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SYNTHESIS AND CHEMICAL BEHAVIORS OF 12-SUBSTITUTED DIBENZ[c,f][1,5]AZASTIBOCINE AND DIBENZ[c,f][1,5]AZABISMOCINE DERIVATIVES: EVIDENCES OF 10-Pn-4 TYPE HYPERVALENT INTERACTION

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Abstract: A series of 12-substituted 6-methyl-5,6,7,12-tetrahydro-12-X-dibenz[c,f][1,5]azastibocine (**1**) and azabismocine (**2**) were prepared. Both ^1H and ^{13}C NMR signals of the N-methyl group were shifted to downfield by electron-withdrawing substituent at the pnictogen atoms and the shift was linearly correlated with Hammett σ_m values.

In a preceding paper, we showed the formation of bicyclic phosphoranes or stiboranes by means of the transannular interaction between the pnictogen atom and the amino group in heterocyclic dibenzocyclooctadiene derivatives.[1ab] All of these compounds are regarded as pentacoordinate hypervalent pnictogen compounds, 10-Pn-5.[1]

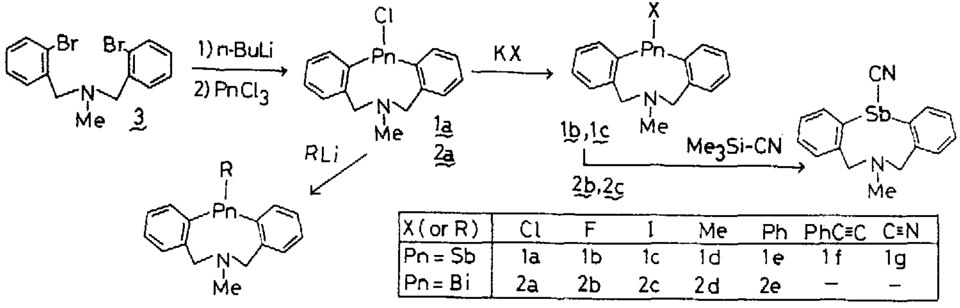
Here, we describe 10-Pn-4 type hypervalent interaction in the title compounds (**1a-g** and **2a-e**) on the basis of substituent effect of ^1H and ^{13}C NMR signals of the N-methyl group as well as chemical behaviors of **1a** and **2a**.

A precursor of tridentate ligand, di(o-bromobenzyl)methylamine (**3**),[1b] was prepared in 60% yield by Menschutkin reaction of o-bromobenzyl bromide with methylamine in dichloromethane solution at room temperature. To a solution of the dilithio derivative prepared from **3** (545 mg, 1.48 mmol) was added antimony trichloride (365 mg, 1.60 mmol) to give 12-chloroaza-stibocine derivative (**1a**) in 58% yield as pure crystals. Treatment of the dilithio derivative with excess bismuth trichloride (3 equiv) afforded 12-chloro azabismocine derivative (**2a**, mp 199-200 °C) in 50% yield. Halogen exchange reaction of **1a** and **2a** with KF in DMF solution afforded the corresponding 12-fluoro derivatives (**1b**, **2b**; X=F) respectively. By the same methodology using KI, 12-iodo derivatives (**1c**, **2c**; X=I) were prepared in moderate yield. Reaction of 12-chloro derivatives (**1a** and **2a**) with lithium reagents (MeLi, PhLi, $PhC\equiv CLi$) gave **1d-f** and **2d,e** in 55-80%.[2] Treatment of 12-fluoro derivative (**1b**) with trimethylsilyl cyanide in

CH_2Cl_2 solution furnished 12-cyano derivative (**1g**) in 80% yield.

