JOC *Article*

A Highly Regio- and Stereoselective Nickel-Catalyzed Ring-Opening Reaction of Alkyl- and Allylzirconium Reagents to 7-Oxabenzonorbornadienes

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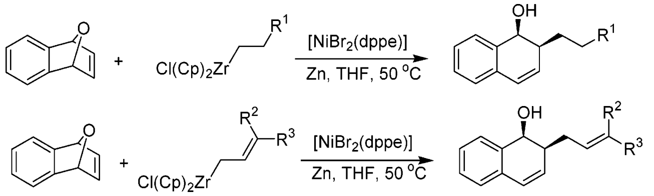
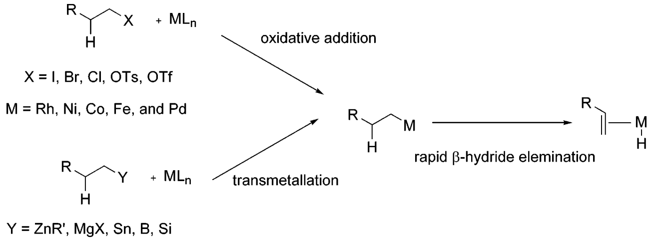


An efficient method for the synthesis of *cis*-2-alkyl- or allyl-1,2-dihydronaphthalenes via a nickel-catalyzed highly regio- and stereoselective ring-opening addition of alkyl- or allylzirconium reagents to 7-oxabenzonorbornadienes is described. Treatment of 7-oxabenzonorbornadienes **1a−c** with various alkylzirconium reagents **2a−j** ($Cp_2ZrClCH_2CH_2R$: R = *tert*-butyl, *n*-butyl, *n*-pentyl, $-(CH_2)_3$-$CH{=}C(CH_3)_2$, $-SiMe_3$, $-CH_2SiMe_3$, $-(CH_2)_3Br$, cyclopentyl, cyclohexyl, and benzyl) in the presence of $NiBr_2$(dppe) and Zn powder in dry THF at 50 °C afforded the corresponding *cis*-2-alkyl-1,2-dihydronaphthalene derivatives **3a−m** in good yields. In addition, allyl zirconium reagents **4a−c** also underwent ring-opening reactions with **1a** and **1c** to give **5a−d** in very good yields. The alkylative ring-opening products from 7-oxabenzonorbornadiene can be further converted to naphthalene derivatives **6a−c**, via an acid-mediated dehydration, in good to excellent yields. A possible mechanism for the present catalytic reaction was proposed.

Introduction

Recently, transition-metal-catalyzed $C_{SP^3-SP^3}$ bond formation reactions have drawn great attention in organic synthesis.[1] The metal-catalyzed C_{SP-SP}, $C_{SP^2-SP^2}$, and C_{SP-SP^2} bond formations are well developed,[2] but $C_{SP^3-SP^3}$ bond formation reactions imposes considerable synthetic limitations such as (a) the relatively slow oxidative addition or transmetalation of the alkyl reagents to metal center and (b) the rapid *β*-hydride elimination of the resulting alkylmetal complex (Scheme 1).

SCHEME 1



The metal-catalyzed ring opening of 7-oxabenzonorbornadienes to give dihydronaphthalene derivatives is an efficient method to construct multiple stereocenters in organic synthesis.[3] The dihydronaphthalene skeleton is found in a wide range of naturally occurring compounds that exhibit diverse biological activities.[4] In this type of

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(1) (a) Bräse, S.; Waegell, B.; de Meijere, A. *Synthesis* **1998**, 148. (b) Cárdenas, D. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 384. (c) Luh, T.-Y.; Leung, M.-K.; Wong, K.-T. *Chem. Rev.* **2000**, *100*, 3187. (d) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726. (e) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662. (f) Jensen, A. E.; Knochel, P. *J. Org. Chem.* **2002**, *67*, 79. (g) Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 511. (h) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.

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(3) (a) White, J. D. *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic Press: New York, 1984; Chapter 13. (b) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (c) Vogel, P.; Fattori, D.; Gasparini, F.; Le Drain, C. *Synlett.* **1990**, 173. (d) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48.

