Allylic Compounds

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Cobalt-Catalyzed Allylation of Heterobicyclic Alkenes: Ligand-Induced Divergent Reactivities

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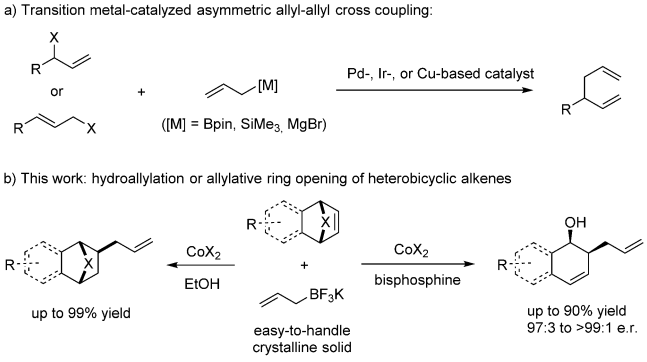
Dedicated to Professor Richard R. Schrock on the occasion of his 70th birthday

Abstract: *The allylation of heterobicyclic alkenes is presented for the first time. By using an inexpensive cobalt salt as the catalyst and easy-to-handle potassium allyltrifluoroborate as the reagent, an unprecedented formal hydroallylation of the bicyclic alkenes is realized in high efficiency. When a chiral cobalt/bis(phosphine) complex is used instead, the alternative ring-opening products can be obtained in high yield and excellent enantioselectivity.*

The stereoselective allylation of carbonyls and imines has been developed into one of the most powerful carbon–carbon bond-forming reactions.[1] The allylation of other π systems such as activated alkenes has also been explored in the forms of conjugate allylation of α,β-unsaturated carbonyls as well as allyl–allyl cross-coupling reactions. Highly stereoselective catalytic systems along these lines have been achieved by the groups of Morken, Carreira, Feringa, and others (Scheme 1 a).[2] In our own efforts in this field of research,[3] we became interested in exploring the allylation of new types of electrophiles and were particularly attracted to strained *meso*-heterobicyclic alkenes. The desymmetrization of these compounds has been developed into highly useful transformations by the group of Lautens and many others.[4,5] The scope of carbon-based nucleophiles used in these studies, however, is largely limited to simple nonfunctionalized arylboronic acid, alkyl zinc, or Grignard reagents.[6–8] As these desymmetrization products are useful building blocks in chemical synthesis and medicinal chemistry,[9] the introduction of new, synthetically versatile nucleophiles will greatly expand the utility of this transformation. We report herein the first catalytic stereoselective allylation of heterobicyclic alkenes using the easy-to-handle potassium allyltrifluoroborate as the allylating reagent (Scheme 1 b).[10] In addition, intriguing divergent reactivities have also been achieved: either the unprecedented hydroallylation of these alkenes or the ring-opening allylation products could be accessed in high efficiency by a simple switch of catalytic reaction conditions.



Scheme 1. Unprecedented cobalt-catalyzed allylation of heterobicyclic alkenes.

In the past few decades, there has been a strong push for the replacement of precious-metal catalysts with the more economical and abundant base-metal catalysts in an effort to promote sustainable chemical synthesis.[11] More specifically, cobalt-based catalysts have been actively pursued for alkene functionalization, an extremely important transformation in organic synthesis. Great progress has been made recently in cobalt-catalyzed hydrogenation, hydroboration, hydroacylation, and related transformation of alkenes,[12] which generally involve hydrocobaltation of alkenes as a key step. In our studies, we have identified cobalt(II) salts as the most effective catalyst for the allylation reactions. This transformation involves a key carbocobaltation step and thus greatly expands the scope of cobalt-catalyzed functionalization of alkenes.

The representative optimization studies for the allylation of the model substrate **1a** are summarized in Table 1. All the metal complexes and potassium allyltrifluoroborate were used as received from commercial sources. Out of the various metal complexes examined initially (entries 1–5), only [{Rh(cod)Cl}$_2$] produced an unexpected hydroallylation product, **2a**, as a single *syn* isomer in moderate yield (entry 3). The anticipated product **3a** was not obtained at all under these reaction conditions. Through a more thorough screening of various metal salts, we were excited to find out that a higher yield of 68% was obtained for **2a** by using cobalt bromide (entry 7), although other cobalt salts, such as cobalt acetate, showed no reactivity under similar reaction conditions (entry 6). Curious about the source of proton for the formation of **2a**, we carried out the same reaction as in entry 7 under strictly moisture-free conditions, and it led to a yield of only 9% for **2a**, thus indicating that an external proton source is needed for the catalytic turnover. Based on this observation, different proton donors were then examined (entries 8 and 9), out of which ethanol proved to be the most