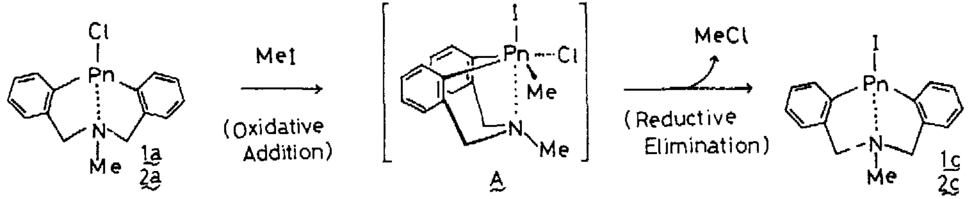
Reaction of **1a** and **2a** with methyl iodide in chloroform solution at 60 °C did not give methylated derivatives but produced the corresponding 12-iodo derivatives (**1c** and **2c**) in quantitative yields. The results must be ascribable to transannular interaction between the pnictogen atom and the amino group, because reaction of methyl iodide with various alkyl amines generally proceeds smoothly (Menschutkin reaction) under mild conditions and also reactivity of methyl iodide with triarylstibine or bismuth compounds is very low.[3] The reaction is rationalized by sequences that oxidative addition of methyl iodide to antimony or bismuth center gives pentacoordinate (or hexacoordinate) **A**, followed by reductive elimination of methyl chloride which is removed from the reaction system due to the volatile properties at reaction temperature (Scheme 2). This is supported by the fact that **1a** and **2a** did not react with methyl tosylate under the same conditions but electron transfer mechanism can not be ruled out at the present stage.

Scheme 1



X (or R)	Cl	F	I	Me	Ph	PhC≡C	C≡N
Pn = Sb	1a	1b	1c	1d	1e	1f	1g
Pn = Bi	2a	2b	2c	2d	2e	–	–

Scheme 2



The ^1H NMR spectral data of **1a-g** and **2a-e** are summarized in Table 1. Structural assignment to **1a** is based upon NMR spectral data and elemental analysis. The methylene protons appear as an AB quartet (J = 14.6 Hz) at δ 3.97 and 4.10 in $CDCl_3$ solution. The two aromatic protons ortho to the pnictogen atom are seen as a multiplet at δ 8.1-8.3: characteristic downfield shift relative to the other aromatic protons.[4] The spectrum of the aromatic protons is quite similar to those of ammoniochlorosulfurane

(**4**), the structure of which was established by means of X-ray analysis.[5] On the other hand, the aliphatic protons appear at slightly upfield relative to those of **4**. All of the other 12-halogeno derivatives (**1b**,**c** and **2a**-**c**) showed almost the same ^{1}H NMR spectral features as that of **1a**. ^{19}F NMR spectra showed a singlet at δ -186 ppm for **1b** and -190 ppm for **2b** in $CDCl_3$ solution (external standard: $CFCl_3$).

Examination of ^{1}H and ^{13}C NMR chemical shifts of **1a**-**e**, **1d**-**g**, and **2a**-**e** reveals the existence of linear relationship for signals of N-methyl groups, δ_{Me}(Sb) and δ_{Me}(Bi), aginst Hammett's σ_m constants of substituents at antimony and bismuth atoms.

For ^{1}H NMR

$$\delta_{Me}(Sb) = 0.79\,\sigma_m + 2.46 \quad (r = 0.972 \text{ for } \mathbf{1a}\text{-}\mathbf{e})$$
$$\delta_{Me}(Sb) = 0.30\,\sigma_m + 2.46 \quad (r = 0.988 \text{ for } \mathbf{1d}\text{-}\mathbf{g})$$
$$\delta_{Me}(Bi) = 1.00\,\sigma_m + 2.47 \quad (r = 0.996 \text{ for } \mathbf{2a}\text{-}\mathbf{e})$$

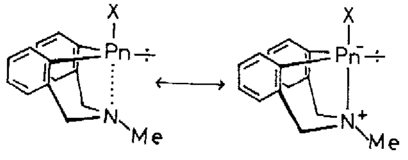
For ^{13}C NMR

$$\delta_{Me}(Sb) = 5.87\,\sigma_m + 41.6 \quad (r = 0.993 \text{ for } \mathbf{1a}\text{-}\mathbf{e})$$
$$\delta_{Me}(Sb) = 1.79\,\sigma_m + 41.5 \quad (r = 0.993 \text{ for } \mathbf{1d}\text{-}\mathbf{g})$$
$$\delta_{Me}(Bi) = 5.62\,\sigma_m + 42.3 \quad (r = 0.984 \text{ for } \mathbf{2a}\text{-}\mathbf{e})$$

Table 1. Selected NMR spectral data of **1a**-**g** and **2a**-**e** in $CDCl_3$ (δ).

