DOI: 10.1002/adsc.201100612

Sodium Borohydride-Nickel Chloride-Methanol Catalytic System for Regioselective Reduction of Electron-Rich Conjugated Dienes and Reductive Cleavage of Allyl Esters Involving π-Allylnickel Intermediates

Biao-Lin Yin,[a,*] Cong-Bi Cai,[a] Jin-Qiang Lai,[a] Ze-Ren Zhang,[a] Li Huang,[a] Li-Wen Xu,[b] and Huan-Feng Jiang[a]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
Fax: (+ 86)-20-8711-3735; phone: (+86)-20-8711-3735; e-mail: blyin@scut.edu.cn
[b] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, Peoples Republic of China

Received: August 2, 2010; Published online: December 6, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201100612.

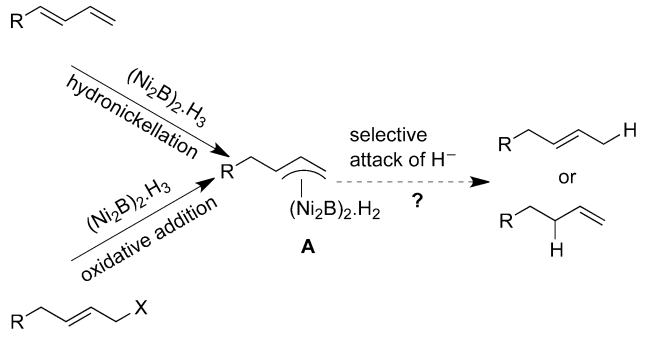
Abstract: The regioslective reduction of electron-rich dienes to monoolefins and the reductive cleavage of allyl esters were fulfilled by employing a sodium borohydride-nickel chloride-methanol catalytic system with exceedingly simple manipulations and high functional group tolerability. Both of the reductive reactions may involve π-allylnickel intermediates generated from fresh nickel boride.

Keywords: allylic esters; π-allylnickel intermediate; hydrogenation; selective reduction; sodium borohydride-nickel chloride

The combination of $NaBH_4$ with a catalytic amount of $NiCl_2$, which generates a highly reactive nickel boride species *in situ*, has been extensively employed to reduce functional groups that are inert to sodium borohydride alone.[1] For example, several groups have reported the reduction of the C=C double bonds of α,β-unsaturated esters with $NaBH_4$-$NiCl_2$ in the synthesis of numerous natural and unnatural bioactive molecules.[2] The $NaBH_4$-$NiCl_2$ system has also been used in the reduction of aliphatic nitro groups or nitroarenes to amines,[3] α-amino acids to 1,2-amino alcohols,[4] 4,5-dihydro-2-oxazole to oxazolidine,[5] and in desulfurization processes.[6] This system is especially attractive for its low cost, simple manipulations (air atmosphere and moisture tolerant), non-pyrophoric nature, short reaction times (generally requiring only a few minutes). Therefore, expanding the application of this reducing system in organic synthesis is of great practical significance. However, to the best of our knowledge, little attention has been paid to the regioselectivity and stereoselectivity of these reductive reactions involving the $NaBH_4$-$NiCl_2$ system.

It is well known that π-allylnickels can be obtained by a hydronickellation of dienes or an oxidative addition of allyl substrates to Ni(0) species. This complex can be coupled with both electrophiles as well as nucleophiles in a regioselective or (and) stereoselective fashion and has been extensively used in organic synthesis.[7] Previous studies demonstrated that the fresh nickel boride had the composition of $(Ni_2B)\cdot H_3$ and it might be transformed into a nickel hydride during the reaction process.[8] We envisaged that the reaction of fresh nickel boride with dienes or allylic substrates would also produce a π-allylnickel complex **A** *via* a hydronickellation of diene or an oxidative addition of allyl substrate (Scheme 1). After the selective attack of hydride on the complex, the regioselective hydrogenation of dienes or reductive cleavage of allyl esters could be fulfilled. Developing alternative methods for these two reductive reactions and improving their selectivities are highly desirable.[9,10] In this communication, we describe our findings on the regioselective reduction of electron-rich conjugated dienes to monoolefins and the reductive cleavage of allylic esters with the $NaBH_4$-$NiCl_2$-MeOH system.