(4) (a) Johnson, B. M.; Chang, P. T. L. *Anal. Profiles Drug Subst. Excipients* **1996**, *24*, 443. (b) Kamal, A.; Gayatri, L. *Tetrahedron Lett.* **1996**, *37*, 3359. (c) Synder, S. E. *J. Med. Chem.* **1995**, *38*, 2395. (d) Kim, K.; Guo, Y.; Sulikowski, G. A. *J. Org. Chem.* **1995**, *60*, 6866. (e) Perrone, R. J. *J. Med. Chem.* **1995**, *38*, 942.

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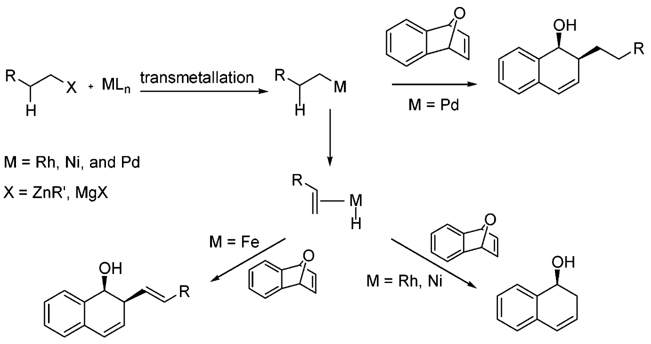
SCHEME 2

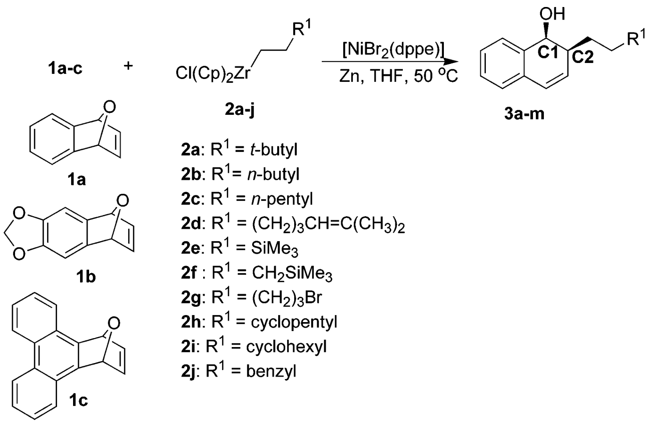


reaction, palladium, nickel, and rhodium catalysts were widely used. Pioneering works in this area have been undertaken by several research groups.[5,6] We have developed the ring-opening reactions of bicyclic alkenes with various electrophiles[7] (aryl and alkenyl halides), the reductive coupling with propiolates,[8] and addition of terminal acetylenes.[9] While various types of aryl, alkynyl (C_{sp}), and alkenyl (C_{sp^2}) addition to bicyclic alkenes have been explored, alkylative (C_{sp^3}) addition to oxabicyclic alkenes has not been well explored. In addition, the allylic addition to bicyclic alkenes is not known in the literature.

Recently, Lautens and Hiebert have reported a palladium-catalyzed alkylative ring-opening reaction of bicyclic alkenes with dialkylzinc[10] to give alkylative ring-opening products. However, this reaction is limited to only simple dialkylzinc reagents (R_2Zn, where R = Et, *n*-Pr). As the alkyl chain increased, the reaction did not proceed smoothly due to the steric hindrance of dialkylzinc reagents. The addition of alkyl Grignard reagents to oxabicyclic alkenes in the presence of $FeCl_3$ catalyst was reported, but the reaction gave the vinylated instead of the alkylated products (Scheme 2).[11] For the alkylative ring-opening reactions of bicyclic alkenes, only limited success has been achieved.

