Diarylrhodates as Promising Active Catalysts for the Arylation of Vinyl Ethers with Grignard Reagents

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S *Supporting Information*

ABSTRACT: Anionic diarylrhodium complexes, generated by reacting $[RhCl(cod)]_2$ with 2 equiv of aryl Grignard reagents, were found to be effective active catalysts in cross-coupling reactions of vinyl ethers with aryl Grignard reagents, giving rise to the production of vinyl arenes. In this catalytic system, vinyl-O bonds were preferably cleaved over Ar–O or Ar–Br bonds. A lithium rhodate complex was isolated, and its crystal structure was determined by X-ray crystallography.

Arylrhodium(I) complexes (**B**) are readily formed by the transmetalation of the corresponding rhodium salts (**A**) with various organometallic reagents[1] and play important roles as key catalytic species in C–C bond forming reactions.[2] Some useful examples include the addition of aromatic moieties to carbonyl groups and enones (1,2- and 1,4-addition),[3,4] alkenes (also Heck-type reactions),[5] and alkynes.[6] Asymmetric addition to carbonyl compounds provides a powerful tool for creating chiral carbon centers.[4] Another fundamental reaction course of arylrhodium(I) complexes is oxidative addition with organo (pseudo)halides to give Rh(III) complexes, which is involved as a key process in cross-coupling reactions.[7]

In our previous studies, we reported that anionic transition-metal species such as nickelate,[8a−c] palladate,[8d] and cobaltate[9] complexes efficiently catalyze cross-coupling reactions of unactivated alkyl (pseudo)halides with organometallic reagents. Despite the importance and usefulness of Rh catalysts in organometallic chemistry and in organic synthesis, anionic diarylrhodium complexes **C** and their potent catalytic activities remained undeveloped in sharp contrast with neutral and cationic rhodium species.[1] Garcia et al. synthesized anionic diarylrhodium complexes and revealed a crystal structure of a bimetallic complex having Ag within the sum of covalent radii of Rh and Ag but their catalytic activities were not examined.[10] Here we report on the first examples in which anionic rhodium(I) species **C**, generated by the addition of arylmetal reagents to Rh salts **A** via arylrhodium(I) **B** (Scheme 1, **A** to **B** to **C**), play important roles as an active catalytic intermediate in cross-coupling reactions of vinyl ethers with aryl Grignard reagents.[11−13]

Scheme 1. Organorhodiums (L = ligand)
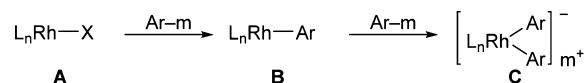
In our previous work on anionic transition-metal-catalyzed C–C bond formation, unsaturated hydrocarbon additives were employed as the ligand or ligand precursor,[8,9,14] to stabilize the complexes by withdrawing electrons through π-back-donation from the anionic metal center. Therefore, our initial efforts involved reacting $[RhCl(cod)]_2$ with PhMgBr to generate a rhodate species, followed by its application to cross-coupling reactions. When phenyl vinyl ether (**1a**) was reacted with PhMgBr in the presence of 1 mol % of $[RhCl(cod)]_2$ (2 mol % based on metal), a coupling reaction via C–O bond cleavage proceeded giving styrene (**2a**) in 64% yield, accompanied by a 3% yield of stilbene (**3a**) formed probably by the Heck-type arylation of the coupling product **2a** with PhMgBr (Table 1,