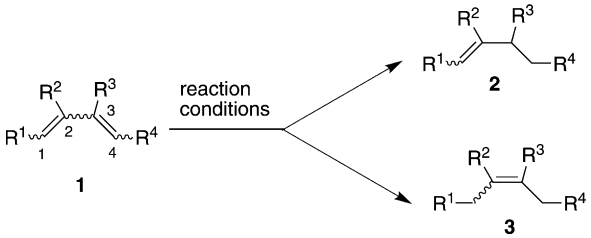
Initially, a series of dienes **1a**–**1g** with an electron-donating group (alkylamino, alkyloxy, or silyloxy) at the 1-position were chosen as substrates. As shown in Table 1, upon treatment with $NaBH_4$-$NiCl_2$ at room temperature in MeOH/DME (1/1, v/v), the evaluated



Scheme 1. Possible pathways for the reaction of dienes or allylic substrates with fresh nickel boride resulted from the system of $NaBH_4$-$NiCl_2$-MeOH.

dienes afforded high yields of monoolefins within 5 min, and the 3,4-carbon carbon double bonds (including mono-, di- and tri-substituted) were selectively hydrogenated (entries 1–7). Furthermore, even when the amount of $NaBH_4$ was increased to 10 equivalents, no over-reduction was observed. During the reaction, the isolated double-bond of **1e** was not influenced. Interestingly, when a large excess of $NaBH_4$ (20 equiv.) was used, reduction of the isolated double bond of **1g** was observed, producing **2g** in excellent yield (90%). Notably, the hydrogenation did not give rise to the cleavage of the protective groups of Cbz and Bn (entries 2, 4 and 6). For dienes with an alkyloxy group at the 2-position and a bulky phenyl group at the 1-position, their 3,4-double bonds were selectively reduced, providing **2h**–**2l** in fair to

Table 1. Regioselective reduction of **1** with the $NaBH_4$-$NiCl_2$-MeOH system.[a]



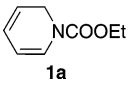
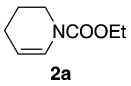
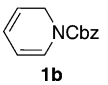
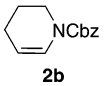
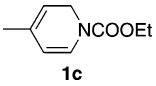
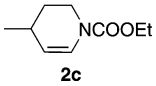
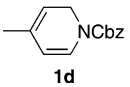
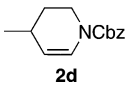
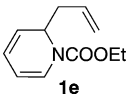
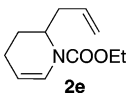
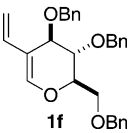
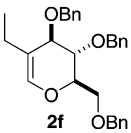
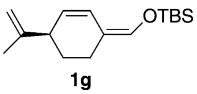
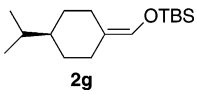
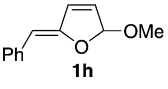
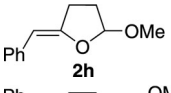
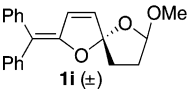
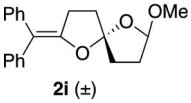
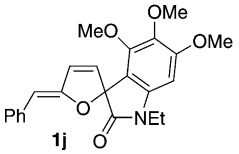
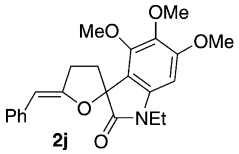
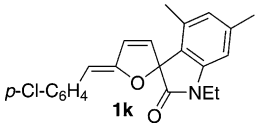
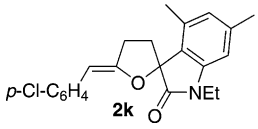
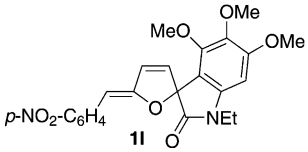
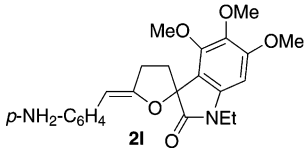
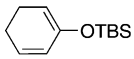
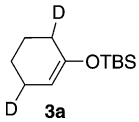
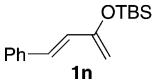
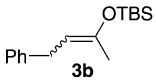
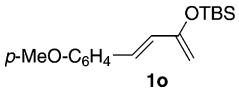
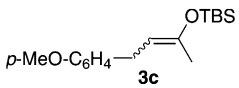
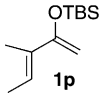
Entry	Diene	Product	Yield [%][b]
1	 **1a**	 **2a**	85
2	 **1b**	 **2b**	78
3	 **1c**	 **2c**	76
4	 **1d**	 **2d**	81
5	 **1e**	 **2e**	84
6	 **1f**	 **2f**	93
7[c]	 **1g**	 **2g**	90
8	 **1h**	 **2h**	77
9[d]	 **1i** (±)	 **2i** (±)	81