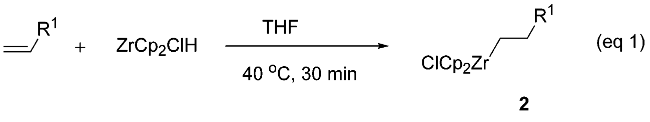
Very recently, we have reported a nickel-catalyzed ring-opening reaction of alkenylzirconium reagents to bicyclic alkenes to give highly regio- and stereoselective alkenyl ring-opening products.[12] Our continuous interest in this type of reactions prompted us to explore the possibility of using alkyl- and allylzirconium reagents as substrates for ring-opening reactions. In this paper, we wish to report a highly regio- and stereoselective ring opening of oxabicyclic alkenes with alkylzirconium reagents in the presence of nickel complexes to afford *cis*-2-alkyl-1,2-dihydronaphthalene derivatives. This reaction is applicable to various longer and bulkier alkylzirconium reagents. In addition, this ring-opening reaction is successfully extended into various allylzirconium reagents.

SCHEME 3



Results and Discussion

The reaction of 7-oxabenzonorbornadiene (**1a**) (1.50 mmol) with 3,3-dimethylbutylzirconium reagent (**2a**) (1.00 mmol) (freshly prepared[13a] from 3,3-dimethyl-but-1-ene and Cp_2ZrClH in dry THF (eq 1)) in the presence of $NiBr_2(dppe)$ (10 mol %) and zinc powder (20 mol %) in THF at 50 °C furnished the ring-opening addition product **3a** in 82% isolated yield based on the amount of zirconium hydride used (Scheme 3, and Table 1, entry 1). Product **3a** was thoroughly characterized by its NMR and mass data. The *cis* stereochemistry of this product was established on the basis of the coupling constants (~4.0 Hz) of two protons at C1 and C2 positions (Scheme 3).



To optimize the present reaction, the catalytic activities of various nickel complexes for the ring-opening reaction of **1a** with **2a** were investigated. In the absence of nickel catalyst no reaction occurs, whereas the omission of zinc powder gave a trace of product **3a**. If zinc powder was replaced by $ZnCl_2$ (20 mol %) and NEt_3 (1.60 mmol), the catalytic reaction also proceeded smoothly leading to the formation of **3a** in 70%. Simple nickel complex $Ni(acac)_2$ was totally inactive for this ring-opening reaction. Monodentate phosphine complex $NiCl_2(PPh_3)_2$ gave a trace amount of product **3a**. Bidentate phosphine complexes $NiCl_2(dppe)$ afforded **3a** in 38% yield, whereas $NiBr_2(dppe)$ furnished **3a** in 86% yield. Addition of 1 equiv of dppe to the $NiBr_2(dppe)$ system totally inhibited the ring-opening reaction. In addition to the above nickel com-

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(5) (a) Leong, P.; Lautens, M. *J. Org. Chem.* **2004**, *69*, 2194. (b) Lautens, M.; Dockendorff, C. *Org. Lett.* **2003**, *5*, 3695. (c) Lautens, M.; Dockendorff, C.; Fagnou, K.; Malicki, A. *Org. Lett.* **2002**, *4*, 1311. (d) Lautens, M.; Fagnou, K.; Rovis, T. *J. Am. Chem. Soc.* **2000**, *122*, 5650. (e) Lautens, M.; Ma, S. *J. Org. Chem.* **1996**, *61*, 7246. (f) Lautens, M.; Chiu, P.; Ma, S.; Rovis, T. *J. Am. Chem. Soc.* **1995**, *117*, 532. (g) Lautens, M.; Hiebert, S.; Renaud, J. L. *Org. Lett.* **2000**, *2*, 1971.

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(8) Rayabarapu, D. K.; Chiou, C.-F.; Cheng, C.-H. *Org. Lett.* **2002**, *4*, 1679.

(9) Rayabarapu, D. K.; Cheng, C.-H. *Chem. Eur. J.* **2003**, *9*, 3164.

