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Synthesis of a new class of bidentate Lewis acids based on boronic esters and zirconocene

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Abstract

Hydrozirconation of various alkenylboronic esters **1** with $H(Cl)ZrCp_2$ produces a new class of bidentate Lewis acids as crystalline solids or oils, **2**, in 81–96% yield. Products **2** were characterized by IR, NMR, and in selected cases elemental analysis.

Key words: Boron; Zirconium; Alkenylboronic ester; Bimetallics; Diastereoselective hydrozirconation; Hydroboration

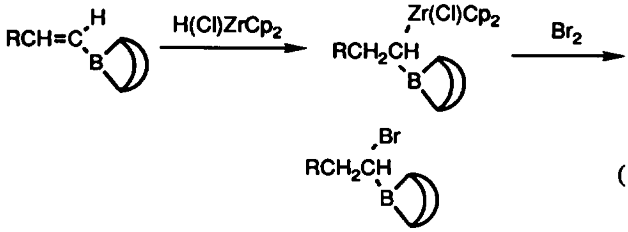
1. Introduction

Interest has been growing in the synthesis of organozirconium compounds as a result of recent reports of their applications in bond-breaking reactions [1], insertion reactions [2], conjugate additions [3], olefin cross-coupling reactions [4], Grignard-type additions [5], and especially in their potential applications as catalysts for stereo- or regio-selective polymerization of olefins [6].

1,1-Bimetallics of transition metals are well known to serve a wide range of applications [7] towards organic synthesis. However, the chemistry of 1,1-bimetallics containing zirconium has not been extensively studied, and only a few cases have been reported, including zirconium with zinc [4b,4e] as well as aluminium [4b–d]. Examples of the use of boron in organic synthesis are legion [8]. In order to extend organozirconium-boron chemistry, it would be of great value to develop a novel class of 1,1-bimetallics based on zirconium and boron. Since both zirconium and boron are Lewis acids, it is reasonable to expect that zirconium and boron bimetallics could be potentially applied in organic synthesis as stoichiometric reagents and in polymerization of olefins as Lewis acid catalysts.

2. Results and discussion

We recently reported that zirconium-boron bimetallic reagents prepared by hydrozirconation of various alkenyl-9-BBN derivatives were selectively cleaved with bromine to furnish α-bromo-9-BBN derivatives (eqn. (1)) [9].



(1)

While this route offers a method for preparation of the bimetallics based on zirconium and trialkylboranes, it suffers from the poor stability of these bimetallics. Thus these compounds are not only sensitive to moisture and oxygen, but decompose fairly rapidly in $CDCl_3$. Efforts to characterize and determine the structure of these bimetallics were unsuccessful. To achieve the successful application of the bimetallics in chemistry, it is essential to develop a new type of bimetallics with high thermal stability and better chemical properties. Oxygenated boranes are more stable than trialkylboranes, more readily available and are synthetically more useful. In our continuing studies of the synthesis and utility of bimetallic reagents, we therefore began to

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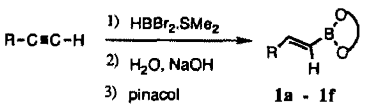
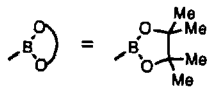
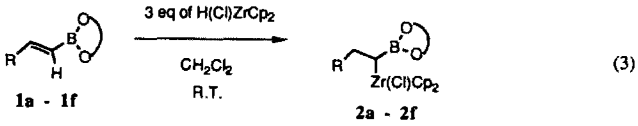


1a - 1f



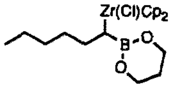
1a: R = n-Bu; 78%
1b: R = $(CH_2)_3Cl$; 73%
1c: R = $CH(CH_3)CH_2CH_3$; 65%
1d: R = $CH(CH_2)_4$; 67%
1e: R = t-Bu; 63%
1f: R = $(CH_2)_3Ph$; 64%



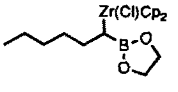
1a - 1f

2a - 2f

2a: R = n-Bu
2b: R = $(CH_2)_3Cl$
2c: R = $CH(CH_3)CH_2CH_3$
2d: R = $CH(CH_2)_4$
2e: R = t-Bu
2f: R = $(CH_2)_3Ph$



3a



3b

Scheme 1.

synthesize these types of compounds based on boronic esters and zirconocene with the aim of achieving better thermal stability and chemical properties. Herein we describe the synthesis of a new class of relatively stable bidentate Lewis acids based on boronic esters and zirconocene (Scheme 1).

