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Rhodium-Catalyzed Oxidative C–H Allylation of Benzamides with 1,3-Dienes by Allyl-to-Allyl 1,4-Rh(III) Migration

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Supporting Information Placeholder

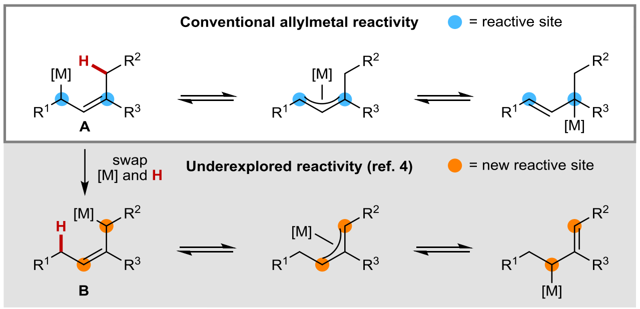
ABSTRACT: The Rh(III)-catalyzed oxidative C–H allylation of *N*-acetylbenzamides with 1,3-dienes is described. The presence of allylic hydrogens *cis*- to the less substituted alkene of the 1,3-diene is important for the success of these reactions. With the assistance of reactions using deuterated 1,3-dienes, a proposed mechanism is provided. The key step is postulated to be the first reported examples of allyl-to-allyl 1,4-Rh(III) migration.

INTRODUCTION

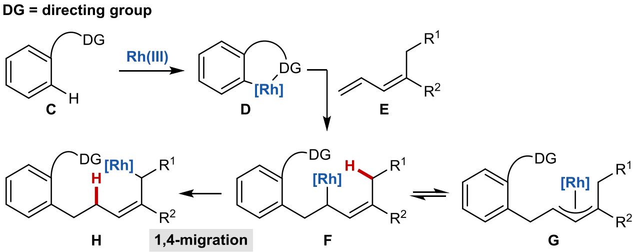
Allylmetal species are important intermediates in organic synthesis.[1,2] For example, π-allylmetal species are usually electrophilic, and can be intercepted by diverse nucleophiles in allylic substitutions.[1] On the other hand, σ-allylmetal species are usually nucleophilic, and can be employed in a huge range of allylations of π-electrophiles.[2] Numerous catalytic, diastereoselective, and/or enantioselective variants of these processes have also been reported.[1,2]

A well-recognized feature of allylmetal reactivity is the often facile 1,3-transposition of the metal from one end of the allylic fragment to the other, which potentially enables new bond-forming reactions at either side (Scheme 1, top). Isomerizations of allylmetal species that open up reactions at sites *beyond* those resulting from conventional 1,3-allylic transposition would be highly enabling for reaction discovery.[3,4,5] As part of a program in enantioselective rhodium-catalyzed additions of allylboron reagents to imines,[3,4,6] we have described the allyl-to-allyl 1,4-Rh(I) migration of allylrhodium(I) species (as in **A** to **B**, Scheme 1).[4,7] This isomerization allows subsequent carbon–carbon bond formation at sites not immediately expected from the structure of the allylboron reagents (Scheme 1, bottom). Given the synthetic potential of this underexplored mode of reactivity, its investigation in other classes of reactions is warranted. In particular, demonstration of metals other than Rh(I) to engage in allyl-to-allyl 1,4-migration would be highly valuable.