Table 1. (Continued)

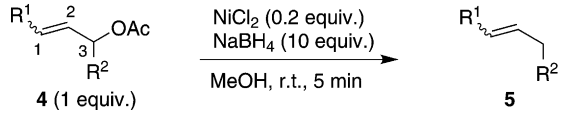
Entry	Diene	Product	Yield [%][b]
10	 **1j**	 **2j**	70
11	 **1k**	 **2k**	75
12	 **1l**	 **2l**	60
13[d]	 **1m**	 **3a**	84
14	 **1n**	 **3b**	81[e]
15	 **1o**	 **3c**	73[f]
16	 **1p**	 **3d**	67 [g]

[a] Unless otherwise noted, the reaction conditions were: 1 mmol of **1**, 0.2 mmol of $NiCl_2$, 10 mmol of $NaBH_4$, 5 mL of MeOH/DME (1/1, v/v), room temperature, and 5 min.
[b] Isolated yield.
[c] 20 mmol of $NaBH_4$.
[d] $NaBD_4$ and CD_3OD were used.
[e] $Z/E = 1/1$.
[f] $Z/E = 1/1$.
[g] $Z/E = 1/6$.

good yields (entries 8–16) and with the enol ether being left intact. Except for the nitro group, which was reduced to an amino group, other functional groups such as acetals, aryl chlorides, and amides were tolerated under these reaction conditions. Interestingly, for conjugated 2-silyloxydienes **2m**–**2p**, selective 1,4-reduction was observed, resulting in the corresponding mono-silyl enol ethers **3a**–**3d** in good yields. The conjugated silyloxydiene has a high electron density, and its selective hydrogenation has never been reported before. The conventional preparation of silyl enol ethers involves silylation of the enolates generated from the corresponding ketones and a strong bulky base. For unsymmetrical ketones, the less-substituted silyl enol ethers are preferentially formed. Importantly, this protocol provided the hitherto unknown 1,4-reduction of electron-rich 2-silyloxydienes, allowing for the preparation of more-substituted silyl enol ethers.

