

Methoxy-Directed Aryl-to-Aryl 1,3-Rhodium Migration

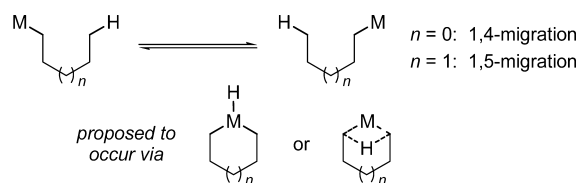
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S Supporting Information

ABSTRACT: Through-space metal/hydrogen shift is an important strategy for transition-metal-catalyzed C–H bond activation. Here we describe the synthesis and characterization of a Rh(I) 2,6-dimethoxybenzoate complex that underwent stoichiometric rearrangement via a highly unusual 1,3-rhodium migration. This aryl-to-aryl 1,3-Rh/H shift was also demonstrated in a Rh(I)-catalyzed decarboxylative conjugate addition to form a C–C bond at a *meta* position instead of the *ipso*-carboxyl position. A deuterium-labeling study under the conditions of Rh(I)-catalyzed protodecarboxylation revealed the involvement of an *ortho*-methoxy group in a multistep pathway of consecutive sp^3 and sp^2 C–H bond activations.

Transition-metal-catalyzed direct functionalization of C–H bonds has become a powerful tool for organic synthesis.¹ An important method for intramolecular C–H bond activation is the “through-space” metal/hydrogen shift, most commonly at 1,4- and 1,5-positions of a hydrocarbon backbone (1,4- and 1,5-migrations, Scheme 1).² These rearrangement processes

Scheme 1. Intramolecular C–H Bond Activation via Metal–Hydrogen Shifts



allow functionalization of C–H bonds that are difficult to activate directly. Catalytic 1,4-rhodium migration was first reported in 2000 by Miura et al. in the reaction between arylboronic acids and norbornenes.^{3a} In the same year, Larock et al. reported the first catalytic 1,4-palladium migration in coupling between aryl iodides and alkynes.^{4a} Since these pioneering studies, catalytic 1,4-migrations of various late transition-metal centers such as Rh(I),³ Pd(II),⁴ Pt(II),^{5a,b} and Ni(I)^{5c} have been successfully explored for selective functionalization of sp^2 and sp^3 C–H bonds to form carbon–carbon and carbon–heteroatom bonds. Several examples of catalytic 1,5-migrations have also been reported for Rh(I)^{6a} and Pd(II)^{6b–d} intermediates.

In contrast to the well-established 1,4- and 1,5-migrations, other forms of metal/hydrogen shifts are very rare. In particular,

1,3-migration has not been reported with any transition-metal species. From the reaction mechanism perspective, 1,4- and 1,5-migrations have been proposed to be facilitated by stabilized 5- or 6-membered metallacycle intermediates and transition states (Scheme 1).² In comparison, DFT calculations suggest that direct 1,3-metal/hydrogen shifts would require highly strained 4-member cyclic transition states with prohibitively high activation energies.^{6c,d,7} On the other hand, the classic 1,3-shifts of transition-metal allyl species only involve migration of metal centers but not hydrogen atoms.⁸ We herein describe stoichiometric and catalytic rearrangement processes that occur by a formal aryl-to-aryl 1,3-rhodium migration in Rh(I)-mediated decarboxylation. Mechanistic results from deuterium labeling studies suggest a highly unusual, “double 1,4-Rh migration” pathway that involves sp^3 C–H bond activation at the methoxy group.⁹