Scheme 1. Allylmetal Reactivity



Scheme 2. System to Test Allyl-to-Allyl 1,4-Rh(III) Migration

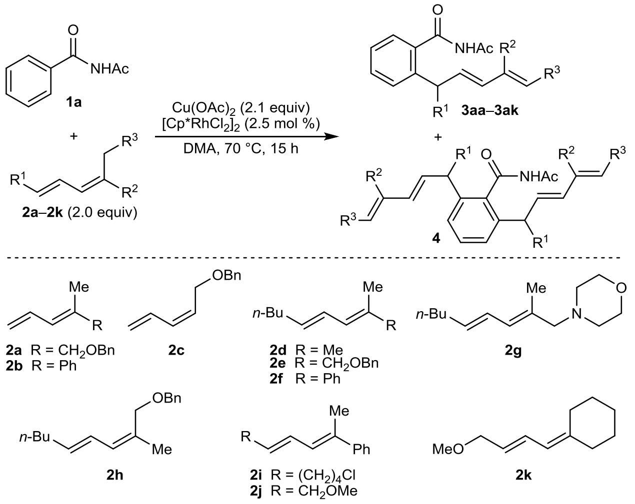


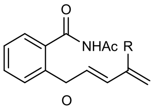
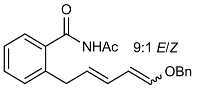
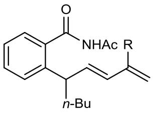
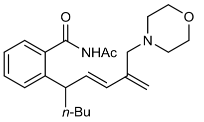
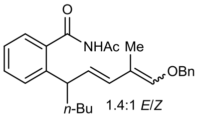
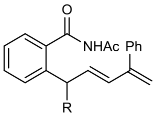
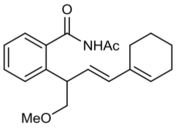
In connection with our work on Rh(III)-catalyzed C–H functionalization[8,9] in combination with alkenyl-to-allyl 1,4-Rh(III) migration to prepare heterocyclic[10] and carbocyclic[11] products, we became interested in whether allyl-to-allyl 1,4-Rh(III) migrations would be possible.[12] Our design for investigating the feasibility of this migration is shown in Scheme 2. The directing-group-assisted cyclorhodation of substrate **C** with a Rh(III) complex to give rhodacycle **D** is well-known.[8] Migratory insertion of **D** with a 1,3-diene **E**, which contains allylic hydrogens *cis*- to the less-substituted alkene, would give allylrhodium species **F**, which is likely to be in equilibrium with the π-haptomer **G**.[13] If allyl-to-allyl 1,4-Rh(III) migration of **F** were then to occur, a new allylrhodium species **H** would form. Although the final fate of **H** could not be predicted, this process could serve as a valuable addition to the currently limited number of catalytic C–H functionalizations involving 1,3-dienes,[14] provided that high overall chemo-, regio-, and stereoselectivity is exhibited. Herein, we describe the successful use of allyl-to-allyl 1,4-Rh(III) migration in the oxidative C–H allylation of benzamides with 1,3-dienes. These reactions are distinct from other metal-catalyzed C–H allylations of arenes, which employ allylic electrophiles,[15] allenes,[16] or terminal alkenes[17] as the reaction partners.

RESULTS AND DISCUSSION

After attempting Rh(III)-catalyzed reactions of various aromatic substrates of type **C** with 1,3-dienes of type **E** (see Scheme 2),[18] we found that *N*-acetylbenzamides **1** gave productive reactions under oxidative conditions to form allylation products **3**. For example, the reaction of *N*-acetylbenzamide **1a**

Table 1. Scope of the 1,3-Diene[a]



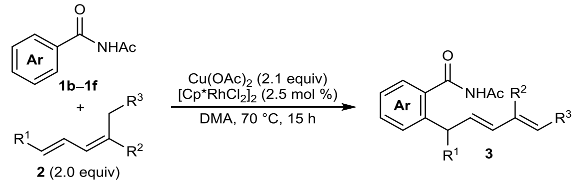
entry	1,3-diene	product		R	yield (%)[b]
1[c]	**2a**		**3aa**	CH_2OBn	50
2	**2b**		**3ab**	Ph	69 (27)[d]
3[c]	**2c**		**3ac**		61
4	**2d**		**3ad**	Me	77
5	**2e**		**3ae**	CH_2OBn	77
6[c]	**2f**		**3af**	Ph	63
7	**2g**		**3ag**		60
8	**2h**		**3ah**		31
9[c]	**2i**		**3ai**	$(CH_2)_4Cl$	62
10[c]	**2j**		**3aj**	CH_2OMe	76
11	**2k**		**3ak**		82

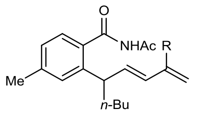
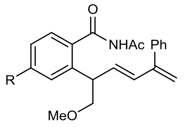
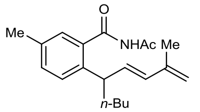
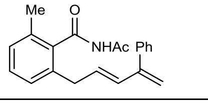
[a] Unless stated otherwise, reactions were conducted using 0.30 mmol of **1a** and 0.60 mmol of **2**. [b] Yield of isolated product. [c] Conducted using 0.60 mmol of **1a** and 0.30 mmol of **2**. [d] Values in parentheses refer to the yield of the product **4ab** resulting from reaction at both *ortho*-positions of **1a**.

with diene **2a** in the presence of $[\mathrm{Cp^*RhCl_2}]_2$ (2.5 mol %) and $\mathrm{Cu(OAc)_2}$ (2.1 equiv) in DMA at 70 °C for 15 h gave product **3aa** in 50% yield (Table 1, entry 1). Other dienes **2b**–**2k**, containing either a methyl or a methylene group *cis*- to the less-substituted alkene, are also effective and gave products **3ab**–**3ak** in 31–82% yield (Table 1, entries 2–11). The mass balance in these reactions was mainly composed of unreacted starting materials. In some cases, a 1:2 ratio of benzamide and diene, respectively, was optimal to maximize the yield of the products **3** (entries 2, 4, 5, 7, 8, and 11). However, in other cases a 2:1 ratio of **1a**:**2** was chosen to minimize the formation of products **4**, which result from C–H functionalization at both *ortho*-positions of **1a** (entries 1, 3, 6, 9, and 10). In one reaction, the diallylated product **4ab** was isolated (entry 2). Dienes containing a terminal alkene are effective (entries 1–3), and hydrogen, phenyl, and various alkyl groups at the alkenes are well-tolerated. With **2a**, the product **3aa** is derived from loss of a hydrogen atom from the methyl substituent *cis*- to the vinyl group, rather than from the benzyloxymethyl substituent *trans*- to the vinyl group (entry 1). Diene **2c**, which contains a 1,2-disubstituted *Z*-alkene, reacted to give dienol benzyl ether **3ac** as a 9:1 mixture of *E*/*Z* isomers, along with traces of unidentified decomposition products (entry 3). Dienes **2d**–**2k**, which contain a 1,2-disubstituted alkene and a trisubstituted alkene, were also effective (entries 4–11). Here, carbon–carbon bond formation occurs exclusively at the 1,2-disubstituted alkene, at the carbon distal to the trisubstituted alkene. As with diene **2a** (entry 1), when there are different geminal alkyl groups at the trisubstituted alkene, the products are derived from loss of a hydrogen atom at the alkyl group *cis*- to the disubstituted alkene (entries 4, 5, 7, and 8). This point is further exemplified by the outcomes with dienes **2e** and **2h**, which are geometric isomers of each other (entries 5 and 8). The reaction with **2h** did not go to completion but dienol benzyl ether **3ah** was obtained in 31% yield as a 1.4:1 mixture of *E*:*Z* isomers (entry 8). No evidence of **3aa** was detected in this reaction.