The (E)-alkenylboronic esters (**1**) were prepared by hydroboration [10] of alkynes with $HBBr_2 \cdot Me_2S$ followed by the conversion of the intermediate dibromoboronic esters to the corresponding alkenylboronic acids by esterification with diols (eqn. (2)). The bimetallics **2** were synthesized in 81–96% yield by hydrozirconation [11] of the resulting esters **1** with 3 equiv of $Cp_2Zr(H)Cl$ [12] using CH_2Cl_2 as solvent (eqn. (3)). As expected, these bimetallics based on boronic esters are fairly stable, and can be kept for seven days in $CDCl_3$ with no significant changes in their ^1H NMR spectra. The result of the synthesis of a series of bidentate compounds are summarized in Table 1. It is of interest to note that compound **2b** and **2e** appear as yellow crystalline solids which are stable even in dry air for a couple of days. The remaining compounds are green oils.

Monitoring the hydrozirconation process (eqn. (3)) by ^1H NMR, we found that one equivalent of $Cp_2Zr(H)Cl$ did not fully consume the alkenylboronic esters **1**. To complete hydrozirconation, 3 equiv of $Cp_2Zr(H)Cl$ were required. We consider that this is probably due to the coordination of $Cp_2Zr(H)Cl$ with the two oxygens in the boronic ester. Also coordination may be the reason why hydrozirconation of alkenylboronic esters is considerably slower than hydroboration of alkenyl-9-BBN derivatives [9].

Compound **3a** (Scheme 1) was unambiguously characterized by ^1H-^1H double quantum filtered COSY, and ^{13}C-^1H heteronuclear chemical shift correlation NMR spectroscopy [13]. The NMR study accurately showed that the methine proton (δ, 1.86 ppm) was attached to the α-carbon, and that two protons (δ, 1.96, 1.39 ppm) were attached to the β-carbon, which indicated that the zirconium atom was placed on the terminal carbon of the alkenyl chain in the hydrozirconation step. Furthermore, bromination *in situ* was carried out and the reaction mixture was analyzed by GC-MS before work-up. The only major peak in the spectra was α-bromoboronic ester (> 98% yield). No

TABLE 1. Preparation of bidentate compounds by hydrozirconation of alkenylboronic esters

Entry	R in Alkenyl- boronic ester	Moiety of Ester	Hydrozirconation Time, h	Product	Yield [a] %
1	n-butyl	pinacol	0.7	**2a**	96
2	3-chloropropyl	pinacol	0.7	**2b**	89
3	1-methylpropyl	pinacol	2	**2c**	91
4	cyclopentyl	pinacol	2	**2d**	86
5	t-butyl	pinacol	12 [b]	**2e**	81
6	3-phenylpropyl	pinacol	1.5	**2f**	85
7	n-butyl	1,3-propanediol	0.3	**3a**	86
8	n-butyl	ethylene glycol	0.3	**3b**	82

[a] Crude yields, percent based on alkenylboronic ester. Satisfactory spectral data (IR, ^1H-, ^{11}B- and ^{13}C-NMR) were obtained for all compounds.
[b] Reacted at 40°C, 4 equiv of $Cp_2Zr(H)Cl$ required.

alkene or bromoboronic ester were detected. The latter would be the expected products of β-elimination of β-bromoboranes from bimetallics if zirconium had added to the β-caron in hydrozirconation step. Therefore, hydrozirconation of these alkenylboronic esters is assumed to be regiospecific.

A solvent study showed that there was no hydrozirconation of alkenylboronic ester with $Cp_2Zr(H)Cl$ in hexanes. In diethyl ether, the reaction was extremely slow and incomplete. Both THF and benzene are suitable solvents for hydrozirconation of alkenylboronic esters. However, whereas hydrozirconation of **1a** in CH_2Cl_2 required 40 min at 25°C, the reaction took 1 h in THF and 4 h in benzene under the same conditions with 3 equiv of $Cp_2Zr(H)Cl$. CH_2Cl_2 appears to be the solvent of choice for hydrozirconation of 1-alkenylboronic esters, which is consistent with recent reports [2e,4e,5,14].

