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An Unexpected Trimethylstannylpyrrole from a Stannylated Derivative of Tosylmethyl Isocyanide (TosMIC) and Chalcone

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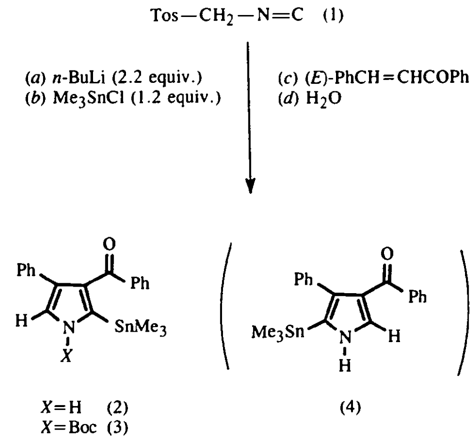
Abstract

The structure of the title compound, *tert*-butyl 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole-*N*-carboxylate, [$Sn(CH_3)_3(C_{22}H_{20}NO_3)$], is one of the first in which the stannyl group is attached to a C atom of the pyrrole ring. There appears to be an intramolecular interaction between the Sn atom and the carbonyl O atoms of both the benzoyl and the *tert*-butoxycarbonyl substituents. The compound was prepared by a base-induced cycloaddition of a stannylated derivative of tosylmethyl isocyanide to chalcone.

Comment

(Trialkylstannyl)pyrroles are of use in palladium-catalyzed cross-coupling reactions (Stille, 1986) for the preparation of oligo- and polypyrroles (Martina, Enkelmann, Wegner & Schlütter, 1992). We are presently engaged in developing new routes to stannylated azoles using tosylmethyl isocyanide [TosMIC; (1)] and trialkylstannyl halides. In one case, a stannylated synthon was prepared *in situ* by double deprotonation of TosMIC, followed by addition of one equivalent of trimethylstannyl chloride in tetrahydrofuran (THF) at 203 K (see reaction scheme). Chalcone (*E*)-PhCH=CHCOPh was then added at the same temperature to give a pyrrole, (2), which was converted to a stable crystalline *N*-*tert*-butoxycarbonyl (Boc) derivative, (3), using Boc_2O (Grehn & Ragnarsson, 1984). Compound (3) was crystallized from petroleum ether (b.p. 313–333 K).



So far, trisubstituted pyrroles prepared by the same approach (from Michael acceptors and monosubstituted derivatives of TosMIC) always carry the third substituent (introduced *via* monosubstituted TosMIC) at the position β to the electron-withdrawing group of the Michael acceptor (Possel & van Leusen, 1977; van Leusen & van Leusen, 1995*a*). By extrapolation, the initial reaction product of the reaction scheme was expected to be 4-benzoyl-3-phenyl-2-(trimethylstannyl)pyrrole, (4), rather than 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole, (2), through regiospecific cycloaddition of $TosCLi(SnMe_3)N{\equiv}C$, (5). To confirm the inconclusive spectroscopic evidence for (4), the X-ray structure of the *N*-Boc derivative was determined, which surprisingly proved to be compound (3) and not the *N*-Boc derivative of (4). This means that stannylation of dilithio–TosMIC probably leads to reaction at the isocyano C atom (unlike all previously known alkylations) to give $TosCLi{=}N^+{=}C^-{-}SnMe_3$, (6), as the synthon prepared *in situ*. Alternative explanations, such as a reversal of the regioselective addition of (5) or a migration of the trimethylstannyl group in (4), seem much less likely. The actual structure of the corresponding silylated TosMIC derivative, so far considered to be $TosCLi(SiMe_3)N{\equiv}C$ (van Leusen & Wildeman, 1982), remains to be seen. Trisubstituted pyrroles similar to (2), with Ph, Me, MeO and MeS substituents in place of Me_3Sn, have been prepared previously using different synthons of the *N*-tosylmethyliminocarbonate and *N*-tosylmethylthiobenzimidate types, for example, $TosCH_2N{=}C(SMe)Ph$ (Houwing & van Leusen, 1981; van Leusen & van Leusen, 1995*b*).