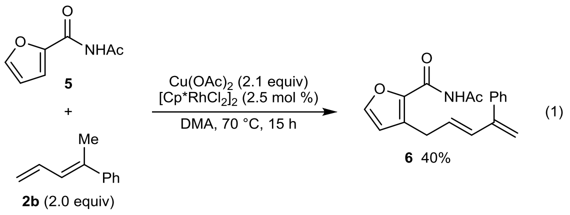
Attention was then turned to the scope of the reaction with respect to the *N*-acetylbenzamide (Table 2). Benzamides containing a methyl group at the *para*-, *meta*-, or *ortho*-positions (entries 1, 2, 5, and 6) are tolerated, as are those bearing *para*-methoxy (entry 3) or *para*-nitro substituents (entry 4). Electron-withdrawing substituents on the aromatic ring of the benzamide appear to be beneficial, as shown by the formation of **3dj** in 75% yield compared with a 46% yield for **3cj** (compare

Table 2. Scope of the *N*-Acetylbenzamide[a]



entry	1,3-diene	product		R	yield (%)[b]
1	**2d**		**3bd**	Me	53
2	**2e**		**3be**	CH_2OBn	53
3[c]	**2j**		**3cj**	OMe	46
4[c]	**2j**		**3dj**	NO_2	75
5	**2d**		**3ed**		64
6	**2b**		**3fb**		98

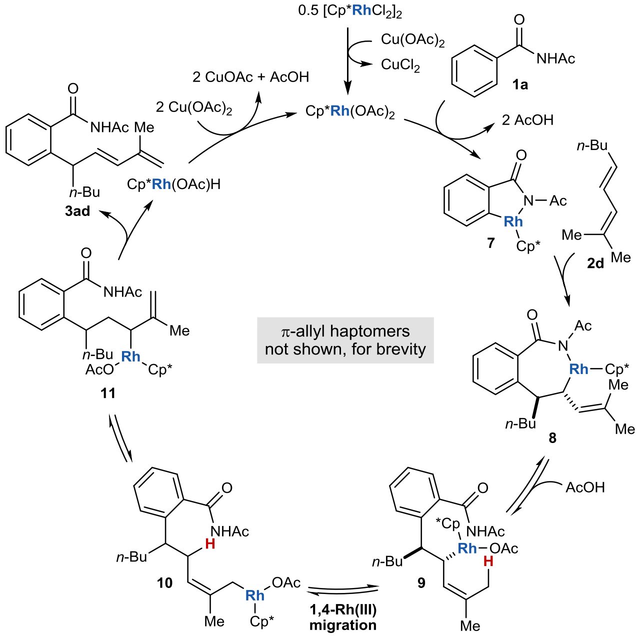
[a] Unless stated otherwise, reactions were conducted using 0.30 mmol of **1** and 0.60 mmol of **2**. [b] Yield of isolated product. [c] Conducted using 0.60 mmol of **1** and 0.30 mmol of **2**.



entries 3 and 4). C–H functionalization of a furan-containing substrate **5** is also possible, although the yield of the product **6** was modest (eq 1).

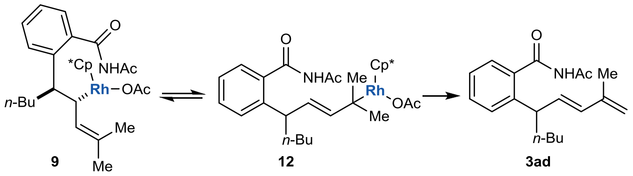
A possible catalytic cycle for these reactions begins with formation of Cp*Rh(OAc)$_2$ from [Cp*RhCl$_2$]$_2$ and Cu(OAc)$_2$ (Scheme 3), which reacts with *N*-acetylbenzamide **1a** to give rhodacycle **7** and AcOH. Coordination and migratory insertion of 1,3-diene **2d** at the less-substituted alkene gives rhodacycle **8**, in which there is also an allylrhodium(III) moiety. Acetolysis of **8** gives allylrhodium(III) species **9**, which can undergo 1,4-Rh(III) migration[10,11,12] to the *cis*-allylic carbon to give a new σ-allylrhodium intermediate **10**. A σ-π-σ isomerization of **10** provides σ-allylrhodium species **11**, which undergoes *β*-hydride elimination to give product **3ad** and Cp*Rh(OAc)H. Reaction of Cp*Rh(OAc)H with Cu(OAc)$_2$ (2.0 equiv) leads to reductive elimination to give AcOH and Cp*Rh(I), which is oxidized to regenerate Cp*Rh(OAc)$_2$. Although we have proposed the acetolysis of **8** into **9**, we cannot discount the possibility that the directing group remains coordinated to rhodium in one or more of the subsequent intermediates.