We have also investigated the effect of the ester moiety in **1**. We have found that hydrozirconation of 1-hexenyl-1,3,2-benzodioxaborole with $Cp_2Zr(H)Cl$ gave complex products. Hydrozirconation of 1,3-propanediol 1-hexenylboronate and ethylene glycol 1-hexanylboronate occurred smoothly, and was faster than the pinacol counterpart **1a**. The reactions were completed in 15 min at ambient temperature, and gave the corresponding, specific bidentate products **3a**, **3b** (Scheme 1). These products, however, were less stable than complex **2a**. They decomposed in $CDCl_3$ within one day. The ester moiety therefore influences both the rate of hydrozirconation and the stability of the products. The alkenylboronate with the substituted ester ring underwent relatively slow hydrozirconation, but the products are more stable apparently due to steric hindrance.

In conclusion, we have synthesized a novel class of bidentate compounds. The further synthetic scope of these compounds is under investigation in our laboratories.

3. Experimental section

3.1. General comments

All reactions were carried out under argon. Solvents were freshly distilled from the appropriate drying agent (CH_2Cl_2, CaH_2; THF, sodium and benzophenone; diethyl ether, sodium and benzophenone; hexanes, sodium; benzene, sodium). All reagents were obtained from Aldrich Chemical Co. with exception of the alkynes which were obtained from Lancaster, and used after distillation from CaH_2. $Cp_2Zr(Cl)H$ was prepared as described in ref. 12.

The NMR solvent $CDCl_3$ was dried over CaH_2. All NMR spectra were taken on a Varian VXR-400. ^1H NMR spectra operated at 400 MHz, ^{13}C NMR spectra at 100.6 MHz, ^{11}B NMR spectra at 128.3 MHz. All chemical shifts were references to residual proton or carbon signals in the deuterated solvent (^1H and ^{13}C NMR) or to external boron trifluoride dimethyl etherate (^{11}B NMR). Infrared spectra were obtaining using a Nicolet Model 60SX spectrometer. Elemental analyses were performed in a Perkin-Elmer Model 2400 CHN.

3.2. General preparation of alkenylboronic esters

The following procedure, given for the preparation of (E)-pinacol 1-hexenylboronate (**1a**) is representative of the general procedure used to synthesize alkenylboronic esters. Yields for each compounds are given in Scheme 1.

A dried reaction flask fitted with a septum inlet and stirring bar was charged under argon with 1-hexyne (3.30 g, 40 mmol) in dry CH_2Cl_2 (20 ml) and cooled to 0°C. A 3.2 M solution of $HBBr_2 \cdot Me_2S$ in CH_2Cl_2 (15 ml, 40 mmol) was then added. The reaction mixture was stirred for 3 h at room temperature and poured into a mixture of ice (200 g) and NaOH (4.0 g, 100 mmol) and stirred for 3 min. Ethyl acetate (100 ml) was added and aqueous layer was washed with ethyl acetate (2 × 75 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was dissolved in ethyl ether (40 ml) and hexanes (10 ml), and stirred for 1 h with pinacol (5.67 g, 48 mmol) and $MgSO_4$ (10 g). Water (40 ml) was added, and stirred for 2 min. After separation, organic layer was evaporated off the solvents. The crude oil was distilled under vacuum affording pure **1a** (6.55 g, 78%).

3.3. General preparation of 1,1-bimetallics 2 and 3

The following procedure, given for the preparation of compound **2a**, is a typical procedure used to synthesize 1,1-bimetallics based on zirconocene and boronic esters. Details of reaction times, reaction temperatures, number of equiv of $Cp_2Zr(H)Cl$ required, and yields for each compounds are given in Scheme 1 and Table 1.

A suspension of 0.350 g (1.36 mmol) of $H(Cl)ZrCp_2$ in 2.8 ml of dry CH_2Cl_2 was stirred at ambient temperature under an atmosphere of argon. A 0.9 ml of 0.5 M solution of (E)-pinacol 1-hexenylboronate (**1a**) (0.45 mmol) in CH_2Cl_2 was then added. The reaction mixture was stirred for 40 min, and became a clear green-yellow solution. Evaporation of the solvent gave a yellow oil-solid mixture. Dry hexanes (4 × 6 ml) were added to extract the resulting mixture. Pumping off the hexanes from the filtrate afforded green oil of **2a** (0.203 g, 96%).

