Journal of Organometallic Chemistry, 453 (1993) C11-C12

JOM 23645PC

Preliminary Communication

The reaction of $Sn[CH(SiMe_3)_2]_2$ with ethyne: formation of $(HC{\equiv}C)Sn[CH(SiMe_3)_2]_2(\mu\text{-}trans\text{-}CH{=}CH)Sn[CH(SiMe_3)_2]_2(CH{=}CH_2)$

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(Received January 21, 1993)

Abstract

The reaction of $Sn[CH(SiMe_3)_2]_2$ and ethyne at ambient temperature affords a mixture of products, from which the title compound has been separated and identified by IR, ^1H, and ^{13}C NMR spectroscopy.

The stannylenes $Sn[CH(SiMe_3)_2]_2$ [1] and $Sn[C_6H_2\text{-}(2,4,6\text{-}^iPr)_3]_2$ (generated from the trimer) [2] and the tin(II)diamide $Sn[N(^tBu)]_2SiMe_2$ [3] react with strained cyclic alkynes [4] to afford either stannacyclopropenes (which dissociate readily in solution [5]) or distannacyclobutenes [6,7]. The intrinsic instability of these compounds has been explained in terms of MO calculations performed on the hypothetical stannacyclopropene derived from H_2Sn and C_2H_2 [8]. This aspect was dealt with in a recent review [9]. In addition, we recently described reactions of the nickel(0) ethyne complex $(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_2)$ with $Sn[CH(SiMe_3)_2]_2$. Below −30°C a kinetically controlled reaction yields a nickela(II)stanna(II)cyclobutene complex that is in equilibrium with the starting components. At 20°C, in a slow irreversible reaction, the stannylene is inserted into a C–H bond of the ethyne ligand to form a tin(IV) ethynyl nickel(0) complex [10]. In the case of palladium(0), the reaction of $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_2)$ with $Sn[CH(SiMe_3)_2]_2$ affords a thermally stable pallada(II)stanna(II)cyclobutene complex, which upon reaction with ethyne is reconverted to $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_2)$ with concomitant catalytic formation of the *C*-unsubstituted stannole $(C_4H_4)Sn[CH(SiMe_3)_2]_2$ [11]. These studies prompted us to examine the course of the reaction of $Sn[CH(SiMe_3)_2]_2$ and ethyne in the absence of a transition metal species [12].

Treatment of the red-violet THF solution (25 ml) of $Sn[CH(SiMe_3)_2]_2$ (1.75 g, 4.0 mmol) with ethyne (200 ml, excess) at 20°C led to a gradual loss of colour until, after 3 days, an almost colourless solution was obtained along with only minor amounts of insoluble material. The reaction starts at about −10°C and is solvent dependent; for example, in pentane a detectable reaction (at 20°C) was observed only after addition of an equal volume of THF. Following completion of the reaction, evaporation of the THF under vacuum afforded a residue that was largely soluble in pentane (25 ml). When the solution was filtered through silica gel (Florisil; Roth) and kept at −78°C, after 2 days, colourless crystals were present and these were separated, and dried under vacuum to yield 630 mg of pure **1** (33%). According to its elemental analysis **1** [†] comprises two stannylene and three ethyne molecules. Some other products apparently containing similar structural units to those in **1** were present in the mother liquor as indicated by the ^1H NMR spectrum. However, no signals from the stannole $(C_4H_4)Sn[CH(SiMe_3)_2]_2$ were detected, and so a [2 + 2 + 1] cyclization reaction [13*] of the stannylene and two equivalents of ethyne can be *excluded*.

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[†] Analytical and spectroscopic data for **1**: Colourless microcrystals; m.p. 136–140°C. Anal. Calcd for $C_{34}H_{82}Si_8Sn_2$ (953.1): C, 42.85; H, 8.67; Si, 23.57; Sn, 24.91. Found: C, 42.81; H, 8.76; Si, 23.42; Sn, 24.94]. IR see text; ^1H NMR (400 MHz, THF-d_8) δ 7.68 [d, 1H, ^3J 21 Hz, $^2J(^{119}SnH)$ 76.5 Hz, $^3J(^{119}SnH)_{cis}$ 63.0 Hz, Sn–CH=C*H*–Sn_{vinyl}], 7.21 [d, 1H, $^2J(^{119}SnH)$ 93.5 Hz, $^3J(^{119}SnH)_{cis}$ 58.0 Hz, Sn–CH=C*H*–$Sn_{ethynyl}$], 6.69 [m, 1H, $^2J(^{119}SnH)$ 51.0 Hz, H_2C=C*H*–Sn], 6.22 [m, 1H, ^3J 13.7 Hz, $^3J(^{119}SnH)_{trans}$ 90.0 Hz, H_EHC=CH–Sn], 5.86 [m, 1H, ^3J 20.4 Hz, $^3J(^{119}SnH)_{cis}$ 43.5 Hz, HH_ZC=CH–Sn], 2.72 [s, 1H, $^3J(^{119}SnH)$ 15.2 Hz, HC≡C–Sn], 0.23, 0.18, 0.17, 0.16 [each s, 18H; two pairs of diastereotopic $SiMe_3$], −0.24 [s, 2H, $^2J(^{119}SnH)$ 43.0 Hz, Sn_{vinyl}CH], −0.26 [s, 2H, $^2J(^{119}SnH)$ 45.5 Hz, $Sn_{ethynyl}$CH]. ^{13}C NMR (100.6 MHz, THF-d_8) δ 156.4 [1C, $^1J(^{119}SnC)$ 385 Hz, $^2J(^{119}SnC)$ 60 Hz, Sn–CH=*C*H–Sn_{vinyl}], 153.0 [1C, $^1J(^{119}SnC)$ 468 Hz, $^2J(^{119}SnC)$ 43 Hz, Sn–CH=*C*H–$Sn_{ethynyl}$], 143.4 [1C, $^1J(^{119}SnC)$ 428 Hz, H_2C=*C*H–Sn], 135.4 [1C, ^2J(SnC) not obs., H_2*C*=CH–Sn], 102.1 [1C, ^1J(CH) 235 Hz, ^2J(SnC) 71 Hz, H*C*≡C–Sn], 92.4 [1C, $^1J(^{119}SnC)$ 410 Hz, HC≡*C*–Sn], 6.31 [2C, $^1J(^{119}SnC)$ 201 Hz, $Sn_{ethynyl}$CH], 4.75 [2C, $^1J(^{119}SnC)$ 167 Hz, Sn_{vinyl}CH], 4.53, 4.33, 4.12, 3.93 [each 6C; two pairs of diastereotopic $SiMe_3$].

