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Nickel-Catalyzed Addition of Alkenylzirconium Reagents to Bicyclic Olefins: A Highly Regio- and Stereoselective Ring-Opening Reaction

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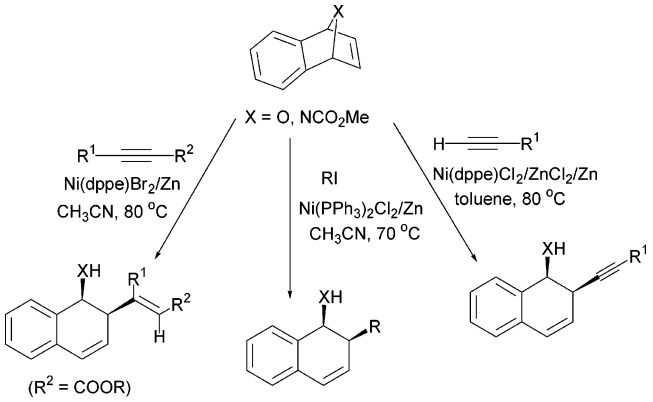
A highly regio- and stereoselective ring-opening addition of alkenylzirconium reagents to bicyclic olefins catalyzed by nickel complexes was described. Treatment of 7-oxa- and 7-azabenzonorbornadienes (**1a**−**e**) with various terminal alkenylzirconium reagents **2a**−**f** ($Cp_2ZrClCH{=}CHR$; R = *t*-Bu, *n*-Pr, *n*-Oct, 1-cyclohexenyl, $SiMe_3$, and Ph) in the presence of $Ni(PPh_3)_2Cl_2$ and Zn powder (or a combination of $ZnCl_2$ and NEt_3) in dry THF at 50 °C afforded the corresponding *cis*-2-alkenyl-1,2-dihydronaphthalene derivatives **3a**−**l** in moderate to excellent yields. Under similar reaction conditions, internal alkenylzirconium reagents **2g**,**h** ($Cp_2ZrClCR{=}CHR$: R = Et and *n*-Pr) also undergo ring-opening addition to oxanorbornadienes **1a** and **1d** to give *cis*-2-alkenyl-1,2-dihydronaphthalene derivatives **4a**−**c** in good yields. Possible pathways involving the transfer of alkenyl group in the alkenylzirconium reagent to the Ni(II) center followed by migration of the alkenyl group from the Ni(II) center to the carbon−carbon double bond of 7-oxanorbornadiene or the reaction of 7-oxanorbornadiene with Ni(0) to form a Ni(II)-π-allyl prior to the transfer of the alkenyl group as key steps for the catalytic reaction were proposed and discussed.

Introduction

Stereocontrolled synthesis of cyclic and acyclic compounds with multiple stereocenters can be achieved efficiently by ring-opening addition reaction of bicyclic alkenes.[1,2] Lautens' group has completed considerable work in the ring opening of oxabicyclic alkenes, including transition-metal-catalyzed enantioselective ring opening of oxabicyclic alkenes with DiBAL-H, Grignard, organolithium, organozinc, organoboronic acid, and various nucleophilic reagents.[3−8] We have successfully used electrophilic aryl, alkenyl, and alkyl halides as reagents for the ring-opening addition of oxabicyclic alkenes in the presence of a palladium[9] or nickel catalyst[10] (Scheme 1).

SCHEME 1



(1) (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.

(2) (a) Oxabicyclics as valuable intermediates, see: B. H. Lipshutz, *Chem. Rev.* **1986**, *86*, 795. (b) Vogel, P.; Fattori, D.; Gasparini, F.; Le Drian, C. *Synlett* **1990**, 173. (c) Lautens, M. *Synlett* **1993**, 177. (d) Arjona, O.; Dios de, A.; Fernandez de la Pradilla, R.; Plumet, J.; Viso, A. *J. Org. Chem.* **1994**, *59*, 3906.

(3) For a review on ring-opening chemistry of oxabicyclic alkenes, see: Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48.

(4) (a) Leong, P.; Lautens, M. *J. Org. Chem.* **2004**, *69*, 2194. (b) Lautens, M.; Dockendorff, C. *Org. Lett*. **2003**, *5*, 3695.

(5) (a) Lautens, M.; Dockendorff, C.; Fagnou, K. Malicki, A. *Org. Lett*. **2002**, *4*, 1311. (b) Lautens, M.; Fagnou, K. *Tetrahedron* **2001**, *57*, 5067. (c) Lautens, M.; Fagnou, K.; Taylor, M.; Rovis, T. *J. Organomet. Chem.* **2001**, *624*, 259. (d) Lautens, M.; Renaud, J.-L.; Hiebert, S. *J. Am. Chem. Soc*. **2000**, *122*, 1804. (e) Lautens, M.; Fagnou, K.; Rovis, T. *J. Am. Chem. Soc.* **2000**, *122*, 5650. (f) Lautens, M.; Fagnou, K.; Taylor, M. *Org. Lett.* **2000**, *12*, 1677. (g) Lautens, M.; Hiebert, S.; Renaud, J.-L. *Org. Lett*. **2000**, *13*, 1971.

