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

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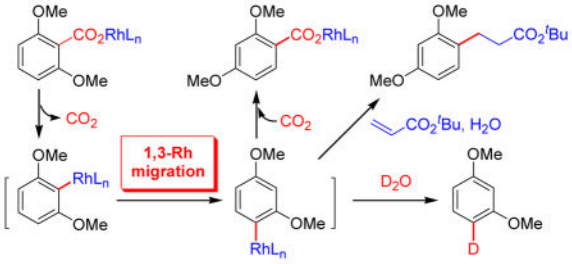
## Abstract

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 multi-step 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 allow functionalization of C-H bonds that are difficult to activate directly. Catalytic 1,4-rhodium migration was first reported in 2000 by Miura and coworkers in the reaction between arylboronic acids and norbornenes.[3a] In the same year, Larock and coworkers 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

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Supporting Information

Experimental procedures, spectral data, and structural parameters of compounds **2b**, **3b** and **4b** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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,6d,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]

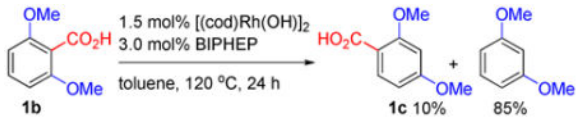
Over the past decade, late transition metal-mediated decarboxylation of benzoic acids has generated much interest as a non-conventional approach towards reactive metal aryl intermediates in catalysis.[10–12] A very important structural motif for decarboxylation is *ortho*-substitution of benzoic acids. 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, $\kappa^2$-carboxylates **2a** and **2b** were prepared by reactions between $[(cod)Rh(\mu\text{-}OH)]_2$ (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) $\kappa^2$- benzoates (**2**) and pyridine would lead to the formation of pyridine-ligated $\kappa^1$-benzoate complexes (**3**). Indeed, we have observed clean formation of **3a** and **3b** by $^{31}$P NMR (Scheme 2). The *in situ* formed **3a** underwent quantitative decarboxylation that was consistent with our previous observation.[13a] In sharp contrast, thermolysis of *in situ* formed $\kappa^1$-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 $\kappa^1$-2,4- dimethoxybenzoate **4b** in 34% yield as the only detectable Rh(I) species by $^{31}$P NMR analysis. Interestingly, the yield of **4b** was improved to 71% when the thermolysis was carried out under 1 atm of $CO_2$ instead of $N_2$. Structures of isolated **2b**, **3b** and **4b** were determined by single crystal X-ray diffraction (see Supporting Information for details). In

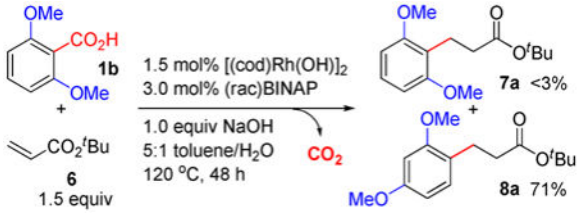
the solid state, the chelating carboxylato ligand in **2b** led to a significantly distorted square planar geometry. In comparison, **3b** and **4b** adopt near square-planar geometry with monodentate carboxylato ligands.

Based on the yield improvement of **4b** under $CO_2$ atmosphere, we propose a multi-step pathway for the 1,3-carboxyl migration as described in Scheme 3. Decarboxylation of **3b** was 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 $CO_2$ insertion into the Rh-aryl linkage[15] to give carboxylation product **4b** as the most stable Rh(I) species in the reaction system. With lower $CO_2$ concentration in a non-$CO_2$ 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 non-rearrangement 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/$H_2O$ mixed solvent at 120 °C. Notably, this reaction occurred in good selectivity and without the formation of corresponding Heck-Mizoroki olefination products.[12]




(1)




(2)

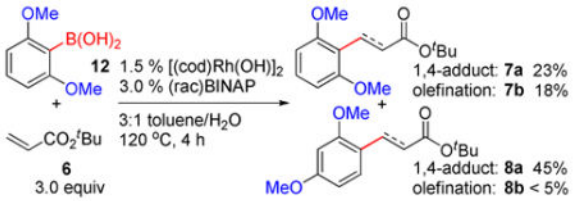
We have considered several possible pathways for the proposed 1,3-Rh migration with arylrhodium(I) intermediate **5a** in decarboxylative transformations of **1b** (Scheme 4). A direct 1,3-Rh/H shift (path A) requires a 4-membered cyclometalated Rh(III) hydrido intermediate **A** or a σ-bond metathesis 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 $sp^3$ 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 released steric crowding with mono- vs. di-methoxy 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 towards 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,3c,4g,4h] 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]

Protodecarboxyation 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(diphenylphosphino) ethane), 1 equiv of $Na_2CO_3$ additive in 6:1 toluene/ $H_2O$ at 120 °C to give 1,3-dimethoxybenzene (**9a**) in 64% isolated yield. Using $D_2O$ in place of $H_2O$ 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 $D_2O$. The catalytic protodecarboxylation was then studied with two siteselective 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 $OCD_3$ 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,4h,4i] 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/$D_2O$ 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.




