Nickel-catalysed reactions with trialkylboranes and silacyclobutanes

Koji Hirano, Hideki Yorimitsu* and Koichiro Oshima*

Received (in Cambridge, UK) 25th February 2008, Accepted 18th March 2008
First published as an Advance Article on the web 12th May 2008
DOI: 10.1039/b803172j

Nickel catalysis enables us to develop new reactions with trialkylboranes and silacyclobutanes of modest reactivity. A combination of $Ni(cod)_2$ and tri-*tert*-butylphosphine catalyses alkylation reactions of aldehydes and α,β-unsaturated esters with various trialkylboranes of modest reactivity, suppressing conceivable β-hydride elimination from alkylnickel intermediates. A nickel catalyst is also useful for 1,4-addition of bis(pinacolato)diboron to α,β-unsaturated esters and amides. Nickel-catalysed reaction of silacyclobutanes with aldehydes results in ring opening to afford the corresponding alkoxyallylsilanes. In contrast, the ring expansion reaction of benzosilacyclobutene with aldehydes yields benzoxasilacyclohexenes. A nickel catalyst prepared from $Ni(cod)_2$ and tricyclohexylphosphine realises direct silylation of terminal alkenes with silacyclobutane furnishing vinylsilanes.

1 General introduction

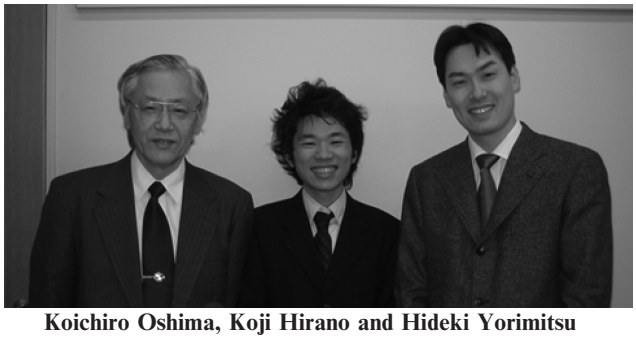
Taking advantage of their excellent and/or unique reactivity, molecular nickel catalysts have been attracting increasing attention in organic synthesis.[1] Among nickel-catalysed reactions, cross-coupling and carbometalation reactions, in a broad sense, with organometallic reagents provide powerful and reliable tools for carbon–carbon bond formation. A variety of organometallic reagents such as organomagnesium, -zinc, -aluminium, -silicon and -boron reagents are now available for use under nickel catalysis. However, to expand scope, and to establish universal organic synthesis, further studies on nickel-catalysed reactions are essential. In light of the importance of moderately reactive organoboron and -silicon reagents, we have focused on nickel-catalysed reactions with these reagents. This account consists of two sections. The former section deals with nickel-catalysed alkylation reactions of carbonyl compounds with trialkylboranes. The latter describes nickel-catalysed reactions of unsaturated compounds with silacyclobutanes.

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan. E-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp; oshima@orgrxn.mbox.media.kyoto-u.ac.jp; Fax: +81-75-383-2438; Tel: +81-75-383-2441

2 Nickel-catalysed alkylation reactions with trialkylboranes

2.1 Overview of organoborons under nickel catalysis

Compared to palladium[2] and rhodium,[3] nickel catalysts were far less frequently used for reactions with organoborons: cross-coupling reactions of aryl tosylates and mesylates[4] and alkyl halides,[5] allylic arylation,[6] 1,2- and 1,4-addition,[7] carboboration,[8] and three-component coupling of carbon–carbon multiple bonds, carbonyls and arylboron reagents.[9] It is worth noting that all the reactions utilise aryl- or alkenylboron reagents and that few reports of alkylation reactions with alkylboron reagents have appeared.[5] For instance, nickel-

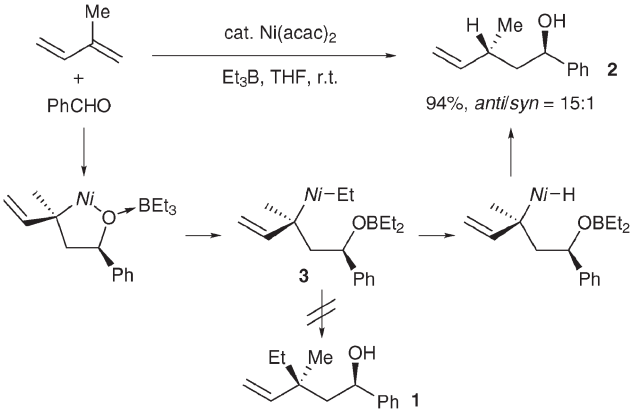


Koichiro Oshima, Koji Hirano and Hideki Yorimitsu

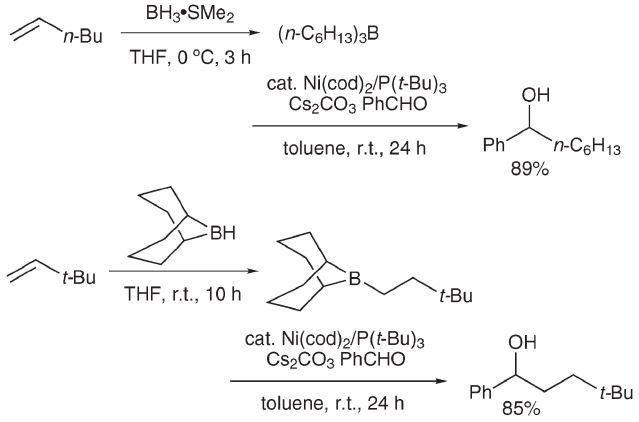
Koji Hirano (middle) received his BS at Kyoto University and has just obtained his PhD degree under Professor Koichiro Oshima. He has been a JSPS research fellow since 2005, involved in the development of transition-metal-catalysed reactions. He is currently a JSPS postdoctoral fellow working with Professor Tamio Hayashi at Kyoto University.

Hideki Yorimitsu (right) received his PhD under Prof. Koichiro Oshima at Kyoto University in 2002. He served as a JSPS postdoctoral fellow, working with Prof. Eiichi Nakamura at the University of Tokyo and is presently an Assistant Professor at Kyoto University. His research program focuses on the development of new organic reactions useful for synthesizing biologically interesting compounds, novel coordinating structures, and organometallic compounds.

Koichiro Oshima (left) received his BS and PhD degrees from Kyoto University under the guidance of Professor Hitosi Nozaki. After a spell as a postdoctoral fellow with Professor Barry Sharpless at MIT he returned to Kyoto University where he has been a Professor since 1993. His current research interests include the development of new synthetic methods via radical reactions and organometallic reagents.