(6) (a) Lautens, M.; Rovis, T. *J. Am. Chem. Soc.* **1997**, *119*, 11090. (b) Lautens, M.; Chiu, P.; Ma, S.; Rovis, T. *J. Am. Chem. Soc.* **1995**, *117*, 532. (c) Lautens, M.; Ma, S. *J. Org. Chem.* **1996**, *61*, 7246. (d) Lautens, M.; Rovis, T. *J. Org. Chem.* **1997**, *62*, 5246.

(7) (a) Lautens, M. *Pure Appl. Chem*. **1992**, *64*, 1873. (b) Lautens, M.; Ma, S. *Tetrahedron Lett*. **1996**, *37*, 1727. (c) Woo, S.; Keay, B. A. *Synthesis* **1996**, 669. (d) Arjona, O.; Conde, S.; Plumet, J.; Viso, A. *Tetrahedron Lett*. **1995**, *36*, 6157. (e) Lautens, M.; Fillon, E.; Sampat, M. *J. Org. Chem*. **1997**, *62*, 7080. (f) Gillespie, D. G.; Wlaker, B. J.; Stevens, D.; McAuliffe, C. A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1697. (g) Cuny, G. D.; Buchwald, S. L. *Organometallics* **1991**, *10*, 363. (h) Moinet, C.; Fiaud, J. C. *Tetrahedron Lett.* **1995**, *36*, 2051. (i) Fugami, K.; Hagiwara, S.; Oda, H.; Kosugi, M. *Synlett*. **1998**, 477. (j) Lautens, M.; Klute, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 442.

(8) (a) Millward, D. B.; Sammis, G.; Waymouth, R. M. *J. Org. Chem.* **2000**, *65*, 3902. (b) Murakami, M.; Igawa, H. *J. Chem. Soc., Chem. Commun.* **2002**, 390.

(9) (a) Duan, J. P.; Cheng, C. H. *Tetrahedron Lett.* **1993**, *34*, 4019. (b) Duan, J. P.; Cheng, C. H. *Organometallics* **1995**, *14*, 1608.

(10) Feng, C. C.; Nandi, M.; Sambaiah, T.; Cheng, C. H. *J. Org. Chem*. **1999**, *64*, 3538.

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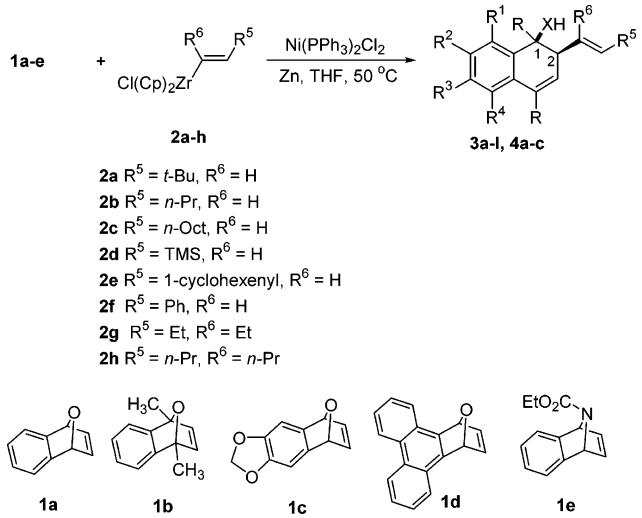
SCHEME 2



In addition, we have shown the addition of terminal acetylenes[11] to bicyclic alkenes and the reductive coupling[12] of propiolates and bicyclic alkenes catalyzed by nickel complexes (Scheme 1). However, to date, no report has appeared using alkenylzirconium complexes as reagents for the ring-opening addition of bicyclic alkenes. In this paper, we wish to disclose for the first time the addition of alkenylzirconium reagents to oxa- and azabicyclic alkenes in the presence of nickel complexes and zinc metal powder to afford ring-opening addition products with remarkable diastereoselectivity. The present nickel-catalyzed reaction provides a convenient and general route to *cis*-2-alkenyl-1,2-dihydronaphthalene derivatives in good to excellent yields and in high stereoselectivities from easily accessible starting materials. Moreover, the dihydronaphthalene skeleton was found in a wide range of naturally occurring compounds that exhibit diverse biological activities.[13]