Compd. (mp, °C)	Pn-X (or Pn-R)	^{1}H NMR N-methyl	^{1}H NMR methylene	^{1}H NMR aromatic (ortho)	^{13}C NMR N-methyl
1a (172-174)	Cl	2.76	3.97, 4.10 J=14.6 Hz	8.1-8.3	43.6
1b (200-200.5)	F	2.71	3.90, 4.04 J=14.6, 1.2 Hz	7.8-8.0	43.8
1c (215-217.5)	I	2.76	3.92, 4.09 J=14.5 Hz	8.3-8.5	43.7
1d (74-75)	Me	2.42	3.63, 3.81 J=14.5 Hz	7.4-7.7	41.4
1e (117-118)	Ph	2.49	3.69, 3.95 J=14.3 Hz	7.5-7.7	41.5
1f (134-136)	PhC≡C	2.54	3.73, 3.89 J=14.5 Hz	8.2-8.4	42.0
1g (169-172)	CN	2.62	3.81, 3.96 J=14.8 Hz	8.1-8.3	42.5
2a (199-200)	Cl	2.83	4.13, 4.21 J=14.7 Hz	8.45-8.65	44.3
2b (216-219)	F	2.80	4.08, 4.17 J=14.7 Hz	8.05-8.3	44.4
2c (246 dec.)	I	2.85	4.07, 4.18 J=14.7 Hz	8.8-9.1	44.3
2d (219-222)	Me	2.44	3.63, 3.74 J=14.3 Hz	7.7-7.8	42.1
2e (213-215)	Ph	2.52	3.72, 3.91 J=14.4 Hz	7.75-7.95	42.2

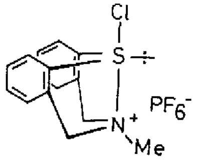
The above linear relationship reflects the change of electron density around the amino group with the substituent at the pnictogen atoms. The relationships also suggest that these compounds maintain at least an analogous conformation in solution and that the electronic effect of the substituent at the pnictogen atoms is transmitted to the N-methyl group. A very analogous phenomenon has also been observed in dibenzo-[b,g][1,5]thiazocine system (**4**), in which the amino group donates electron to the *sulfonio* group.^{5} The most reasonable structure of these compounds, therefore, is depicted as 10-Pn-4 type hypervalent molecule in which the amino group donates electron to the *trivalent* antimony or bismuth atoms, which is a quite unique and unprecedented feature for large metalloidal main group elements.



1a-**g** and **2a**-**e**

10-Pn-4

Pn = Sb and Bi



4 10-S-4

References and Notes

1) (a) K-y. Akiba, K. Okada, and K. Ohkata, *Tetrahedron Lett.*, **27**, 5221 (1986). (b) K. Ohkata, M. Ohnishi, and K-y. Akiba, *Tetrahedron Lett.*, **29**, 5401 (1988). (c) L. E. Carpenter II and J. G. Verkade, *J. Am. Chem. Soc.*, **107**, 7084 (1985).

2) Analytical and spectral data for all new compounds were fully compatible with the given assignments.

3) R. C. Poller,"Comprehensive Org. Chem.", D. N. Jones ed. Pergamon Press., Oxford, Vol 3, 1111 (1979).

4) The downfield shift can be attributed to the deshielding anisotropic effect of hypervalent bond (X-Pn-N) in **1a**-**c**, **1fg**, and **2a**-**c**. cf; G. W. Astrolonges and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 4390 (1977).

5) K-y. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, *J. Am. Chem. Soc.*, **108**, 6320 (1986).

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