Over the past decade, late transition-metal-mediated decarboxylation of benzoic acids has generated much interest as a nonconventional approach toward reactive metal aryl intermediates in catalysis.^{10–12} A very important structural motif for decarboxylation is *ortho*-substitution of benzoic acids. In particular, *ortho*-methoxy and *ortho*-fluorine groups have been shown to significantly promote decarboxylation reactivity with various transition-metal catalysts.¹⁰ We have previously reported Rh(I)-catalyzed decarboxylative transformations of 2,6-difluorobenzoic acids including conjugate addition, oxidative olefination,^{12a} and protodecarboxylation.¹³ As part of our efforts to gain mechanistic insights into Rh(I)-mediated decarboxylation, we have synthesized (bis)phosphine-ligated Rh(I) benzoate complexes for direct observation of stoichiometric decarboxylation. As described in Scheme 2, κ^2 -carboxylates **2a** and **2b** were prepared by reactions between $[(\text{cod})\text{Rh}(\mu\text{-OH})]_2$ (cod: 1,4-cyclooctadiene), BIPHEP (2,2'-bis(diphenylphosphino)-1,1'-biphenyl), and 2,6-difluorobenzoic acid (**1a**) or 2,6-dimethoxybenzoic acid (**1b**), respectively. As we reported previously,^{13a} 2,6-difluorobenzoate **2a** underwent stoichiometric decarboxylation at 120 °C with 1 equiv of added pyridine in toluene, giving the corresponding arylrhodium(I) complex **4a** in quantitative conversion.

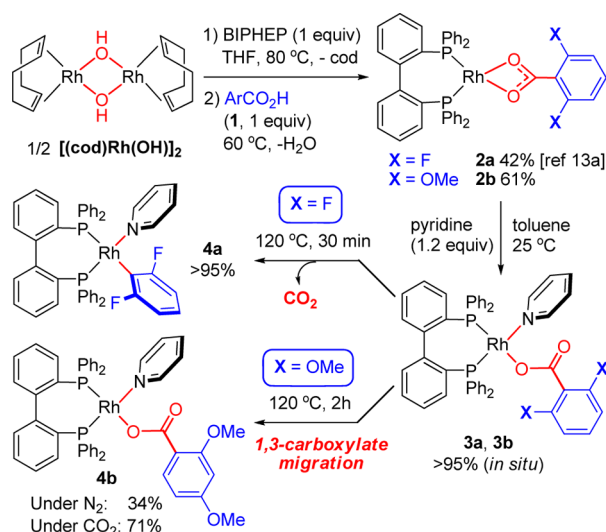
We envisioned that the reaction between Rh(I) κ^2 -benzoates (**2**) and pyridine would lead to the formation of pyridine-ligated κ^1 -benzoate complexes (**3**). Indeed, we have observed clean formation of **3a** and **3b** by ³¹P NMR (Scheme 2). The *in situ*

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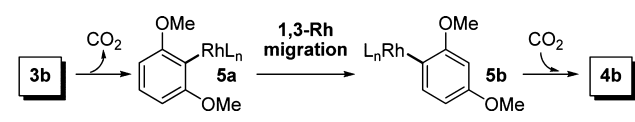


Scheme 2. Synthesis and Thermal Transformation of 2,6-Disubstituted Rh(I) Benzoates



formed **3a** underwent quantitative decarboxylation that was consistent with our previous observation.^{13a} In sharp contrast, thermolysis of *in situ* formed κ^1 -2,6-dimethoxybenzoate **3b** at 120 °C in toluene did not generate the expected Rh(I) 2,6-dimethoxyphenyl complex by decarboxylation.¹⁴ Instead, a novel “1,3-carboxylate migration” appeared to occur, leading to the formation of κ^1 -2,4-dimethoxybenzoate **4b** in 34% yield as the only detectable Rh(I) species by ³¹P NMR analysis. Interestingly, the yield of **4b** was improved to 71% when the thermolysis was carried out under 1 atm of CO₂ instead of N₂. Structures of isolated **2b**, **3b**, and **4b** were determined by single crystal X-ray diffraction (details in SI). In the solid state, the chelating carboxylate ligand in **2b** led to a significantly distorted square planar geometry. In comparison, **3b** and **4b** adopt near square-planar geometry with monodentate carboxylate ligands.