Results and Discussion

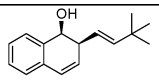
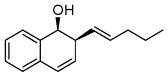
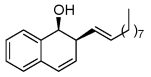
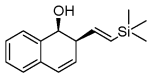
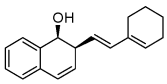
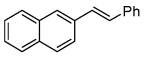
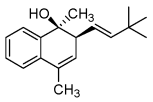
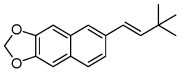
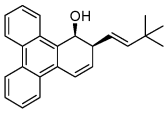
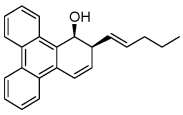
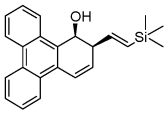
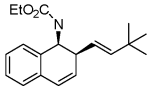
Treatment of 7-oxabenzonorbornadiene (**1a**) (1.00 mmol) with alkenylzirconium reagent **2a** (1.25 mmol), freshly prepared by treating 3,3-dimethylbut-1-yne (2.00 equiv) with Cp_2ZrClH (1.00 equiv) in dry THF (1.5 mL) at room temperature for 1 h,[14] in the presence of $NiCl_2(PPh_3)_2$ (5.0 mol %) and zinc powder (10.0 mol %) in THF (3.0 mL) at 50 °C for 12 h led to the formation of the ring-opening addition product **3a** in 62% isolated yield based on the amount of zirconium hydride used (Scheme 2, Table 1). The yield of **3a** increased greatly to 89%, if the amounts of **1a** and **2a** for the reaction were changed to 1.50 and 1.00 mmol, respectively. Product **3a** was fully characterized by its NMR and mass data. The cis stereochemistry of the two protons at C1 and C2 positions in this product was established based on the coupling constants (~6.0 Hz) of the two protons (Scheme 2), whereas the *E* stereochemistry of the alkenyl group was established based on the coupling constant (J = 16.0 Hz) of the two olefinic protons in the ^{1}H NMR spectrum.

To understand the nature of this nickel-catalyzed ring-opening reaction of **1a** with **2a**, the effect of reaction conditions on the product yield was investigated (see Table 1, footnote *a* for the standard catalytic reaction conditions). In the absence of nickel catalyst no reaction occurs, while the omission of zinc powder gave ~4% of product **3a**. Although the presence of zinc powder is important for the reaction, the amount of zinc powder used (0.10−2.75 mmol) shows no essential effect on the yield of **3a**. The replacement of zinc powder by $ZnCl_2$ (10.0 mol %) and NEt_3 (80.0 mol %) in the catalytic reaction also effectively led to the formation of **3a** in 88%. Nickel complex $NiBr_2$(dppe) with a bidentate phosphine ligand afforded a trace amount of **3a**, while $Ni(acac)_2$ and $Ni(COD)_2$ were totally inactive for this ring-opening addition. The use of $NiBr_2(PPh_3)_2$ and $NiI_2(PPh_3)_2$ gave **3a** in 42% and 15% yields, respectively. The most active nickel complex for this reaction appears to be $NiCl_2(PPh_3)_2$, furnishing **3a** in 95% yield. Thus, the halide on nickel complex $NiX_2(PPh_3)_2$ appears to show profound effect on the yield of **3a**, but the exact reason is not yet clear. Addition of 2 equiv of PPh_3 to the $NiCl_2(PPh_3)_2$ system strongly retarded the reaction giving **3a** in only 28% yield. The solvent employed for the reaction using $NiCl_2(PPh_3)_2$/Zn as the catalyst is crucial for the yield of **3a**. THF was the solvent of choice giving **3a** in 95% yield. The other solvents CH_3CN, and DMF were totally inactive, whereas toluene afforded only a trace amount of **3a**.

Table 1 summarizes the results of ring-opening addition reaction of various oxabenzonorbornadienes with alkenylzirconium reagents. Thus, treatment of **1a** with different alkenylzirconium reagents **2b**−**d** ($Cp_2ZrClCH$=CHR: R = *n*-Pr, *n*-Oct, and $SiMe_3$) (Scheme 2, Table 1, entries 2−4) furnished the corresponding *cis*-2-alkenyl-1,2-dihydronaphthalene derivatives **3b**−**d** in 59, 73, and 80% yields, respectively. Likewise, the reaction of **1a** with dienyl zirconium reagent **2e** afforded the corresponding ring-opening addition product **3e** containing a triene functionality in 76% yield (entry 5). In the reaction of **1a** with styryl zirconium reagent **2f**, (*E*)-2-styrylnaphthalene **3f** was obtained in 88% yield (entry 6). This product was formed as a result of dehydration of the corresponding 1,2-dihydronaphthalen-1-ol. Substituted oxabenzonorbornadiene **1b** bearing two methyl groups at the bridgehead carbons also reacted with **2a** smoothly to give highly substituted *cis*-2-alkenyl-1,2-dihydronaphthalene system **3g** in 78% yield. Similar to the result in entry 6, the reaction of **1c** with **2a** produced dehydrated product 6-[(*E*)-3,3-dimethyl-1-butenyl]naphtho[2,3-*d*][1,3]-dioxole (**3h**) in 43% yield. The addition reaction was further applied to bulkier 1,4-oxa-1,4-dihydrotriphenylene **1d**. Thus, the reaction of **1d** with **2a**, **2b**, and **2d** furnished the corresponding *cis*-2-alkenyl-1,2-dihydrotriphenylene derivatives **3i**−**k** in 73−84% yields. Similar to 7-oxabenzonorbornadienes, 7-azabenzonorbornadiene **1e** cleanly undergoes addition reaction with alkenylzirconium reagent **2a** in the presence of $Ni(PPh_3)_2Cl_2$, and Zn powder in THF at 50 °C to give *cis*-2-alkenyl-1,2-