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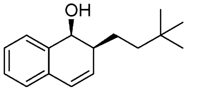
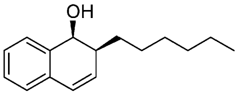
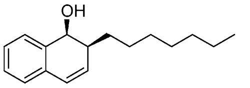
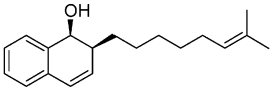
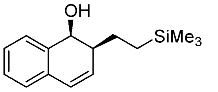
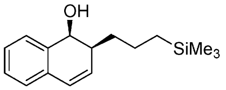
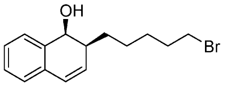
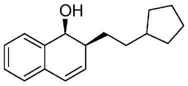
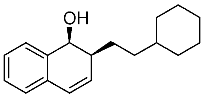
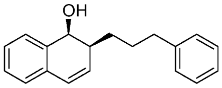
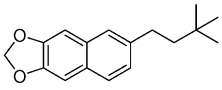
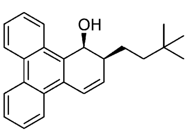
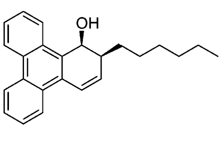
(11) Nakamura, M.; Matsuo, K.; Inoue, T.; Nakamura, E. *Org. Lett.* **2003**, *5*, 1373.

(12) Wu, M.-S.; Rayabarapu, D. K.; Cheng, C.-H. *J. Org. Chem.* **2004**, *69*, 8407.

(13) (a) Ni, Y.; Amarasinghe, K. K. D.; Montgomery, J. *Org. Lett.* **2002**, *4*, 1743. (b) Wipf, P.; Smitroiuch, J. H. *J. Org. Chem.* **1991**, *56*, 6494.

TABLE 1. Results of Nickel-Catalyzed Addition of Alkyl Zirconium Reagents 2 to Oxabenzonorbornadienes 1[a]

Entry	1	2	Product		Yield (%)[b]
1	**1a**	**2a**		**3a**	82 (86)
2	**1a**	**2b**		**3b**	76 65[c] 49[c]
3	**1a**	**2c**		**3c**	73
4	**1a**	**2d**		**3d**	72
5	**1a**	**2e**		**3e**	76
6	**1a**	**2f**		**3f**	62
7	**1a**	**2g**		**3g**	52
8	**1a**	**2h**		**3h**	79
9	**1a**	**2i**		**3i**	77
10	**1a**	**2j**		**3j**	72
11	**1b**	**2a**		**3k**	83
12	**1c**	**2a**		**3l**	78
13	**1c**	**2b**		**3m**	72

[a] All reactions were carried out using $NiBr_2(dppe)$ (10 mol %), Zn (20 mol %), 7-oxabenzanorbornadienes (**1**) (1.50 mmol), and alkylzirconium reagent **2** (1.00 mmol) in THF (2.0 mL) at 50 °C under N_2 for 12 h. [b] Isolated yields; yields in parentheses were determined by ^1H NMR using mesitylene as an internal standard. [c] Corresponding alkylzirconium reagents were derived from 2-hexene and 3-hexene.

plexes, various Pd catalysts $Pd(dba)_2$, $PdCl_2(PPh_3)_2$, and $PdCl_2(dppe)$ were also tested for the catalytic reaction. However, none of these palladium complexes showed catalytic activity for the ring-opening reaction of **1a** with

2a. It is important to point out that in the ring-opening reaction with dialkylzinc,[10] palladium complexes are the best catalysts, compared to nickel or rhodium species, because in the transmetalation step dialkylzinc readily underwent β-hydride elimination with nickel or rhodium catalysts to give rhodium or nickel hydride species prior to the carbon−carbon bond formation (Scheme 2). In contrast, in the present case, nickel complexes are much more efficient than palladium complexes. The solvent employed for the reaction using $NiBr_2(dppe)/Zn$ as the catalyst is crucial for the yield of **3a**. THF was the solvent of choice giving **3a** in 86% yield. The other solvents CH_3CN and DMF tested were totally ineffective, whereas toluene afforded 36% of **3a**. Based on these optimization studies, we choose $NiBr_2(dppe)$ as the catalyst and THF as the solvent in the presence of Zn for this ring-opening reaction.

