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Platinum complex catalyzed reaction of tributyltin cyanide with alkynes

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Abstract

In the presence of a catalytic amount (5 mol%) of a platinum complex, tributyltin cyanide (**1**) reacts with dimethyl- (**2a**) or diethyl acetylenedicarboxylate (**2b**) to afford cyanostannylation adducts (**3a, b**) in excellent yields. The reaction proceeds highly selectively affording only a (*Z*)-isomer. The compounds **3a**, **b** are novel products which possess synthetically useful cyano, alkenylstannyl and alkoxycarbonyl functionalities in the same molecule. Two alkoxycarbonyl functionalities may be indispensable on each alkyne carbon to accomplish the cyanostannylation reaction. Reaction with terminal alkynes gave the stannylated product (**6**).

Keywords: Cyanostannylation; Tributyltin cyanide; Transition-metal-complex catalyst; Internal alkyne; Terminal alkyne

1. Introduction

Tributyltin cyanide (Bu_3SnCN, **1**) is a commercially available air and moisture stable reagent. This is in sharp contrast to trimethylsilyl cyanide (Me_3SiCN), which is a useful reagent [1], but easily hydrolyzed to poisonous HCN even in the presence of a small amount of water. Therefore, **1** has been successfully used as a safe cyano source [2] as well as a catalyst [3] in organic synthesis.

On the other hand, much less attention has been paid to cyanostannylation reaction using **1**, in which the stannyl and the cyano functionalities of **1** are introduced simultaneously to unsaturated substrates. Recently, as the first example of cyanostannylation across carbon–carbon unsaturated bonds using **1**, Lukashev reported a reaction of **1** with ynamines [4]. Ynamines were very reactive toward 1 and the reaction proceeded without a catalyst.

We have recently developed transition-metal-catalyzed reactions using Me_3SiCN [5], acylsilanes [6], and acylstannanes [7]. Furthermore, transition metal-catalyzed carbostannylation of alkynes and dienes have been reported by Shirakawa and Hiyama [8]. During the course of these studies, we found **1** is a suitable substrate for catalytic transformations. In this paper we report the first example of transition-metal complex catalyzed cyanostannylation of acetylenedicarboxylate using **1**. The reaction provides cyanostannylated products as a single isomer in high yields at room temperature. Furthermore, terminal alkynes were also reacted with **1** to give stannylated products. All the alkynes used in this study afforded neither cyanostannylated, cyanated, nor stannylated products in the absence of a transition-metal complex catalyst.

2. Results and discussion

2.1. Reaction with dimethyl- or diethyl acetylenedicarboxylate

When **1** was allowed to react with dimethyl acetylenedicarboxylate (**2a**) in the presence of a catalytic amount (5 mol%) of $PtCl_2(PPh_3)_2$ in THF at room temperature, a single cyanostannylation adduct (**3a**) was obtained selectively in nearly quantitative yield (Eq. (1)). Analytically pure product was isolated by column chromatography and was fully characterized by spectro-

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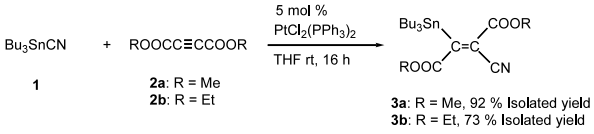
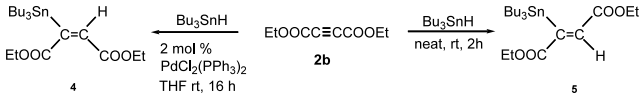
scopic method as well as elemental analysis. Noteworthy is that **3a** is a novel product which possesses synthetically useful cyano, alkenylstannyl and methoxycarbonyl functionalities in the same molecule. Similarly, reaction of **1** with diethyl acetylenedicarboxylate (**2b**) afforded the corresponding cyanostannylated product (**3b**) as a single product in high yield.