(11) Rayabarapu, D. K.; Chiou, C. F.; Cheng, C. H. *Org. Lett.* **2002**, *4*, 1679.
(12) Rayabarapu, D. K.; Cheng, C.-H. *Chem. Eur. J.* **2003**, *9*, 3164.
(13) For dihydronaphthalene skeleton in natural products, see: (a) Johnson, B. M.; Chang, P. T. L. *Anal. Profiles Drug Subst. Excipients* **1996**, *24*, 443. (b) Synder, S. E. *J. Med. Chem.* **1995**, *38*, 2395. (c) Kamal, A.; Gayatri, L.; *Tetrahedron Lett.* **1996**, *37*, 3359. (d) Kim, K.; Guo, Y.; Sulikowski, G. A. *J. Org. Chem.* **1995**, *60*, 6866. (e) Perrone, R. *J. Med. Chem.* **1995**, *38*, 942.
(14) Ni, Y.; Amarasinghe, K. K. D.; Montgomery, J. *Org. Lett.* **2002**, *4*, 1743.

TABLE 1. Results of Nickel-Catalyzed Addition of Alkenylzirconium Reagents 2 to Oxa- and Azabicyclic Olefins 1[a]

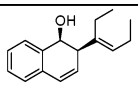
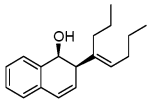
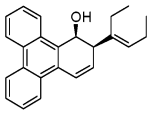
entry	alkene (**1**)	alkenyl zirconium reagent (**2**)	product (**3**)	yield[b] (%)
1	**1a**	**2a**		**3a** 89 (95)
2	**1a**	**2b**		**3b** 59 (65)
3	**1a**	**2c**		**3c** 73 (83)
4	**1a**	**2d**		**3d** 80 (87)
5	**1a**	**2e**		**3e** 76
6	**1a**	**2f**		**3f** 88
7	**1b**	**2a**		**3g** 78
8	**1c**	**2a**		**3h** 43
9	**1d**	**2a**		**3i** 75
10	**1d**	**2b**		**3j** 84
11	**1d**	**2d**		**3k** 73
12	**1e**	**2a**		**3l** 83

[a] Unless stated otherwise, all reactions were carried out using $Ni(PPh_3)_2Cl_2$ (5.0 mol %), Zn (10.0 mol %), 7-oxa- and 7-azanorbornadienes (**1**) (1.50 mmol), and alkenylzirconium reagent **2** (1.00 mmol) in THF (3.0 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.

dihydronaphthalenyl carbamate derivative **3l** in 83% yield (entry 12). In these reactions, the alkenylzirconium reagents were freshly prepared by treating the corresponding terminal alkynes (2.00 equiv) with Cp_2ZrClH (1.00 equiv) in dry THF (1.5 mL) at room temperature for 1 h. The yields of the ring-opening addition products **3** were based on the amount of zirconium hydride Cp_2ZrClH. It appears that the freshness of this hydride, which is sensitive to moisture and air, greatly affects the yields of **3**.