Encouraged by the above results, we next investigated the reductive cleavages of allyl esters using $NaBH_4$-$NiCl_2$ system. As shown in Table 2, in the presence of 10 equivalents of $NaBH_4$ and a catalytic amount of $NiCl_2$ (0.2 equiv.) in MeOH at room temperature, the acetyloxy and benzoyloxy groups placed at the allylic position of variously protected glycals were removed successfully in 5 min, producing the corresponding 3-deoxy glycals with good to excellent yields (Table 2, entries 1–7). 3-Acetoxy glycals generally led to higher yields than 3-benzoyloxy glycals (**5b** > **5c**; **5d** > **5e**; and **5f** > **5g**), which may be due to the better leaving ability of acetoxy group than that of benzoyloxy group. Using this protocol, a variety of hydroxy-protecting groups (e.g., Ac, Bz, TBDPS,

Table 2. Reductive cleavage of allyl esters with the $NaBH_4$-$NiCl_2$-MeOH system.[a]



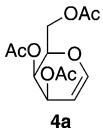
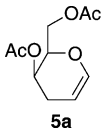
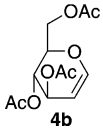
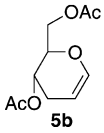
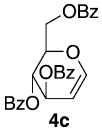
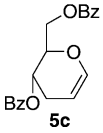
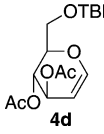
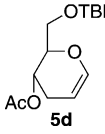
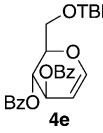
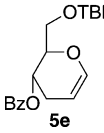
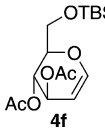
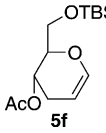
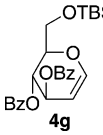
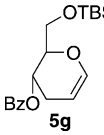
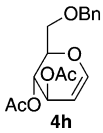
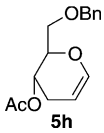
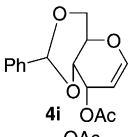
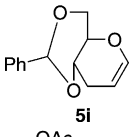
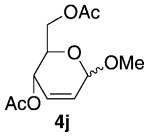
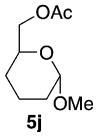
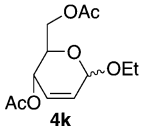
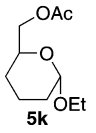
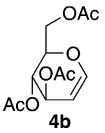
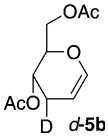
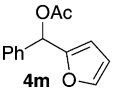
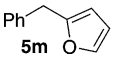
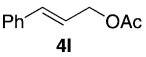
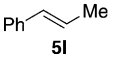
Entry	Allyl ester	Product	Yield [%][b]
1	 **4a**	 **5a**	88
2	 **4b**	 **5b**	93
3	 **4c**	 **5c**	84
4	 **4d**	 **5d**	89
5	 **4e**	 **5e**	83
6	 **4f**	 **5f**	95
7	 **4g**	 **5g**	85
8	 **4h**	 **5h**	92
9	 **4i**	 **5i**	84
10	 **4j**	 **5j**	84
11	 **4k**	 **5k**	79

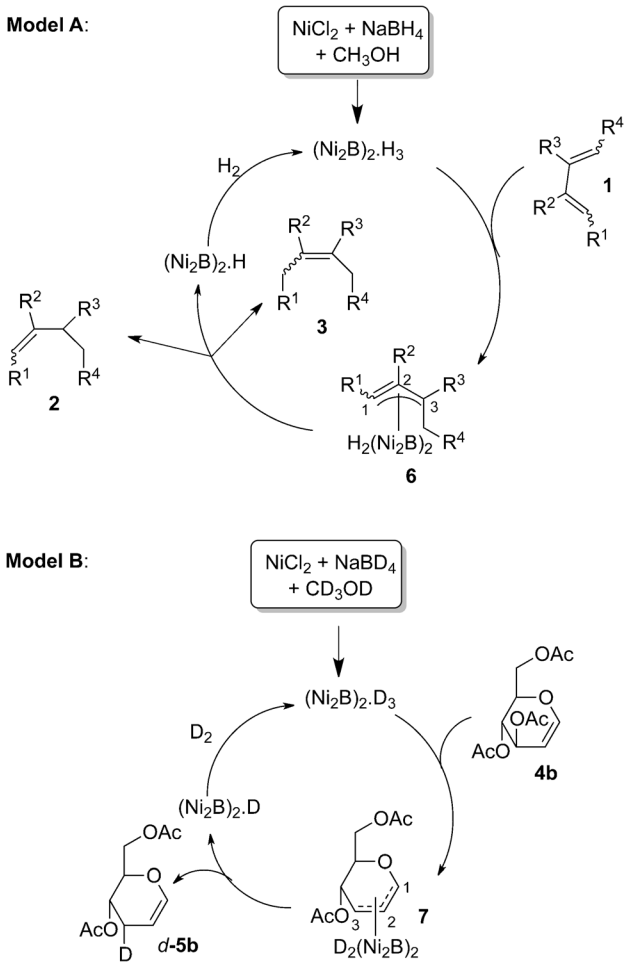
Table 2. (Continued)