Table 1. Cross-Coupling of Vinyl Ethers with PhMgBr[a]

catalyst (2 mol %)
(based on metal)
$\diagup\!\!\diagup$ OR + Ph–MgBr $\xrightarrow{\text{THF, rt, 1 h}}$ $\diagup\!\!\diagup$ Ph + Ph $\diagdown\!\!\diagup\!\!\diagdown$ Ph
1 (0.5 mmol) (1.0 mmol)   **2a**   **3a**
R = Ph (**1a**), n-Bu (**1b**), Cy (**1c**), t-Bu (**1d**)

entry	1	catalyst (mol %)	2a (%)[b]	3a (%)[b]
1	1a	$[RhCl(cod)]_2$ (1)	64	3
2	1b	$[RhCl(cod)]_2$ (1)	9	<1
3	1c	$[RhCl(cod)]_2$ (1)	6	<1
4	1d	$[RhCl(cod)]_2$ (1)	<1	<1
5	1a	$RhCl(PPh_3)_3$ (2)	49	1
6	1a	$[Rh(OAc)_2]_2$ (1)	65	2
7	1a	$Rh(acac)_3$ (2)	65	3
8	1a	$[Cp*RhCl_2]_2$ (1)	48	2

[a]Reaction conditions: **1** (0.5 mmol), PhMgBr (in THF, 1.0 mmol), catalyst (0.01 mmol on metal), rt, 1 h. [b]Determined by GC. Cp*: pentamethylcyclopentadienyl.

entry 1).[5] The fact that a biphenyl derivative was not formed suggests that the reaction proceeded via the cleavage of the vinylic carbon–oxygen bond in **1a** rather than the aryl-oxygen bond.[15] Reactions using vinyl ethers having a primary, secondary, or tertiary alkyl group resulted in poor yields, presumably due to β-hydrogen elimination of alkoxyrhodium intermediates and/or steric hindrance (entries 2–4). When a diaryl ether or an aryl methyl ether was employed, no coupling reaction occurred and the starting compounds were recovered. Other rhodium salts $[Rh(OAc)_2]_2$ and $Rh(acac)_3$ also gave similar results (entries 6, 7) although Rh complexes carrying PPh_3 or Cp* ligands afforded

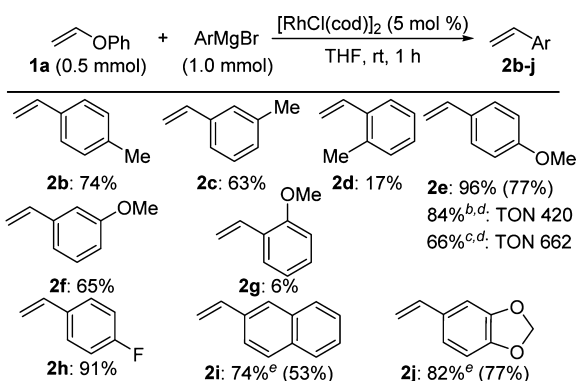slightly lower yields (entries 5, 8). The use of Co, Ru, or Pd salts resulted in poor yields, and Ir was completely ineffective.[16]

The scope of the reaction with respect to Grignard reagents is shown in Table 2. Aryl Grignard reagents having either an

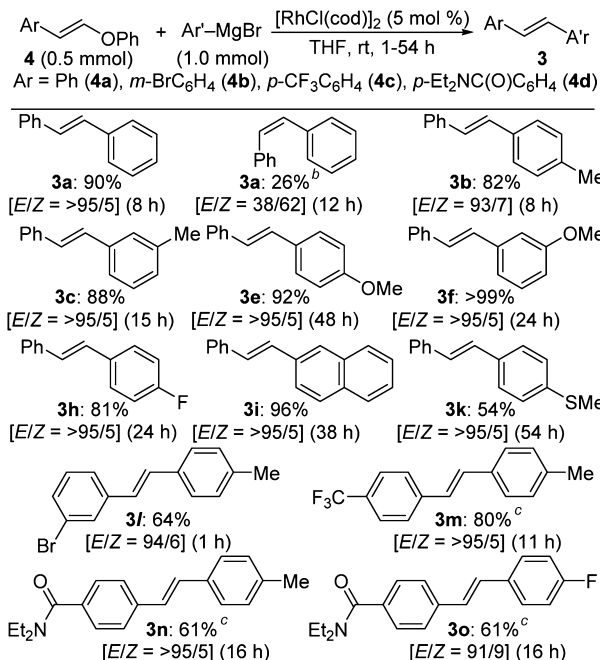**Table 2. Scope of Grignard Reagents[a]**