Scheme 3. Postulated Catalytic Cycle



An alternative mechanism involves the isomerization of **9** into σ-allylrhodium species **12**, which undergoes *β*-hydride elimination to give **3ad** (Scheme 4). If this mechanism was operative, it would be expected that dienes **2e** and **2h**, which differ only in the geometry of the trisubstituted alkene, would react to provide similar outcomes. The fact that different products are obtained in their reactions with **1a** (Table 1, entries 5 and 8) suggests this pathway is less likely.

Scheme 4. Alternative Mechanistic Pathway



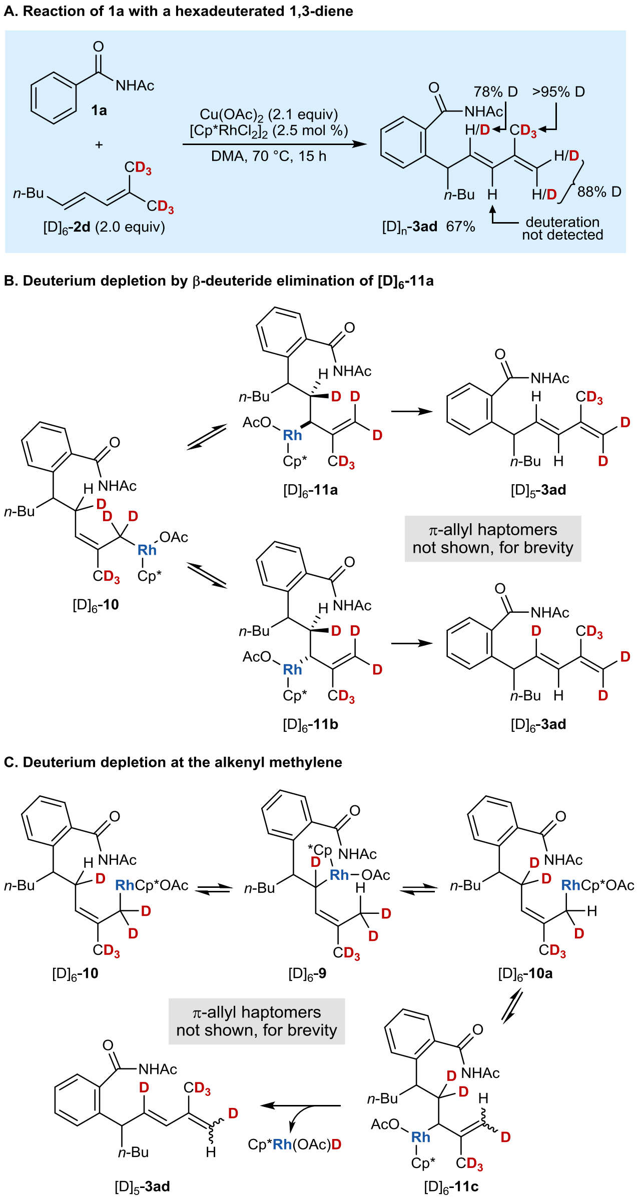


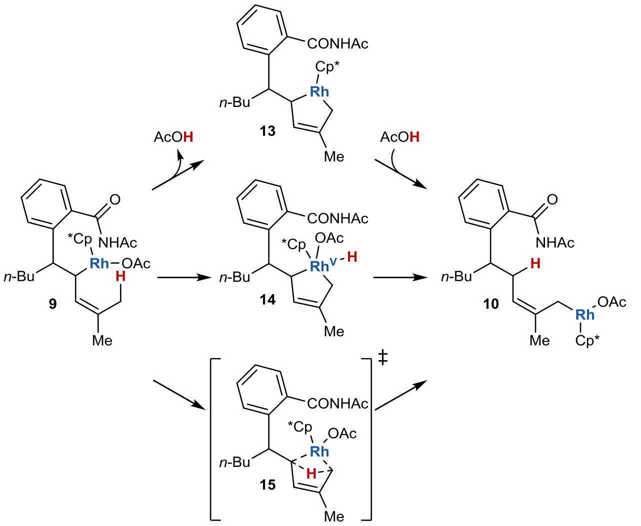
Figure 1. Investigation of deuterium transfer with 1,3-diene [D]$_6$-**3ad** and mechanistic rationale.

Further support for the mechanism proposed in Scheme 3 is provided by the reaction of **1a** with the hexadeuterated diene [D]$_6$-**2d** (Figure 1A). This experiment gave [D]$_n$-**3ad** in 67% yield, in which there was significant, but incomplete, deuterium transfer (78% D) from one of the CD$_3$ groups to the alkenyl carbon proximal to the benzene ring. This outcome may be rationalized by considering that σ-π-σ-isomerization of [D]$_6$-**10** could provide [D]$_6$-**11a** or [D]$_6$-**11b** (Figure 1B). Deuterium depletion can then occur by *β*-deuteride elimination of [D]$_6$-**11a** to give [D]$_5$-**3ad**, whereas *β*-hydride elimination of [D]$_6$-**11b** would give [D]$_6$-**3ad**.