Entry	Allyl ester	Product	Yield [%][b]
12[c]	 **4b**	 ***d*-5b**	90
13	 **4m**	 **5m**	84
14	 **4l**	 **5l**	77

[a] Unless otherwise noted, the reaction conditions were: 1 mmol of **4**, 0.2 mmol of $NiCl_2$, 10 mmol of $NaBH_4$, 5 mL of MeOH, room temperature, 5 min.
[b] Isolated yield.
[c] $NaBD_4$ and CD_3OD were used.

TBS, and Bn) were tolerated. Known methods for 3-deoxygenation of glycals usually involve the formation of π-allyl-Pd complexes that are then attacked by a hydride under strong acidic conditions.[10] This reductive system provided an alternative access to diversified 3-deoxy glycals conveniently under mild basic conditions. For 1-alkyloxy-2,3-unsaturated monosaccharides **4i** and **4j**, both the reductive cleavage at the 3-position and hydrogenation of the C=C double bond occurred, giving rise to **5i** and **5j** in good yields (entries 10 and 11). In addition, 3-phenylallyl acetate **4l** and furan-2-yl-phenylmethyl acetate **4m** were also reduced under these reaction conditions (entries 13 and 14). To study the stereochemistry of this cleavage, the reaction of **4b** with $NaBD_4/NiCl_2$ in CD_3OD was performed. To our delight, *d*-**5b** was produced with complete inversion of the configuration at the C-3 position (Table 2, entry 12). The stereochemistry of *d*-**5b** was verified *via* NOESY experiments and by comparison of their NMR spectra with those reported in the literature.[10a]

Although the $NaBH_4$-$NiCl_2$ system has been extensively used in organic synthesis, its reaction mechanism is still under discussion.[11] Based on the above outcomes, two preliminary mechanisms are proposed for the reductions (Scheme 2). For these dienes, a hydronickellation of $(Ni_2B)_2{\cdot}H_3$ with dienes gives rise to a π-allylnickel complexs of **6**. When R^1 is an electron-donating group, hydride attacks exclusively at the 3-postion of the complex, leading to the formation of **2**.[12] If R^2 is an electron-donating group and R^1 is a phenyl group , due to the steric bulk of R^1 and (or) its conjugated effect with the olefin, hydride also attacks exclusively at the 3-postion to form **2**. But when R^1 is an alkyl group, hydride attacks exclusively at the 1-postion, giving rise to double bond isomerization and forming **3**.[13] For allyl esters, an oxidative addition of



Scheme 2. Proposed mechanistic pathway for the reductive reactions.

the allylic substrate **4b** to $(Ni_2B)_2{\cdot}D_3$ species on the back side of the 3-acetoxy gives the π-allylnickel complex **7**. Then hydride attacks exclusively at the 3-position of the complex to liberate the olefin *d*-**5b** with the generation of the $(Ni_2B)_2{\cdot}D$ which reacts with D_2 and carries on the catalytic cycle.