2b: 74%   2c: 63%   2d: 17%   2e: 96% (77%) 84%[b,d]: TON 420 66%[c,d]: TON 662

2f: 65%   2g: 6%   2h: 91%   2i: 74%[e] (53%)   2j: 82%[e] (77%)

[a]Yields were determined by GC. Isolated yields are in parentheses. [b]0.10 mol % of [RhCl(cod)]$_2$. [c]0.05 mol % of [RhCl(cod)]$_2$. [d]24 h. [e]NMR yield.

electron-withdrawing or -donating substituent at the *p*-position afforded the coupling products **2b,e,h** in excellent yields. The present catalyst showed high catalytic performance with TONs of up to 662. A substituent at the *m*-position had no effect on the reaction giving **2c,f** in good yields, although the reaction was sluggish when *o*-tolyl and *o*-anisyl Grignard reagents were employed affording **2d,g** in low yields. A 2-naphthyl group was vinylated efficiently, and an acetal functionality survived under the present conditions giving rise to **2i** and **2j**, respectively.
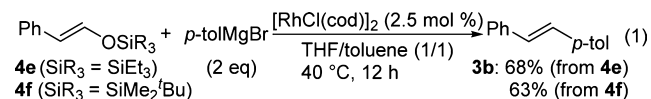
As shown in Table 3, the *trans* enriched *β*-styryl phenyl ethers **4** afforded *trans*-stilbenes as the major products in all cases. The stereochemistry of these products was found to be kinetically controlled because *cis*-stilbene was recovered with only 1% isomerization when a reaction of **4a** with *p*-tolMgBr was conducted for 4 h forming 79% of **3b** in the presence of *cis*-stilbene. The net retention of stereochemistry of the present coupling reaction was confirmed using a *cis*-rich *β*-d_1-vinyl ether (DHC=CHOAr, *E/Z* = 19/81) giving rise to the corresponding *cis*-rich *β*-d_1-styrene (*E/Z* = 27/73) in 69% yield.[16] When *cis* enriched **4a** (*E/Z* = 13/87) was employed, however, the reaction was slow and **3a** was obtained only in a poor yield (26%, *E/Z* = 38/62) after 12 h. The use of the naphthyl Grignard reagent required a longer reaction time but gave the desired product **3i** in nearly quantitative yield. It is noteworthy that cross-coupling took place exclusively at the vinylic carbon, when a *β*-styryl ether having a Br substituent on the aromatic ring was employed. Styryl ethers having CF$_3$ or an amide substituent **4c,d** also coupled with aryl Grignard reagents to give the coupling products **3m–o**.[17]

It is of great synthetic importance that this present cross-coupling reaction could be successfully applied to silyl vinyl ethers which can be readily prepared from the corresponding aldehydes. For example, when *trans*-silyl enol ethers having TES (**4e**) and TBDMS (**4f**) were employed, the corresponding coupling products were obtained in 68% and 63% yields, respectively, with complete stereoretention (eq 1). Styryl-OTs (*E/Z* = 66/34) and *β*-bromostyrene (*E/Z* = 84/16) also gave stilbene **3a** in 51% yield (*E/Z* = 66/34) and 71% yield (*E/Z* = 89/11), respectively.

Table 3. Arylation of *β*-Styryl Ethers[a]

Ar = Ph (**4a**), *m*-BrC$_6$H$_4$ (**4b**), *p*-CF$_3$C$_6$H$_4$ (**4c**), *p*-Et$_2$NC(O)C$_6$H$_4$ (**4d**)

3a: 90% [*E/Z* = >95/5] (8 h)   **3a**: 26%[b] [*E/Z* = 38/62] (12 h)   **3b**: 82% [*E/Z* = 93/7] (8 h)

3c: 88% [*E/Z* = >95/5] (15 h)   **3e**: 92% [*E/Z* = >95/5] (48 h)   **3f**: >99% [*E/Z* = >95/5] (24 h)