Scheme 1 Nickel-catalysed reductive coupling reaction with triethylborane.



Scheme 2 Alkylations of aldehydes with alkylboranes prepared by hydroboration.

catalysed reaction of isoprene with benzaldehyde in the presence of triethylborane failed to afford the corresponding ethylated three-component coupling product **1**, and did result in reductive coupling yielding **2** (Scheme 1).[10,11] Fast β-hydride elimination from an ethylnickel intermediate **3** is inevitable, which renders the use of alkylboron reagents under nickel catalysis as alkylating agents difficult. During the last few years, we have successfully developed simple yet unprecedented nickel-catalysed alkylation reactions with trialkylboranes, overcoming the competitive β-hydride elimination.

2.2 Nickel-catalysed alkylation of aldehydes with trialkylboranes

Alkylation of aldehydes with organometallic reagents is a basic and thus important reaction in organic chemistry. Conventional alkylboron reagents do not react with aldehydes, due to their modest reactivity. Based on reports of nickel catalysis for arylation of aldehyde with arylboron reagents[7] as well as alkylations of aldehydes with dialkylzinc[12] and trialkylaluminium[13] reagents, we envisioned that a nickel catalyst can facilitate alkylation with alkylboron reagents. By suppressing undesirable β-hydride elimination from alkylnickel intermediates, we indeed developed such an alkylation reaction.

Treatment of aldehydes with tri-*n*-butyl- or triethylborane in the presence of caesium carbonate and catalytic amounts of $Ni(cod)_2$ and $P(t\text{-}Bu)_3$ in toluene at room temperature for 24 h afforded the corresponding alkylated products in good yields

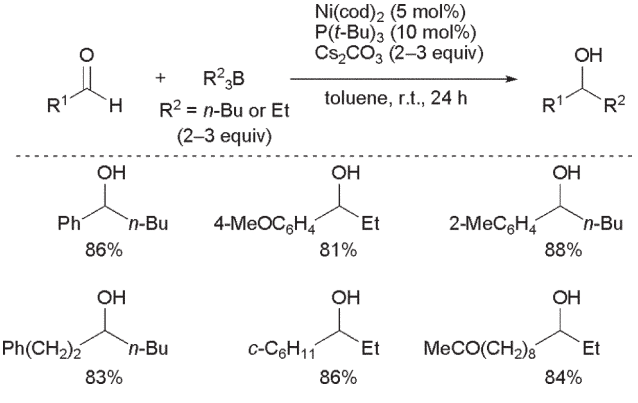
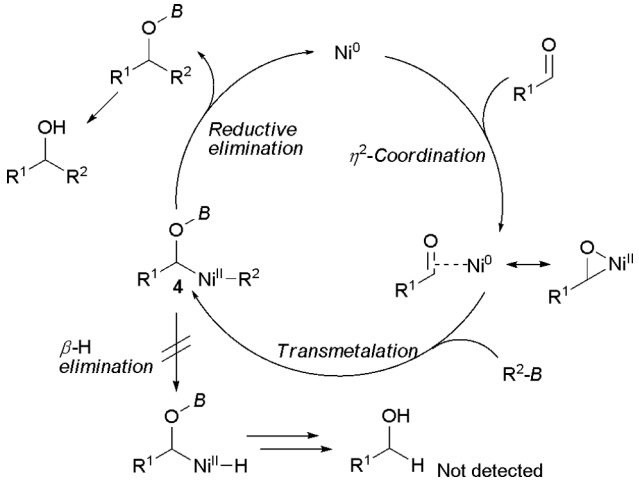


Fig. 1 Nickel-catalysed alkylation of aldehydes.

(Fig. 1).[14] A variety of aldehydes, including keto aldehyde, underwent the alkylation. The key for the successful alkylation is the combination of $P(t\text{-}Bu)_3$ and caesium carbonate. Other ligands such as PPh_3, $P(n\text{-}Bu)_3$ and $P(c\text{-}C_6H_{11})_3$ were ineffective. In the absence of caesium carbonate or with potassium carbonate instead of caesium carbonate, no butylated alcohols were obtained.

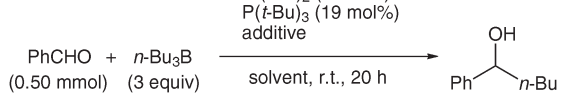
Trialkylboranes prepared by hydroboration from hydroboranes and alkenes can be employed for the reaction (Scheme 2). Trihexylborane, prepared from borane-dimethyl sulfide complex and 1-hexene, reacted with benzaldehyde to afford 1-phenyl-1-heptanol in excellent yield. Alkylboranes, prepared from 9-borabicyclo[3.3.1]nonane (9-BBN) and 3,3-dimethyl-1-butene, transferred the 3,3-dimethyl-1-butyl group selectively.

Mechanistic work by Ogoshi *et al.*[15] on nickel(η^2-aldehyde) complexes promoted us to propose the following mechanism for the alkylation reaction (Scheme 3). A nickel(0) species initially reacts with aldehyde to generate a η^2-coordinated complex or its resonance form. Subsequent transmetalation with trialkylborane or its borate formed by the action of caesium carbonate yields intermediate **4**. $P(t\text{-}Bu)_3$ highly promotes reductive elimination from **4** to provide the corresponding alcohol and the initial nickel complex. No primary alcohol R^1CH_2OH was detected, which would be formed if β-hydride



Scheme 3 Plausible mechanism for alkylation of aldehydes.

Table 1 Butylation of benzaldehyde in water



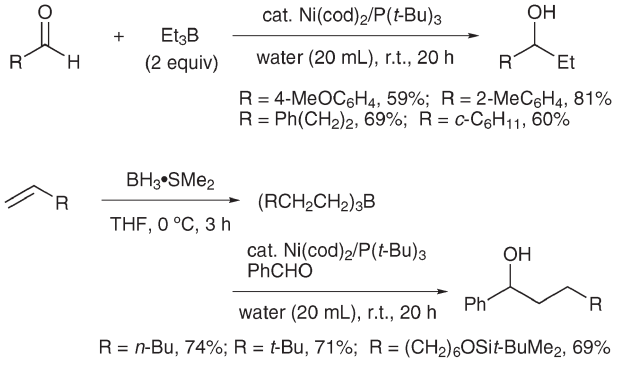
Entry	Solvent	Additive	Yield (%)
1	Toluene (10 mL)	None	<2
2	Toluene (10 mL)	Cs_2CO_3 (3 equiv.)	88
3	Toluene (10 mL)	H_2O (3 equiv.)	<2
4	Water (5 mL)	None	33
5	Water (10 mL)	None	63
6	Water (20 mL)	None	90

elimination from the intermediate **4** could occur. The exact role of caesium carbonate is not clear. Formation of a borate complex from $R^2{}_3B$ and Cs_2CO_3 could facilitate the transmetalation step.