In summary, for the first time, we used fresh nickel boride, generated *in situ* from the combination of $NaBH_4$ with $NiCl_2$, to fulfill the regioselective reduction of electron-rich conjugated dienes to monoolefins and reductive cleavage of allyl esters with exceedingly simple manipulations. Both of these reactions may involve the generation of π-allylnickel complexes *via* the hydronickellation of dienes and the oxidative addition of the ally ester, respectively. The selectivity strongly depends on the features of the substrates. The selective attack of hydride on the allylnickel complexes is responsible for the selectivity. The studies give us hints that the fresh nickel boride is a Ni(0) species with high catalytic activity and it can catalyze some useful allylation reactions. Further studies on the detailed mechanism and design of some novel nickel-catalyzed coupling reactions involving the $NaBH_4$-$NiCl_2$ system are ongoing in our lab, and the results will be reported in due course.

Experimental Section

Typical Procedure for the Reduction of Dienes with $NaBH_4$-$NiCl_2$ System (to form 2f)

To a solution of **1f** (442 mg, 1 mmol) in 5 mL of MeOH/DME (1/1, v/v) was added $NiCl_2$ (26 mg 0.2 mmol), then $NaBH_4$ (380 mg, 10 mmol) in portions over 5 min at room temperature with the formation of a black solid and evolution of hydrogen. After additional stirring for 5 min, the reaction was quenched with 10 mL H_2O. The resulting mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvents yielded a crude product, which was purified by column flash chromatography on silica gel to afford **2f** as colourless oil; yield: 411 mg (93%); $[\alpha]_D^{23}$: −3.6 (*c* 0.5 g mL^{-1}, CH_3COCH_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 15H), 6.30 (s, 1H), 4.79–4.52 (m, 6H), 4.21–4.15 (m, 1H), 4.12–4.11 (d, J = 4.8 Hz, 1H), 4.01–3.98 (dd, J = 6.8 Hz, 4.8 Hz, 1H), 3.86–3.82 (dd, J = 10.4 Hz, 5.6 Hz, 1H), 3.78–3.74 (dd, J = 10.8 Hz, 4.0 Hz, 1H), 2.11–2.05 (m, 2H), 1.05–1.01 (t, J = 7.4 H z, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 138.3, 138.0, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 113.9, 76.0, 75.7, 73.7, 73.3, 72.8, 71.3, 68.3, 21.9, 12.8; HR-MS (ESI): *m/z* = 445.2371, calcd. for $C_{29}H_{33}O_4$ $[M+H]^+$: 445.2379.

Typical Procedure for the $NiCl_2$-Catalyzed Reductive Cleavage of Allyl Esters

To a solution of **4d** (1 mmol) in MeOH (3 mL) was added $NiCl_2$ (26 mg 0.2 mmol), then $NaBH_4$ (10 mmol) in portions over 5 min at room temperature. After additional stirring of 5 min, the reaction was quenched with 10 mL H_2O. The resulting mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvents yielded a crude product, which was purified by column flash chromatography on silica gel to afford **5d** as a colorless oil; yield: 366 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.71 (m, 4H), 7.46–7.42 (m, 6H), 6.36 (d, J = 6.4 Hz, 1H), 5.31–5.26 (m, 1H), 4.65–4.62 (m, 1H), 4.06–4.02 (m, 1H), 3.91–3.82 (m, 2H), 2.46–2.40 (m, 1H), 2.10–2.06 (m, 4H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 142.8, 135.7, 133.3, 129.8, 127.8, 97.1, 76.2, 66.0, 62.6, 26.8, 24.8, 21.2, 19.3; HR-MS (ESI): *m/z* = 411.1988, calcd for $C_{29}H_{33}O_4$ $[M + H]^+$ 411.1992.

Acknowledgements

This work was support by Doctoral Fund of Ministry of Education of China (200805611041), Fundamental Research Funds for the Central Universities (2009M0241), the National Natural Science Foundation of China (No. 21072062), the

Natural Science Foundation of Guangdong Province, China (10351064101000000).

