TRANSANNULAR BOND FORMATION BETWEEN THE ANTIMONY AND THE NITROGEN
ATOMS IN DIBENZ[c,f][1,5]AZASTIBOCINE SYSTEM.
FORMATION OF X-Sb-X AND X-Sb-N+ HYPERVALENT BOND

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Abstract: 6-Methyl-5,6,7,12-tetrahydro-12-p-tolyldibenz[c,f][1,5]azastibocine
(1) was prepared by means of one-pot reaction of di(o-bromobenzyl)methylamine
(2), butyllithium, and antimony trichloride, followed by p-tolyllithium in 23%
yield. Halogenation of 1 afforded the corresponding dihalide (4a-c and 5d)
and the reaction of 4b and 4c with SbCl₅ or AgBF₄ resulted in the formation of
X-Sb-N+ bond (5b,c).

In a preceding paper, we showed the formation of bicyclic phosphoranes by
means of the transannular interaction between the phosphorus and the nitrogen
atoms in dibenz[c,f][1,5]azaphosphocine derivatives.[1] Recently, considerable
attention has been paid to such a transannular bond formation in various eight
membered ring systems containing main group elements below the second row,
e.g. Si, P, S, Sn, etc.[2] Here, we describe the formation of hypervalent bond
(halogen-Sb-N+) by transannular interaction in the title compound (1).

An important precursor of tridentate ligand, aminodibromide (2), was
synthesized in 28% overall yield from o-bromobenzoic acid by stepwise
procedures. Treatment of 2 with 2 equiv of n-butyllithium gave dilithio
derivative which was confirmed by quenching experiments with silylating
reagents to afford disilyl derivative (3a) and azasilocine derivative (3b) in
63 and 20 % yield, respectively. The heterocyclic compound (3b) had been
prepared by an alternative route and the structure was discussed by means of
NMR and X-ray analyses.[2a] To a solution of the dilithio derivative prepared
from 2 (450 mg, 1.23 mmol) was added antimony trichloride (280 mg, 1.25 mmol),
followed by treatment with an ethereal solution of p-tolyllithium (1.23 mmol).
Azastibocine derivative (1) was obtained in 23% yield after usual workup.[3]
Reaction of 1 with halogenating reagents (SO₂Cl₂, Br₂, I₂) in CH₂Cl₂ solution
smoothly proceeded to furnish dihalide (4b,c and 5d), respectively. Treatment
of 4b (X=Cl) with KF in DMF solution afforded difluoro compound (4a; X=F).
Treatment of 4b and 4c with SbCl₅ or AgBF₄ gave 5b and 5c, respectively.
Scheme 1 and 2 show synthetic routes and the ^{1}H NMR spectral data of 1, 4a-c,
and 5b-d are summarized in Table 1.

Scheme 1 [a]
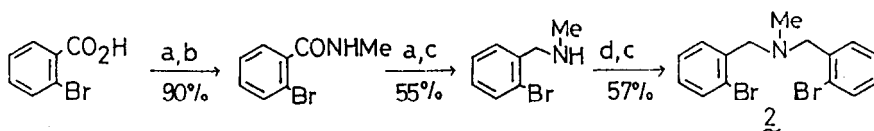
[a]: (a) $SOCl_2$; (b) 40% aq. $MeNH_2$; (c) $LiAlH_4$, THF, -15 °C;
(d) o-bromobenzoyl chloride, THF, r.t.