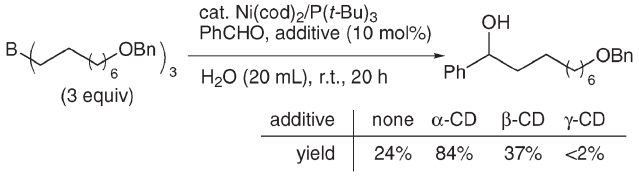
Water is not only cheap, nontoxic, and nonflammable solvent but also offers extraordinary solvent effects on reactions.[16] The additions of organometallic reagents to aldehydes in aqueous media have also been widely explored.[17,18] However, alkylation of aldehydes in water is not a trivial reaction. We disclosed that nickel-catalysed alkylation reactions of aldehydes with trialkylboranes proceed smoothly in water (Table 1).[19] Intriguingly, the reaction in water took place in the absence of caesium carbonate (entries 1, 2 and 5), which is different from the alkylation in toluene. The amount of water also dramatically influenced the yield. An addition of 3 equiv. of water in toluene had no effect (entry 3). The larger the amount of water was, the higher the yield was (entries 4–6).

It is worth noting that benzaldehyde, tri-*n*-butylborane, and the nickel catalyst were completely insoluble in water, and the reaction proceeded in a biphasic system, of organic droplets in water. The effect of water as a reaction medium is not clear. Water can enhance the η^2-coordination step and/or the transmetalation step. These steps cause the reduction of the total volume of the organic components, which water would enhance due to hydrophobic interaction.[16,20] Moreover, an aqua complex $(n\text{-}Bu)_3B{\cdot}OH_2$ can more readily undergo the transmetalation.

Scope of the alkylation in water was similar to that in toluene with the aid of caesium carbonate (Fig. 1 and Scheme 2 *vs*. Scheme 4), although the yields obtained in water were generally lower.



Scheme 4 Nickel-catalysed alkylation with trialkylboranes in water.



additive	none	α-CD	β-CD	γ-CD
yield	24%	84%	37%	<2%

Scheme 5 Effect of cyclodextrins in nickel-catalysed alkylation in water.

The reaction with trialkylborane having a benzyloxy moiety resulted in low yield (Scheme 5). To our delight, an addition of a catalytic amount of α-cyclodextrin (α-CD) dramatically improved the yield to 84%. Additions of β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD) showed less efficiency. The exact role of α-CD is not clear. α-CD is known to accommodate a phenyl ring in its cavity most tightly among CDs.[21] We suppose that interaction between the benzyloxy group and the nickel or boron centre might suppress the transmetalation step to result in low yield and that the inclusion of the benzyloxy group in α-CD would help blocking out the unfavourable interaction.

2.3 Nickel-catalysed 1,4-addition of trialkylboranes to α,β-unsaturated esters

Transition-metal-catalysed 1,4-addition of alkylmetals is among the most powerful and promising C–C bond formations in organic synthesis. In particular, copper-catalysed addition of alkylmagnesium, alkylzinc and alkylaluminium reagents have been widely studied and accomplished asymmetric induction using a variety of chiral ligands.[22] 1,4-Addition reactions with trialkylboranes have been less explored,[23] although 1,4-addition of aryl- and alkenylboronic acid derivatives under rhodium,[3] palladium,[24] and nickel[7] catalysis has been established.

On the basis of results obtained in the previous section, we have developed nickel-catalysed 1,4-addition of trialkylboranes to α,β-unsaturated esters (Fig. 2).[25] Treatment of benzyl crotonate with triethylborane in the presence of a $Ni(cod)_2$/$P(t\text{-}Bu)_3$ catalyst and caesium carbonate in toluene at room temperature for 17 h afforded the 1,4-adduct **5a** in 88% yield. The addition of caesium carbonate was essential to attain satisfactory yield. The chlorobenzyl moiety of **5d** remained untouched, and the conceivable Suzuki–Miyaura cross-coupling product was not obtained. Not only crotonic acid esters

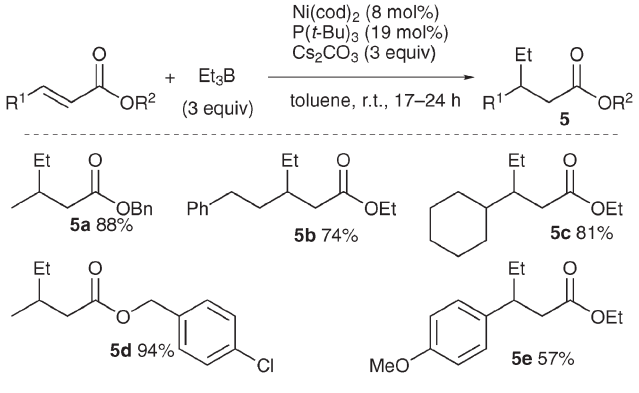
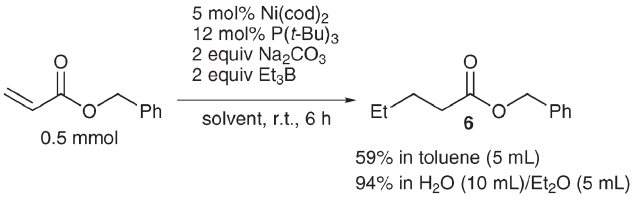


Fig. 2 Nickel-catalysed 1,4-addition of triethylborane.



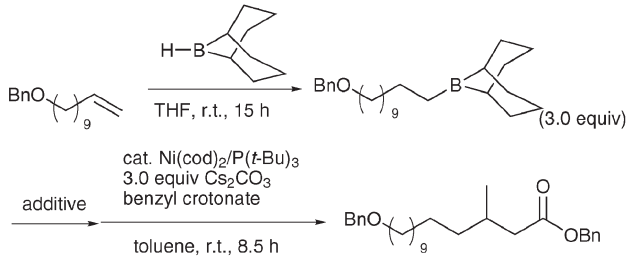
Scheme 6 1,4-Addition to acrylate ester in water/ether biphasic solvent.

but also unsaturated esters having a larger alkyl group at the β position participated in the reaction. For instance, cyclohexyl-substituted ester **5c** was obtained in 81% yield. Methoxy-substituted cinnamate ester also reacted to yield **5e** in 57% yield.