References

[1] Concerning the preparation and properties of nickel borides, see: a) C. A. Brown, H. C. Brown, *J. Am. Chem. Soc.* **1963**, *85*, 1003–1005; b) H. C. Brown, C. A. Brown, *J. Am. Chem. Soc.* **1963**, *85*, 1005–1006; c) C. A. Brown, V. K. Ahuja, *J. Org. Chem.* **1973**, *38*, 2226–2230; d) P. C. Maybury, R. W. Mitchell, M. F. Hawthome, *J. Chem. Soc. Chem. Commun.* **1974**, 534–535; e) B. Ganem, J. O. Osby, *Chem. Rev.* **1986**, *86*, 763–780; f) Y. Okamoto, Y. Nitta, T. Imanaka, S. Teranishi, *J. Chem. Soc. Faraday Trans. 1* **1979**, *75*, 2027–2039; g) C. M. Belisle, Y. M. Young, B. Singaram, *Tetrahedron Lett.* **1994**, *35*, 5595–5598; h) G. N. Glavee, K. J. Klabunde, C. M. Sorensen, G. C. Hadjipanayis, *Langmuir* **1994**, *10*, 4726–4730; i) Z.-J. Wu, S.-H. Ge, M.-H. Zhang, W. Li, S.-C. Mu, K.-Y. Tao, *J. Phys. Chem. C*: **2007**, *111*, 8587–8593; j) J. Geng, D. A. Jefferson, B. F. G. Johnson, *Chem. Commun.* **2007**, 969–971.

[2] a) S. Watanabe, S.; Ikishima, T. Matsuo, K. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 8402–8403; b) P. A. Jacobi, K. Lee, *J. Am. Chem. Soc.* **2000**, *122*, 4295–4303; c) P. A. Jacobi, K. Lee, *J. Am. Chem. Soc.* **1997**, *119*, 3409–3410; d) Y. Moritani, C. Fukushima, T. Miyagishima, H. Ohmizu, T. Iwasaki, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2281–2286; e) Y. Morimoto, K. Nishida, Y. Hayashi, H. Shirahama. *Tetrahedron Lett.* **1993**, *34*, 5773–5776.

[3] a) D. Setamdideh, B. Khezri, *Asian J. Chem.* **2010**, *22*, 5575–5580; b) N. P. Bandgar, S. M. Nikat, P. P. Wadgaonker, *Synth. Commun.* **1995**, *25*, 863–869; c) A. Nose, T. Kudo, *Chem. Pharm. Bull.* **1988**, *36*, 1529–1533; d) A. Nose, T. Kudo, *Chem. Pharm. Bull.* **1981**, *29*, 1159–1161; e) S. Saeki, T. Oka, T. Hayakawa, K. Sakai, *Chem. Pharm. Bull.* **1989**, *37*, 2207–2208.

[4] A. S. Demir, I. M. AKHmedov, Ö. Sesenoglu, *Turk J. Chem.* **1999**, *23*, 123–126.

[5] B. Das, H. Holla, Y. Srinivas, K. Venkateswarlu, *Indian J. Heterocycl. Chem.* **2007**, *17*, 1–6.

[6] a) W. E. Truce, F. M. Perry, *J. Org. Chem.* **1965**, *30*, 1316–1317; b) J. Schut, J. B. F. N. Engberts, H. Wynberg, *Synth. Commun.* **1972**, *2*, 415–421; c) R. B. Boar, D. W. Hawkins, J. F. McGhie, D. H. R. Barton, *J. Chem. Soc. Perkin Trans. 1* **1973**, 654–656; d) M. R. Euerby, R. D. Waigh, *Synth. Commun.* **1986**, *16*, 779–784; e) F. S., Jr. Guziec, L. M. Wasmund, *Tetrahedron Lett.* **1990**, *31*, 23.