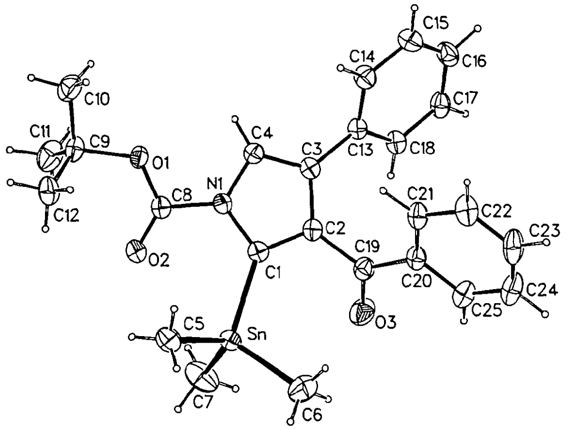
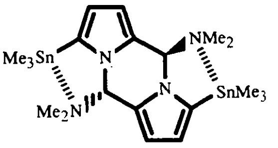


Fig. 1. Perspective *ORTEP* drawing (Johnson, 1965) of the title compound. All non-H atoms are represented by displacement ellipsoids drawn to encompass 50% of the electron density. The H atoms are drawn with an arbitrary radius.

A search of the January 1996 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) and of *Chemical Abstracts* revealed several X-ray structures of *N*-(trimethylstannyl)pyrroles, but only two with the trimethylstannyl group attached to a pyrrole ring C atom (Hillmann, Hausen, Schwarz & Weidlein, 1995). Of these, one paper refers to a 2-(trimethylstannyl)pentapyrrole derivative but there are no structural data (Martina *et al.*, 1992), whereas the other describes 5,10-bis(dimethylamino)-3,8-bis(trimethylstannyl)-5*H*,10*H*-dipyrrolo[1,2-*a*:1′,2′-*d*]pyrazine, (7), a compound containing two 2-(trimethylstannyl)-pyrrole moieties (Veith *et al.*, 1993).



(7)

Some aspects of the structure data of (3) other than the unexpected position of the trimethylstannyl group at C1 (as discussed above) are of interest. The aromatic pyrrole ring is essentially flat, as are the two benzene rings. The pyrrole ring of compound (3) has to accommodate four bulky substituents, which is possible only by rotating the two carbonyl-derived substituents and the phenyl ring at C3 out of the pyrrole plane, apparently at the expense of resonance stabilization. Furthermore, three of the four substituents are tilted slightly out of the plane of the pyrrole ring. Only the C19 atom of the benzoyl group lies effectively in this plane. The trimethylstannyl group is bent to one side, the distance of the Sn atom to the least-squares pyrrole plane being 0.257 (1) Å. The Boc group at N1 and the phenyl group at C3 are on the opposite side, with distances to the least-squares plane of 0.138 (2) for C8 and 0.143 (2) Å for C13. The carbonyl O2 atom of the Boc group is in close contact with the Sn atom, with an Sn···O2 distance of 3.0265 (16) Å, as compared with the sum of the corresponding van der Waals radii (Bondi, 1964) of 3.78 Å. The distance between O2 and the methyl C12 atom of the Boc group of 2.966 (3) is shorter than the sum of the corresponding van der Waals radii (3.22 Å); the same is true for the O2 atom and one of the H atoms at C12 [2.50 (4) *versus* 2.72 Å]. On the other hand, the distances of O2 to the trimethylstannyl H atoms are greater than the sum of the van der Waals radii. This, however, is not the case for the benzoyl O3 atom, which is at a distance of 2.56 (4) Å from one of the trimethylstannyl H atoms of C6 (*cf* 2.72 Å). Also, the Sn···O3 distance of 3.440 (2) Å is shorter than the van der Waals sum (3.78 Å), but longer than the Sn···O2 distance above. The C1—C2—C19—O3 torsion angle of 47.1 (3)° indicates that the carbonyl of the benzoyl group lies much further out of the pyrrole plane than the Boc carbonyl group, which has a C1—N1—C8—O2 torsion angle of −14.2 (3)°. The carbonyl O2 atom of the Boc group more or less bisects the C5—Sn—C7 angle. Although otherwise rather different, pyrrole (3) and pyrrole (7) reported by Veith *et al.* (1993) both exhibit a close contact between the Sn atom and a hetero atom of a neighbouring substituent. In the latter, the distance from the Sn atom to the N atom of the dimethylamino side chain [a five-membered ring-forming interaction, as found for O2 and O3 in compound (3)] of 3.101 (5) Å is shorter than the sum of the corresponding van der Waals radii (3.75 Å).