Scheme 2 [a]
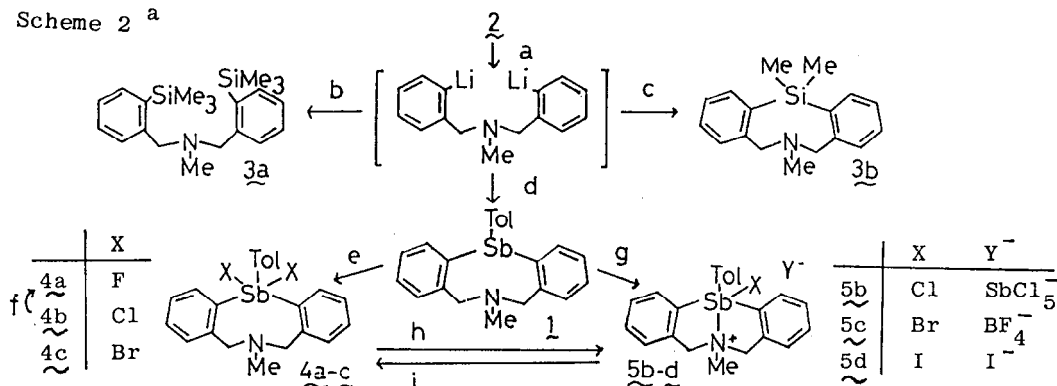
[a]: (a) n-BuLi, Et_2O; (b) Me_3SiCl; (c) Me_2SiCl_2; (d) $SbCl_3$, then TolLi;
(e) SO_2Cl_2 or Br_2, CH_2Cl_2; (f) KF, DMF; (g) I_2, Et_2O; (h) $SbCl_5$ or
$AgBF_4$, CH_2Cl_2; (i) $PhCH_2N^+Et_3Cl^-$, $CHCl_3$.

Structural assignment to 4a is based upon ^{1}H NMR spectral data and its
chemical behavior. Considerations by molecular model indicate that the twist
boat (TB) conformation is relatively free of serious nonbonded interactions,
when compared with the boat chair (BC) form. The methylene protons appear as
an AB quartet (J = 14.1 Hz) at δ 4.05 and 4.48 in $CDCl_3$ solution. The two
ortho protons in the tolyl group are seen as a doublet (J = 8.1 Hz) at δ 7.99
; the downfield shift relative to the other aromatic protons can be attributed
to the deshielding anisotropic effect of F–Sb–F hypervalent bond in the TB
conformer.[4] Both dichloride (4b) and dibromide (4c) showed almost the same [1]H
NMR spectral features as that of difluoride (4a) but the anisotropic effect
was slightly more effective than for 4a. ^{19}F NMR spectrum of 4a showed an AB
quartet (J = 87.5 Hz) at δ -127.9 and -140.6 in $CDCl_3$ solution (external
standard: $CFCl_3$). These indicate that the exact geometry around antimony may
be distorted trigonal bipyramidal (rectangular pyramidal, RP) rather than
typical TBP as judged by the large difference of the chemical shifts in [19]F
NMR spectrum.[5] In such a distorted TBP geometry, the amino group can interact

^{1}H NMR Spectral Data of 1, 4a-c, and 5b-d in CDCl$_3$ (δ).

Compd. (mp, °C)	Methyl	Methylene	Aromatic
1 (143.5-144)	2.40 (s, 3H) 2.48 (s, 3H)	3.67 and 3.93 (ABq, J=14.5 Hz, 4H)	6.8-7.4 (m, 8H) 7.21 and 7.55 (ABq, J=7.9 Hz, 4H)
4a (273-275)	2.37 (d, J=2.0 Hz, 3H) 2.46 (s, 3H)	4.05 and 4.48 (ABq, J=14.1 Hz, 4H)	7.1-7.6 (m, 8H) 7.41 and 7.99 [a] (ABq, J=8.1 Hz, 4H)
4b (300-302)	2.47 (s, 6H)	4.03 and 4.78 (ABq, J=14.2 Hz, 4H)	7.1-7.6 (m, 8H) 7.43 (d, J=8.3 Hz, 2H) 8.44 (d, J=8.3 Hz, 2H) [a]
4c (295-296)	2.48 (s, 6H)	4.00 and 4.81 (ABq, J=14.2 Hz, 4H)	7.1-7.6 (m, 8H) 7.47 (d, J=8.1 Hz, 2H) 8.49 (d, J=8.1 Hz, 2H) [a]
5b (215-217)	2.41 (s, 3H) 2.45 (s, 3H)	4.35 and 4.56 (ABq, J=15.3 Hz, 4H)	7.33 and 7.40 [a] (ABq, J=6.3 Hz, 4H) 7.6-7.9 (m, 6H) 8.15-8.4 (m, 2H) [b]
5c	2.46 (s, 3H) 2.48 (s, 3H)	4.44 and 4.50 (ABq, J=14.4 Hz, 4H)	7.43 and 7.45 [a] (ABq, J=6.3 Hz, 4H) 7.6-7.9 (m, 6H) 8.0-8.2 (m, 2H) [b]
5d (206.5-207)	2.45 (s, 3H) 2.46 (s, 3H)	4.55 and 4.82 (ABq, J=14.9 Hz, 4H)	7.27 and 7.38 [a] (ABq, J=6.3 Hz, 4H) 7.6-7.9 (m, 6H) 8.1-8.6 (m, 2H) [b]