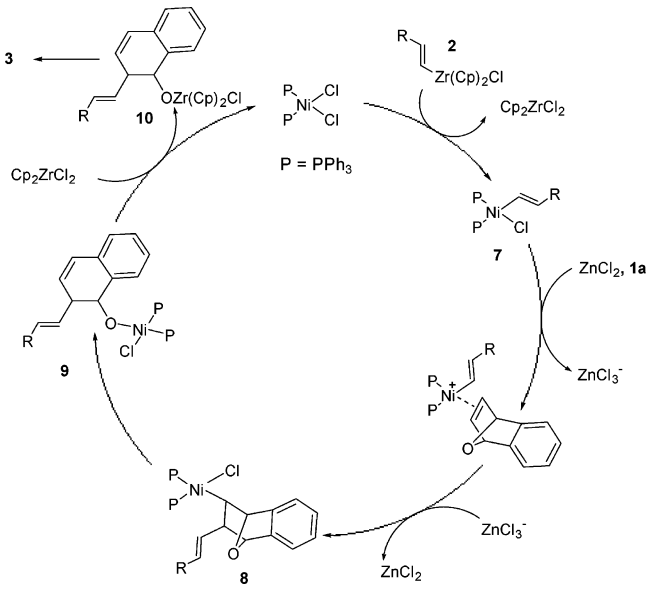
The present methodology was successfully implemented to internal alkenylzirconium reagents $Cp_2ZrClCR{=}CHR$. Thus, the reaction of 7-oxabenzonorbornadiene (**1a**) with alkenylzirconium **2g** and **2h** under

TABLE 2. Results of Nickel-Catalyzed Addition Reaction[a]

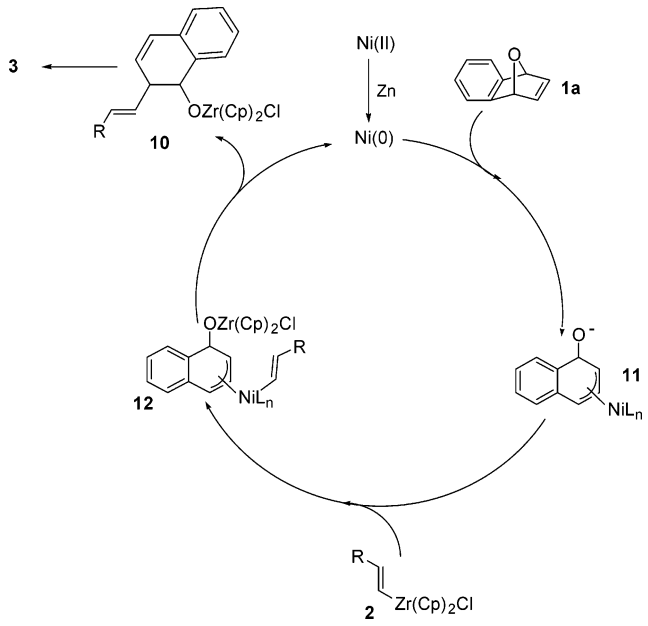
entry	alkene (**1**)	**2**	product (**4**)	yield[b](%)
13	**1a**	**2g**		**4a** 70
14	**1a**	**2h**		**4b** 81
15	**1d**	**2g**		**4c** 72

[a] The same conditions as mentioned in Table 1 were used. [b] Isolated yields.

SCHEME 3



SCHEME 4



standard conditions afforded the functionalized dihydronaphthalenes **4a** and **4b** in 70% and 81% yields, respectively. The zirconium reagents **2g** and **2h** were generated from 3-hexyne and 4-octyne, respectively, and zirconium hydride Cp_2ZrClH. The yields of **4a** and **4b** were based on the amount of zirconium hydride used (Table 2, entries 13 and 14). Similarly, when oxaphenanthronorbornadiene **1d** was treated with **2g**, the corresponding ring-opening addition product **4c** was produced in 72% yield.

While the detailed pathways are not clear, the key pathways are proposed as shown in Scheme 3.[16] The catalysis is likely initiated by transmetalation of alkenylzirconium reagent ($Cp_2ZrClCH{=}CHR$) with nickel(II) species to give nickel(II) alkenyl intermediate **7**. Coordination of 7-oxabenzonorbornadiene via the exo face of the carbon−carbon double bond to the Ni center and insertion of the double bond to the Ni-alkenyl bond results in the formation of intermediate **8**. Subsequent β-heteroatom elimination leads to intermediate **9**, which then undergoes transmetalation with Cp_2ZrCl_2 to give the nickel(II) catalyst and zirconium alkoxide **10**. The latter is converted to the final desired alkenyl product **3** by protonation.

There are several pieces of evidence that support the proposed mechanism. (1) The reaction of 7-oxabenzonorbornadiene (**1a**) with $Cp_2ZrClCH{=}CH^tBu$ (**2a**) in the presence of $NiCl_2(PPh_3)_2$ (5.0 mol %) and $ZnCl_2$ (10.0 mol %) afforded 27% of ring-opening addition product **3a** and 21% of the corresponding dehydrated product. (2) By reducing the amount of $ZnCl_2$ to 3.0 mol % or by reducing the Lewis acidity of $ZnCl_2$ (10.0 mol %) with addition of Et_3N (80.0 mol %) the addition reaction afforded **3a** in 79% and 88% yields, respectively. (3) Stoichiometric reaction of **1a** (1.50 mmol), **2a** (1.00 mmol based on Cp_2-

(15) For review on application of organozirconium, see: Wipf, P.; Jahn, H. *Tetrahedron* **1996**, *52*, 12853.
(16) For mechanistic studies, see: Lautens, M.; Hiebert, S.; Renaud, J.-L. *J. Am. Chem. Soc*. **2001**, *123*, 6834.