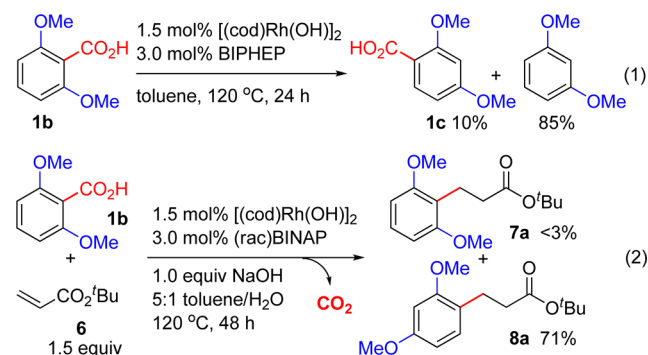
Based on the yield improvement of **4b** under CO₂ atmosphere, we propose a multistep pathway for the 1,3-carboxyl migration as described in Scheme 3. Decarboxylation of **3b** was

Scheme 3. Proposed Pathway for Isomerization of Rh(I) Carboxylates **3b** To Form **4b**

expected to generate a Rh(I) 2,6-dimethoxyphenyl intermediate **5a**,¹⁴ which underwent rearrangement by 1,3-Rh/H shift (1,3-Rh migration) to form Rh(I) 2,4-dimethoxyphenyl complex **5b**. With the reduced steric crowding around Rh center in **5b** compared to **5a**, the decarboxylation/carboxylation thermodynamics was shifted to favor CO₂ insertion into the Rh-aryl linkage¹⁵ to give carboxylation product **4b** as the most stable Rh(I) species in the reaction system. With lower CO₂ concentration in a non-CO₂ atmosphere, **5b** underwent competitive protonation of the Rh–C bond to generate 1,3-dimethoxybenzene that was detected as the major byproduct.

We envisioned that the proposed 1,3-Rh migration could be exploited catalytically to give novel rearrangement products. For example, the 1,3-carboxyl migration of **3b** (Scheme 2) could proceed catalytically to allow isomerization of 2,6-dimethoxybenzoic

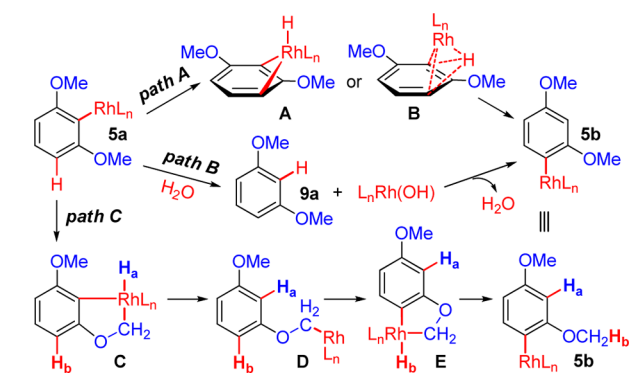
acid (**1b**) to form 2,4-dimethoxybenzoic acid (**1c**) (eq 1). However, 1,3-dimethoxybenzene was formed as the major



product by competitive protodecarboxylation. In comparison, a catalytic decarboxylative 1,4-addition^{13a} of **1b** with *t*-butyl acrylate (**6**) was successfully carried out to give 1,3-migration product **8a** in 71% yield and >20:1 selectivity over the nonrearrangement product **7a** (eq 2). This reaction was promoted by 1.5 mol % [(cod)Rh(OH)]₂, 3.0 mol % BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), 1.0 equiv NaOH additive, and 5:1 toluene/H₂O mixed solvent at 120 °C. Notably, this reaction occurred in good selectivity and without the formation of corresponding Heck–Mizoroki olefination products.^{12a,13a}

We have considered several possible pathways for the proposed 1,3-Rh migration with arylrhodium(I) intermediate **5a** in decarboxylative transformations of **1b** (Scheme 4). A direct

