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

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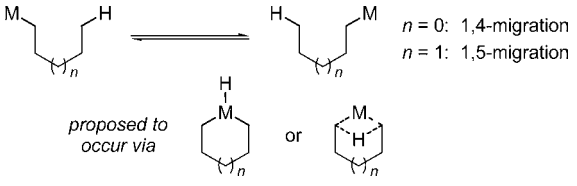
Supporting Information

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 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.

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



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 $[(cod)Rh(\mu\text{-}OH)]_2$ (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) 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 ^{31}P NMR (Scheme 2). The *in situ*

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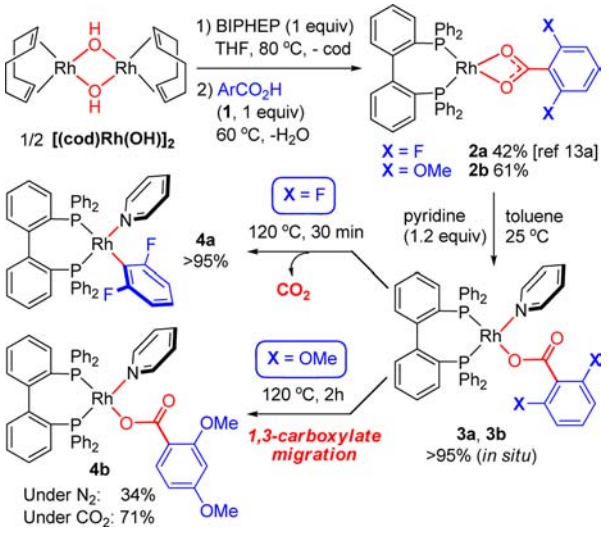
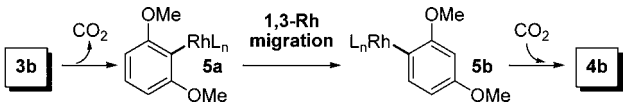
Scheme 2. Synthesis and Thermal Transformation of 2,6-Disubstituted Rh(I) Benzoates



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 ^{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 (details in SI). 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.

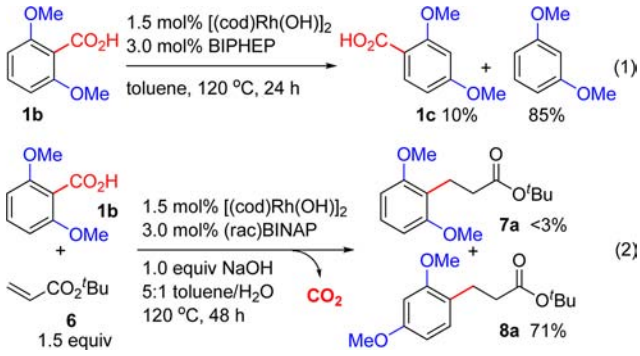
Based on the yield improvement of **4b** under CO_2 atmosphere, we propose a multistep pathway for the 1,3-carboxyl migration as described in Scheme 3. Decarboxylation of **3b** was

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 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.

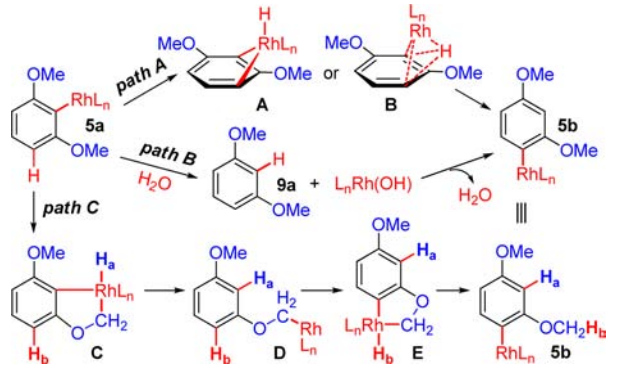
We envisioned that the proposed 1,3-Rh migration could be exploited catalytically to give novel rearrangement products. For example, the 1,3-carboxyl migration of **3b** (Scheme 2) could proceed catalytically to allow isomerization of 2,6-dimethoxybenzoic acid (**1b**) to form 2,4-dimethoxybenzoic acid (**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 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/H_2O 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 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

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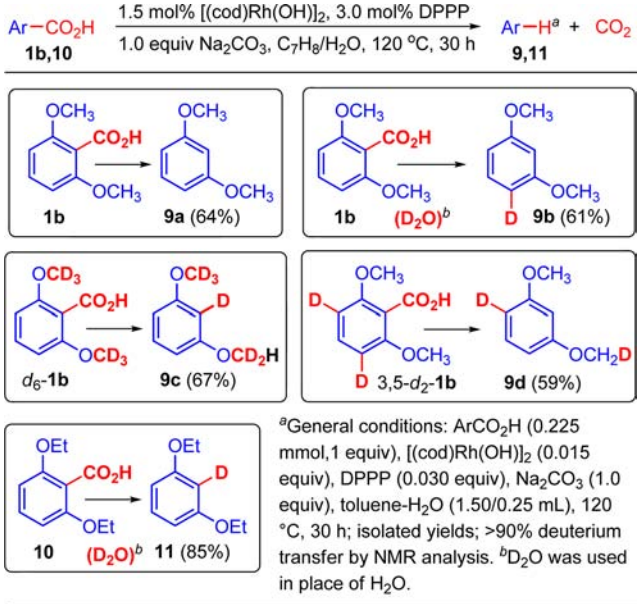
intermediate **D**, which undergoes further aromatic C−H bond activation at the less hindered *meta* position to form another cyclometalated Rh(III) intermediate **E**. **E** then undergoes C−H reductive elimination at the methoxy position to form **5b**. Notably, the proposed transformations of **5a**→**D** 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]

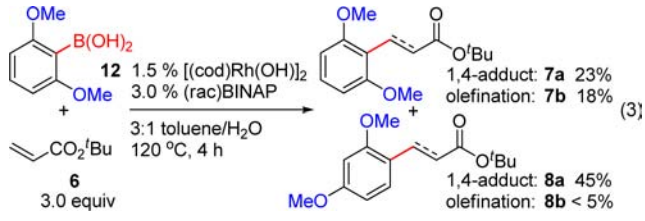
Scheme 5. Deuterium-Labeling Study on Rh(I)-Catalyzed Hydrodecarboxylation



[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.

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(diphenyl-phosphino)-propane), 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 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 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,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/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.

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

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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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