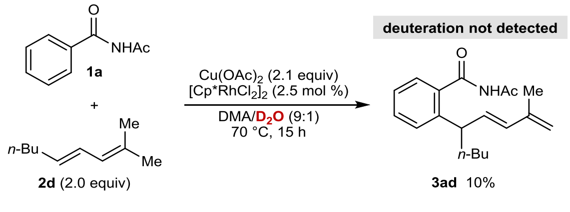
Another outcome of the experiment shown in Figure 1A is partial deuterium depletion (88% D) at the alkenyl methylene of $[D]_n$-**3ad**. This result may be explained by reversible allyl-to-allyl 1,4-migration between $[D]_6$-**10**, $[D]_6$-**9**, and $[D]_6$-**10a**, which leads to deuterium–hydrogen exchange between the two *cis*-allylic substituents (Figure 1C).[4] σ-π-σ-Isomerization of $[D]_6$-**10a** would provide $[D]_6$-**11c**, from which *β*-deuteride elimination would give $[D]_5$-**3ad**, in which there is deuterium depletion at the alkenyl methylene group.

Regarding the actual mechanism of allyl-to-allyl 1,4-Rh(III) migration, there are a number of possibilities (Scheme 5). First, in a manner similar to that proposed for the alkenyl-to-allyl 1,4-Rh(III) migrations we described previously,[10,11] an acetate-promoted, concerted metalation–deprotonation of $[D]_6$-**9** would give rhodacycle **13**, which could undergo acetolysis to give **10**. Alternatively, **9** could undergo a C–H oxidative addition to give a Rh(V) hydride species **14**, which can then form **10** by a C–H reductive elimination. The participation of Rh(V) intermediates has been suggested in various other Rh(III)-catalyzed C–H functionalization reactions[19] and has gained some experimental and theoretical support.[20] Finally, **9** could undergo a σ-complex-assisted metathesis (σ-CAM)[12a,21,22] *via* **15** to give **10**.

Scheme 5. Possible Mechanisms for 1,4-Rh(III) Migration



To investigate the possibility of an acetate-assisted concerted metalation–deprotonation pathway to give **13**, the reaction of *N*-acetylbenzamide **1a** with 1,3-diene **2d** was conducted in in a 9:1 mixture of DMA/D_2O. The presence of D_2O would be expected to provide some of deuterated **3ad** as a result of deuteronolysis of **13**, as we have observed previously in related alkenyl-to-allyl 1,4-Rh(III) migrations.[10,11] In the event, D_2O markedly decreased the efficiency of oxidative C–H allylation. Nevertheless, **3ad** was isolated in 10% yield but no deuterium incorporation was detected. This result suggests that the intermediacy of **13** is less likely and that C–H oxidative addition/reductive elimination or σ-CAM pathways may be more probable mechanisms for allyl-to-allyl 1,4-Rh(III) migration.



(2)

Thus far, all of the 1,3-dienes tested contain allylic hydrogens *cis*- to the less-substituted alkene, which enables facile allyl-to-allyl 1,4-Rh(III) migration. To test whether 1,3-dienes lacking this structural feature would also be effective substrates, the reaction of **1a** (2.0 equiv) with 1,3-diene **14**, the *E*-isomer of diene **2c** (see Table 1, entry 3), was conducted (Figure 2A). This experiment did give allylation product **3ac** as a 9:1 mixture of *E*/*Z* isomers, but in a much lower yield of 31% compared with the 61% yield obtained when the corresponding *Z*-diene **2c** was used (Table 1, entry 3). In addition, alkenylation product **15** was isolated in 12% yield, which is notable as analogous alkenylation products were not formed in any of the reactions examined up till this point. The corresponding reaction conducted with dideuterated diene $[D]_2$-**14** gave deuterated products $[D]_n$-**15** and $[D]_n$-**3ac**, each in 16% yield, in which appreciable 1,4-deuterium transfer was observed (Figure 2B). This time, $[D]_n$-**3ac** was obtained as a 6:1 mixture of *E*/*Z* isomers.

