Palladium(0)-mediated Insertion of Isonitriles into the Silicon–Tin Bond

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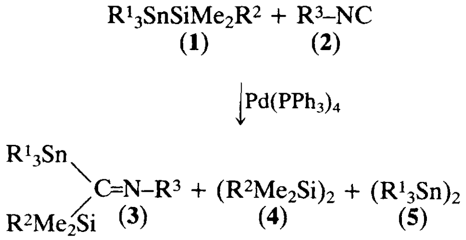
Insertion of isonitriles into the silicon–tin bond of organosilylstannanes is catalysed by palladium(0) to give organosilyl(*N*-substituted imino)stannanes.

Transition metal catalysed additions of silicon–silicon[1] and tin–tin bonds[2] to unsaturated carbon–carbon bonds have provided convenient methods for preparation of organosilicon and organotin compounds including synthetically useful vinylsilanes and vinylstannanes. Recently, it was reported[3] that the silicon–tin bond of organosilylstannanes (**1**) also adds to alkynes in the presence of $Pd(PPh_3)_4$ catalyst to give β-silylvinylstannanes.

We now report that α,α-addition of the silicon–tin bond of organosilylstannanes (**1**)[4] to the isocyano carbon atom of isonitriles (**2**) has been achieved by using a palladium(0) catalyst to afford organosilyl(*N*-substituted imino)stannanes (**3**) in moderate yields.

The α,α-addition reaction proceeded in competition with the disproportionation of (**1**) to give the disilane (**4**) and distannane (**5**). The Pd^0 catalysed reaction of (trimethylsilyl)-

trimethylstannane with t-butyl isocyanide, which is sterically bulky, gave only disproportionation products, with none of the desired isonitrile insertion.



$$R^1{}_3SnSiMe_2R^2 + R^3\text{–}NC \xrightarrow{Pd(PPh_3)_4} (R^1{}_3Sn)(R^2Me_2Si)C{=}N\text{–}R^3 + (R^2Me_2Si)_2 + (R^1{}_3Sn)_2$$

(1) (2) (3) (4) (5)

(**3a**), $R^1 = R^2 = Me$, $R^3 = Pr^i$, 71%
(**3b**), $R^1 = R^2 = Me$, $R^3 =$ hexyl, 59%
(**3c**), $R^1 = R^2 = Me$, $R^3 =$ cyclohexyl, 58%
(**3d**), $R^1 = R^2 = Me$, $R^3 = o\text{-}MeC_6H_4$, 69%
(**3e**), $R^1 = Bu^n$, $R^2 = Me$, $R^3 = Pr^i$, 40%
(**3f**), $R^1 = Me$, $R^2 = Bu^t$, $R^3 = Pr^i$, 28%

Scheme 1

In general, the reactions were carried out by heating a mixture of the isonitrile (2 mmol), organosilylstannane (5.0 mmol) and tetrakis(triphenylphosphine)palladium (0.06 mmol) in toluene (3 ml) or without sovlent at 60 °C for 3 h under argon. The progress can be monitored by g.l.c. analysis of aliquot samples. The insertion product (**3**)† can be isolated by distillation: *e.g.* (**3a**) had b.p. 45 °C at 3 mmHg, and its identity was established by elemental analyses and i.r. ($\nu_{C=N}$ 1556 cm^{-1}) and n.m.r spectroscopy [^{1}H (100 MHz, C_6D_6, cyclohexane as internal reference) δ 0.21 (s, 9H), 0.26 (s, 9H), 1.27 (d, 6H), and 2.92—3.20 (m, 1H); ^{13}C (C_6D_6) δ −5.80, −1.73, 23.93, 71.32, and 202.71.]

The Pd^0 mediated insertion of isonitrile into the Si–Sn bond may be reasonably explained by a mechanism involving the following catalytic cycle: (i) oxidative addition of the organosilylstannane (**1**) onto the Pd^0 catalyst; (ii) insertion of isonitrile (**2**) into the resultant Pd–Sn or Pd–Si linkage; (iii) reductive elimination leading to (**3**) with regeneration of the Pd^0 catalyst. The concomitant disproportionation of (**1**) to give the disilane (**4**) and distannane (**5**) may also involve a palladium intermediate common to the insertion reaction. Analogous Pd^0 catalysed disproportionation of disilanes is known.[1a]

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† The yields are based on isonitrile.

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