Experimental

^{n}BuLi (1.8 ml, 4.5 mmol) was added to a solution of TosMIC (0.39 g, 2.0 mmol) in THF (30 ml) at 198–208 K. After stirring for 5 min at the same temperature, Me$_3$SnCl (0.50 g, 2.5 mmol) in THF (5 ml) was added dropwise, followed, after stirring for another 5 min at the same temperature, by addition of chalcone (0.42 g, 2.0 mmol) in THF (5 ml). The reaction mixture was stirred for 2 h while the temperature was allowed to rise to 233 K. The reaction mixture was quenched with H$_2$O (50 ml) and extracted with ether (3 × 50 ml). The combined organic layers were washed with H$_2$O and brine, dried (MgSO$_4$) and concentrated. The yellow solid residue was crystallized from CH$_2$Cl$_2$/hexane (1:2) to give compound (2) as a white solid (m.p. 445–447 K), pure according to ^{1}H NMR. The yield before crystallization was 0.66 g (1.6 mmol, 80%). Compound (2) was converted into compound (3) using Boc$_2$O in CH$_3$CN (Grehn & Ragnarsson, 1984). The product was crystallized from petroleum ether (b.p. 313–333 K) giving (3) as transparent colourless crystals (m.p. 391–392 K).

Crystal data

[Sn(CH$_3$)$_3$(C$_{22}$H$_{20}$NO$_3$)]
M_r = 510.22

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/a$
a = 13.4950 (10) Å
b = 9.6660 (10) Å
c = 19.7180 (10) Å
β = 109.108 (5)°
V = 2430.4 (2) Å^3
Z = 4
D_x = 1.394 Mg m^{-3}
D_m not measured

Cell parameters from 22 reflections
θ = 17.97–20.08°
μ = 1.08 mm^{-1}
T = 130 K
Parallelepiped
0.50 × 0.45 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans with ω width (0.85 + 0.34tanθ)°
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.225, $T_{\max}$ = 0.478
6512 measured reflections

5285 independent reflections
4542 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0357
$\theta_{\max}$ = 26.98°
$h = 0 \rightarrow 17$
$k = -1 \rightarrow 12$
$l = -25 \rightarrow 23$
3 standard reflections
frequency: 180 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R(F)$ = 0.0249
$wR(F^2)$ = 0.0586
S = 1.083
5010 reflections
387 parameters
H atoms refined freely with individual isotropic displacement parameters

