Note

Palladium-catalyzed novel addition–elimination reaction of alkenyltin reagents to norbornene

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The present letter is dedicated to Professor J.P. Genêt on the occasion of his 60th birthday

Abstract

Palladium-catalyzed reaction between 1-alkenyltin trichlorides and norbornene resulted in stereoselective formation of 3-alkylidenepentacyclo[9.2.1.^{5,8}1.^{1,11}0.^{2,10}0^{4,9}]pentadecane instead of an expected simple alkenylstannylation product. Generation of trichlorostannane and its decomposition product, tin(II) chloride, was confirmed by trapping it with methyl propiolate and norbornene and analysis of the reaction by ^{119}Sn NMR, respectively.
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We have recently developed carbostannylation reactions of norbornene using aryltin trichlorides and a combination of allylic halides and tin(II) chloride [1–3]. The reaction of the former reagent afforded a mixture of the product with one norbornene moiety (**1**) and that with two norbornene moieties (**2**), while that of the latter gave the adduct with one norbornene, exclusively. The product ratio between **1** and **2** showed a certain level of dependence on electronic character of the aromatic substituent. Namely, the more the aromatic substituent possesses electron-releasing character, the higher the proportion of the product **2** was. That result suggests that sp^2 carbon attached directly to the norbornene ring carbon adjacent to that the tin moiety is attached to played an important role in the production of the adduct **2** [4]. Thus we next examined the reaction between 1-alkenyltin trichloride and norbornene (Eq. (1)).


(1)
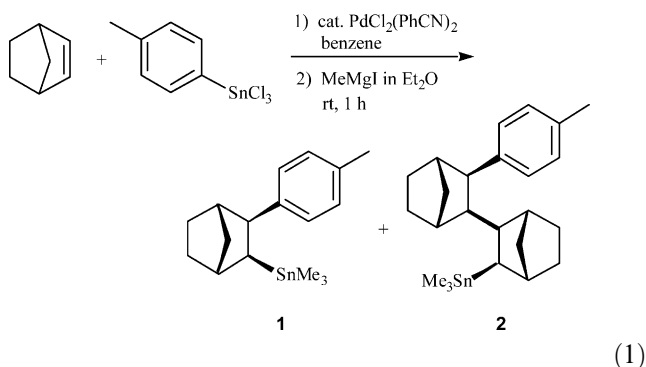
To our surprise, the sole product obtained by the reaction did not contain tin atom, at all. The structure of the product obtained by the reaction of in situ generated 2-phenylethenyltin trichloride was exactly the same as that obtained by Catellani's Mizoroki–Heck reaction between 2-phenylethenyl bromide and norbornene (Eq. (2)) [5].

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(2)

Scheme 1. A plausible reaction pathway.
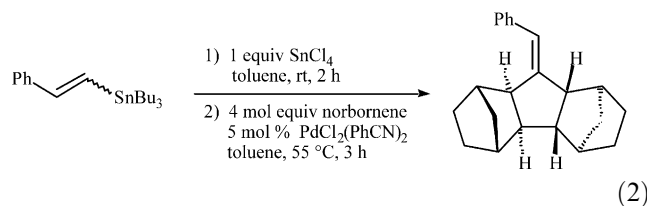
Our representative results are summarized in Table 1. A typical experiment was performed as follows: to a toluene solution (2.5 cm^3) of norbornene (1.5 mmol) and dichlorobis(benzonitrile)palladium (2.5×10^{-2} mmol) was added 1-propenyltin trichloride (0.5 mmol). The resulting brown colored solution was stirred at 55 °C for 2 h. Then, the reaction became a dark gray suspension. It was poured into water and the crude product was extracted by ether. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo (Table 1, run 1). The product was purified by silica gel column chromatography using hexane as an eluent.

All the reactions were perfectly stereoselective, giving *exo*-*exo*-*cis*-*trans*-*cis* isomers, exclusively. No other isomers were detected, at all, in any case.