Under the optimized reaction conditions, substituted alkylzirconium reagents also underwent ring-opening reactions with **1a** to afford the corresponding ring-opening products with high yields. The reaction of **1a** with linear alkyl zirconium reagents **2b**−**c** ($Cp_2ZrClCH_2CH_2R$: R = *n*-butyl and *n*-pentyl) (Scheme 3, Table 1, entries 2−3) furnished the corresponding *cis*-2-alkyl-1,2-dihydronaphthalene derivatives **3b**,**c** in 76 and 73% yields, respectively. Again, **2b**,**c** was prepared from the insertion of 1-hexene and 1-heptene into zirconium hydride Cp_2ZrClH, and the yields of **3b**,**c** were based on the Cp_2ZrClH used (eq 1). Interestingly, 2-hexene or 3-hexene also can be used for the preparation of zirconium reagent **3b** presumably via successive insertion and β-hydride elimination steps. The zirconium reagent **2b** prepared from 2-hexene and 3-hexene then reacted with **1a** to give ring-opening product **3b** in 65 or 49% yields (entry 2). The observed difference in the yield of product **3b** indicates that 1-hexene > 2-hexene > 3-hexene in the reaction rate with Cp_2ZrClH to give **2b**. This is expected in view of the fact that 2-hexene and 3-hexene require more reaction steps to reach **2b**. Under similar reaction conditions, zirconium reagent **2d** consisting of a 7-methyloct-6-enyl group underwent ring-opening addition to **1a** to afford **3d** in 72% yield (entry 4). Similarly, bromide- and silyl-substituted alkylzirconium reagents ($Cp_2ZrClCH_2CH_2R$: R = $SiMe_3$, CH_2SiMe_3, $(CH_2)_3Br$) react successfully with **1a** to furnish corresponding ring opening products **3e**−**g** in 76, 62, and 52% yields, respectively (entries 5−7). These results show the catalytic reaction is compatible with silyl and bromo functionalities. The ring-opening reaction of **1a** also can be extended to zirconium reagents[13b] **2h**−**j** ($Cp_2ZrClCH_2CH_2R$: R = cyclopentyl, cyclohexyl, and benzyl) to give products **3h**−**j** in 79, 77, and 72% yields, respectively (entries 8−10). In addition to **1a**, substituted oxabenzonorbornadienes **1b**,**c** were successfully used for the ring opening with zirconium reagents. Thus, 6,7-methylenedioxy-substituted oxabenzonorbornadiene **1b** reacts with **2a** to afford dehydrated naphthalene product **3k** in 83% yield (entry 11), while bulkier 1,4-oxa-1,4-dihydrotriphenylene **1c** with zirconium reagents **2a** and **2b** afforded the corresponding products **3l** and **3m** in 78 and 72% yields, respectively (entries 12−13). In these reactions, the alkylzirconium reagents were freshly prepared by treating the corresponding alkenes (2.00 equiv) with Cp_2ZrClH (1.00 equiv) in dry THF (1.5 mL) at 40 °C for 30 min (eq 1). The yields of the ring-opening products **3** were based on the amount of zirconium hydride Cp_2ZrClH used.

SCHEME 4

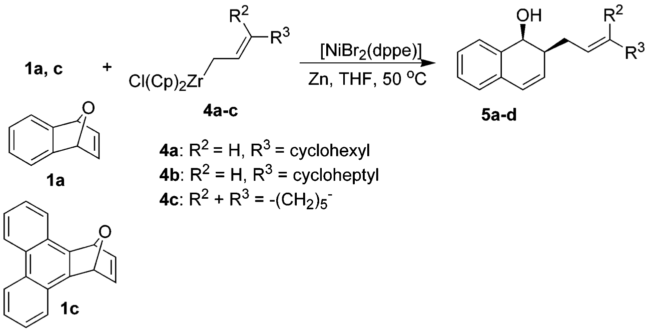
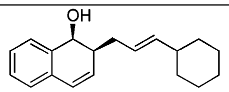
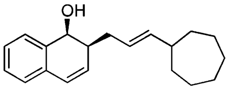
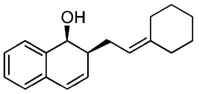
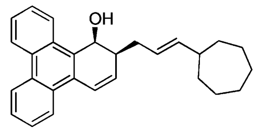
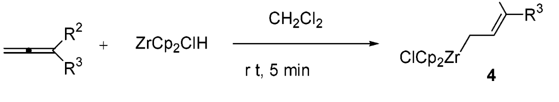