1,4-Addition of triethylborane to benzyl acrylate is challenging because acrylate can undergo radical and anionic polymerisation much more readily. 1,4-Adduct **6** was indeed obtained in only 59% yield under similar conditions (Scheme 6). About half of the starting ester underwent the undesired polymerisation. The addition of the initially formed boryl enolate to acrylate ester would cause the side reaction. Considering that smooth protonolysis of the intermediate was essential, we performed the reaction in an aqueous/organic biphasic system.[26] To our delight, the desired product **6** was obtained in 94% yield under water/Et_2O biphasic conditions.

Initial attempts to perform sequential hydroboration/1,4-addition resulted in failure (Scheme 7). No 1,4-addition took place, and the starting material was completely recovered. After many experiments, we finally found that an addition of 4.0 equiv. of methanol dramatically enhanced the reaction. Interestingly, a large amount of methanol prevented the reaction completely. Other alcohols such as *tert*-butyl alcohol and phenol had no influence on the yield. The use of *N*,*N*-dimethylacetamide (DMA) and water led to slight improvement of the yield. A much stronger Lewis base, pyridine, did not work to promote the reaction.

With the optimal methanol-promoted conditions, 1,4-addition of several 9-alkyl-9-BBN reagents to benzyl crotonate was examined (Fig. 3). The advantage of the reaction is facile introduction of functionalised alkyl groups. For instance, alkylborane having an C(sp^3)–Br bond, which the corresponding alkylmagnesium halide and dialkylzinc are difficult to prepare, underwent 1,4-addition smoothly.



additive	none	methanol (4 equiv)	water (4 equiv)	DMA (4 equiv)
yield	0%	96%	24%	65%

Scheme 7 Effect of additive in sequential hydroboration/nickel-catalysed 1,4-addition.

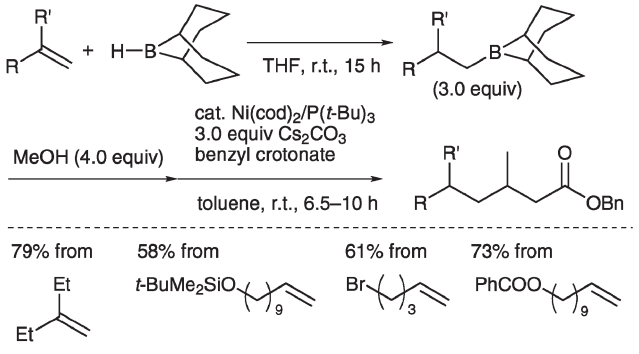
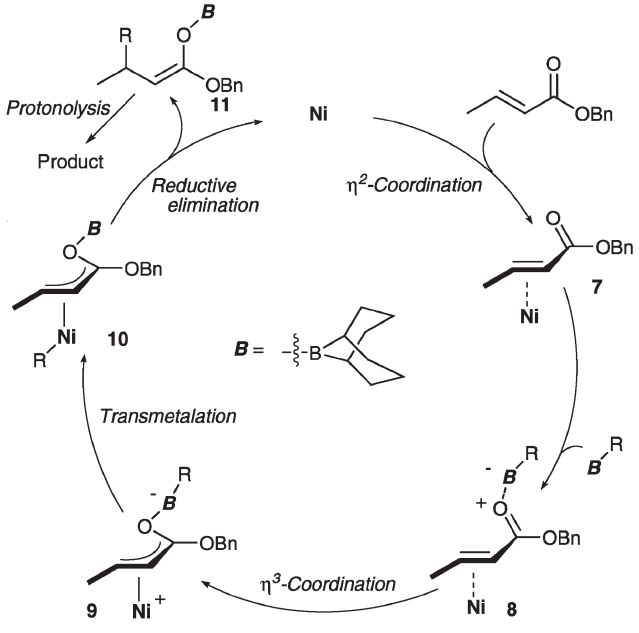


Fig. 3 Methanol-promoted nickel-catalysed 1,4-addition of functionalised alkylborane reagents.



Scheme 8 Plausible mechanism of 1,4-addition.

We are tempted to assume the mechanism of the reaction with 9-alkyl-9-BBN as follows (Scheme 8). Formation of a nickel(η^2-alkene) complex initially took place. Coordination of the carbonyl moiety of **7** to alkylborane affords the intermediate **8** and then η^3-coordinated complex **9**.[27] Transfer of the R group on the boron to nickel furnishes an alkylnickel species **10**. Finally, reductive elimination from **10** affords **11** and regenerates the initial nickel complex. Protonolysis of **11** would provide the product. The exact roles of caesium carbonate and methanol are not clear at this stage. They can enhance the transmetalation step through their coordination to the boron centre of **9**. Moreover, methanol can be a good proton source for intermediate **11**.

2.4 Nickel-catalysed 1,4-addition of bis(pinacolato)diboron to α,β-unsaturated esters and amides

Platinum-, rhodium- and copper-catalysed 1,4-additions of diborons to α,β-unsaturated aldehydes and ketones are important procedures for the preparation of organoboranes having carbonyl functionalities at the β position.[28] However,

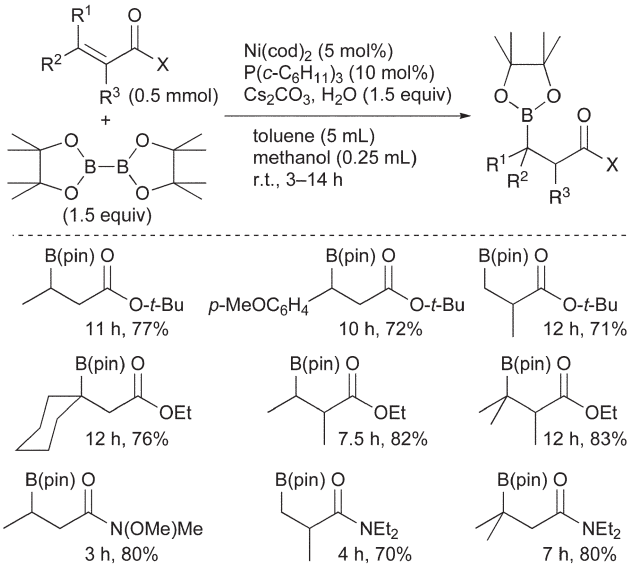


Fig. 4 β-Boration of α,β-unsaturated esters and amides.

similar additions to α,β-unsaturated esters and amides have been still challenging. Moreover, the reaction of sterically demanding multisubstituted esters and amides is not trivial. Considering the similarity in the Lewis acidic character between trialkylboranes ($R–BR_2$) and bis(pinacolato)diboron [(pin)B–B(pin), pin = pinacolato], we expected that the nickel-catalysed conditions developed in the previous section would be applicable to 1,4-addition of bis(pinacolato)diboron to α,β-unsaturated esters.

