditions.

(11) Selected examples of *ortho* C−H activation by rhodiium(III) directed by an *N*-oxyimino or imino group. See: (a) Fukutani, T.;

DOI: 10.1021/acs.organomet.6b00311
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(12) For reviews, see: (a) Lapointe, D.; Fagnou, K. *Chem. Lett.* **2010**, *39*, 1118−1126. (b) Bouffard, J.; Itami, K. *Top. Curr. Chem.* **2009**, *292*, 231−280. (c) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315−1345. (d) Sperger, T.; Sanhueza, I. A.; Kalvet, I.; Schoenebeck, F. *Chem. Rev.* **2015**, *115*, 9532−9586.

(13) Simmons, E. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066−3072.

(14) The possibility that the coordination of rhodium to oxime esters is rate-determining cannot be excluded with the present results.

(15) The *E*/*Z* isomerization of oxime esters was also observed in the reaction of (*E*)-**1**-d_5 with $RhCl(PPh_3)_3$ (Figure S14 in the Supporting Information) despite no thermal isomerization of these oxime esters under the reaction conditions. This result is also consistent with the reversibility of N−O bond cleavage.

(16) For eqs 6 and 7, see the screening of the reaction conditions in the Supporting Information.

(17) Isoquinoline synthesis by the stoichiometric alkyne insertion to a five-membered rhodacycle intermediate with a Cp* ligand has been reported by Jones et al. See: Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414−12419.

(18) For reviews on rhodium(III)-catalyzed formation of isoquinolines via a five-membered rhodacycle intermediate, see: (a) He, R.; Huang, Z.-T.; Zheng, Q.-Y.; Wang, C. *Tetrahedron Lett.* **2014**, *55*, 5705−5713. (b) Mo, J.; Wang, L.; Liu, Y.; Cui, X. *Synthesis* **2015**, *47*, 439−459 See also ref 6.

DOI: 10.1021/acs.organomet.6b00311
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