(1)

Determination of (*E*) or (*Z*) stereochemistry of the cyanostannylated products (**3a**, **b**) were carried out by comparing ^{13}C-NMR spectra, $^{3}J_{Sn-C}$ in particular, of **3a**, **b** with those of model compounds: **4** for (*E*)-isomer and **5** for (*Z*)-isomer. The model compounds **4** and **5** were prepared by hydrostannylation of **2b** using Bu_3SnH according to the published methods: **4** was obtained in the presence of $PdCl_2(PPh_3)_2$ as a catalyst [9] and **5** was obtained without a catalyst [10] (Eq. (2)). In ^{13}C-NMR spectrum of **4**, the carbonyl carbon *trans* to the Bu_3Sn moiety has $^{3}J_{Sn-C(trans)}$ value of 56 Hz, which is considerably larger than $^{3}J_{Sn-C(cis)}$ value (15 Hz) of the carbonyl carbon *cis* to the Bu_3Sn moiety in ^{13}C-NMR spectrum of **5** (Scheme 1). This difference as well as $^{3}J_{Sn-H(trans\ or\ cis)}$ is most diagnostic to differentiate (*E*) and (*Z*)-isomers of alkenylstannanes [11]. With this consideration in mind, we compared the two $^{3}J_{Sn-C(trans)}$ and $^{3}J_{Sn-C(cis)}$ values of **3a**, **b**. As shown in Scheme 1, the $^{3}J_{C-Sn}$ values of the cyano carbons of **3a**, **b** are 11 Hz, while one of the carbonyl carbons of the alkoxycarbonyl moieties of **3a**, **b** has much smaller $^{3}J_{Sn-C}$ value (<1 Hz). Therefore, in **3a**, **b**, the cyano and the alkoxycarbonyl moieties must be *trans* and *cis* to the Bu_3Sn ((*Z*)-isomer), respectively, as shown in Scheme 1. Note that the J_{Sn-C} values observed with **3a**, **b** are smaller than those with **4** and **5**. It is reported that absolute values of J_{Sn-H} were considerably reduced by introducing electronwithdrawing substituents such as cyano group on olefinic carbon [12]. Actually, $^{1}J_{117Sn-C(olefin)}$ values for **4** and **5** are 210 and 235 Hz, while those for **3a** and **3b** both decreased to 111 and 115 Hz, respectively.

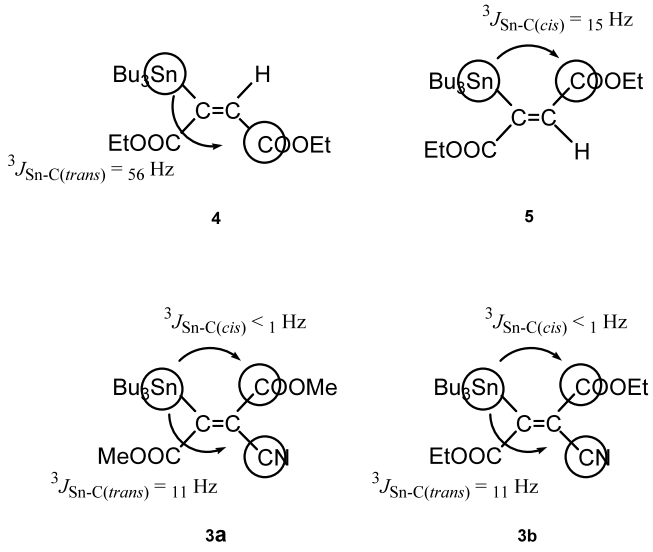


(2)

2.2. Effect of reaction conditions in the cyanostannylation

Effect of catalyst precursors and solvents for the synthesis of **3a** is listed in Table 1. As for a catalyst precursor, $PtCl_2(PPh_3)_2$ in THF showed the best activity (entry 1). The corresponding palladium analogues, $PdCl_2(PPh_3)_2$, showed similar catalytic activity (entry 2). However, other platinum and palladium complexes listed in Table 1 showed much lower activity (entries 3–11). Note that in the absence of a catalyst, the alkynes did not provide any cyanostannylation products at all.