ZrClH used) and $NiCl_2(PPh_3)_2$ (1.00 mol) in THF at 50 °C for 12 h produced **3a** in 73% yield. (4) A catalytic amount of $Ni(COD)_2$/2 PPh_3 does not catalyze the present reaction.

The above results indicate that Ni(II) with a mild Lewis acid is required for this ring-opening reaction. The presence of $ZnCl_2$ assists the catalytic reaction, but excess $ZnCl_2$ led to the dehydration of **3a**. The addition of a suitable base to reduce the acidity of Zn^{2+} effectively prevents the formation of the dehydration product. However, it should be noted that the reactions of 7-oxabenzonorbornadienes with alkenylzirconium reagents can also be carry out in the presence of $NiCl_2(PPh_3)_2$ and zinc metal powder instead of $ZnCl_2$ as well to give the expected ring-opening addition products (Tables 1 and 2). The role of zinc powder in these reactions is not entirely clear. One possibility is that the Zn metal powder interacts with Cp_2ZrCl_2 or Zr(IV) species formed in the reactions to give a mixture that can act as a mild Lewis acid.[17] to effectively promote the ring-opening addition reaction of alkenylzirconium reagent **2** to bicyclic **1**.

The above proposed mechanism involves the transfer of alkenyl group in the zirconium reagent to Ni(II) species and insertion of the carbon−carbon double bond in the bicyclic alkene into the Ni(II)-alkenyl bond as key steps. A mechanism was used to explain the results of addition of alkenylzirconium reagents to conjugated enones and enesters.[19] In addition, we have used this type of pathway (insertion of a bicyclic alkene into a M(II)−carbon bond) to account for the addition of aryl and alkenyl halides to bicyclic alkenes catalyzed by nickel and palladium complexes in the presence of zinc metal powder.[9,10] The same regio- and stereoselectivity were observed for the addition of an alkenylzirconium complex and an aryl halide to a bicyclic alkene catalyzed by nickel complexes, although one is a nucleophilic reagent and the other is an electrophile.

Another possible mechanism for the present nickel-catalyzed ring-opening addition of an alkenylzirconium reagent to 7-oxabenzonorbornadiene involves first the reduction of $NiCl_2(PPh_3)_2$ to a Ni(0) species by zinc metal or the alkenylziconium reagent, followed by the oxidative addition of 7-oxabenzonorbornadiene with nickel(0) species to yield a (π-allyl)nickel(II) complex **11**.[6c] This species then undergoes transmetalation with alkenylzirconium reagent ($Cp_2ZrClCH{=}CHR$) to give (alkenyl)(π-allyl)-nickel(II) intermediate **12**. Reductive elimination affords the ring-opening addition product and regenerates the nickel(0) species (Scheme 4).

A similar mechanism has been proposed by Lautens and co-workers to account for the ring-opening addition of organometallic reagents to bicyclic alkenes catalyzed by nickel complexes.[6b,c] Moreover, this type of pathway was also employed to explain the results of addition of various organometallic reagents to bicyclic alkenes catalyzed by palladium[5d] and rhodium[5e] complexes. However, recent mechanistic studies of the palladium-catalyzed addition of dialkylzinc to oxabicyclic alkenes carried out by the same group[16] strongly favor the mechanism via transmetalation of the organometallic reagent to palladium(II) followed by insertion of the carbon−carbon double bond in the bicyclic alkene into the palladium-(II)-carbon bond similar to those steps shown in Scheme 3. In view of the same regio and stereochemistry for the palladium-catalyzed addition of dialkylzinc to oxabicyclic alkenes[16] and our present nickel-catalyzed alkenylzirconium addition, the mechanism in Scheme 3 is more favorable than the one involves a π-allyl nickel intermediate as shown in Scheme 4.

Conclusion

In conclusion, we have developed a novel nickel-catalyzed ring-opening addition of alkenyl zirconium reagents to oxa- and azabicyclic alkenes to afford products with extremely high stereoselectivity in good to excellent yields. This addition reaction offers a convenient method for the synthesis of functionalized 1,2-dihydronaphthalene derivatives and the mechanistic pathway is highly interesting. Studies on the asymmetric version of this nickel-catalyzed reaction and the application in organic synthesis are in progress.