3h: 81% [*E/Z* = >95/5] (24 h)   **3i**: 96% [*E/Z* = >95/5] (38 h)   **3k**: 54% [*E/Z* = >95/5] (54 h)

3l: 64% [*E/Z* = 94/6] (1 h)   **3m**: 80%[c] [*E/Z* = >95/5] (11 h)

3n: 61%[c] [*E/Z* = >95/5] (16 h)   **3o**: 61%[c] [*E/Z* = 91/9] (16 h)

[a]**4a** (*E/Z* = 93/7), **4b** (*E/Z* = >99/1), **4c** (*E/Z* = 95/5), or **4d** (*E/Z* = 72/28) was used unless otherwise stated. Yields were determined by GC. *E/Z* ratios were determined by ^{1}H NMR. [b]**4a** (*E/Z* = 13/87) was used. [c]Isolated yield.

$$\text{Ph} \diagup \text{OSiR}_3 + p\text{-tolMgBr} \xrightarrow[\text{THF/toluene (1/1)}]{[\text{RhCl(cod)}]_2 \text{ (2.5 mol \%)}}_{40\,°C,\ 12\ h} \text{Ph} \diagup p\text{-tol} \quad (1)$$

4e (SiR$_3$ = SiEt$_3$)   (2 eq)   **3b**: 68% (from **4e**)
4f (SiR$_3$ = SiMe$_2$^{t}Bu)   63% (from **4f**)

An interesting chemoselectivity of the Rh catalyst was noted, compared to Ni and Pd which have been utilized for cross-coupling reactions of ethers and esters with organometallic reagents.[11,12a–d] Results for some competitive reactions of vinyl ether **1a** and *p*-bromotoluene with PhMgBr in the presence of Rh, Ni, or Pd catalysts are summarized in eq 2. In the case of Rh,
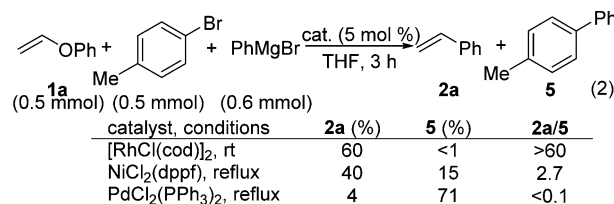
the vinyl ether **1a** was selectively coupled with PhMgBr to give the styrene **2a** in 60% yield accompanied by only a trace amount of the biaryl derivative **5**, as expected from the successful site-selective cross-coupling of **4b** leading to **3l** in Table 3. In contrast, the Ni catalyst gave a mixture of **2a** and **5** in 40% and 15% yields, respectively, and the Pd catalyst selected the bromoarene in preference to the vinyl ether to give **5** exclusively in 71% yield.

To determine the actual catalytic species in this reaction, we conducted stoichiometric reactions using [RhCl(cod)]$_2$, **1a**, and 1 to 4 equiv of PhMgBr (Table 4). When 1 equiv of PhMgBr was added to an equimolar mixture of [RhCl(cod)]$_2$ (based on Rh) and **1a**, the styrene (**2a**) and stilbene (**3a**) were both produced in small amounts and 79% of **1a** was recovered (entry 1), suggesting that the arylrhodium complex **B** is not an active catalyst for the arylation of vinyl ethers under the present conditions.[13a,b] When
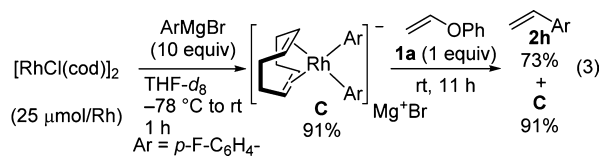
$$\text{(eq 2 scheme)}$$

catalyst, conditions	2a (%)	5 (%)	2a/5
[RhCl(cod)]$_2$, rt	60	<1	>60
NiCl$_2$(dppf), reflux	40	15	2.7
PdCl$_2$(PPh$_3$)$_2$, reflux	4	71	<0.1