Effect of solvent was examined for the synthesis of **3a** using $PtCl_2(PPh_3)_2$ or $PdCl_2(PPh_3)_2$ as catalyst precursors. Similar solvent effect was observed in each catalyst system. THF gave the best yield (entries 1 and 2), while



Scheme 1.

Table 1
Effect of catalyst precursor and solvent [a]

Entry	Catalyst precursor	Solvent	Yield (%) [b]
1	$PtCl_2(PPh_3)_2$	THF	> 99
2	$PdCl_2(PPh_3)_2$	THF	94
3	$PdCl_2(COD)_2$	THF	47
4	$Pt(CO)_2(PPh_3)_2$	THF	25
5	$Pt(DBA)_2$	THF	19
6	$PdCl_2(PMePh_2)_2$	THF	13
7	$Pd(DBA)_2+4PEt_3$	THF	10
8	$Pd(DBA)_2$	THF	7
9	$Pd(PPh_3)_4$	THF	5
10	$Pd(OAc)_2$	THF	0
11	$PdCl_2$	THF	0
12	$PtCl_2(PPh_3)_2$	DMF	63
13	$PdCl_2(PPh_3)_2$	DMF	50
14	$PtCl_2(PPh_3)_2$	Dioxane	39
15	$PdCl_2(PPh_3)_2$	Dioxane	35
16	$PtCl_2(PPh_3)_2$	Toluene	58
17	$PdCl_2(PPh_3)_2$	Toluene	34
18	$PtCl_2(PPh_3)_2$	CH_2Cl_2	2
19	$PdCl_2(PPh_3)_2$	CH_2Cl_2	4

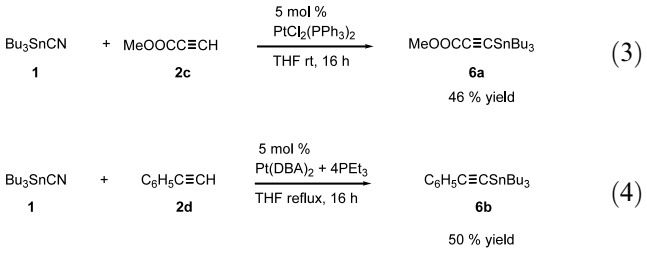
[a] Conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), catalyst precursor (0.05 mmol), and solvent (4.0 ml) at room temperature for 16 h.
[b] Yield of **3a** by GLC.

other solvents such as DMF, dioxane, toluene, and CH_2Cl_2 lowered the yields significantly (entries 12–19).

2.3. Reaction with other internal acetylenes and terminal acetylenes

Nature of substituents on alkynes is of critical importance in determining reactivity of the alkyne in the present reaction. When the reaction was carried out with internal hydrocarbon alkynes such as 4-octyne, 1-phenyl-1-propyne, and diphenylacetylene, conversions of the alkynes were low and no cyanostannylated products were obtained. Two alkoxycarbonyl functionalities may be indispensable on each alkyne carbon like **3a** and **3b** to accomplish the cyanostannylation reaction, since methyl 2-butynoate (only one methoxycarbonyl moiety on the alkyne carbon) and 1,4-diphenyl-2-butyne-1,4-dione (two benzoyl moieties on the alkyne carbons) did not provide any products which contain cyano and/or stannyl moieties.

Reactions of **1** with terminal alkynes were also carried out. When methyl propiolate (**2c**) was employed, stannylated product (**6a**) was obtained in 46% yield using $PtCl_2(PPh_3)_2$ as a catalyst precursor under the standard reaction conditions (Eq. (3)). In this case, no cyanostannylated product was obtained. On the other hand, terminal alkynes without alkoxycarbonyl functionality such as phenylacetylene (**2d**) afforded low yield of stannylated product (**6b**) (yield < 5%) under the standard reaction conditions. However, yield of **6b** increased to 50% when the Pt(0)–PEt_3 catalyst system was employed (Eq. (4)).