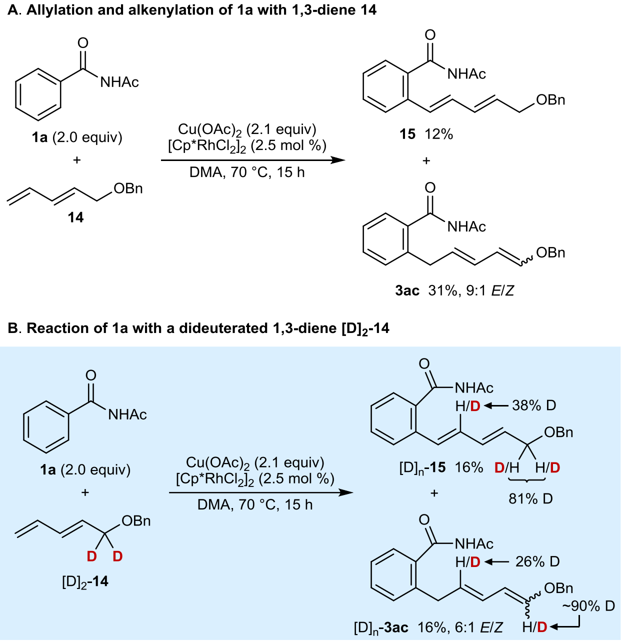
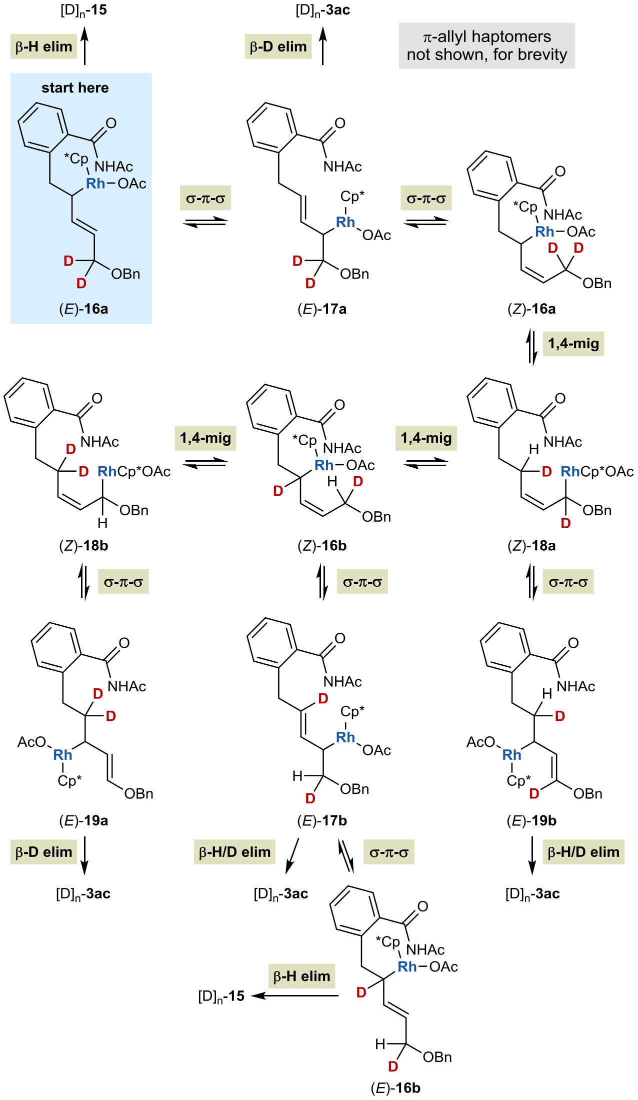


Figure 2. Reaction of a 1,3-diene lacking *cis*-allylic hydrogens.

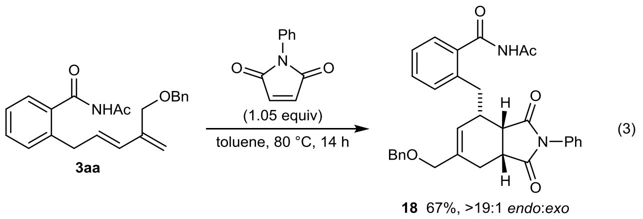
The appreciable 1,4-deuterium transfer in both $[D]_n$-**15** and $[D]_n$-**3ac** suggests a complex mechanism is operative, involving the interconversion between numerous allylrhodium(III) species by σ-π-σ isomerization (1,3-allylic transposition), *E*/*Z* isomerization, and allyl-to-allyl 1,4-Rh(III) migration pathways (Scheme 6). First, the reaction of **1a**, $[D]_2$-**14**, and $[Cp^*RhCl_2]_2$ following the initial steps of the catalytic cycle shown in Scheme 3 leads to the formation of (*E*)-**16a**, which can give a dideuterated isomer of alkenylation product $[D]_n$-**15** by *β*-hydride elimination. Intermediate (*E*)-**16a** can also undergo σ-π-σ isomerization into (*E*)-**17a**, which, after *β*-deuteride elimination, would give a monodeuterated allylation product $[D]_n$-**3ac**. Alternatively, (*E*)-**16a** can undergo σ-π-σ isomerization with concomitant *E*/Z isomerization to give (*Z*)-**16a**, from which a series of reversible allyl-to-allyl 1,4-Rh(III) migrations involving either a 1,4-deuterium or a 1,4-hydrogen shift can give new allylrhodium(III) species (*Z*)-**18a**, (*Z*)-**16b**,

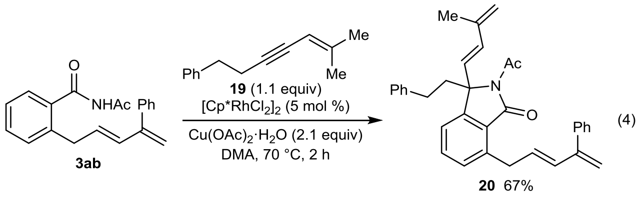
Scheme 6. Mechanistic Rationale to Explain the Outcome of the Reaction of 1a with [D]$_2$-14



and (*Z*)-**18b**. These latter three intermediates can undergo σ-π-σ isomerization to provide (*E*)-**19a**, (*E*)-**17b**, and (*E*)-**19b**, respectively, from which *β*-hydride or *β*-deuteride elimination would give various mono- and dideuterated isomers of [D]$_n$-**3ac**. Finally, σ-π-σ isomerization of (*E*)-**17b** into (*E*)-**16b** followed by β-hydride elimination would provide a dideuterated isomer of [D]$_n$-**15**.