Experimental Section

Synthesis of Alkenylzirconium Reagent. A terminal/internal alkyne (RC≡CH/ RC≡CR, 2.00 mmol) was added to a suspension of Cp_2ZrHCl (1.00 mmol) in THF (1.5 mL) at room temperature. The resulting mixture was stirred at room temperature for 1 h. During the reaction, light yellow color of the solution was developed. The solution was evacuated to remove the excess alkyne and solvent. Then freshly distilled THF (2.0 mL) was added, and this resulting mixture ($Cp_2ZrClCH{=}CHR/Cp_2ZrClCR{=}CHR$) was used for the subsequent nickel-catalyzed reaction. This procedure of generating alkenylzirconium reagent ($Cp_2ZrClCH{=}CHR/Cp_2ZrClCR{=}CHR$) was used for all alkynes except terminal acetylenes (R = Ph, 1-cyclohexenyl, *n*-Oct) and internal acetylene (R = *n*-Pr). The alkenylzirconium reagents from these acetylenes were generated using 1.00 mmol of the alkyne, and no further evacuation or addition of THF was done.

Procedure for Nickel-Catalyzed Ring-Opening Reaction. A round-bottom sidearm flask (25 mL) containing $NiCl_2(PPh_3)_2$ (0.05 mmol, 5.0 mol %) and zinc powder (0.10 mmol, 10.0 mol %) was evacuated and purged with nitrogen gas three times. To the system were added freshly distilled THF (1.0 mL), an oxabenzonorbornadiene (1.50 mmol), and alkenylzirconium reagent (1.00 mmol in 2.0 mL THF) sequentially, 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) 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 hexanes−ethyl acetate (19:1) as eluent to afford the ring-opening product **3**. Compounds **3a**−**l** and **4a**−**c** were synthesized according this procedure, and the spectral data of representative compounds are as follows.

2-[(*E*)-3,3-Dimethyl-1-butenyl]-1,2-dihydro-1-naphthalenol (3a): oil; TLC (hexane/ethyl acetate, 6:1) $R_f = 0.54$; ^1H NMR (500 MHz, $CDCl_3$) δ 0.93 (9H, s), 1.69 (1H, d, J = 8.5 Hz), 3.03−3.05 (1H, m), 4.70 (1H, dd, J_1 = 2.0 Hz, J_2 = 6.0 Hz), 5.20 (1H, dd, J_1 = 7.0 Hz, J_2 = 16.0 Hz), 5.71 (1H, d, J =

(17) Tour, J. M.; Bedworth, P. V.; Wu, R. *Tetrahedron Lett.* **1989**, *30*, 3927.

(18) A combination of $ZnCl_2$ and Et_3N was used for the palladium-catalyzed ring-opening of oxabenzonorbornadienes with aryl halides; see ref 9.

(19) (a) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. (b) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333.

16.0 Hz), 5.85 (1H, dd, J_1 = 5.0 Hz, J_2 = 10.0 Hz), 6.43 (1H, dd, J_1 = 1.5 Hz, J_2 = 10.0 Hz), 7.00−7.02 (1H, m), 7.17−7.18 (2H, m), 7.35−7.36 (1H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 29.7, 33.4, 44.7, 70.2, 120.3, 126.1, 126.2, 127.1, 127.7, 127.9, 129.8, 132.5, 137.0, 147.4; HRMS (*m/e*) calcd for $C_{16}H_{20}O$ 228.1514, found 228.1507.

2-[(*E*)-3,3-Dimethyl-1-butenyl]-1,4-dimethyl-1,2-dihydro-1-naphthalenol (3g): oil; TLC (hexane/ethyl acetate, 19:1) R_f = 0.38; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (9H, s), 1.43 (3H, s), 2.04 (4H, s), 2.77−2.81 (1H, m), 4.92 (1H, dd, J_1 = 5.6 Hz, J_2 = 9.6 Hz), 5.71−5.77 (2H, m), 7.19−7.26 (3H, m), 7.58−7.60 (1H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 19.1, 28.4, 29.7, 33.3, 51.8, 72.5, 121.1, 123.1, 124.1, 127.0, 127.2, 127.8, 130.7, 133.6, 142.8, 148.6; HRMS (*m/e*) calcd for $C_{18}H_{24}O$ 256.1827, found 256.1823.

6-[(*E*)-3,3-Dimethyl-1-butenyl]naphtho[2,3-*d*][1,3]-dioxole (3h): solid; mp 102−104 °C; TLC (hexane/ethyl acetate, 19:1) R_f = 0.18; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (9H, s), 6.00 (2H, s), 6.32 (1H, d, J = 16.0 Hz), 6.40 (1H, d, J = 16.0 Hz), 7.05 (2H, s), 7.41−7.43 (1H, m), 7.54−7.58 (2H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 29.5, 29.7, 33.4, 100.9, 103.8, 103.9, 122.6, 124.6, 126.7, 127.4, 129.5, 130.7, 134.2, 141.5, 147.2, 147.7; HRMS (*m/e*) calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1308.