3. Conclusions

We successfully demonstrated the new catalytic cyanostannlylation of alkyne with **1**. Nature of substituents on an alkyne affects its reactivity drastically in the present reaction. Highly π-acidic alkynes with two alkoxycarbonyl substituents (**2a**, **b**) are suitable substrates for the cyanostannylation. Thus, in these cases, coordination of the alkynes to the metal center might initiate the catalytic cycle. Then an oxidative addition of **1** to the metal center followed by a reductive elimination affords the cyanostannylation products (**3**) and regenerates the active catalyst species. On the other hand, reaction of terminal alkynes with **1** afforded the stannylated products in moderate yields with proper choice of a platinum catalyst.

4. Experimental

4.1. General

All manipulations were performed under argon atmosphere in conventional Schlenk-type glasswares on a dual-manifold Schlenk line. The reagents and the solvents were dried and purified before use by the usual procedures [13]. Tributyltin cyanide (**1**) was purchased from Aldrich. 1,4-Diphenyl-2-butyne-1,4-dione was prepared according to published method [14]. The following catalyst precursors and complexes were prepared by the published methods: $PtCl_2(PPh_3)_2$ [15], $Pt(CO)_2(PPh_3)_2$ [16], $Pt(DBA)_2$ [17], $PdCl_2(PPh_3)_2$ [18], $PdCl_2(COD)$ [19], $PdCl_2(PMePh_2)_2$ [20], $Pd(DBA)_2$ [21], $Pd(PPh_3)_4$ [22], $Pd(OCOCH_3)_2$ [23]. **6a** [24] and **6b** [25] were identified by comparing their spectral data with reported values.

4.2. Analytical procedures

NMR spectra were recorded on a Bruker ARX-400 (^1H, 400 MHz; ^{13}C, 100 MHz). The mass spectra were measured on a Shimadzu QP-5050A (EI) and a JEOL

JMS-700TZ (HRMS, EI). The GLC analysis was made on a Shimadzu GC-8APF equipped with an integrator (C-R6A) with a column (3 mm i.d. × 3 m) packed with Silicon OV-17 (2% on Uniport HP, 60/80 mesh) or Apiezon Grease L (5% on Uniport HP, 60/80 mesh). IR spectra were measured on a Shimadzu FTIR-8300. Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University.

4.3. Reaction *1* with *2a*

A mixture of **1** (316 mg, 1.00 mmol), **2a** (142 mg, 1.00 mmol), $PtCl_2(PPh_3)_2$ (40 mg, 0.05 mmol), THF (4.0 ml), and a magnetic stirring bar was placed under an argon flow in a 20 ml round-bottomed flask, and was stirred for 16 h at room temperature (r.t.). After the reaction, the whole mixture was filtered through a short Celite pad to afford a red orange solution. GLC analysis with naphthalene as an internal standard showed **3a** was formed in quantitative yield. The product (**3a**) was isolated by column chromatography (silica gel with Hexane–EtOAc = 98:2) in 92% yield as colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 0.84 (t, $J = 7$ Hz, 9H), 1.04 (t, $J = 7$ Hz, $^2J_{H-Sn} = 53$ Hz, 6H), 1.21–1.28 (m, 6H), 1.38–1.46 (m, 6H), 3.83 (s, 3H), 3.87 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 12.6 (CH_2, $^1J_{C-117Sn} = 349$ Hz, $^1J_{C-119Sn} = 365$ Hz,), 13.5 (CH_3), 27.0 (CH_2, $^2J_{C-Sn} = 63$ Hz), 28.5 (CH_2, $^3J_{C-Sn} = 20$ Hz), 52.4 (CH_3), 53.7 (CH_3), 112.7 (–C=*C*(C(=O)OMe)CN, $^2J_{C-Sn} = 34$ Hz), 114.5 (–*C*N, $^3J_{C-Sn} = 11$ Hz), 163.0 (*C*=O), 170.3 (*C*=O, $^2J_{C-Sn} = 17$ Hz), 182.8 (–Sn–*C*=C–, $^1J_{C-117Sn} = 111$ Hz, $^1J_{C-119Sn} = 117$ Hz); IR (neat, cm^{-1}) 2224 ($\nu_{C=N}$), 1732 ($\nu_{C=O}$); FDMS (relative intensity) *m*/*z* 459 [M^+(as ^{120}Sn), 3], 457 [M^+(as ^{118}Sn), 3], 406 (21), 404 (19), 402 (100), 401 (41), 400 (74), 399 (33), 398 (47); Anal. Calc. for $C_{19}H_{33}NO_4Sn$: C, 49.81; H, 7.26; N, 3.06. Found: C, 49.66; H, 7.35; N, 2.88%.