Data for **2a**: green oil; IR (neat) 3114, 2977, 2958, 2927, 2856, 1443, 1347, 1308, 1268, 1238, 1216, 1146, 1019, 967, 891, 812, 737, 606, 465 cm^{-1}. ^{1}H NMR δ 0.82 (t, 3H), 0.86–0.98 (m, 1H), 1.02–1.19 (m, 4H), 1.20 (s, 6H), 1.23 (s, 6H), 1.29–1.36 (m, 1H), 1.44–1.50 (m, 1H), 1.93 (d, 1H), 1.98–2.06 (m, 1H), 6.29 (s, 5H), 6.35 (s, 5H); ^{11}B NMR δ 33.7; ^{13}C NMR δ 14.03, 22.61, 24.55, 25.15, 31.61, 33.97, 34.10, 61.52–62.26 (broad, weak), 81.41, 112.20, 113.23. Anal. Calcd. for $C_{22}H_{34}BClO_2Zr$: C, 56.45; H, 7.34. Found: C, 56.39; H, 7.49%.

Data for **2b**: yellow crystal; mp 122–125°C (sealed); IR (KBr) 3114, 2975, 2934, 2858, 2362, 1455, 1441, 1380, 1345, 1322, 1308, 1279, 1260, 1223, 1144, 1017, 969, 882, 812, 754, 702, 460 cm^{-1}. ^{1}H NMR δ 1.02–1.12 (m, 1H), 1.21 (s, 6H), 1.24 (s, 6H), 1.25–1.30 (m, 1H), 1.48–1.58 (m, 1H), 1.64–1.72 (m, 2H), 1.95 (d, 1H), 2.05–2.16 (m, 1H), 3.46 (t, 2H), 6.31 (s, 5H), 6.37 (s, 5H); ^{11}B NMR δ 33.6; ^{13}C δ 24.67, 25.32, 31.58, 32.38, 33.21, 45.38, 60.02–60.90 (broad, weak), 81.64, 112.38, 113.46.

Data for **2c**: green oil; IR (neat) 3114, 2975, 2960, 2931, 2871, 1480, 1461, 1443, 1370, 1354, 1343, 1269, 1235, 1216, 1187, 1144, 1110, 1071, 1019, 969, 880, 814, 739, 673, 608, 579, 448 cm^{-1}. ^{1}H NMR δ 0.69 (d, 3H), 0.77 (t, 3H), 1.21 (d, 6H), 1.23 (s, 6H), 1.34–1.40 (m, 1H), 1.55–1.62 (m, 1H), 1.79–1.92 (m, 2H), 1.99–2.11 (m, 2H), 6.30 (d, 5H), 6.36 (d, 5H); ^{11}B NMR δ 33.5; ^{13}C NMR δ 11.52, 11.76, 18.91, 19.34, 24.67, 24.75, 25.16, 25.22, 28.91, 29.31, 38.85, 39.19, 39.86, 40.34, 58.60–59.51 (broad, weak), 81.48, 112.11, 112.19, 113.28.

Data for **2d**: green oil; IR (neat) 3110, 2977, 2948, 2865, 1482, 1466, 1443, 1378, 1353, 1341, 1310, 1269, 1243, 1216, 1200, 1144, 1104, 1019, 969, 882, 810, 739, 670, 604, 579, 477 cm^{-1}. ^{1}H NMR δ 0.89–0.98 (m, 1H), 1.01–1.09 (m, 1H), 1.21 (s, 6H), 1.24 (s, 6H), 1.35–1.45 (m, 3H), 1.56–1.68 (m, 5H), 1.99 (d, 1H), 2.03–2.11 (m, 1H), 6.30 (s, 5H), 6.36 (s, 5H); ^{11}B NMR δ 33.7; ^{13}C NMR δ 24.73, 24.77, 25.10, 25.15, 31.82, 32.62, 39.51, 44.39, 60.51–61.22 (broad, weak), 81.49, 112.15, 113.28.