This was indeed the case, and after screening reaction conditions, we realised efficient borations of a wide range of α,β-unsaturated esters and amides (Fig. 4).[29] The substitution patterns of the substrates had little influence on reaction efficiency. *tert*-Alkyl-substituted pinacolatoborons were obtained in high yields. A plausible reaction mechanism would be similar to that described in Scheme 8.

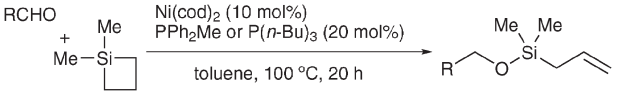
3 Nickel-catalysed reactions with silacyclobutanes

3.1 Overview of silacyclobutanes under transition-metal catalysis

Organosilicon compounds have generally high thermal and chemical stabilities, compared to other organometallic reagents. Especially, tetraalkylsilanes are quite stable and inert to water and oxygen. Their low reactivity often becomes problematic from the synthetic point of view. However, silacyclobutanes have quite interesting reactivity based on their ring strain and high Lewis acidity, and thus are useful in organic synthesis.[30]

Platinum- and palladium-catalysed transformations of silacyclobutanes are well known, and usually begin with oxidative addition of silacyclobutanes to low valent transition metals.[31,32] In contrast, nickel-catalysed reactions of silacyclobutanes have not been explored, although nickel belongs to the same group, group 10. Considering the Lewis acidity of silacyclobutanes that is comparable to that of trialkylboranes,

Table 2 Nickel-catalysed reaction of silacyclobutane with aldehydes



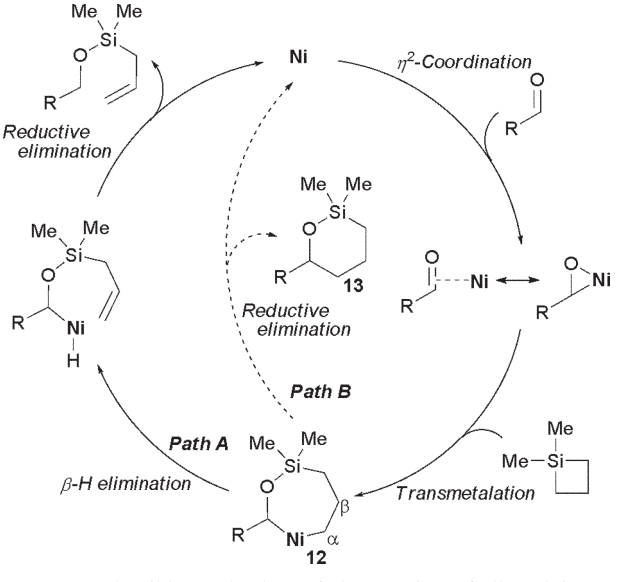
Entry	RCHO	Ligand	Yield (%)
1	PhCHO	PPh_2Me	88
2	$2\text{-}MeC_6H_4CHO$	PPh_2Me	85
3	$4\text{-}MeOCOC_6H_4CHO$	$P(n\text{-}Bu)_3$	53
4	$Ph(CH_2)_2CHO$	$P(n\text{-}Bu)_3$	73
5	$c\text{-}C_6H_{11}CHO$	$P(n\text{-}Bu)_3$	69
6	*trans*-PhCH=CHCHO	PPh_2Me	51

we started to develop nickel-catalysed reactions of silacyclobutanes with carbonyl compounds.

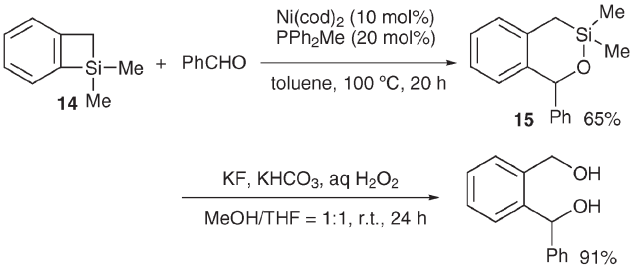
3.2 Nickel-catalysed reactions of silacyclobutanes with aldehydes

Treatment of 1,1-dimethylsilacyclobutane with benzaldehyde in the presence of catalytic amounts of $Ni(cod)_2$ and PPh_2Me in toluene at 100 °C afforded allylbenzyloxydimethylsilane in high yield (Table 2, entry 1).[33] Ester functionality could survive under the reaction conditions (entry 3). Aliphatic aldehydes as well as aromatic aldehydes were converted to alkoxyallylsilanes (entries 4 and 5). In the reaction of *trans*-cinnamaldehyde, 1,2-reduction predominated to afford the corresponding allylcinnamyloxysilane as the sole product (entry 6).

Apparently, nickel-catalysed carbon–silicon bond cleavage is involved in this transformation. In analogy with the mechanism in Scheme 3, we propose the following mechanism (Scheme 9). A nickel(0) species initially reacts with aldehyde to generate η^2-coordinated complex or its resonance form. Subsequent transmetalation with silacyclobutane gives the intermediate **12**. Following β-hydride elimination and reductive elimination furnish allyl(alkoxy)silane and regenerate the



Scheme 9 Plausible mechanism of the reaction of silacyclobutane with aldehydes.



Scheme 10 Nickel-catalysed ring-expansion.

initial low-valent nickel (path A). Direct reductive elimination (path B) is much slower than β-hydride elimination.

If the intermediate **12** had no hydrogens at the β-position, reductive elimination could proceed to afford the ring-expanded product like **13** (path B). As expected, benzosilacyclobutene **14** reacted with benzaldehyde under similar conditions to afford benzoxasilacyclohexene **15** in good yield (Scheme 10). Interestingly, regioselective cleavage of the sp^2 carbon–silicon bond occurred. Tamao–Fleming oxidation could transform **15** to the corresponding diol. The overall transformation is equivalent to 2-(hydroxymethyl)phenylation of aldehydes.