(3)

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 structurereactivity correlations in this novel isomerization process and seek broader applications in synthetic chemistry.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

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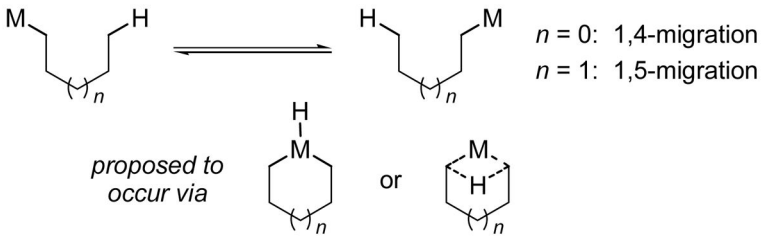
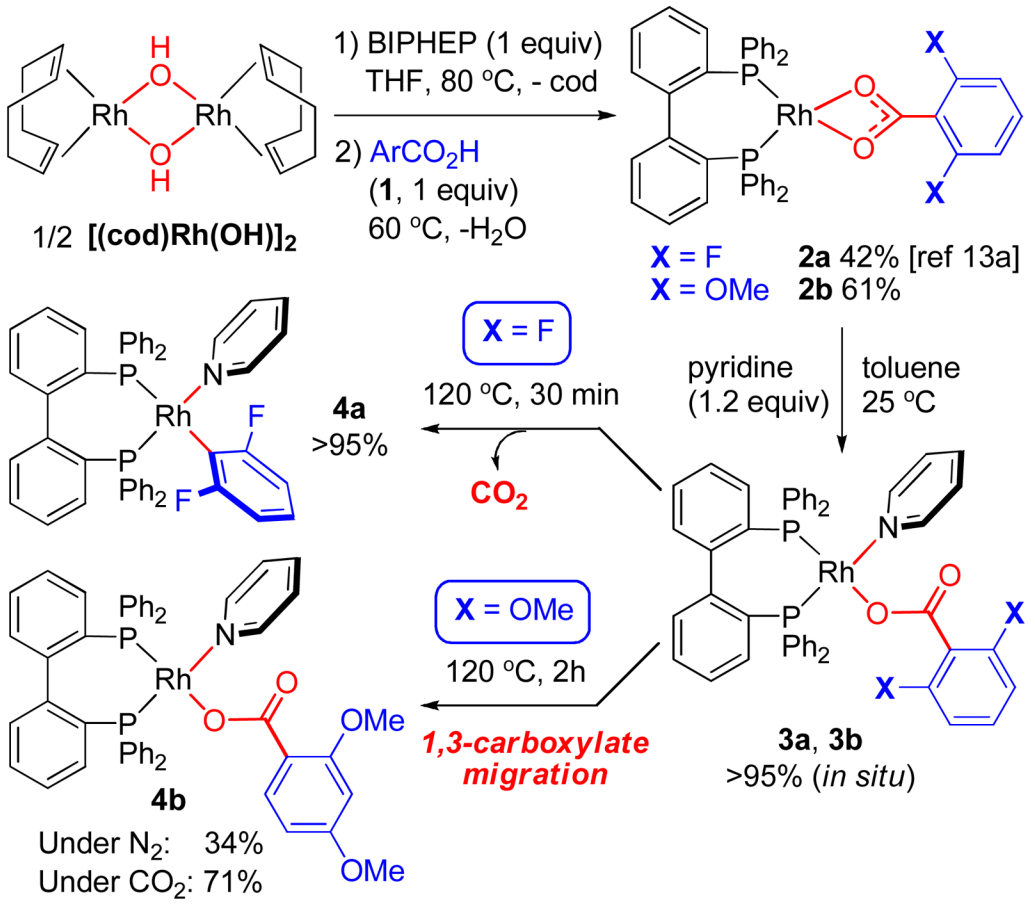