4.4. Reaction of *1* with *2b*

In the similar manner in the preparation of **3a**, the cyanostannylated product (**3b**) was obtained as colorless liquid (73%); ^{1}H-NMR ($CDCl_3$) δ 0.86 (t, $J = 7$ Hz, 9H), 1.06 (t, $J = 7$ Hz, $^2J_{H-Sn} = 53$ Hz, 6H), 1.22–1.28 (m, 6H), 1.30–1.37 (m, 6H), 1.42–1.47 (m, 6H), 4.27–4.36 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 12.6 (CH_2, $^1J_{C-117Sn} = 349$ Hz, $^1J_{C-119Sn} = 365$ Hz), 13.5 (CH_3), 14.0 (CH_3), 14.1 (CH_3), 27.1 (CH_2, $^2J_{C-Sn} = 63$ Hz), 28.6 (CH_2, $^3J_{C-Sn} = 21$ Hz), 61.8 (CH_2), 63.2 (CH_2), 112.7 (–C=*C*(C(=O)OEt)CN, $^2J_{C-Sn} = 36$ Hz), 114.7 (–*C*N, $^3J_{C-Sn} = 11$ Hz), 162.6 (*C*=O), 170.0 (*C*=O, $^2J_{C-Sn} = 17$ Hz), 182.5 (–Sn–*C*=C–, $^1J_{C-117Sn} = 115$ Hz, $^1J_{C-119Sn} = 121$ Hz); IR (neat, cm^{-1}) 2224 ($\nu_{C=N}$), 1720 ($\nu_{C=O}$); EIMS (relative intensity) *m*/*z* 487 [M^+(as ^{120}Sn), 4], 485 [M^+(as ^{118}Sn), 17], 483 [M^+(as ^{116}Sn), 21], 434 (17), 432 (16), 431 (19), 430 (100), 429 (39), 428 (75), 427 (31), 426 (43), 402 (17), 400 (13), 233 (11), 179 (17), 177 (38), 176 (13), 175 (28), 173 (16), 165 (17), 163 (12), 152 (13), 137 (10), 124 (12), 121 (12), 119 (10), 57 (21), 41 (27); HRMS (EI) calcd for $C_{21}H_{37}NO_4^{120}Sn$: 487.1745. Found: 487.1744; Anal. Calc. for $C_{21}H_{37}NO_4Sn$: C, 51.87; H, 7.67; N, 2.88. Found: C, 51.63; H, 7.42; N, 2.64%.