3.3 Nickel-catalysed regio- and stereoselective silylation of terminal alkenes with silacyclobutanes for the synthesis of vinylsilanes from alkenes

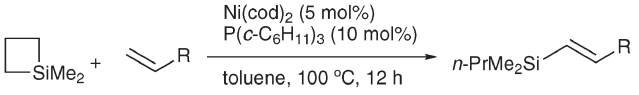
Vinylsilanes are very useful organometallic reagents. Methods for the synthesis of vinylsilanes are thus extensively studied. Regio- and stereoselective direct silylation of alkenes is an ideal route to vinylsilanes. Transition-metal-catalysed dehydrogenative silylation of alkenes with hydrosilanes sounds attractive (Scheme 11).[34] However, the substrates were limited to activated alkenes such as α,β-unsaturated esters and styrenes. Moreover, the dehydrogenative silylations required a large excess of alkenes because the alkenes were hydrogen acceptors as well as substrates to be silylated. During the investigation of nickel-catalysed reactions of silacyclobutanes with aldehydes, we found nickel-catalysed silylation of alkenes with silacyclobutanes.[35] The reaction provides a facile and straightforward access to vinylsilanes from a variety of terminal alkenes without formation of byproducts such as alkanes.

Table 3 displays the broad scope of the silylation reaction with silacyclobutane. Except for the silylation of acrylamide (entry 2), the reactions proceeded in high yields with exclusive *E* selectivity. Not only acrylates, acrylamide, and styrenes (entries 1–6) but also unactivated alkenes such as 1-tetradecene were efficiently silylated (entries 7–10). Functional groups such as pyridyl, ester and silyl ether were compatible under the reaction conditions.

Notably, benzosilacyclobutene **14** was also the suitable silylating agent (eqn (1)). Styrene reacted with **14** to furnish

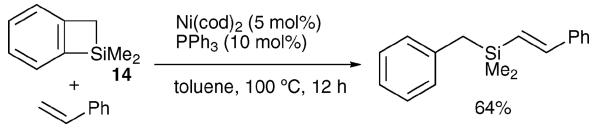
Scheme 11 Dehydrogenative silylation.

Table 3 Nickel-catalysed silylation of terminal alkenes with silacyclobutane



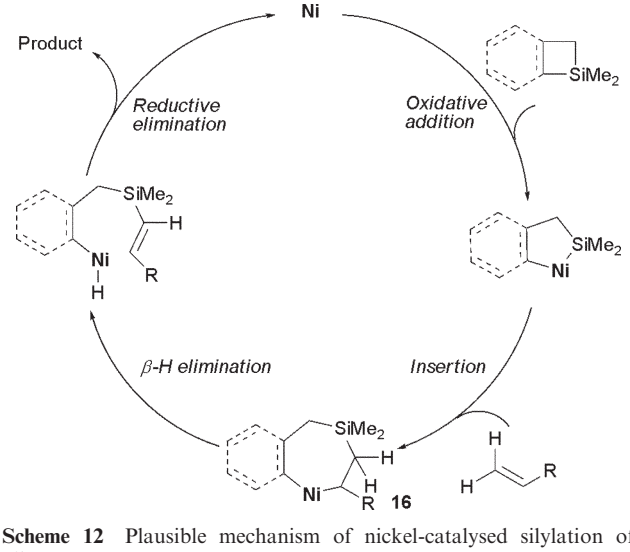
Entry	R	Yield (%)	*E* : *Z*
1	CO_2CH_2Ph	95	>99 : 1
2	$CONEt_2$	82	88 : 12
3	Ph	98	>99 : 1
4	2-MeC_6H_4	99	>99 : 1
5	4-$MeOC_6H_4$	93	>99 : 1
6	2-Pyridyl	71	>99 : 1
7	*n*-$C_{12}H_{25}$	93	>99 : 1
8	CH_2SiMe_2Ph	82	>99 : 1
9	$(CH_2)_9OSi$*t*-$BuMe_2$	93	>99 : 1
10	$(CH_2)_9OCO$*t*-Bu	81	>99 : 1

the benzyldimethylsilyl-substituted styrene regio- and stereoselectively. In this case, $Ni(cod)_2/2PPh_3$ catalyst gave the better result. The palladium-catalysed cross-coupling reaction of benzyl-substituted vinylsilane with aryl halides[36] would be applicable to the product.



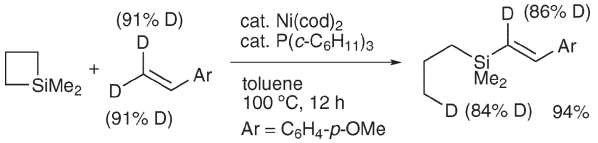
(1)

The reaction would proceed as follows (Scheme 12). Oxidative addition of silacyclobutanes to zerovalent nickel followed by insertion of alkene to the Si–Ni bond of the intermediate affords nickelasilacycloheptane **16**. In the case of benzosilacyclobutane **14**, the oxidative addition of the $C(sp^2)$–Si bond to Ni(0) predominates over that of the benzylic $C(sp^3)$–Si bond. Subsequent β-H elimination followed by reductive elimination produces product to complete the catalytic cycle. The result of the silylation of terminally deuterated styrene was consistent



Scheme 12 Plausible mechanism of nickel-catalysed silylation of alkenes.

with our plausible mechanism (eqn (2)).



(2)

4 Conclusions

We have focused on the reactivity of electron-rich low valent nickel complexes and succeeded in the activation of trialkylboranes, diboron and silacyclobutanes by the nickel catalysts. The new modes of activation enabled several synthetically useful reactions with these reagents for carbon–carbon, –boron, and –silicon bond formations, which exhibited the interesting nature of the nickel complexes. Detailed mechanistic studies and further applications including asymmetric reactions are awaited.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research, COE Research, Global COE Research from MEXT and JSPS. K. H. acknowledges JSPS for financial support.