Data for **2e**: yellow crystal; mp 130–134°C (sealed); IR (KBr) 3123, 2985, 2962, 2946, 2906, 2883, 2863, 2838, 1476, 1441, 1389, 1378, 1349, 1312, 1291, 1279, 1268, 1235, 1215, 1198, 1144, 1106, 1017, 969, 880, 937, 812, 675 cm^{-1}. ^{1}H NMR δ 0.73 (s, 9H), 1.21 (s, 6H), 1.23 (s, 6H), 1.59 (d, 1H), 1.92 (m, 1H), 2.02 (d, 1H), 6.31 (s, 5H), 6.38 (s, 5H); ^{11}B NMR δ 31.1; ^{13}C NMR δ 24.92, 25.19, 28.96, 33.93, 46.01, 55.02–55.98 (broad, weak), 81.51, 112.06, 113.34. Anal. Calcd for $C_{22}H_{34}BClO_2Zr$: C, 56.45; H, 7.34. Found: C, 56.29; H, 7.52%.

Date for **2f**: green oil; IR (neat) 3109, 3087, 2979, 2931, 2856, 1506, 1453, 1441, 1378, 1347, 1308, 1248, 1213, 1144, 1019, 973, 843, 832, 814, 751, 729, 700 cm^{-1}. ^{1}H NMR δ 0.94–1.05 (m, 1H), 1.16 (s, 6H), 1.20 (s, 6H), 1.22–1.27 (m, 1H), 1.46–1.56 (m, 3H), 1.96 (d, 1H), 2.02–2.13 (m, 1H), 2.52 (t, 2H), 6.29 (s, 5H), 6.34 (s, 5H), 7.10–7.16 (m, 3H), 7.21 -7.26 (m, 2H); ^{11}B NMR δ 33.5; ^{13}C NMR δ 24.57, 25.11, 31.16, 33.92, 34.06, 35.87, 60.57–60.98 (broad, weak), 81.45, 112.26, 113.29, 125.26, 128.00, 128.39, 143.05.

Data for **3a**: yellow crystal; decomposes at 96°C; IR (KBr) 3115, 3099, 2952, 2925, 2892, 2871, 2854, 1452, 1407, 1326, 1292, 1260, 1239, 1208, 1179, 1128, 1017, 830, 805, 751, 668 cm^{-1}. ^{1}H NMR δ 0.84 (t, 3H), 0.90–0.98 (m, 1H), 1.02–1.10 (m, 1H), 1.11–1.28 (m, 4H), 1.35–1.43 (m, 1H), 1.84–1.90 (m, 3H), 1.91–2.02 (m, 1H), 3.99 (t, 4H), 6.28 (s, 5H), 6.32 (s, 5H); ^{11}B NMR δ 30.5; ^{13}C NMR δ 14.15, 22.70, 28.06, 31.85, 33.15, 34.12, 61.33, 66.62–67.42 (broad, weak), 112.16, 113.11. Anal. Calcd. for $C_{19}H_{28}BClO_2Zr$: C, 53.57; H, 6.64. Found: C, 53.26; H, 6.76%.

Data for **3b**: green oil; IR (neat) 3106, 2958, 2927, 2873, 2857, 1638, 1482, 1437, 1397, 1376, 1339, 1300, 1269, 1243, 1214, 1169, 1021, 946, 807, 774, 668, 475, 428 cm^{-1}; ^{1}H NMR δ 0.77 (t, 3H), 0.86–0.96 (m, 1H), 0.99–1.28 (m, 5H), 1.38–1.46 (m, 1H), 1.92–1.98 (m, 2H), 4.03 (s, 4H), 6.22 (s, 5H), 6.26 (s, 5H); ^{11}B NMR δ 34.5; ^{13}C NMR δ 14.13, 22.68, 31.76, 33.93, 34.36, 58.46–59.31 (broad, weak), 64.76, 112.36, 113.44.

Acknowledgments

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References

1 (a) D.W. Hart and J. Schwartz, *J. Am. Chem. Soc., 96* (1974) 8115; (b) T.F. Blackburn, J.A. Labinger and J. Schwartz, *Tetrahedron Lett., 16* (1975) 3041; (c) C.A. Bertelo and J. Schwartz, *J. Am. Chem. Soc., 98* (1976) 262.