2-[(*E*)-3,3-Dimethyl-1-butenyl]-1,2-dihydro-1-triphenylenol (3i): oil; TLC (hexane/ethyl acetate, 19:1) R_f = 0.25; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (9H, s), 1.82 (1H, d, J = 6.8 Hz), 3.32−3.33 (1H, m), 5.33 (1H, dd, J_1 = 2.0 Hz, J_2= 6.0 Hz), 5.85−5.90 (2H, m), 6.22 (1H, dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz), 7.41 (1H, dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz), 7.64−7.71 (4H, m), 8.25−8.34 (2H, m), 8.70−8.74 (2H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 29.8, 33.3, 44.3, 66.7, 122.6, 122.9, 123.0, 123.3, 123.7, 123.9, 124.1, 124.3, 126.3, 126.5, 126.7, 126.8, 127.0, 127.2, 129.9, 130.5, 131.2, 145.2; HRMS (*m/e*) calcd for $C_{24}H_{24}O$ 328.1827, found 328.1831.

2-[(*E*)-2-(1,1,1-Trimethylsilyl)-1-ethenyl]-1,2-dihydro-1-triphenylenol (3k): oil; TLC (hexane/ethyl acetate, 19:1) R_f = 0.28; ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (9H, s), 1.82 (1H, d, J = 6.0 Hz), 3.39−3.41 (1H, m), 5.42 (1H, dd, J_1 = 2.0 Hz, J_2 = 6.0 Hz), 6.17 (1H, d, J = 16.0 Hz), 6.28 (1H, dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz), 6.55 (1H, dd, J_1 = 6.4 Hz, J_2 = 16.0 Hz), 7.44 (1H, dd, J_1 = 2.8 Hz, J_2 = 9.6 Hz), 7.61−7.69 (4H, m), 8.25−8.35 (2H, m), 8.69−8.73 (2H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ −1.09, 47.1, 66.1, 122.9, 123.1, 123.4, 123.8, 124.0, 126.0, 126.5, 126.6, 126.9, 127.1, 127.5, 128.7, 129.3, 129.8, 129.9, 130.5, 130.6, 133.6, 144.2; HRMS (*m/e*) calcd for $C_{23}H_{24}OSi$ 344.1596, found 344.1584.

Ethyl *N*-{2-[(*E*)-3,3-Dimethyl-1-butenyl]-1,2-dihydro-1-naphthalenyl}carbamate (3l): oil; TLC (hexane/ethyl acetate, 19:1) R_f = 0.21; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (9H, s), 1.23 (3H, t, J = 7.2 Hz), 3.08−3.10 (1H, m), 4.11 (2H, Q, J_1 = 6.8 Hz, J_2 = 6.8 Hz), 4.91−5.01 (2H, m), 5.12 (1H, dd, J_1 = 7.2 Hz, J_2 = 16.0 Hz), 5.65 (1H, d, J = 16.0 Hz), 5.92 (1H, dd, J_1 = 4.8 Hz, J_2 = 9.6 Hz), 6.47 (1H, dd, J_1 = 1.2 Hz, J_2 = 9.6 Hz), 7.04−7.06 (1H, m), 7.19−7.24 (3H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.6, 29.6, 33.2, 42.6, 51.8, 60.8, 120.4, 125.8, 126.3, 127.3, 127.6, 127.8, 130.1, 133.0, 135.1, 146.2, 156.4; HRMS (*m/e*) calcd for $C_{19}H_{25}NO_2$ 299.1885, found 299.1886.

2-[(*E*)-1-Ethyl-1-butenyl]-1,2-dihydro-1-naphthalenol (4a): oil; TLC (hexane/ethyl acetate, 19:1) R_f = 0.35; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, t, J = 7.6 Hz), 1.00 (3H, t, J = 7.6 Hz), 1.93−1.98 (2H, m), 2.10−2.24 (3H, m), 3.28−3.30 (1H, m), 4.61 (1H, dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz), 5.50 (1H, t, J = 3.6 Hz), 5.88 (1H, dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz), 6.58 (1H, dd, J_1 = 2.4 Hz, J_2 = 7.2 Hz), 7.12−7.13 (1H, m), 7.22−7.29 (2H, m), 7.31−7.38 (1H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 13.9, 14.7, 21.2, 47.2, 47.5, 67.8, 126.6, 127.4, 127.8, 128.3, 128.7, 129.7, 130.0, 132.5, 135.3, 138.4; HRMS (*m/e*) calcd for $C_{16}H_{20}O$ 228.1514, found 228.1514.

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Supporting Information Available: Spectral data for compounds **3b**−**f**,**j** and **4b**,**c** and ^1H NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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