Scheme 4. Proposed Pathways for 1,3-Rh Migration

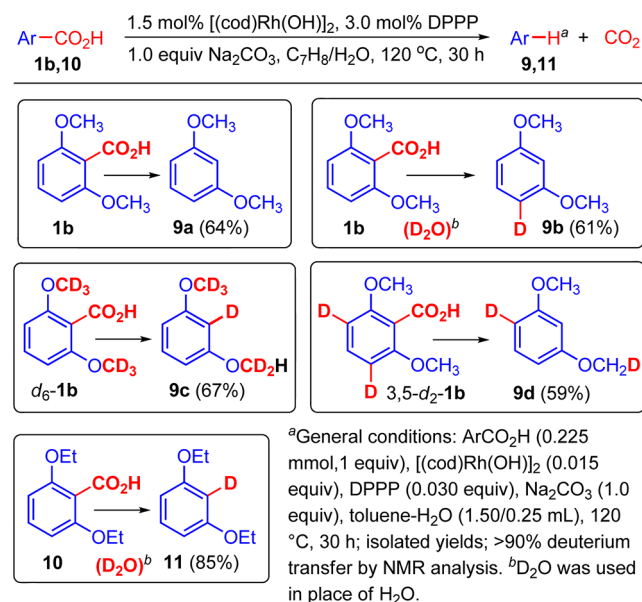


1,3-Rh/H shift (path A) requires a 4-membered cyclometalated Rh(III) hydrido intermediate **A** or a σ -bond metathesis transition-state **B**.² Both structures would be extremely strained due to the inherent aromatic planarity and rigidity, making this pathway a highly unlikely scenario.⁷ Path B involves protonation of the Rh–C bond in **5a** by hydrolysis to form 1,3-dimethoxybenzene (**9a**) and a Rh(I) hydroxo intermediate. **5b** is then formed via aromatic C–H bond activation of **9a** by Rh(I) hydroxide,¹⁶ with the regioselectivity determined by *ortho*- and *para*-directing methoxy groups in an electrophilic aromatic substitution (S_EAr) mechanism. In path C, **5a** undergoes cyclometalation to activate a methoxy sp³ C–H bond at the *ortho* position and forms a Rh(III) hydrido intermediate **C**.⁹ Subsequent C–H reductive elimination at the original *ipso* position generates a Rh(I) aryloxyalkyl

intermediate **D**, which undergoes further aromatic C–H bond activation at the less hindered *meta* position to form another cyclometalated Rh(III) intermediate **E**. **E** then undergoes C–H reductive elimination at the methoxy position to form **5b**. Notably, the proposed transformations of **5a**→**D** and **D**→**5b** represent formal 1,4-Rh migrations and could also occur by single-step σ -bond metathesis and without involvement of Rh(III) hydrido intermediates.² In all three possible pathways, the individual steps are possibly reversible and the driving force for formation of **5b** over **5a** is most likely the partly relieved steric hindrance with mono- vs dimethoxy groups at *ortho* positions.

To evaluate the feasibility of path B, we have attempted coupling reaction with *t*-butyl acrylate (**6**) using 1,3-dimethoxybenzene (**9a**) in place of **1b** under catalytic conditions shown in eq 2. No reaction was observed, and **9a** was fully recovered, which strongly argues against path B. Regarding path C, our efforts toward a direct observation of the proposed stoichiometric transformations were hampered by failed attempts for an independent synthesis of intermediate **5a**. However, the proposed intramolecular transfer of H atoms (H_a and H_b) provides a suitable target for deuterium labeling studies.^{3b,c,4g,h} Thus, path C was further evaluated by a catalytic deuterium transfer process described below, using a modified procedure of Rh(I)-catalyzed protodecarboxylation previously reported by our group (Scheme 5).^{13b,17}

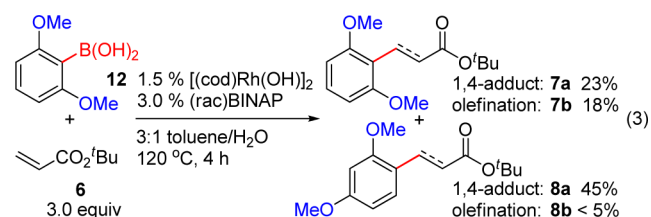
Scheme 5. Deuterium-Labeling Study on Rh(I)-Catalyzed Hydrodecarboxylation