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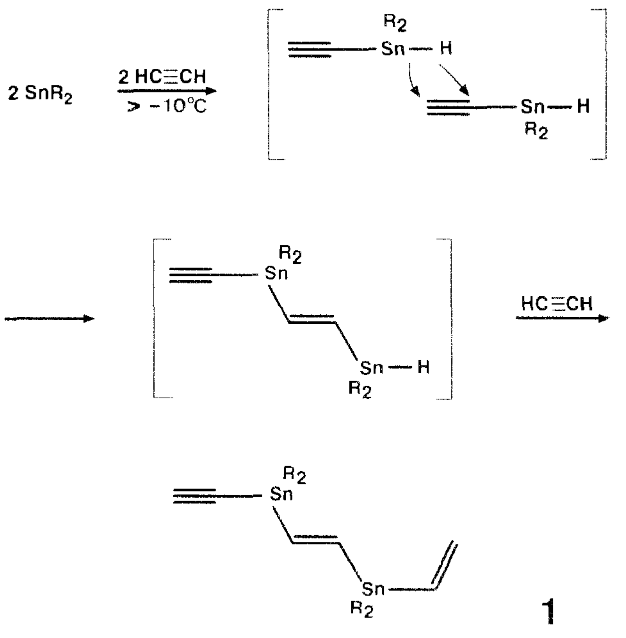

R = $CH(SiMe_3)_2$ (1)

The IR spectrum (KBr) of **1** shows absorption bands for ≡C–H (3280), =C–H (3050), C≡C (2005), and *trans*-substituted C=C (1580 cm^{-1}, weak) bonds. Elucidation of the structure of **1**, with full assignment of the H and C carbon atoms, was facilitated by correlated ^1H, ^{13}C NMR spectroscopy.

The ^1H NMR spectrum shows two resonances δ 7.68 and 7.21 [^3J 21 Hz] corresponding to the protons of a *trans*-Sn–CH=CH–Sn unit. Three signals at δ 6.69, 6.22, and 5.86, can be assigned to an Sn–CH=CH_2 group, and a single resonance δ 2.72 to an Sn–C≡CH group. The analysis of this part of the spectrum is complicated by overlapping couplings of the protons with the ^{119}Sn and ^{117}Sn nuclei of one or both tin atoms[††]. A C–C linkage between the original ethyne molecules can be excluded because of the absence of H,H couplings between the three structural C_2 elements. Furthermore, the ^{13}C NMR spectrum shows six signals of equal intensity for the *trans*-Sn–CH=CH–Sn (δ 156.4, 152.9), Sn–CH=CH_2 (δ 143.4, 135.4), and Sn–C≡CH (δ 102.1, 92.4) entities. The assignment[†] of the protons and carbon atoms is unambiguous in the light of the long range couplings in the C,H correlated spectra. In addition, the ^1H and ^{13}C NMR spectra exhibit two SnCH and four $SiMe_3$ resonances arising from two different $RR'Sn[CH(SiMe_3)_2]_2$ moieties with diastereotopic $SiMe_3$ groups. Thus, **1** which is composed of two SnR_2 [R = $CH(SiMe_3)_2$] and three ethyne molecules has a linear chain structure with a central *trans*-SnR_2–CH=CH–SnR_2 moiety and a vinyl substituent on one Sn^{IV} atom and an ethynyl substituent on the other.

The formation of **1** can be accounted for in terms of a sequence of oxidative addition and hydrostannylation reactions, as indicated in eqn. (1). In the first step an oxidative addition of an ethyne C–H bond to the stannylene occurs to form the ethynylstannane intermediate $[(Me_3Si)_2CH]_2Sn(H)(C{\equiv}CH)$. This dimerizes by cis addition of a Sn–H bond to the neighbouring ethynyl group, resulting in the dinuclear *trans* ethenediyl skeleton with an ethynyl substituent on one tin atom. This species undergoes a final insertion of ethyne into the Sn–H bond of the second tin atom to give the vinyl substituent present in **1**.

Obviously, closely related side reactions also take place to give various by-products, which have not been isolated. Although the yield of **1** is only moderate, it appears to be the main product, and it is the most readily isolated.

References and notes

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[*] Reference number with asterisk indicates a note in the list of references.

[††] The coupling $J(Sn–H)$ follows the known sequence $^3J_{trans} > {^2J_{gem}} > {^3J_{cis}}$ [14].