[a], ortho protons of tolyl. [b], H$_o$ of dibenzazastibocine part.

Scheme 3
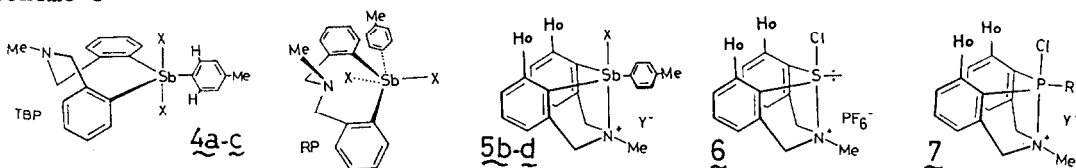
easily with the electron-deficient antimony center in 4a-c.

On the other hand, the most reasonable structure of the compound obtained from 1 and I$_2$ was determined to be ammonioiodo stiborane (5d) as shown in scheme 3 on the basis of the following spectral features. Thus, the ortho protons in the dibenzazastibocine part appear as a multiplet at δ 8.1-8.6; the downfield shift relative to the other aromatic protons is attributable to the anisotropic effect resulted from the transannular hypervalent bond (I-Sb-N$^+$). The methylene protons are seen as an AB quartet (J = 14.9 Hz) at δ 4.55 and 4.82, which show distinct downfield shift relative to those of 4 and are almost the same as those of 6.[2d] The aromatic protons are quite similar to

those of ammoniochloro sulfurane (6) or phosphorane (7).[1] But, the N^+-Me protons appear as a singlet at δ 2.45 which is in upfield different from the expected normal value for the ammonium methyl (δ ~3.1).[2d] The abnormal upfield shift is understandable in terms of the shielding effect of tolyl group in 5d.[1] Almost the same ^{1}H NMR spectra were observed for 5b and 5c. Therefore, it indicates that removal of one of halogen atoms as an anion (Cl^- or Br^-) from 4b,c resulted in the transannular bond formation ($X-Sb-N^+$) such as 5b,c. The compound 5b was converted to 4b by benzyltrimethylammonium chloride. These are probably caused by the relative stability between X-Sb-X hypervalent bond and $X-Sb-N^+$ transannular bond in the present system which is influenced by the halide ion (X^-). Thus, the $X-Sb-N^+$ bonding structure is preferable to the X-Sb-X bonding one in diiodo derivative (5d), while the relative stability is inversed in difluoro, dichloro, and dibromo derivatives. The tendency would be associated with the bond energy of antimony penta-halide.[6]

References and Notes

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6)   Sb-X bond energy (kcal/mol): Sb-F = 96 in SbF_5, Sb-F = 105 in SbF_3, Sb-Cl = 59.4 in $SbCl_5$, Sb-Cl = 75.2 in $SbCl_3$, Sb-Br = 44 in $SbBr_5$, Sb-Br = 62.1 in $SbBr_3$, and Sb-I = 46.6 in SbI_3, referred from "Inorganic Chemistry, Principles of Structure and Reactivity" by J. E. Huheey, Harper & Row, Publishers, Inc., (1983).
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