2 (a) M. Kubora and D.M. Blake, *J. Am. Chem. Soc., 93* (1971) 1368; (b) C.A. Bertelo and J. Schwartz, *J. Am. Chem. Soc., 97* (1975) 228; (c) T. Matsumoto, M. Katsuki and K. Suzuki, *Tetrahedron Lett., 29* (1988) 6935; (d) T. Matsumoto, T. Hosoya and K. Suzuki, *J. Am. Chem. Soc., 114* (1992) 3568; (e) P. Wipf and W.J. Xu, *J. Org. Chem., 58* (1993) 825.

3 (a) J. Schwartz, M.J. Loots and H. Kosugi, *J. Am. Chem. Soc., 102* (1980) 1333; (b) B.H. Lipschutz and E.L. Ellsworth, *J. Am. Chem. Soc., 112* (1990) 7440.

4 (a) E. Negishi and D.E. Van Horn, *J. Am. Chem. Soc., 99* (1977) 3168; (b) F.W. Hartner and J. Schwartz, *J. Am. Chem. Soc., 103* (1981) 4979; (c) T. Yashida and E. Negishi, E. *J. Am. Chem. Soc., 103* (1981) 1276; (d) F.W. Hartner, J. Schwartz and S.M. Clift, *J. Am. Chem. Soc., 105* (1983) 640; (e) C.E. Tucker and P. Knochel, *J. Am. Chem. Soc., 113* (1991) 9888.

5 (a) H. Maeta, T. Hashimoto, T. Hasegawa and K. Suzuki, *Tetrahedron Lett., 33* (1992) 5965; (b) H. Maeta and K. Suzuki, *Tetrahedron Lett., 33* (1992) 5969.

6 (a) H. Sin and W. Kaminsky, *Adv. Organomet. Chem., 18* (1980) 99; (b) G. Erker, *Pure Appl. Chem., 63* (1991) 797; (c) J. Chowdhury and S. Moore, *Chem. Engineering*, (1993) April 34.

7 (a) S.M. Clift and J. Schwartz, J. *J. Am. Chem. Soc., 106* (1984) 8300; (b) T. Kaufmann, T. Moller, H. Rennefeld, S. Welke and R. Wieschollek, *Angew. Chem. Int. Ed. Engl., 24* (1985) 368; (c) L.R. Gilliom and R.H. Grubbs, *J. Am. Chem. Soc., 108* (1986) 733; (d) A. Aguero, J.A. Kress and J.A. Osborn, *J. Chem. Soc., Chem. Commun.*, (1986) 531; (e) P. Knochel and J.F. Normant, *Tetrahedron Lett., 27* (1986) 4431; (f) J.R. Wass, A.R. Sidduri and P. Knochel, *Tetrahedron Lett., 33* (1992) 3717; (g) L. Labaudiniere, J. Hanaizi and J.F. Normant, *J. Org. Chem., 57* (1992) 6903; (h) C.E. Tucker and P. Knochel, *Synthesis*, (1993) 530.

8 A. Pelter, K. Smith and H.C. Brown, In *Borane Reagents*, Academic Press, London, 1988.

9 B. Zheng and M. Srebnik, *Tetrahedron Lett., 34* (1993) 4133.

10 (a) H.C. Brown and H. Ravindran, *Inorg. Chem., 16* (1977) 2938; (b) H.C. Brown and J.B. Campbell Jr., *J. Org. Chem., 45* (1980) 384; (c) H.C. Brown and J. Chandrasekharan, *J. Org. Chem., 48* (1983) 644.

11 (a) J. Schwartz and J.A. Labingert, *Angew. Chem. Int. Ed. Engl., 15* (1976) 333; (b) J. Schwartz, *Pure Appl. Chem., 52* (1980) 733; (c) U.M. Dzhemilev, O.S. Vostrikova and A.G. Ibragimov, *Russian Chem. Rev., 55* (1985) 66; (d) E. Negishi and T. Takahashi, *Synthesis*, (1988) 1; (e) S.L. Buchwald and R.B. Nielsen, *Chem. Rev., 88* (1988) 1047.

12 S.L. Buchwald, S.J. LaMaire, R.B. Nielsen, B.T. Watson and S.M. King, *Tetrahedron Lett., 28* (987) 3895.

13 B.V. Cheesman, B. Zheng and M. Srebnik, The details of these results will be published separately.

14 H. Maeta and K. Suzuki, *Tetrahedron Lett., 34* (1993) 341.