Notes and references

1. *Modern Organonickel Chemistry*, ed. Y Tamaru, Wiley-VCH, Weinheim, 2005; R. M. Moslin, K. Miller-Moslin and T. F. Jamison, *Chem. Commun*., 2007, 4441–4449; S. Ikeda, *Acc. Chem. Res*., 2000, **33**, 511–519; J. Montgomery, *Acc. Chem. Res*., 2000, **33**, 467–473; T. F. Jamison, *Tetrahedron*, 2006, **62**, 7503.
2. N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457–2483.
3. K. Fagnou and M. Lautens, *Chem. Rev*., 2003, **103**, 169–196; T. Hayashi and K. Yamasaki, *Chem. Rev*., 2003, **103**, 2829–2844.
4. V. Percec, J.-Y. Bae and D. H. Hill, *J. Org. Chem*., 1995, **60**, 1060–1065; M. Ueda, A. Saitoh, S. Oh-tani and N. Miyaura, *Tetrahedron*, 1998, **54**, 13709–13086; D. Zim, V. R. Lando, J. Dupont and A. L. Monterio, *Org. Lett*., 2001, **3**, 3049–3051; Z.-Y. Tang and Q.-S. Hu, *J. Am. Chem. Soc*., 2004, **126**, 3058–3059.
5. J. Zhou and G. C. Fu, *J. Am. Chem. Soc*., 2004, **126**, 1340–1341; F. Gonzalez-Bobes and G. C. Fu, *J. Am. Chem. Soc*., 2006, **128**, 5360–5361; B. Saito and G. C. Fu, *J. Am. Chem. Soc*., 2007, **129**, 9602–9603.
6. Y. Kobayashi and E. Ikeda, *J. Chem. Soc., Chem. Commun*., 1994, 1789–1790; H. Chen and M.-Z. Deng, *J. Organomet. Chem*., 2000, **603**, 189–193; Y. Kobayashi, R. Mizojiri and E. Ikeda, *Synlett*, 1995, 571–572; Y. Kobayashi, Y. Tokoro and K. Watatani, *Eur. J. Org. Chem*., 2000, 3825–3834.
7. G. Takahashi, E. Shirakawa, T. Tsuchimoto and Y. Kawakami, *Chem. Commun*., 2005, 1459–1460; E. Shirakawa, Y. Yasuhara and T. Hayashi, *Chem. Lett*., 2006, **35**, 768–769; T. Arao, K. Kondo and T. Aoyama, *Tetrahedron Lett*., 2007, **48**, 4115–4117.
8. E. Shirakawa, G. Takahashi, T. Tsuchimoto and Y. Kawakami, *Chem. Commun*., 2002, 2210–2211; G. Takahashi, E. Shirakawa, T. Tsuchimoto and Y. Kawakami, *Adv. Synth. Catal*., 2006, **348**, 837–840; M. Suginome, A. Yamamoto and M. Murakami, *J. Am. Chem. Soc*., 2003, **125**, 6358–6359; M. Suginome, M. Shirakura and A. Yamamoto, *J. Am. Chem. Soc*., 2006, **128**, 14438–14439.
9. M. Kimura, S. Matsuo, K. Shibata and Y. Tamaru, *Angew. Chem., Int. Ed*., 1999, **38**, 3386–3388; M. Kimura, K. Shibata, Y. Kobayashi and Y. Tamaru, *Tetrahedron Lett*., 2000, **41**, 6789–6793; K. Shibata, M. Kimura, K. Kojima, S. Tanaka and Y. Tamaru, *J. Organomet. Chem*., 2001, **624**, 348–353; S. J. Patel and T. F. Jamison, *Angew. Chem., Int. Ed*., 2003, **42**, 1364–1367; S. J. Patel and T. F. Jamison, *Angew. Chem., Int. Ed*., 2004, **43**, 3941–3944; T. T. Jayanth and C.-H. Cheng, *Angew. Chem., Int. Ed*., 2007, **46**, 5921–5924.
10. M. Kimura, A. Ezoe, K. Shibata and Y. Tamaru, *J. Am. Chem. Soc*., 1998, **120**, 4033–4034; M. Kimura and Y. Tamaru, *Top. Curr. Chem*., 2007, **279**, 173–207.
11. Other reductive coupling reactions that employ trialkylboranes as reducing agents: Y. Sato, M. Takimoto and M. Mori, *Tetrahedron Lett*., 1996, **37**, 887–890; W.-S. Huang, J. Chan and T. F. Jamison, *Org. Lett*., 2000, **2**, 4221–4223; M. Kimura, A. Ezoe, S. Tanaka and Y. Tamaru, *Angew. Chem., Int. Ed*., 2001, **40**, 3600–3602; K. M. Miller, W.-S. Huang and T. F. Jamison, *J. Am. Chem. Soc*., 2003, **125**, 3442–3443; T. Luanphaisarnnont, C. O. Ndubaku and T. F. Jamison, *Org. Lett*., 2005, **7**, 2937–2940; K. M. Miller and T. F. Jamison, *Org. Lett*., 2005, **7**, 3077–3080; A. Herath and J. Montgomery, *J. Am. Chem. Soc*., 2006, **128**, 14030–14031; A. Herath, B. B. Thompson and J. Montgomery, *J. Am. Chem. Soc*., 2007, **129**, 8712–8713.
12. M. I. Burguete, M. Collado, J. Escorihuela, F. Galindo, E. Garcíaverdugo, S. V. Luis and M. J. Vicent, *Tetrahedron Lett*., 2003, **44**, 6891–6894.
13. T. Ichiyanagi, S. Kuniyama, M. Shimizu and T. Fujisawa, *Chem. Lett*., 1998, 1033–1034; K. Biswas, O. Prieto, P. J. Goldsmith and S. Woodward, *Angew. Chem., Int. Ed*., 2005, **44**, 2232–2234.
14. K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett*., 2005, **7**, 4689–4691.
15. S. Ogoshi, M. Oka and H. Kurosawa, *J. Am. Chem. Soc*., 2004, **126**, 11802–11803.
16. C.-J. Li and T.-H. Chan, *Organic Reactions in Aqueous Media*, John Wiley & Sons, New York, 1997; P. A. Grieco, *Organic Synthesis in Water*, Blackie Academic & Professional, London, 1998; A. Lubineau and J. Auge, *Modern Solvents in Organic Synthesis*, ed. P Knochel, Springer-Verlag, Berlin/Heidelberg, 1999.
17. Allylation with allylmetals: J. Nokami, J. Otera, T. Sudo and R. Okawara, *Organometallics*, 1983, **2**, 191–193; C. Petrier and J. L. Luche, *J. Org. Chem*., 1985, **50**, 910–912; C.-J. Li and T.-H. Chan, *Tetrahedron Lett*., 1991, **32**, 7017–7020; M. Sugiura, K. Hirano and S. Kobayashi, *J. Am. Chem. Soc*., 2004, **126**, 7182–7183; T. Tsuji, S. Usugi, H. Yorimitsu, H. Shinokubo, S. Matsubara and K. Oshima, *Chem. Lett*., 2002, 2–3, and references cited therein.
18. Catalytic arylation or alkenylation with organoboronic acid derivatives, see refs. 3 and 7.
19. K. Hirano, H. Yorimitsu and K. Oshima, *Adv. Synth. Catal*., 2006, **348**, 1543–1546.
20. H. Yorimitsu, T. Nakamura, H. Shinokubo, K. Oshima, K. Omoto and H. Fujimoto, *J. Am. Chem. Soc*., 2000, **122**, 11041–11047; H. Yorimitsu, H. Shinokubo, S. Matsubara, K. Oshima, K. Omoto and H. Fujimoto, *J. Org. Chem*., 2001, **66**, 7776–7785; H. Kinoshita, T. Nakamura, H. Kakiya, H. Shinokubo, S. Matsubara and K. Oshima, *Org. Lett*., 2001, **3**, 2521–2524.
21. F. Hapiot, S. Tilloy and E. Monflier, *Chem. Rev*., 2006, **106**, 767–781.
22. A. Alexakis and C. Benhaim, *Eur. J. Org. Chem*., 2002, 3221–3236; B. E. Rossiter and N. M. Swingle, *Chem. Rev*., 1992, **92**, 771–806; S. Woodward, *Angew. Chem., Int. Ed*., 2005, **44**, 5560–5562.
23. There are a few examples of the 1,4-additions of trialkylboranes to α,β-unsaturated aldehydes and ketones under radical conditions. However, the radical conditions are not applicable to the addition to α,β-unsaturated esters because they are prone to undergo radical polymerisation, H. C. Brown and G. W. Kabalka, *J. Am. Chem. Soc*., 1970, **92**, 714–716.
24. C.-S. Cho, S. Motofusa, K. Ohe and S. Uemura, *J. Org. Chem*., 1995, **60**, 883–888; T. Nishikata, Y. Yamamoto and N. Miyaura, *Angew. Chem., Int. Ed*., 2003, **42**, 2768–2770; T. Nishikata, Y. Yamamoto and N. Miyaura, *Organometallics*, 2004, **23**, 4317–4324; X. Lu and S. Lin, *J. Org. Chem*., 2005, **70**, 9651–9653; F. Gini, B. Hessen and A. J. Minnaard, *Org. Lett*., 2005, **7**, 5309–5312; T. Yamamoto, M. Iizuka, T. Ohta and Y. Itoh, *Chem. Lett*., 2006, **35**, 198–199; P. He, Y. Lu, C.-G. Dong and Q.-S. Hu, *Org. Lett*., 2007, **9**, 343–346.
25. K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett*., 2007, **9**, 1541–1544.