Protodecarboxylation of 2,6-dimethoxybenzoic acid (**1b**) was effectively promoted by a catalyst system of 1.5 mol % [(cod)-Rh(OH)₂], 3.0 mol % DPPP ligand (1,2-bis(diphenyl-phosphino)propane), 1 equiv of Na₂CO₃ additive in 6:1 toluene/H₂O at 120 °C to give 1,3-dimethoxybenzene (**9a**) in 64% isolated yield. Using D₂O in place of H₂O in the solvent system led to the exclusive formation of 4-*d*-1,3-dimethoxybenzene (**9b**) in 61% yield. Such regioselective deuterium incorporation confirmed the involvement of 1,3-Rh migration to form intermediate **5b** (Scheme 3), which underwent subsequent deuteration of the Rh-aryl bond with D₂O. The catalytic protodecarboxylation was then studied with two site-selective deuterium-labeled

derivatives of 2,6-dimethoxybenzoic acid (**1b**), and both results supported the proposed intramolecular H-atom transfers by path C: (1) Substrate *d*₆-**1b** (fully deuterium-labeled methoxy groups) underwent intramolecular deuterium transfer from a OCD₃ group to the original *ipso* position, forming hydrodecarboxylation product **9c** in 67% yield. This result was consistent with the proposed (*ipso*)aryl/methoxy 1,4-Rh/H shift in path C (Scheme 4, **5a**→**D**). (2) Substrate 3,5-*d*₂-**1b** (deuterium labeling at both *meta* positions relative to the carboxyl group) underwent deuterium transfer from one of the *meta* positions to the nearby methoxy group, forming hydrodecarboxylation product **9d** in 59% yield. This result was consistent with the proposed methoxy/(*meta*)aryl 1,4-Rh/H shift in path C (Scheme 4, **D**→**5b**). It is noteworthy that the individual steps of **5a**→**D** and **D**→**5b** have been reported for Pd(II)-catalyzed rearrangement processes by aryl-to-alkyl^{4d,h,i} and alkyl-to-aryl^{4c} 1,4-Pd migrations, respectively. However, a formal 1,3-migration by two consecutive 1,4-migrations has not been reported. The highly selective formation of **9b** suggested that both steps of 1,4-migration were impressively rapid processes that effectively prevented competitive protonation of intermediates **5a** or **D**, which would allow incorporation of external deuteriums at *ortho* and methoxy positions. In addition, catalytic hydrodecarboxylation of 2,6-diethoxybenzoic acid (**10**) in toluene/D₂O did lead to exclusive *ipso*-deuteration to form 2-*d*-1,3-diethoxybenzene (**11**) as the only detectable product. Thus, the target 1,3-Rh migration process appears to rely on a delicate balance on steric effects of the *ortho*-substituents: significant steric crowding (OMe vs F) is needed to slow down *ipso*-functionalization and promote rapid, consecutive Rh/H shifts, whereas too much steric crowding (OEt vs OMe) inhibits the first Rh/H shift step and shuts down the overall migration process.

Based on the proposed mechanism, we envisioned that 1,3-Rh migration is not limited to decarboxylation process and could occur with analogous Rh(I) aryl species generated by other transformations. Indeed, preliminary results showed that methoxy-directed 1,3-migration also occurred in Rh(I)-catalyzed coupling of arylboronic acids with olefins (eq 3),



where arylrhodium(I) species were formed by B-to-Rh transmetalation.^{18,19} A catalyst system of [(cod)Rh(OH)₂] precursor and racemic BINAP ligand promoted the reaction between 2,6-dimethoxyphenylboronic acid (**12**) and *t*-butyl acrylate (**6**) at 120 °C to form a mixture of *ipso* products (**7a**, **7b**) and *meta* products (**8a**, **8b**) by competitive 1,4-addition and Heck–Mizoroki olefination. The tandem 1,3-migration/1,4-addition product **8a** was isolated as the major component in 45% yield. Despite the moderate selectivity, this result serves as a proof-of-concept for methoxy-directed 1,3-Rh migration in general coupling reactions that may be exploited for site-selective arene functionalization.

In summary, we report a novel 1,3-migration of rhodium that was demonstrated in several stoichiometric and catalytic

isomerization processes involving proposed Rh(I) 2,6-dimethoxyphenyl intermediates. Mechanistic results from a deuterium-labeling study support a highly unusual, "consecutive 1,4-migration" pathway via sp^3 C–H bond activation of the methoxy group. With ongoing studies on further mechanistic details, we aim to better understand structure–reactivity correlations in this novel isomerization process and seek broader applications in synthetic chemistry.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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