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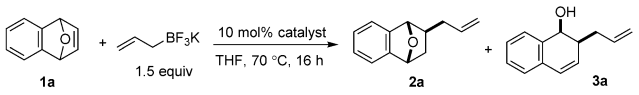
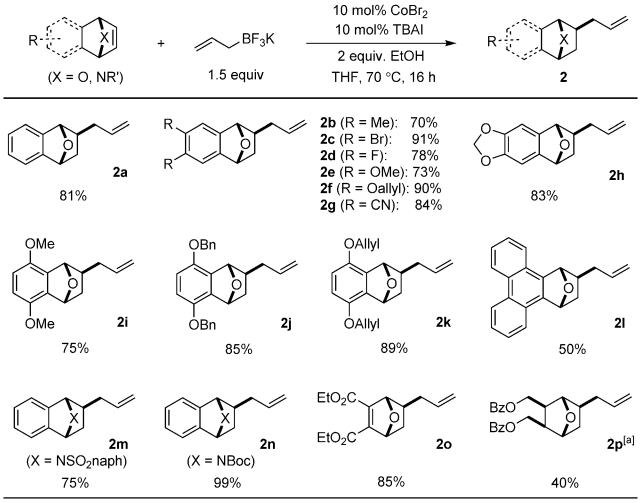
Table 1: Identification of divergent cobalt-catalyzed allylation of **1a**.



Entry	Metal	Additive	**2a** Yield [%][a]	**3a** Yield [%][a]
1	$[Pd_2(dba)_3]$	–	< 2	< 2
2	$[\{Ir(cod)Cl\}_2]$	–	< 2	< 2
3	$[\{Rh(cod)Cl\}_2]$	–	50	< 2
4	CuCl	–	< 2	< 2
5	$Sc(OTf)_3$	–	< 2	< 2
6	$Co(OAc)_2$	–	< 2	< 2
7	$CoBr_2$	–	68 (9)[b]	< 2
8	$CoBr_2$	2 equiv H_2O	38	< 2
9	$CoBr_2$	2 equiv EtOH	72	< 2
10[c]	$CoBr_2$	2 equiv EtOH	81	< 2
11	$CoBr_2$	20 mol% PPh_3	< 2	30
12	$CoBr_2$	10 mol% dppp	< 2	75
13[d]	$CoBr_2$	10 mol% dppp	< 2	75

[a] Yield of isolated product. [b] The number within parentheses was obtained when the reaction was carried out under strictly moisture-free conditions. [c] With 10 mol% TBAI. [d] With 2 equiv EtOH. cod = 1,5-cyclooctadiene, dba = dibenzylidene acetone, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.



Scheme 2. Scope of cobalt-catalyzed hydroallylation. See the Supporting Information for a detailed procedure. [a] 30 mol% $CoBr_2$. Boc = *tert*-butoxycarbonyl, Bz = benzoyl, TBAI = tetra-*n*-butylammonium iodide.

effective choice. Considering the limited solubility of potassium allyltrifluoroborate in THF, we tested the use of phase-transfer catalysts such as tetrabutylammonium iodide (TBAI).[13] This modification further improved the yield of **2a** to 81% (entry 10). The effect of various phosphine ligands was also examined for the allylation reaction. For the reaction catalyzed by the rhodium complex, addition of a bis(phosphine) ligand, such as 1,3-bis(diphenylphosphino)propane (dppp), completely shut down the reaction. When the corresponding cobalt-catalyzed reaction was carried out in the presence of either PPh_3 or dppp, however, an intriguing complete shift of the reaction outcome was observed: the alcohol **3a** was produced exclusively as a single diastereomer (entries 11 and 12). By the use of dppp, a good yield of 75% could be obtained for **3a**. In contrast to the formation of **2a**, this ring-opening reaction turned out to be insensitive to moisture. Addition of other proton donors such as ethanol also showed no effect on the reaction outcome (entry 13).