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References

[1] (a) W.P. Weber, Silicon Reagents for Organic Synthesis, Springer-Verlag, Berlin, 1983, pp. 6–20;
(b) E.W. Colvin, Silicon in Organic Synthesis, Butterworth, London, 1981.
[2] (a) H. Ishitani, S. Komiyama, S. Kobayashi, Angew. Chem. Int. Ed. Engl. 37 (1998) 3186;
(b) S. Kobayashi, T. Busujima, Chem. Commun. (1998) 981;
(c) M.P. Dillon, H. Maag, D.M. Muszynski, Tetrahedron Lett. 36 (1995) 5469;
(d) R. Herranz, J. Castro-Pichel, T. Garcia-Lopez, Synthesis (1989) 703;
(e) D.F. Eaton, J. Am. Chem. Soc. 102 (1980) 3278;
(f) M. Kosugi, T. Ogata, H. Tamura, H. Sano, T. Migita, Chem. Lett. (1986) 1197;
(g) M. Tanaka, Tetrahedron Lett. 21 (1980) 2959.
[3] (a) D.-S. Shin, Y.-S. Jung, J.-J. Kim, C. Ahn, Bull. Korean Chem. Soc. 19 (1998) 119;
(b) M. Scholl, C.-K. Lim, G.C. Fu, J. Org. Chem. 60 (1995) 6229;
(c) M. Scholl, G.C. Fu, J. Org. Chem. 59 (1994) 7178;
(d) P.J. Lennon, D.P. Mack, Q.E. Thompson, Organometallics 8 (1989) 1121.
[4] N.V. Lukashev, A.V. Kazantsev, A.A. Borisenko, I.P. Beletskaya, Tetrahedron 57 (2001) 10309.
[5] (a) Y. Tsuji, M. Taniguchi, T. Yasuda, T. Kawamura, Y. Obora, Org. Lett. 2 (2000) 2635;
(b) Y. Tsuji, T. Kusui, T. Kojima, Y. Sugiura, N. Yamada, S. Tanaka, M. Ebihara, T. Kawamura, Organometallics 17 (1998) 4835;
(c) Y. Tsuji, N. Yamada, S. Tanaka, J. Org. Chem. 58 (1993) 16.
[6] Y. Obora, Y. Ogawa, Y. Imai, T. Kawamura, Y. Tsuji, J. Am. Chem. Soc. 123 (2001) 10489.
[7] Y. Obora, M. Nakanishi, M. Tokunaga, Y. Tsuji, J. Org. Chem. 67 (2002) 5835.
[8] E. Shirakawa, T. Hiyama, Bull. Chim. Soc. Jpn. 75 (2002) 1435.
[9] H.X. Zhang, F. Guibé, G. Balavoine, Tetrahedron Lett. 29 (1988) 619.
[10] S.P. Bew, J.B. Sweeney, Synlett (1991) 109.
[11] (a) T.N. Mitchell, W. Reimann, Organometallics 5 (1986) 1991;
(b) J.C. Cochran, L.E. Williams, B.S. Bronk, J.A. Calhoun, J. Fassberg, K.G. Clark, Organometallics 8 (1989) 804.
[12] A.J. Leusink, H.A. Budding, J.W. Marsman, J. Organomet. Chem. 9 (1967) 285.

[13] W.L.F. Armagego, D.D. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth-Heinemann, Oxford, UK, 1997.
[14] J.J. Zhang, G. Schuster, J. Am. Chem. Soc. 111 (1989) 7149.
[15] J.A. Rahn, L. Baltusis, J.H. Nelson, Inorg. Chem. 29 (1990) 750.
[16] P. Chini, G. Longoni, J. Chem. Soc. (A) (1970) 1542.
[17] W.J. Cherwinski, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1974) 1405.
[18] F.R. Hertley, The Chemistry of Platinum and Palladium, Applied Science, London, 1973, p. 458.
[19] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52.
[20] J.M. Jenkins, J.G. Verkade, Inorg. Synth. 11 (1968) 108.
[21] (a) Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, J. Chem. Soc. Chem. Commun. (1970) 1065;
(b) M.F. Rettig, P.M. Maitlis, Inorg. Synth. 17 (1977) 134.
[22] D.R. Coulson, Inorg. Synth. 13 (1972) 121.
[23] S. Murata, Y. Ido, Bull. Chem. Soc. Jpn. 67 (1994) 1746.
[24] (a) B. Jousseaume, P. Villeneuve, Tetrahedron Lett. 45 (1989) 1145;
(b) M.W. Logue, K. Teng, J. Org. Chem. 47 (1982) 2549;
(c) B. Jousseaume, J. Chem. Soc. Chem. Commun. (1984) 1452;
(d) B.L. Williamson, P.J. Stang, Synlett (1992) 199.
[25] (a) W.P. Newmann, F.G. Kleimer, Tetrahedron Lett. 49 (1964) 3779;
(b) J. Lorberth, J. Organomet. Chem. 16 (1969) 327 (and references therein).