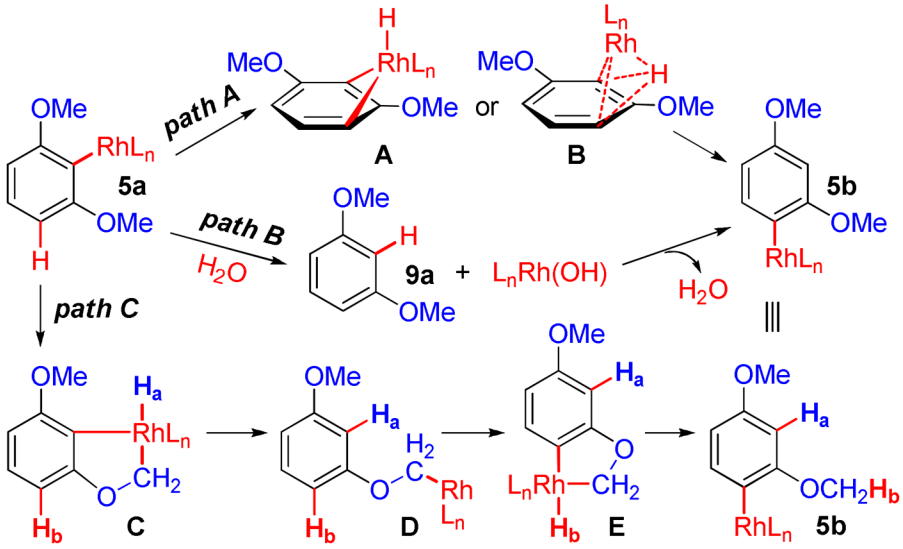

**Scheme 1.**
Intramolecular C-H bond activation via metal-hydrogen shifts.




**Scheme 2.**
Synthesis and thermal transformation of 2,6-disubstituted Rh(I) benzoates.

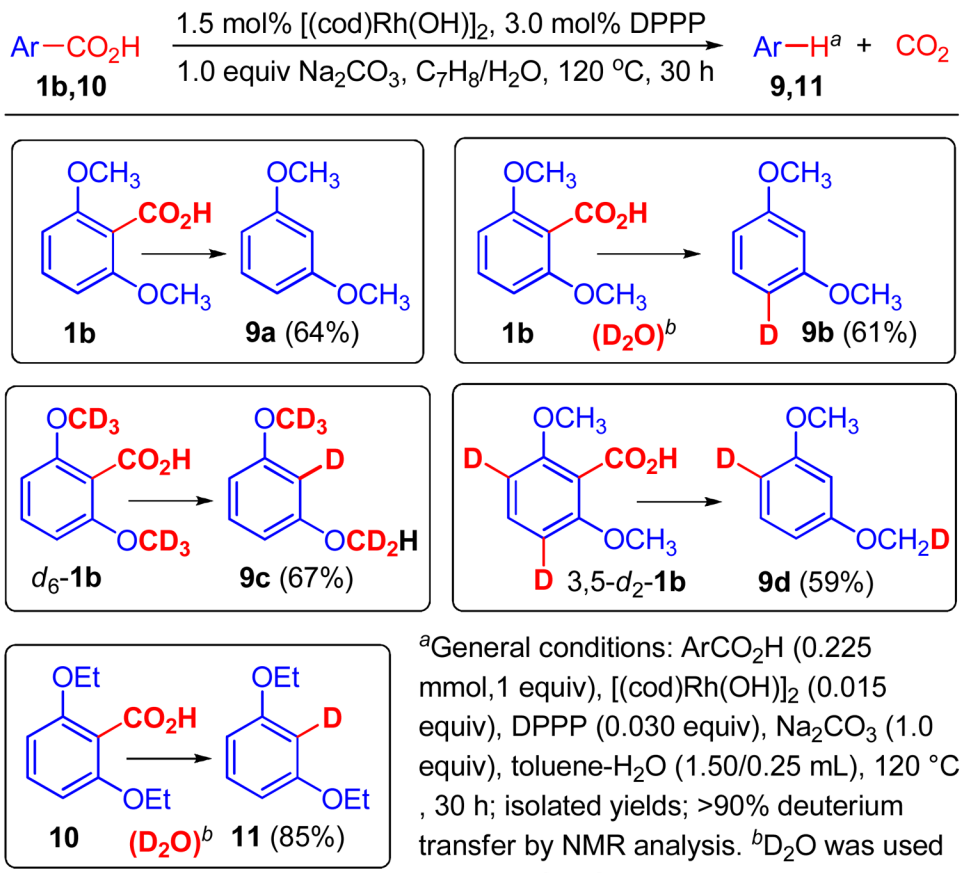

**Scheme 3.**

Proposed pathway for isomerization of Rh(I) carboxylates 3b to form 4b.




**Scheme 4.**

Proposed pathways for 1,3-Rh migration.




**Scheme 5.**

Deuterium labeling study on Rh(I)- catalyzed hydrodecarboxylation.

[a]General conditions: $ArCO_2H$ (0.225 mmol,1 equiv), $[(cod)Rh(OH)]_2$ (0.015 equiv), DPPP (0.030 equiv), $Na_2CO_3$ (1.0 equiv), toluene-$H_2O$ (1.50/0.25 mL), 120 °C, 30 h; isolated yields; >90% deuterium transfer by NMR analysis. [b]$D_2O$ was used in place of $H_2O$.