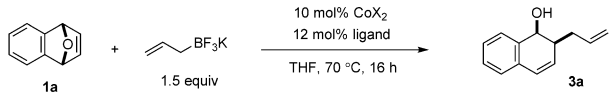
As the hydroallylation product **2a** represents a rare example of its kind and is potentially highly useful in organic synthesis, the scope of this reaction was explored (Scheme 2). Under the optimal reaction conditions using catalytic $CoBr_2$ and TBAI, a wide range of benzofused, oxabicyclic alkenes underwent efficient hydroallylation to produce **2a–l** in good to high yields. While it is well established that the less strained azabicyclic alkenes, as well as non-benzofused oxabicylic alkenes, are much less reactive substrates, we were delighted to find that the hydroallylation of these compounds proceeded smoothly to deliver **2m–o** in good to excellent yields. Only for the much less strained **2p**, a moderate yield of 40% was obtained, even with a higher catalyst loading. It is also noteworthy that various functionalities including ethers, esters, sulfonamide, and carbamate, within the substrates were well-tolerated.[14]

Notably, all the hydroallylation products were obtained as a single *syn* diastereomer, thus implying that the heteroatom in the substrate structure may interact with the cobalt catalyst and direct the allyl addition on the same side in the key carbocobaltation step. Consistent with this hypothesis, when benzonorbornadiene (analogue of **1a** with a methylene bridge) was tested as the substrate, no product was obtained at all. Overall, this simple cobalt-catalyzed procedure produced a wide range of novel hydroallylation products in good to excellent efficiency. The development of an enantioselective variant is underway.

As the use of a cobalt/bis(phosphine) complex induced complete divergent reactivity to yield the ring-opening product **3a**, a wide range of chiral bis(phosphine) ligands were tested to realize an enantioselective synthesis of **3**. The representative data of ligand screening is summarized in Table 2. In combination with cobalt bromide, Josiphos and bdpp proved to be the optimal choices for ligands (entries 5 and 8). A good yield of 70% and excellent enantioselectivities were realized in both cases. At this point, different cobalt salts were tested with bdpp, and the use of $CoCl_2$ led to a slight increase in the chemical yield (entry 11). Finally, a more thorough solvent screening was carried out. The mixed solvents of THF and DCE (1:1) proved to be optimal to deliver **3a** in 81% yield with nearly perfect greater than 99:1 e.r. (entry 12).

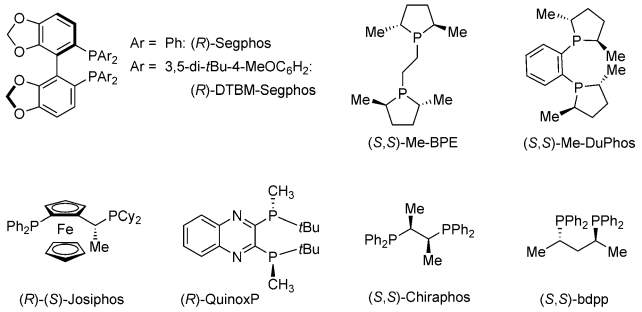
With the optimal reaction conditions in hand, the scope of the enantioselective ring-opening allylation was examined (Scheme 3a). Various allylation products (**3a–h**) bearing electron-neutral, electron-withdrawing, and electron-donating substituents on the aryl structure were produced in uniformly high yield and excellent enantioselectivity through desymmetrization of the *meso* substrates. The extension to the less reactive non-benzofused substrates proved to be partially successful. The highly functionalized cyclohexadiene **3i** was obtained in 74% yield with, again, an excellent

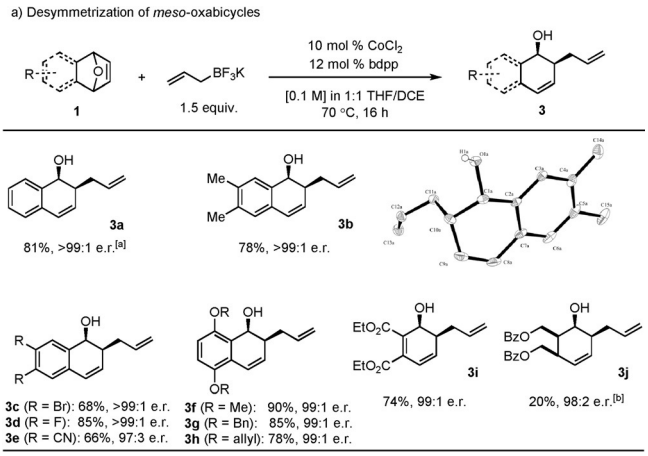
Table 2: Optimization of enantioselective allylative ring opening.