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 1.72P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = −0.002
$\Delta\rho_{\max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\min}$ = −0.57 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sn	0.50364 (1)	0.37525 (2)	0.30485 (1)	0.0256 (1)
O1	0.59182 (11)	0.84319 (15)	0.35658 (8)	0.0250 (4)
O2	0.59820 (12)	0.62275 (16)	0.39744 (8)	0.0307 (5)
O3	0.23548 (15)	0.38371 (18)	0.22607 (9)	0.0411 (5)
N1	0.46205 (13)	0.69696 (18)	0.30121 (9)	0.0220 (5)
C1	0.41862 (16)	0.5680 (2)	0.27833 (11)	0.0224 (6)
C2	0.32113 (16)	0.5949 (2)	0.22913 (11)	0.0221 (5)
C3	0.30463 (15)	0.7418 (2)	0.22267 (10)	0.0210 (5)
C4	0.39314 (16)	0.8021 (2)	0.26748 (11)	0.0223 (6)
C5	0.6616 (2)	0.4016 (3)	0.30737 (14)	0.0327 (7)
C6	0.4366 (3)	0.2301 (3)	0.2200 (2)	0.0520 (10)
C7	0.4827 (3)	0.3050 (4)	0.40195 (17)	0.0467 (10)
C8	0.55805 (16)	0.7148 (2)	0.35735 (11)	0.0229 (5)
C9	0.68998 (17)	0.8906 (2)	0.41272 (11)	0.0279 (6)
C10	0.7008 (2)	1.0369 (3)	0.38912 (16)	0.0396 (8)
C11	0.6734 (3)	0.8874 (3)	0.48500 (14)	0.0437 (9)
C12	0.7817 (2)	0.8021 (3)	0.40997 (15)	0.0385 (8)
C13	0.20732 (15)	0.8146 (2)	0.18208 (10)	0.0213 (5)
C14	0.20894 (17)	0.9315 (3)	0.14155 (12)	0.0281 (6)
C15	0.11693 (19)	0.9988 (3)	0.10341 (13)	0.0332 (7)
C16	0.02152 (18)	0.9514 (3)	0.10673 (13)	0.0320 (7)
C17	0.01893 (17)	0.8361 (3)	0.14741 (12)	0.0284 (6)
C18	0.11076 (16)	0.7671 (2)	0.18446 (11)	0.0237 (6)
C19	0.24989 (16)	0.4815 (2)	0.19155 (11)	0.0255 (6)
C20	0.20134 (16)	0.4827 (2)	0.11170 (11)	0.0252 (6)
C21	0.22717 (16)	0.5789 (3)	0.06789 (12)	0.0278 (6)
C22	0.18252 (19)	0.5696 (3)	−0.00628 (13)	0.0363 (7)
C23	0.1128 (2)	0.4641 (3)	−0.03618 (13)	0.0423 (8)
C24	0.0866 (2)	0.3681 (3)	0.00696 (14)	0.0427 (8)
C25	0.13015 (19)	0.3778 (3)	0.08031 (13)	0.0341 (7)

Table 2. *Selected geometric parameters (Å, °)*

Sn—C1	2.161 (2)	O2—C8	1.196 (3)
Sn—C5	2.131 (3)	O3—C19	1.217 (3)
Sn—C6	2.144 (3)	N1—C1	1.388 (3)
Sn—C7	2.136 (3)	N1—C4	1.391 (3)
O1—C8	1.324 (2)	N1—C8	1.412 (3)
O1—C9	1.493 (3)		
C1—Sn—C5	110.51 (10)	Sn—C1—C2	129.88 (15)
C1—Sn—C6	108.69 (11)	N1—C1—C2	105.26 (17)
C1—Sn—C7	105.99 (12)	N1—C4—C3	107.73 (17)
C5—Sn—C6	105.06 (14)	O1—C8—O2	128.5 (2)
C5—Sn—C7	116.23 (13)	O1—C8—N1	109.66 (17)
C6—Sn—C7	110.23 (14)	O2—C8—N1	121.88 (19)
C8—O1—C9	120.29 (16)	O1—C9—C10	102.16 (18)
C1—N1—C4	110.83 (17)	O1—C9—C11	108.8 (2)
C1—N1—C8	123.07 (17)	O1—C9—C12	109.63 (17)
C4—N1—C8	125.71 (17)	O3—C19—C2	119.32 (19)
Sn—C1—N1	124.15 (15)	O3—C19—C20	120.01 (19)