To demonstrate the synthetic utility of the allylation products, 1,3-diene **3aa** was heated with *N*-phenylmaleimide in toluene at 80 °C to give Diels–Alder adduct **18** in 67% yield with >19:1 *endo*:*exo* selectivity (eq 3). Furthermore, allylation product **3a** reacted smoothly with 1,3-enyne **19** in a Rh(III)-catalyzed oxidative annulation to give isoindolinone **20** in 67% yield (eq 4). In this reaction, 1,3-enyne **19** functions as a one-carbon annulation partner as a result of an alkenyl-to-allyl 1,4-Rh(III) migration.[10]





CONCLUSION

In summary, we have described the oxidative C–H allylation of *N*-acetylbenzamides with 1,3-dienes, which involve, to our knowledge, the first reported examples of allyl-to-allyl 1,4-Rh(III) migration. This new mode of Rh(III) reactivity enables reaction at sites not available from conventional 1,3-allylic transposition. The results of reactions of deuterated 1,3-dienes indicate that reversible interconversion of numerous allylrhodium(III) species by σ-π-σ isomerization, *E*/*Z* isomerization, and allyl-to-allyl 1,4-Rh(III) migration pathways occurs on timescales that are rapid compared to product-forming *β*-hydride (or *β*-deuteride) elimination steps. This work suggests that the possibility that these isomerization processes might occur should be taken into consideration in any future design of new reactions involving allylrhodium(III) species. Further investigation of the synthetic potential of allyl-to-allyl 1,4-metal migrations is ongoing in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and full spectroscopic data for all new compounds

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected reviews on metal-catalyzed enantioselective allylic substitutions, see: (a) Zhuo, C.-X.; Zheng, C.; You, S.-L. *Acc. Chem. Res.* **2014**, *47*, 2558-2573. (b) Tosatti, P.; Nelson, A.; Marsden, S. P. *Org. Biomol. Chem.* **2012**, *10*, 3147-3163. (c) Hartwig, J. F.; Stanley, L. M. *Acc. Chem. Res.* **2010**, *43*, 1461-1475. (d) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258-297. (e) Helmchen, G.; Dahnz, A.; Dubon, P.; Schelwies, M.; Weihofen, R. *Chem. Commun.* **2007**, 675-691. (f) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921-2944. (g) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2002**, *36*, 48-58. (h) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395-422.

(2) For selected reviews on metal-catalyzed enantioselective nucleophilic allylations, see: (a) Ketcham, J. M.; Shin, I.; Montgomery, T. P.; Krische, M. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 9142-9150. (b) Dechert-Schmitt, A.-M. R.; Schmitt, D. C.; Gao, X.; Itoh, T.; Krische, M. J. *Nat. Prod. Rep.* **2014**, *31*, 504-513. (c) Huo, H.-X.; Duvall, J. R.; Huang, M.-Y.; Hong, R. *Org. Chem. Front.* **2014**, *1*, 303-320. (d) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774-7854. (e) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. *Chem. Rev.* **2011**, *111*, 2626-2704. (f) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763-2794.

(3) Martínez, J. I.; Smith, J. J.; Hepburn, H. B.; Lam, H. W. *Angew. Chem., Int. Ed.* **2016**, *55*, 1108-1112.

(4) Hepburn, H. B.; Lam, H. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 11605-11610.

(5) (a) Xue, P.; Bi, S.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2004**, *23*, 4735-4743. (b) Takada, Y.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 2515-2517. (c) Sumida, Y.; Takada, Y.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Chem. Asian. J.* **2008**, *3*, 119-125. (d) Omura, S.; Fukuyama, T.; Horiguchi, J.; Murakami, Y.; Ryu, I. *J. Am. Chem. Soc.* **2008**, *130*, 14094-14095. (e) Smejkal, T.; Han, H.; Breit, B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 10366-10367.

(6) (a) Luo, Y.; Hepburn, H. B.; Chotsaeng, N.; Lam, H. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 8309-8313. (b) Hepburn, H. B.; Chotsaeng, N.; Luo, Y. F.; Lam, H. W. *Synthesis* **2013**, *45*, 2649-2661.

(7) For reviews of 1,4-metal migration, see: (a) Ma, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7512-7517. (b) Shi, F.; Larock, R. C. *Top. Curr. Chem.* **2010**, *292*, 123-164.

(8) For reviews of Rh(III)-catalyzed C–H functionalization, see: (a) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007-1020. (b) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443-1460. (c) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31-41. (d) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212-11222.

(9) For selected recent reviews of catalytic C–H functionalization, see: (a) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107-1295. (b) Gandeepan, P.; Cheng, C.-H. *Chem. Asian. J.* **2015**, *10*, 824-838. (c) Mo, J.; Wang, L.; Liu, Y.; Cui, X. *Synthesis* **2015**, *47*, 439-459. (d) Shi, G.; Zhang, Y. *Adv. Synth. Catal.* **2014**, *356*, 1419-1442. (e) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443-1460. (f) De Sarkar, S.; Liu, W.; Kozhushkov, S. I.; Ackermann, L. *Adv. Synth. Catal.* **2014**, *356*, 1461-1479. (g) Engle, K. M.; Yu, J.-Q. *J. Org. Chem.* **2013**, *78*, 8927-8955. (h) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788-802. (i) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215-1292. (j) Wencel-Delord, J.; Droege, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740-4761. (k) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315-1345.

(10) Burns, D. J.; Lam, H. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 9931-9935.

(11) Burns, D. J.; Best, D.; Wieczysty, M. D.; Lam, H. W. *Angew. Chem., Int. Ed.* **2015**, *54*, 9958-9962.

(12) For stoichiometric 1,4-rhodium(III) migration, see: (a) Ikeda, Y.; Takano, K.; Kodama, S.; Ishii, Y. *Chem. Commun.* **2013**, *49*, 11104-11106. (b) Ikeda, Y.; Takano, K.; Waragai, M.; Kodama, S.; Tsuchida, N.; Takano, K.; Ishii, Y. *Organometallics* **2014**, *33*, 2142-2145.