Entry	Cobalt	Ligand	Yield [%][a]	e.r.[b]
1	$CoBr_2$	(*R*)-Segphos	68	50:50
2	$CoBr_2$	(*R*)-DTBM-Segphos	83	80:20
3	$CoBr_2$	(*S*,*S*)-Me-BPE	< 2	–
4	$CoBr_2$	(*S*,*S*)-Me-DuPhos	< 2	–
5	$CoBr_2$	(*R*)-(*S*)-Josiphos	70	97:3
6	$CoBr_2$	(*R*)-QuinoxP	< 2	–
7	$CoBr_2$	(*S*,*S*)-Chiraphos	40	96:4
8	$CoBr_2$	(*S*,*S*)-bdpp	70	98:2
9	CoI_2	(*S*,*S*)-bdpp	30	82:18
10	CoF_2	(*S*,*S*)-bdpp	< 2	–
11	$CoCl_2$	(*S*,*S*)-bdpp	75	98:2
12[c]	$CoCl_2$	(*S*,*S*)-bdpp	81	> 99:1

[a] Yield of the isolated product. [b] Determined by HPLC analysis using a chiral stationary phase. [c] A mixture solvent (1:1 THF/DCE) was used.



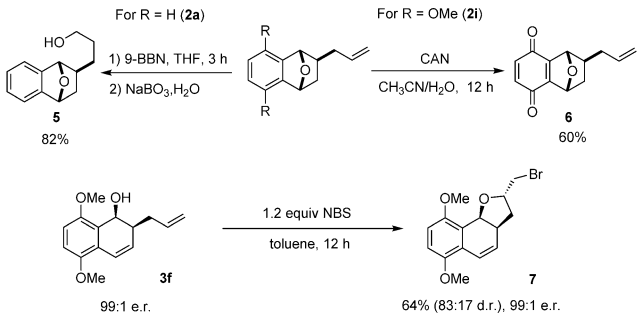


Scheme 3. Scope of the enantioselective allylative ring opening. See the Supporting Information for a detailed procedure. [a] The same reaction was carried out on a scale of 2 mmol **1a**, which produced **3a** in 85% yield with > 99:1 e.r. [b] 20 mol% $CoCl_2$ was used. DCE = 1,2-dichloroethane. Thermal ellipsoids shown at 25% probability.[18]

e.r. value of 99:1. Although **3j** could be accessed in high e.r. value, the efficiency for this reaction requires further optimization. The relative and absolute configuration of **3b** was unambiguously assigned by single-crystal X-ray analysis. The configurations of the other products were assigned by analogy.

In addition to the desymmetrization of *meso* alkenes, the enantioselective allylation was also successfully extended to regiodivergent ring opening of the racemic **4** (Scheme 3b).[15] Two isomeric products, **3k** and **3l**, were produced in good yields (sum of 75%) and with excellent enantioselectivity (> 99:1 e.r.).

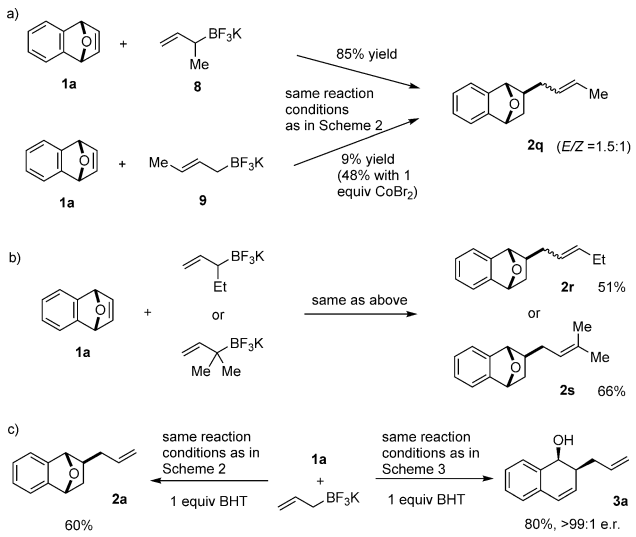
Both series of allylation products are synthetically versatile and representative derivatizations of them are shown in Scheme 4. Hydroboration of the terminal alkene in **2a** followed by oxidation yielded the alcohol **5** in 82% overall yield. In the case of **2i**, bearing *para*-dimethoxy substituents, oxidation using CAN produced the corresponding quinone **6** in reasonable yield. For the ring-opening products, the hydroxy group and the allyl unit can be manipulated in different ways such as the bromoetherification of **3f** to yield **7** in a good d.r. value of 83:17, favoring the diastereomer as shown in Scheme 4.