The title structure was solved by Patterson methods and an extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*94 (Beurskens *et al.*, 1994). Refinement on F^2 was carried out by full-matrix least-squares techniques; the observance criterion $F^2 > 0$ was applied during refinement. Unfortunately, the need for an absorption correction only became apparent to us when residual peaks of up to 1.76 e Å^{-3} persisted near Sn; the only available method was a refined correction using *DIFABS* (Walker & Stuart, 1983). After this was applied, a final electron-density difference map showed no significant peaks above the general background.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1995). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON* (Spek, 1994, 1996).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram of the compound, have been deposited with the IUCr (Reference: BM1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Chloro(methyl)arsino-*N*,*N*′-dimethyl-*N*′-(*p*-tolylthio)urea

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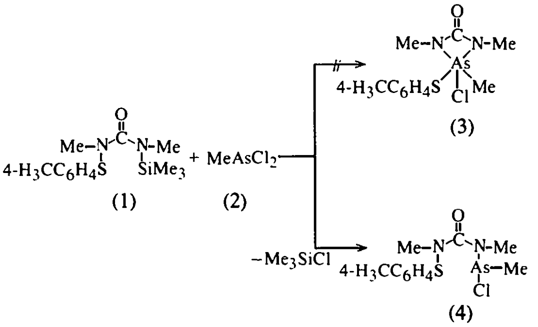
Abstract

The title compound, $C_{11}H_{16}AsClN_2OS$, crystallizes with two independent but closely similar molecules. The pyramidal geometry at arsenic is supplemented by a 1,5-intramolecular interaction with the S atom [2.8682 (13) and 2.8101 (13) Å] and by further weaker intermolecular contacts to oxygen and chlorine.

Comment

We recently reported an intramolecular rearrangement that took place during the phosphorylation of *N*-arylthio-*N*,*N*′-diorgano-*N*′-(trimethylsilyl)ureas with dichlorophosphines. The resulting compounds were shown to be the four-membered cyclic phosphoranes, 2-arylthio-2-chloro-1,2,3-triorgano-1,3,2λ^5-diazaphosphetidin-4-ones (Pinchuk *et al.*, 1994, 1995).

We wished to study the suitability of this synthesis for the preparation of the analogous arsenic derivatives. Some cyclic arsenic compounds based on *N*,*N*′-disubstituted ureas have already been reported (Roesky, Djarrah, Amirzadeh-Asl & Sheldrick, 1981; Vogt, Jones & Schmutzler, 1993). However, the reaction between *N*,*N*′-dimethyl-*N*-(*p*-tolylthio)-*N*′-(trimethylsilyl)-urea, (1), and dichloro(methyl)arsine, (2), did not result in the expected derivative, (3), but instead in the acyclic title compound, (4), the structure of which is reported here.



Compound (4) crystallizes with two independent molecules (Fig. 1) which are closely similar (see Table 2); the conformations are almost identical, with all torsion-angle differences < 8°. The geometry at arsenic is pyramidal, with angles ranging from 93.81 (13) to 97.40 (15)°. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed no other compound with C, N and Cl substituents at three-coordinate arsenic. The As—N and As—Cl bond lengths in compound (4) are similar to the standard values of 1.858 and 2.268 Å quoted by Allen *et al.* (1987).

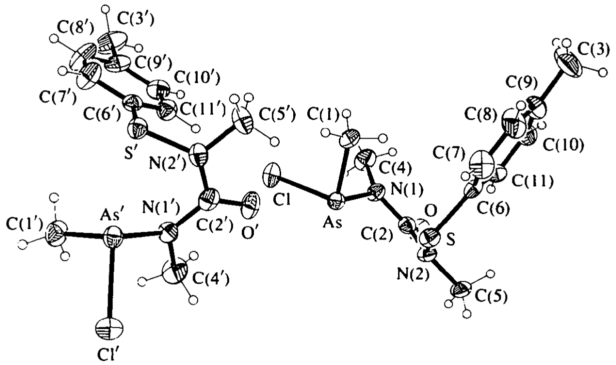


Fig. 1. The two independent molecules of the title compound in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

A feature of both molecules is the short 1,5 contact between the As and S atoms, *trans* to the chlorine sub-