TABLE 2. Results of Nickel-Catalyzed Addition of Allylzirconium Reagents 4 to Oxanorbornadienes 1[a]

Entry	**1**	**4**	Product		Yield (%)[b]
1	**1a**	**4a**		**5a**	85
2	**1a**	**4b**		**5b**	83
3	**1a**	**4c**		**5c**	81
4	**1c**	**4b**		**5d**	80

[a] All reactions were carried out using $NiBr_2(dppe)$ (10 mol %), Zn (20 mol %), alkene (**1**) (1.50 mmol), and allylzirconium reagent **4** (1.00 mmol) in THF (3.0 mL) at 50 °C under N_2 for 12 h. [b] Isolated yields.

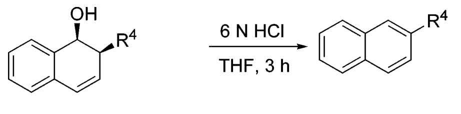
The scope of the present ring-opening reaction can be further extended to allylzirconium reagents. Treatment of 7-oxabenzonorbornadiene (**1a**) (1.50 mmol) with (3-cyclohexylallyl)zirconium reagent (**4a**) (1.00 mmol) (freshly prepared[14] by treating cyclohexylallene (2.00 equiv) with Cp_2ZrClH (1.00 equiv) in dry CH_2Cl_2 (1.5 mL) at room temperature for 5 min (eq 2)) in the presence of $NiBr_2(dppe)$ (10 mol %) and zinc powder (20 mol %) in THF (3.0 mL) at 50 °C for 12 h afforded exclusively *cis* stereochemistry with *E* isomer of allylic addition product **5a** in 85% isolated yield based on the amount of zirconium hydride used (Scheme 4, Table 2, entry 1). Under similar reaction conditions (3-cycloheptylallyl)- and (2-cyclohexylidenethyl)zirconium reagents **4b**,**c** underwent ring-opening reaction with **1a** to provide **5b**,**c** in 83 and 81% yields, respectively (entries 2 and 3). Likewise, the bulkier 1,4-oxa-1,4-dihydrotriphenylene **1c** reacted with **4b** to form **5d** in 80% yield (entry 4).



(eq 2)

The present alkylative ring-opening product from 7-oxabenzonorbornadienes was successfully transformed

SCHEME 5



3a, 3d, 3i **6a-6c**

3a: R^4 = $(CH_2)_2$-*t*-butyl
3d: R^4 = $(CH_2)_5$-C=C$(CH_3)_2$
3i: R^4 = $(CH_2)_2$-cyclohexyl

into 2-alkylnaphthalenes by dehydration in excellent yields. For example, treatment of product **3a** with hydrochloric acid in THF at room temperature for 3 h gave 2-(3,3-dimethylbutyl)naphthalene **6a** in 96% yield (Scheme 5). In addition, treating the reaction mixture of the alkylative ring-opening reaction of **1a** and **2a** with hydrochloric acid also led to the isolation of **6a** in 87% yield. Similarly, on treatment with hydrochloric acid, **3d** and **3i** were converted to the corresponding naphthalene derivatives **6b**,**c** in 75 and 95% yields.