Scheme 4. Derivatization of allylation products. 9-BBN = 9-borabicyclo-[3.3.1]nonane, CAN = ceric ammonium nitrate, NBS = *N*-bromosuccinimide.

To shed some light on the mechanism of this reaction, we tested the reactions with subsituted allylating reagents (Scheme 5a). When potassium α-methylallyltrifluoroborate (**8**) or potassium crotyltrifluoroborate (**9**) were tested under the standard hydroallylation conditions, the same product **2q** (as a mixture of *E*/*Z* isomers) was produced. These results strongly support the intermediate of a cobalt π-allyl species. The reactivity of **9** was much lower than that of **8**. The use of a higher loading of the cobalt catalyst for the reaction using **9**, however, could improve the yield of **2q** to a moderate level. In addition, various substituted reagents such as α-ethylallyltrifluoroborate and α,α-dimethylallyl trifluoroborate also proved to be successful in the hydroallylation to deliver **2r** and **2s**, respectively, in reasonable yields (Scheme 5b).

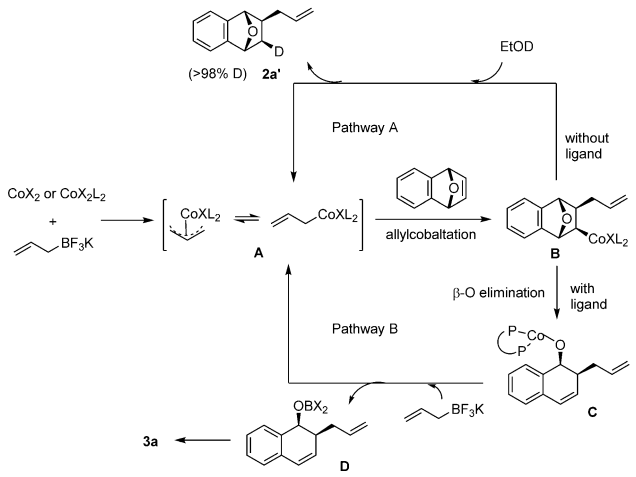
In our reactions readily available cobalt(II) salts were used as the catalyst. The addition of a radical scavenger such as butylhydroxytoluene (BHT) showed no significant influence on the reactivity or selectivity (Scheme 5c), thus implying that no single-electron transfer is involved in this



Scheme 5. Use of substituted allyl reagents and radical scavenger.

reaction. For the ring-opening reaction, the enantioselectivity of the product was found to be directly proportional to the enantiopurity of the chiral ligand (see Figure S1 in the Supporting Information).[16] Based on these preliminary studies we propose that the reaction is catalyzed by the cobalt(II)/bis(phosphine) complex (1:1 ratio).

We propose the reaction pathways shown in Scheme 6 as a working hypothesis. Transmetallation of cobalt salt with allyltrifluoroborate presumably generates the allylcobalt species **A**, the two termini of which can equilibrate through the cobalt π-allyl intermediate for the reaction. *syn*-Allylcobaltation of the alkene substrate by **A** then produces **B** as a common intermediate. In the absence of a ligand, the C–Co bond directly undergoes protonolysis to produce the hydroallylation product **2**. When deuterated ethanol was used as the proton source under otherwise identical conditions, the oxabicycle **2a′** was obtained as a single diastereomer with greater than 98% deterium labelling, thus suggesting a stereoretentive protonolysis. In the presence of a phosphine ligand,



Scheme 6. Proposed catalytic pathways.

in contrast, β-O elimination proceeds instead of protonolysis to yield **C**, which in turn is tranformed into **D**, thus leading to the product **3**. More detailed mechanistic and computational studies will be carried out to better understand the origin of this intriguing divergent reactivity.[17]

In conclusion, we have developed an unprecedented allylation of heterobicyclic alkenes catalyzed by cobalt. Divergent reactivities were realized by using either a cobalt salt or cobalt/bis(phosphine) complex as the catalyst. The procedure uses commercially available and inexpensive catalysts and reagents, and delivers highly synthetically valuable products in high efficiency and stereoselectivity. Current efforts in our laboratories are focused on the extension of this allylcobaltation reaction to other types of alkenes as well as other π-systems.

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[18] CCDC 1423579 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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