Table 4. Stoichiometric Reactions Using 1 to 4 equiv of PhMgBr

$$\text{OPh} + \text{Ph-MgBr} \xrightarrow[\text{THF, }-78\,°C\text{ to rt, 4 h}]{\text{[RhCl(cod)]}_2\ (0.05\ \text{mmol})} \text{Ph} + \text{Ph} \underset{\textbf{3a}}{\diagdown}\text{Ph}$$

1a (0.1 mmol)   2a

entry	PhMgBr	conv. 1a (%)[a]	2a (%)[a]	3a (%)[a]
1	1 equiv	21	1	1
2	2 equiv	68	n.d.	48
3	4 equiv	61	61	n.d.

[a]Determined by GC. n.d.: not detected.

2 equiv of Grignard reagent were used, 68% of **1a** was consumed, but no **2a** was detected, with **3a** being produced in 48% yield, probably via a further Heck type arylation of **2a** (entry 2).[5] In sharp contrast, **2a** was produced as the sole product when 4 equiv of Grignard reagent were used (entry 3). Taking these results into account, RhAr(cod) generated by the transmetalation of "RhCl(cod)" with ArMgBr is catalytically active not for arylation of vinyl ethers but for styrenes.[16] The arylation of vinyl ethers is catalyzed by a diarylrhodate **C**, RhAr₂(cod)⁻·MgBr⁺, generated by the reaction of RhAr(cod) with ArMgBr. In the presence of 2 equiv of PhMgBr, the RhAr₂(cod)⁻·MgBr⁺ was initially generated and reacted with **1a** to give **2a** and RhAr(cod), which react with each other to give **3a**. This was supported by the fact that when *p*-methylstyrene **2b**, in place of **1a**, was subjected to the same conditions as entry 1, **3b** was produced in 56% yield, but **2b** was recovered unreacted when the same reaction was conducted in the presence of 3 equiv of PhMgBr.[16]

When [RhCl(cod)]₂ was treated with *p*-F-C₆H₄MgBr (10 equiv) in THF-*d*₈, the three signals for COD were completely shifted and new peaks appeared in the aromatic region on ¹H NMR, where the aryl group and COD were observed in a 2:1 ratio being assignable to the diarylrhodate **C**.[16] When 1 equiv of the vinyl ether **1a** was added to the solution, the corresponding coupling product **2h** and complex **C** were detected in 73% and 91% yields, respectively (eq 3). These observations along with the results in Table 4 strongly support that a rhodate complex **C** is an active catalytic species.

$$[\text{RhCl(cod)}]_2 \xrightarrow[\substack{\text{THF-}d_8 \\ -78\,°C\text{ to rt} \\ 1\ \text{h} \\ \text{Ar} = p\text{-F-C}_6\text{H}_4\text{-}}]{\substack{\text{ArMgBr} \\ (10\ \text{equiv})}} \left[\text{Rh}\overset{\text{Ar}}{\underset{\text{Ar}}{}}\right]^- \text{Mg}^+\text{Br} \xrightarrow[\text{rt, 11 h}]{\substack{\text{OPh} \\ \textbf{1a}\ (1\ \text{equiv})}} \underset{\substack{\textbf{73\%} \\ + \\ \textbf{C} \\ \textbf{91\%}}}{\overset{\text{Ar}}{\diagup}\textbf{2h}} \quad (3)$$

(25 µmol/Rh)   C
                                        91%

Although all attempts to crystallize the diarylrhodates, generated by Grignard reagents, were fruitless, the structure of the unique anionic diarylrhodium **6** was unambiguously determined by X-ray diffraction analysis using PhLi instead of a Grignard reagent.[17] As shown in Figure 1, the crystal structure of RhPh₂(cod)·Li(dme)₃ (**6**) contains anionic Rh and the Li cation. The Rh center contains one COD and two phenyl groups in a square planar geometry with the sum of the angles around Rh being 360.0°. The rhodium–carbon bond distance (2.062 Å) of **6** is slightly shorter than that of a silver rhodate bimetallic complex (2.093−2.098 Å).[10b,18] The lithium cation is coordinated by three DME ligands. To the best of our knowledge, complex **6** is the first example of a structurally well-defined ion separated anionic diarylrhodium complex.[19]