The reaction pathway could be interpreted as depicted in Scheme 1. The reaction proceeds via oxidative addition of alkenyltin reagent to a catalytic palladium(0) species [6,7]. Subsequent norbornene insertion step appears to conform to carbopalladation, instead of stannylpalladation, to generate the key-intermediate **A**, stereoselectively. In the case of allylstannylation, reductive elimination took place from **A** to give the carbostannylation product, probably because the intermediate that corresponds to complex **A** is so labile owing to inefficient coordination by π-bond of the allylic moiety and β-hydride-elimination is not accessible [1,3]. The above mentioned product ratio of the arylstannylation would indicate that its π-system plays an important role in making the insertion of the second norbornene [2–4]. In the present reaction, however, none of the corresponding alkenylstannylation products were detected, at all, probably because efficient coordination of the
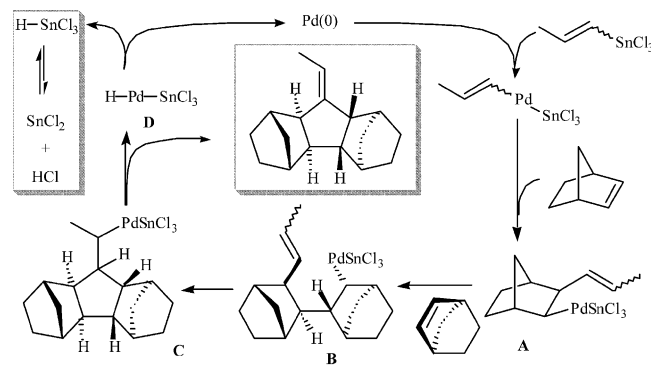
alkene π-bond strongly supports the complex **A** (as well as **B**). The second norbornene insertion undergoes regio- as well as stereoselectively to give **B**, being suffered from the minimum steric hindrance. Now the geometrical arrangement of palladium and carbon–carbon double bond is suitable for intramolecular carbopalladation to generate **C**, which is furnished with a five-membered ring, from which β-hydride-elimination affords the product and hydridopalladium trichlorostannate **D**. Finally, reductive elimination regenerates the catalytic palladium(0) species. We employed a palladium(II) species instead of palladium(0) complexes as a catalyst precursor, because readily available palladium(0) complexes like its phosphine complex and dba complex did not give good results, due to their ligands that disturb the reaction.

This process should discharge trichlorostannane. Thus, we attempted to detect it. After the reaction described as run 3 in Table 1 was completed, the reaction mixture was taken ^{119}Sn NMR to detect an only singlet at δ −205.0 ppm. The signal was assigned to that of tin(II) chloride. THF solution of tin(II) chloride showed a singlet at −209.0 ppm. The deviation was attributed to the existence of a small amount of hydrogen chloride in the reaction mixture. Trichlorostannane has been reported to exist in equilibrium with

Table 1
Palladium-catalyzed reaction between 1-alkenyltin trichloride and norbornene

| Run	1-Alkenyltin reagent	Norbornene/mol. equiv.	Solvent	Temperature (°C)	Time (h)	Yield [a] (%)
1	MeCH=CH−SnCl$_3$	3	Toluene	55	2	73
2	CH$_2$=CH−SnCl$_3$	3	Benzene	55	2	58
3		6	THF	55	5.5	42
4		6	THF	55	22	52
5		6	Et$_2$O	r.t.	16.5	66
6		6	Hexane	r.t.	18.5	Trace
7 [b]	PhCH=CH−SnCl$_3$	4	Benzene	55	10	50
8 [b]	MeOCOCH=CH−SnCl$_3$	6	Et$_2$O	r.t.	22.5	–
9 [b]		6	Benzene	r.t.	17	27

[a] Isolated yields.
[b] The reagent was generated in situ from the corresponding tributyltin reagent by the treatment with 1 mol equiv. of tin(IV) chloride at r.t. for 2 h and used, directly.

Table 2
^{119}Sn NMR of SnCl$_2$ in the presence of HCl

Run	HCl (mol. equiv.)	δ (ppm)
1	0.0	-209
2	0.03	-207
3	0.3	-201
4	2.0	-15

tin(II) chloride and hydrogen chloride [8]. As shown in Table 2, the ^{119}Sn NMR chemical shift depends highly on the coexistence of hydrogen chloride, probably due to the equilibrium. According to Table 2, only a small amount of hydrogen chloride remained in the above reaction. Although hydrogen chloride should be evolved in an equimolar amount to tin(II) chloride, most of it would have been released from the solution during the course of the reaction.

We next tried to detect trichlorostannane by generation of an alkenylstannane. Trichlorostannane adds to the carbon–carbon triple bond of methyl propiolate to give the corresponding alkenyltin trichloride **3** (Eq. (3)) [8]. We therefore employed the present reaction to detect the adduct by formation of **5** (Eq. (4)). The expected product **5** was obtained in 25% yield, based on the yield of **4**. The low yield would presumably be because the reaction of methyl 3-trichlorostannylacrylate is somewhat inherently inefficient (Table 1, runs 8 and 9). Thus, the result would still support our hypothesis, sufficiently.