[7] a) D. J. Krysan, in: *Comprehensive Organometallic Chemistry II*, (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Elsevier, Oxford, UK, **1995**, Vol. 12, p 959; b) *Modern Organonickel Chemistry*, (Ed.:Y. Tamaru), Wiley-VCH, Weinheim, **2005**; c) D. C. Billington, in: *Comprehensive Organic Synthesis*, (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, Vol. 3, p 423; d) G. García-Gómez, J. M. Moréto, *J. Am. Chem. Soc.* **1999**, *121*, 878–879; e) M. L. Nadal, J. Bosch, J. M. Vila, G. Klein, S. Ricart, J. M. Moréto, *J. Am. Chem. Soc.* **2005**, *127*, 10476–10477; f) S. Ikeda, *Acc. Chem. Res.* **2000**, *33*, 511–519.

[8] With respect to the composition of fresh nickel boride as $(Ni_2B)_2{\cdot}H_3$, see: a) W. E. Truce, F. E. Roberta, *J. Org. Chem.* **1963**, *28*, 961–964; b) T. G. Back, K. Yang, H. R. Krouse, *J. Org. Chem.* **1992**, *57*, 1986–1990.

[9] Direct hydrogenation is the conventional method for the reduction of dienes to monoolefins. This method usually leads to the regioselectivities far from satisfactory due to the harsh reaction conditions or the failure to precisely control the amount of hydrogen, and makes the purification tedious. For selected examples, see: a) K. Okura, S. Matsuoka, R. Goto, M. Inoue, *Angew. Chem.* **2010**, *122*, 339–342; *Angew. Chem. Int. Ed.* **2010**, *49*, 329–332; b) C. Gaviglio, F. Doctorovich, *J. Org. Chem.* **2008**, *73*, 5379–5384; c) J. Ornelas, R. Aranzaes, L. Salmon, D. Astruc, *Chem. Eur. J.* **2008**, *14*, 50–64; d) K. Suenaga, S. Kajiwara, S. Kuribayashi, T. Handa, H. Kigoshi, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 3902–3905; e) J. Dupont, P. A. Suarez, A. P Umpierre, R. F. J. Souza, *J. Braz. Chem. Soc.* **2000**, *11*, 293–297; f) T. Mizugaki, M. Ooe, K. Ebitani, K. Kaneda, *J. Mol. Cat. A: Chem.* **1999**, *145*, 329–333; g) M. Murata, Y. Tanaka, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Lett.* **2005**, *34*, 272–273; h) P. P. Zweni, H. Alper, *Adv. Synth. Catal.* **2006**, *348*, 725–731.

[10] For selected references concerning 3-deoxygenation of glycals, see: a) N. Greenspoon, E. Keinan, *J. Org. Chem.* **1988**, *53*, 3723–3731; b) M. Oshima, I. Shimizu, A. Yamamoto, *Organometallics* **1991**, *10*, 1221–1223; c) M. Okabe, R. C. Sun, *Tetrahedron Lett.* **1989**, *30*, 2203–2206.

[11] Concerning a similar mechanism of the $NaBH_4$-Cu_2Cl_2 reductive system, see: M. Narisada, I. Horibe, F. Watanabe, K. Takeda *J. Org. Chem.* **1989**, *54*, 5308–5313.

[12] For related examples about allylation reactions involving π-allylnickel complexes substituted with an electron-donating group at the 1-position, see: a) J. R. Johnson, P. S. Tully, P. B. Mackenzie, M. Sabat, *J. Am. Chem. Soc.* **1991**, *113*, 6172–6177; b) B. A. Grisso, J. R. Johnson, P. B. Mackenzie, *J. Am. Chem. Soc.* **1992**, *114*, 5160–5165.

[13] Other mechanisms cannot be ruled out at this stage. A single electron transfer (SET) mechanism might be a choice, just like that of the Birch reduction.