26. H. Kinoshita, H. Shinokubo and K. Oshima, *J. Am. Chem. Soc.*, 2003, **125**, 7784–7785.
27. S. Ogoshi, T. Yoshida, T. Nishida, M. Morita and H. Kurosawa, *J. Am. Chem. Soc.*, 2001, **123**, 1944–1950; J. A. Marshall, M. Herold, H. S. Eidam and P. Eidam, *Org. Lett.*, 2006, **8**, 5505–5508; B. A. Grisso, J. R. Johson and P. B. Mackenzie, *J. Am. Chem. Soc.*, 1992, **114**, 5160–5165; S. Ikeda and Y. Sato, *J. Am. Chem. Soc.*, 1994, **116**, 5975–5976.
28. N. J. Bell, A. J. Cox, N. R. Cameron, J. S. O. Evans, T. B. Marder, M. A. Duin, C. J. Elsevier, X. Baucherel, A. A. D. Tulloch and R. P. Tooze, *Chem. Commun.*, 2004, 1854–1855; G. W. Kabalka, B. C. Das and S. Das, *Tetrahedron Lett.*, 2002, **43**, 2323–2325; H. Ito, H. Yamanaka, J. Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 2000, **41**, 6821–6825; K. Takahashi, T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2001, **625**, 47–53; S. Mun, J. E. Lee and J. Yun, *Org. Lett.*, 2006, **8**, 4887–4889.
29. K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2007, **9**, 5031–5033.
30. K. Hirano, H. Yorimitsu and K. Oshima, in *Electronic Encyclopedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, P. L. Fuchs, D Crich and G. A. Molander, John Wiley and Sons, 2008, DOI: 10.1002/047084289X.rn00813; J. Hermanns and B. Schmidt, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2209–2230.
31. D. R. Weyneberg and L. E. Nelson, *J. Org. Chem.*, 1965, **30**, 2618–2621; H. Yamashita, M. Tanaka and K. Honda, *J. Am. Chem. Soc.*, 1995, **117**, 8873–8874.
32. H. Sakurai and T. Imai, *Chem. Lett.*, 1975, 891–894; Y. Takeyama, K. Nozaki, K. Matsumoto, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1461–1466; T. Tanaka, H. Yamashita, S. Shimada and M. Tanaka, *Organometallics*, 1997, **16**, 3246–3248; Y. Tanaka, H. Yamashita and M. Tanaka, *Organometallics*, 1996, **15**, 1524–1526; Y. Tanaka and M. Yamashita, *Appl. Organomet. Chem.*, 2002, **16**, 51–54; B. P. S. Chauhan, Y. Tanaka, H. Yamashita and M. Tanaka, *Chem. Commun.*, 1996, 1207–1208; Y. Tanaka, A. Nishigaki, Y. Kimura and M. Yamashita, *Appl. Organomet. Chem.*, 2001, **15**, 667–670; N. P. Reddy, T. Hayashi and M. Tanaka, *Chem. Commun.*, 1996, 1865–1866.
33. K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2006, **8**, 483–485.
34. F. Kakiuchi, Y. Tanaka, N. Chatani and S. Murai, *J. Organomet. Chem.*, 1993, **456**, 45–47; Y. Seki, K. Takeshita, K. Kawamoto, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 928; K. Takeshita, Y. Seki, K. Kawamoto, S. Murai and N. Sonoda, *J. Org. Chem.*, 1987, **52**, 4864–4868; F. Kakiuchi, K. Nogami, N. Chatani, Y. Seki and S. Murai, *Organometallics*, 1993, **12**, 4748–4750; R. Takeuchi and H. Yasue, *Organometallics*, 1996, **15**, 2098–2102.
35. K. Hirano, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2007, **129**, 6094–6095.
36. S. E. Denmark and S. A. Tymonko, *J. Am. Chem. Soc.*, 2005, **127**, 8004–8005.