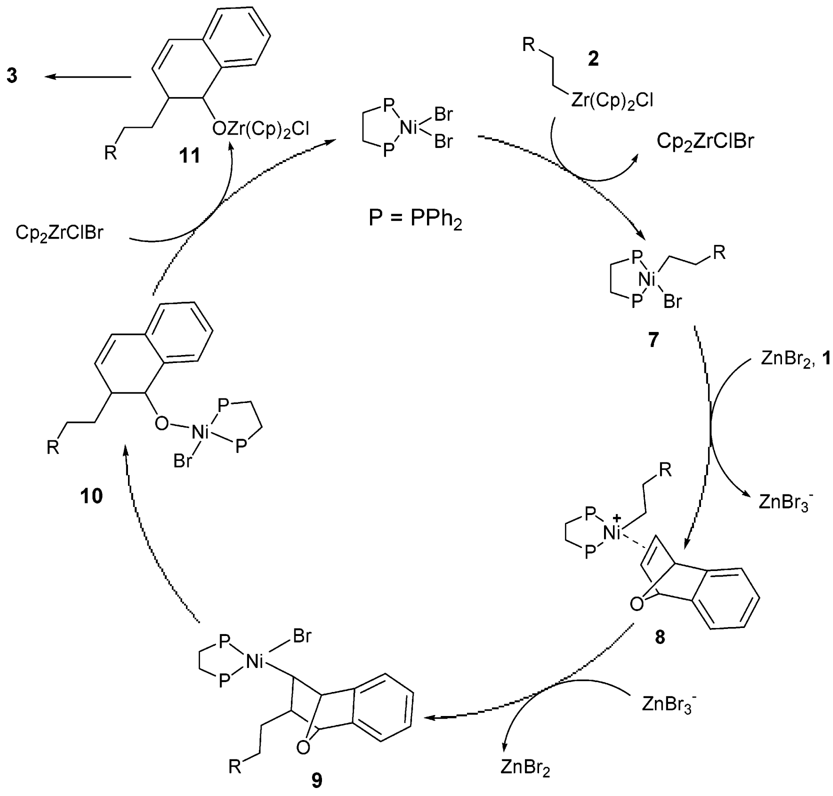
On the basis of the known nickel chemistry and the foregoing results, we proposed the mechanism in Scheme 6 to account for the present alkylative and allylative ring-opening reactions.[7−12] The catalysis is likely initiated by the transmetalation of alkylzirconium reagent with nickel(II) species to give nickel(II) alkyl intermediate **7**. Coordination of 7-oxabenzonorbornadiene via the exo face of the carbon−carbon double bond to the Ni center **8** followed by the insertion of the double bond into the Ni−alkyl bond results in the formation of intermediate **9**. Subsequent β-oxy elimination leads to intermediate **10**, and transmetalation with $Cp_2ZrClBr$ gives the nickel(II) catalyst and zirconium alkoxide **11**. The latter is converted to the final desired alkyl product **3** by protonation after workup.

As indicated in the control reactions, the catalytic reaction requires the presence of zinc powder or a zinc halide in order for the reaction to proceed smoothly. These observations are similar to those for the addition of alkenylzirconium reagents to 7-oxabicyclic alkenes reported previously by us.[12] We proposed that the zinc halide acts as a Lewis acid to assist the removal of a halide from the nickel(II) center and the coordination of the bicyclic alkene. The role of zinc powder is not yet clear, but it likely reacted with $Cp_2ZrClBr$ or the Zr(IV) species formed in the reactions to give an adduct of these two species that act as a mild Lewis acid for removing a coordinated halide and assisting the coordination of the bicyclic alkene. The reaction of Cp_2ZrX_2 by zinc powder was reported,[15] and we also have observed a rapid reaction of zinc powder with Cp_2ZrX_2, although the product is not characterized.