Scheme 2 shows a proposed reaction pathway for this reaction. Transmetalation between [RhCl(cod)]₂ and ArMgBr gives the arylrhodium **B**. Although arylrhodium **B** complexes are
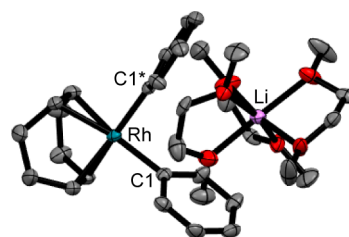
Figure 1. ORTEP drawing of RhPh₂(cod)·Li(dme)₃ (**6**) with thermal ellipsoids at the 50% probability level. H atoms and disordered DME are omitted for clarity.

Scheme 2. A Possible Mechanism
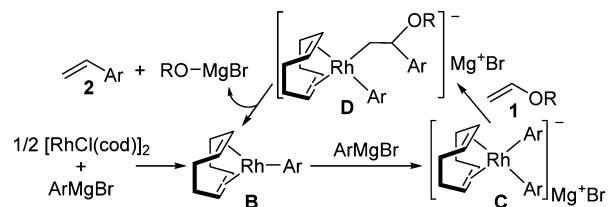
frequently encountered active catalytic species in Rh-catalyzed C−C bond formation, this is not the case in the present reaction system. Thus, the formed arylrhodium **B** reacts with ArMgBr to give the diarylrhodate **C** which adds to the C=C bond of vinyl ethers leading to **D**,[13c,d] and the following β-oxygen elimination affords the product and regenerates **B**, a process that would be more likely to occur than an oxidative addition/reductive elimination pathway.[13a,b] The stereochemistry of net retention of the present reaction can be explained by *syn*-addition followed by *anti*-elimination via **D**.[20] The latter process may be facilitated by the coordination of MgBr⁺ to the oxygen of the intermediate **D** to activate the C−O bond. Although complex **B** functions as a catalyst for the Heck-type arylation of **2** to give stilbene derivatives **3**,[5] it readily reacts with Grignard reagents to form the complex **C** resulting in the suppression of double arylation to form **3**.[16]

In conclusion, we report on the isolation of an anionic diarylrhodium complex and the determination of its structure by X-ray diffraction analysis, confirming that it exists as a separated ion pair. The diarylrhodates **C** efficiently catalyzed the cross-coupling of vinylic ethers with aryl Grignard reagents through vinylic C−O bond cleavage with a high degree of chemoselectivity even in the presence of aromatic C−O as well as C−Br bonds. The present study demonstrates the high synthetic potential of anionic Rh complexes, in that they are capable of performing unique catalytic reactions, in comparison with widely used neutral or cationic organorhodiums.

■ **ASSOCIATED CONTENT**

ⓢ Supporting Information

Detailed experimental results, procedures, characterization data, and crystallographic 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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(16) See Supporting Information (SI).

(17) CCDC-1007198 (**3n**) and -999723 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(18) Carbon—rhodium bond lengths of reported neutral RhArL(cod) are in the range 2.057−2.123 Å. See SI for details.

(19) During isolation processes, **6** lost two DME ligands to give RhPh₂(cod)·Li(dme) (**6′**). The reaction of **6′** with 1.4 equiv of **1a** in THF-d_8 at rt for 1 h gave **2a** in 42% yield (NMR yield based on Rh). When 10 mol % of **6′** was employed for the reaction of **1a** with *p*-F-C₆H₄MgBr (2 equiv) as a catalyst, the reaction completed within 1 h at rt to give **2h** and **2a** in 85% and 6% yields, respectively. These results are consistent with the ones obtained by stoichiometric reactions using different amounts of PhMgBr (entries 2 and 3 in Table 4). See SI for details.

(20) Ohmiya, H.; Ito, H.; Sawamura, M. *Org. Lett.* **2009**, *11*, 5618.