$$(3)$$

$$(4)$$
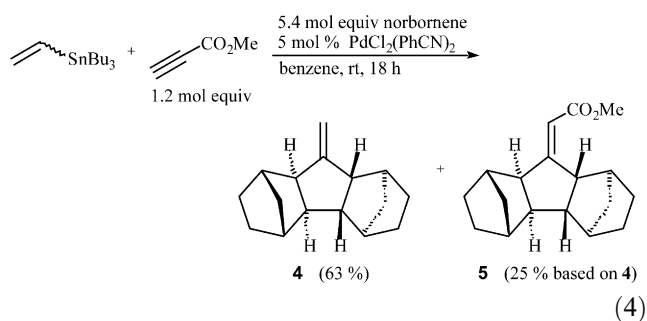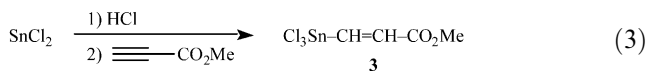
The reaction can be classified as a metallo-Mizoroki–Heck-type reaction [9–16]. This type of reaction usually requires an oxidant to achieve a catalytic system. Oxidant-free system as the present system is quite unusual in this protocol [17–20]. The reaction proceeds faster and at lower temperature than Catellani's Mizoroki–Heck reaction [5]. This would suggest that trichlorostannyl group may be a better leaving group than bromide, which is an ordinary leaving group in the Mizoroki–Heck reaction. Furthermore, the combination of Eqs. (3) and (4) suggests the possibility of a catalytic use of SnCl$_2$ for the present reaction, provided that regenerated trichlorostannane can be effectively recycled. Utility of organotin trichloride toward the Mizoroki–Heck reaction is under investigation.

Acknowledgements

References

[1] K. Fugami, T. Enokido, K. Kawata, M. Kameyama, M. Kosugi, Main Group Met. Chem. 22 (1999) 511.
[2] K. Fugami, Y. Mishiba, S. Hagiwara, D. Koyama, M. Kameyama, M. Kosugi, Synlett (2000) 553.
[3] K. Fugami, K. Kawata, T. Enokido, Y. Mishiba, S. Hagiwara, Y. Hirunuma, D. Koyama, M. Kameyama, M. Kosugi, J. Organomet. Chem. 611 (2000) 433.
[4] C.-S. Li, D.-C. Jou, C.-H. Cheng, Organometallics 12 (1993) 3945.
[5] M. Catellani, G.P. Chiusoli, P. Sgarabotto, J. Organomet. Chem. 240 (1982) 311.
[6] J.W. Labadie, J.K. Stille, J. Am. Chem. Soc. 105 (1983) 6129.
[7] E. Shirakawa, H. Yoshida, T. Hiyama, Tetrahedron Lett. 38 (1997) 5177.
[8] R.E. Hutton, J.W. Burley, V. Oakes, J. Organomet. Chem. 156 (1978) 369.
[9] N. Tuyet, L. Thi, H. Riviere, J. Chem. Soc. Chem. Commun. (1978) 918.
[10] S. Uemura, M. Wakasugi, M. Okano, J. Organomet. Chem. 194 (1980) 277.
[11] C.S. Cho, K. Itotani, S. Uemura, J. Organomet. Chem. 443 (1993) 253.
[12] K. Hirabayashi, Y. Nishihara, A. Mori, T. Hiyama, Tetrahedron Lett. 39 (1998) 7893.
[13] K. Hirabayashi, J. Ando, Y. Nishihara, A. Mori, T. Hiyama, Synlett (1999) 99.
[14] K. Matoba, S. Motofusa, C.S. Cho, K. Ohe, S. Uemura, J. Organomet. Chem. 574 (1999) 3.
[15] K. Hirabayashi, J. Ando, J. Kawashima, Y. Nishihara, A. Mori, T. Hiyama, Bull. Chem. Soc. Jpn. 73 (2000) 1409.
[16] X. Du, M. Suguro, K. Hirabayashi, A. Mori, T. Nishikata, N. Hagiwara, K. Kawata, T. Okeda, H.-F. Wang, K. Fugami, M. Kosugi, Org. Lett. 3 (2001) 3313.
[17] C.S. Cho, S. Uemura, J. Organomet. Chem. 465 (1994) 85.
[18] M. Lautens, A. Roy, K. Fukuoka, K. Fagnou, B.M. Matute, J. Am. Chem. Soc. 123 (2001) 5358.
[19] A. Mori, Y. Danda, T. Fujii, K. Hirabayashi, K. Osakada, J. Am. Chem. Soc. 123 (2001) 10774.
[20] T. Koike, X. Du, T. Sanada, Y. Danda, A. Mori, Angew. Chem. Int. Ed. 42 (2003) 89.