We have employed a similar mechanism to account for the results of addition of alkenyl zirconium reagents to 7-oxabicyclic alkenes and for the addition of aryl or alkenyl halides to bicyclic alkenes. A similar mechanism was also proposed by Lautens and co-workers[16] to explain the addition of organometallic reagents to bicyclic alkenes catalyzed by palladium(II) species. In addition, this type of mechanism have been used to explain the results of addition of alkenylzirconium reagents to conjugated enones and enesters catalyzed by nickel(II) complexes.[17]

Another possible mechanism for the present nickel-catalyzed ring-opening addition of an alkylzirconium reagent to 7-oxabenzonorbornadiene involves the reduction of $NiCl_2(PPh_3)_2$ to a Ni(0) species by zinc metal, followed by the oxidative addition of 7-oxabenzonorbornadiene to nickel(0) species to yield a (π-allyl)nickel(II) complex. This species then undergoes transmetala-

SCHEME 6



tion with alkylzirconium reagent (Cp_2ZrClR) to give an (alkyl)(π-allyl)nickel(II) intermediate. Reductive elimination affords the ring-opening product and regenerates the nickel(0) species. This mechanism cannot be totally ruled out, but it is less likely on the basis of our previous observation.[12]

There are several interesting features for the present catalytic reaction. First, the reaction is highly regio- and stereoselective providing the ring-opening products *cis*-2-alkyl-1,2-dihydronaphthalene with various chain lengths and ring size of the alkyl groups from the zirconium reagents. It is well-known that the transfer of an alkyl group mediated by a transition-metal complex is generally difficult due to the facile β-hydride elimination of a transition-metal alkyl group. The success of the present catalytic reaction indicated that the alkyl groups transferred to the nickel center from zirconium reagents are very effectively trapped by 7-oxabenzonorbornadiene prior to β-hydride elimination. In the earlier reports, the addition of dialkylzinc[10] to oxabicyclic alkenes was not applicable to longer or bulkier carbon chains of dialkylzinc reagents, due to the steric hindrance. On the other hand, the $FeCl_3$-catalyzed ring opening of 7-oxabenzonorbornadienes with alkyl Grignard reagents afforded only vinylated product instead of the alkylative product.[11] Second, the alkylzirconium reagents are easily prepared from the corresponding alkenes and Cp_2ZrHCl under mild reaction conditions (eqs 1 and 2). Third, this is the first report of allyl addition to 7-oxabenzonorbornadienes and also the first time to use allylzirconium reagent as a transmetallating agent for ring-opening reactions.

Conclusion

In conclusion, we have developed a highly regio- and stereoselective nickel-catalyzed ring-opening of alkylzirconium reagents to 7-oxabenzonorbornadienes affording *cis*-2-alkyl-1,2-dihydronaphthalenes in good yields. The ring-opening reaction was successfully extended to various allylzirconium reagents. In addition, alkylative ring-opening products from 7-oxabenzonorbornadienes underwent dehydration readily with HCl to afford the corresponding naphthalene derivatives in excellent yields. Studies on the asymmetric version of this nickel-catalyzed reaction and the application in organic synthesis are in progress.

Experimental Section

Procedure for Nickel-Catalyzed Ring-Opening Reaction. A round-bottom sidearm flask (25 mL) containing $NiBr_2$(dppe) (0.010 mmol, 10.0 mol %), zinc powder (0.020 mmol, 20 mol %), and an 7-oxabenzonorbornadiene (1.50 mmol) was evacuated and purged with nitrogen gas three times. To the system were added sequentially freshly distilled THF (1.0 mL) and alkylzirconium reagent (1.00 mmol in 2.0 mL THF) via syringes, and the reaction mixture was stirred at 50 °C for 12 h. The reaction mixture was cooled to room temperature, 2 or 3 drops of water were added, and the mixture was diluted with a mixture of ethyl acetate and hexane (20:80; ~15 mL) and then stirred in the air for 15 min. The mixture was filtered through a short Celite and silica gel pad and washed with a mixture of ethyl acetate and hexane solution several times. The filtrate was concentrated, and the residue was purified on a silica gel column using a mixture of hexanes−ethyl acetate (19:1) as eluent to afford the ring-opening product **3**. A similar procedure was used in allylzirconium reagents. Compounds **3a**−**m** and **5a**−**d** were synthesized according to this procedure, and the spectral data of these compounds are listed in the Supporting Information.

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Supporting Information Available: General section, synthesis of zirconium reagents, experimental procedure for dehydration reaction, spectral data of compounds **3a**−**m**, **5a**−**d**, and **6a**−**c**, and ^1H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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