(13) For the isolation and characterization of π-allylrhodium(III) species, see: Shibata, Y.; Kudo, E.; Sugiyama, H.; Uekusa, H.; Tanaka, K. *Organometallics* **2016**, *35*, 1547-1552.

(14) For examples of catalytic C–H functionalization reactions involving 1,3-dienes, see: (a) Houlden, C. E.; Bailey, C. D.; Ford, J. G.; Gagné, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.* **2008**, *130*, 10066-10067. (b) Li, Q.; Yu, Z.-X. *J. Am. Chem. Soc.* **2010**, *132*, 4542-4543. (c) Li, Q.; Yu, Z.-X. *Angew. Chem., Int. Ed.* **2011**, *50*, 2144-2147. (d) Nishimura, T.; Ebe, Y.; Hayashi, T. *J. Am. Chem. Soc.* **2013**, *135*, 2092-2095. (e) Nishimura, T.; Nagamoto, M.; Ebe, Y.; Hayashi, T. *Chem. Sci.* **2013**, *4*, 4499-4504. (f) Zhao, D.; Lied, F.; Glorius, F. *Chem. Sci.* **2014**, *5*, 2869-2873. (g) Khan, I.; Chidipudi, S. R.; Lam, H. W. *Chem. Commun.* **2015**, *51*, 2613-2616. (h) Cooper, S. P.; Booker-Milburn, K. I. *Angew. Chem., Int. Ed.* **2015**, *54*, 6496-6500.

(15) For examples of metal-catalyzed C–H allylation of arenes with allylic electrophiles, see: (a) Oi, S.; Tanaka, Y.; Inoue, Y. *Organometallics* **2006**, *25*, 4773-4778. (b) Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**, *13*, 540-542. (c) Kuninobu, Y.; Ohta, K.; Takai, K. *Chem. Commun.* **2011**, *47*, 10791-10793. (d) Yao, T.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2990-2994. (e) Fan, S.; Chen, F.; Zhang, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 5918-5923. (f) Makida, Y.; Ohmiya, H.; Sawamura, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 4122-4127. (g) Wang, H.; Schröder, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 5386-5389. (h) Asako, S.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2013**, *135*, 17755-17757. (i) Cong, X.; Zeng, X. *Org. Lett.* **2014**, *16*, 3716-3719. (j) Suzuki, Y.; Sun, B.; Sakata, K.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 9944-9947. (k) Gensch, T.; Vasquez-Cespedes, S.; Yu, D.-G.; Glorius, F. *Org. Lett.* **2015**, *17*, 3714-3717. (l) Cera, G.; Haven, T.; Ackermann, L. *Angew. Chem., Int. Ed.* **2016**, *55*, 1484-1488.

(16) For examples of metal-catalyzed directing-group assisted C–H allylation of arenes with allenes, see: (a) Zhang, Y. J.; Skucas, E.; Krische, M. J. *Org. Lett.* **2009**, *11*, 4248-4250. (b) Zeng, R.; Fu, C.; Ma, S. *J. Am. Chem. Soc.* **2012**, *134*, 9597-9600. (c) Ye, B.; Cramer, N. *J. Am. Chem. Soc.* **2013**, *135*, 636-639.

(17) (a) Takahama, Y.; Shibata, Y.; Tanaka, K. *Org. Lett.* **2016**, *18*, 2934-2937. (b) Yamaguchi, T.; Kommagalla, Y.; Aihara, Y.; Chatani, N. *Chem. Commun.* **2016**, *52*, 10129-10132.

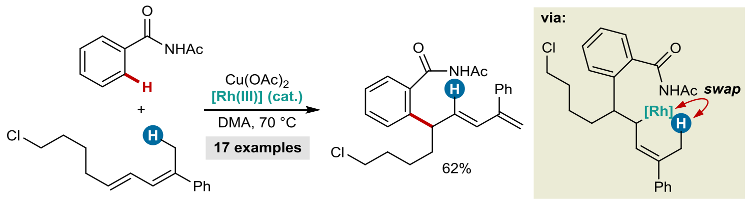
(18) See the Supporting Information for details of other substrates evaluated.

(19) (a) Wencel-Delord, J.; Nimphius, C.; Patureau, F. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 2247-2251. (b) Schröder, N.; Wencel-Delord, J.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 8298-8301. (c) Ryu, J.; Shin, K.; Park, S. H.; Kim, J. Y.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 9904-9908. (d) Shin, K.; Baek, Y.; Chang, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8031-8036.

(20) (a) Xu, L.; Zhu, Q.; Huang, G.; Cheng, B.; Xia, Y. *J. Org. Chem.* **2012**, *77*, 3017-3024. (b) Park, S. H.; Kwak, J.; Shin, K.; Ryu, J.; Park, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 2492-2502. (c) Zhou, T.; Guo, W.; Xia, Y. *Chem. Eur. J.* **2015**, *21*, 9209-9218. (d) Li, J.; Qiu, Z. *J. Org. Chem.* **2015**, *80*, 10686-10693. (e) Yang, Y.-F.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **2016**, *138*, 6861–6868.

(21) Li, Y.; He, G.; Kantchev, E. A. B. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24250-24255.

(22) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578-2592.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