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Synthesis of a New Dibenzobicyclic Stiborane by Way of 10-Sb-4 Hypervalent Intermediate.
1,1-Diaryl-5-aza-2,8-dioxa-1-stiba^V-dibenzo[c,f]bicyclo[3,3]octadiene

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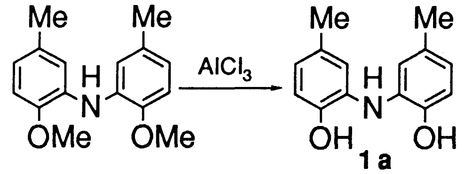
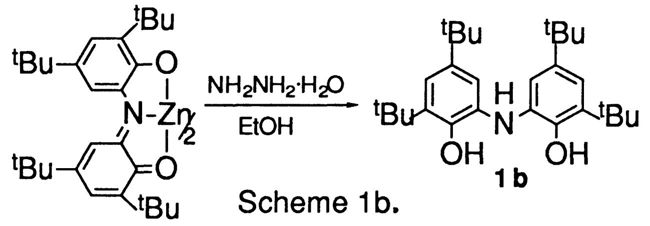
New title dibenzobicyclic stiboranes and related phosphoranes were prepared by means of tridentate 2,2'-diphenolamines. Coordination number of the central pnictogen atoms (Sb and P) changed from three into five during the reaction.

Recently there have been considerable attentions to transannular bond formation in various eight membered ring systems containing main group elements below the second row.1) Here, we describe the changing of coordination number from three to five in an antimony compound by means of transannular bond formation between antimony and nitrogen atoms, which is different from the reaction of the corresponding phosphorus compound.2)

One of the tridentate ligands (**1a**) was obtained by a known procedure as shown in Scheme 1a.3) An analogous ligand (**1b**) was prepared by way of reductive demetallation of the pseudooctahedral zinc complex with hydrazine hydrate in ethanol solution as shown in Scheme 1b.4, 5)



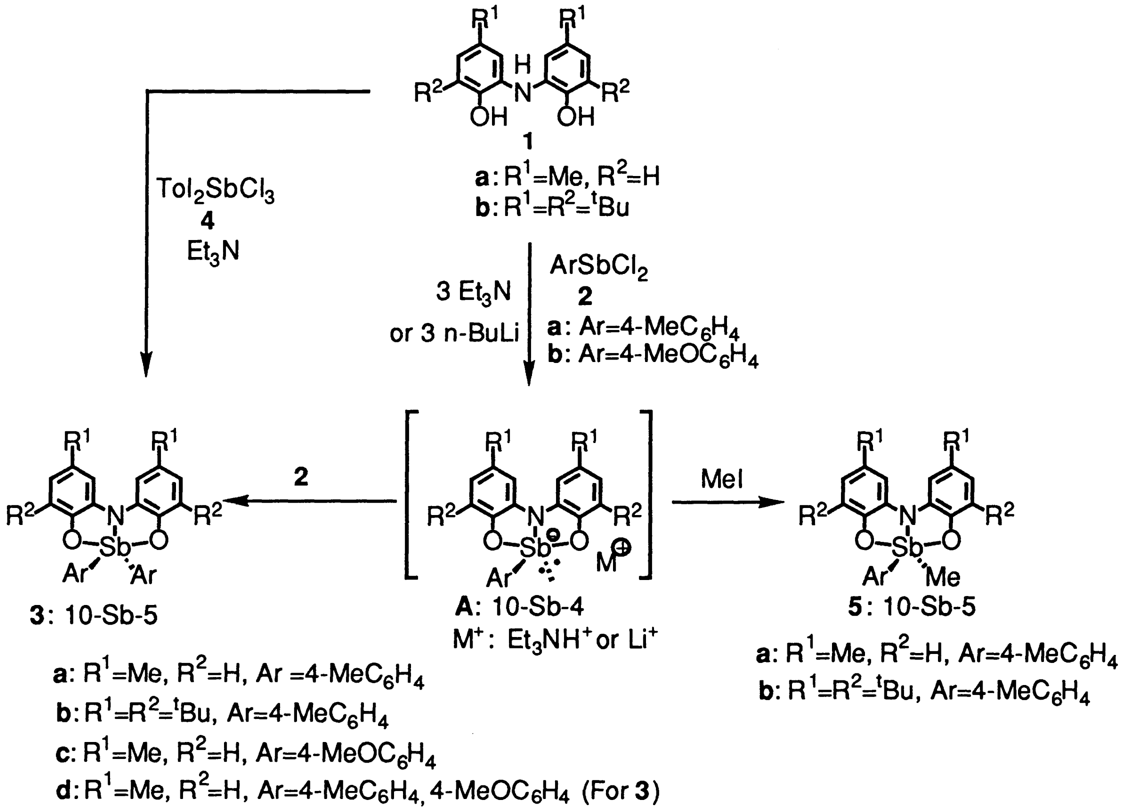
Scheme 1a.



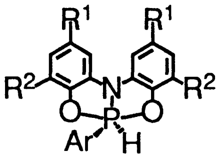
Scheme 1b.

Reaction of the 2,2'-diphenolamine derivatives (**1a,b**) with dichloro(p-tolyl)-antimony (**2a**, 1 equiv.) in the presence of 3 equiv. of triethylamine unexpectedly produced ditolyl derivatives (**3a**; mp 131.5-132.5 °C, **3b**; mp 244-246 °C) in fair yield (11-20%) as a single isolable product, respectively. Under similar conditions, addition of excess antimony compound (**2a**, up to 3 equiv.) increased the yield of **3a** to 49%. The same product (**3a**) was obtained by treatment of trichlorodi(p-tolyl)antimony (**4**) with **1a** in 72% yield. Alternatively, the trianion prepared from **1a** with 3 equiv. of butyllithium in THF reacted with **2a** or p-anisyldichloroantimony (**2b**) to furnish the corresponding diarylantimony derivatives (**3a**, **3c**; mp 108.5-110 °C), respectively.

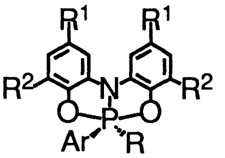
A possible mechanism of the reaction is illustrated in Scheme 2. It can be considered that reaction of aryldichloroantimony (**2a**,**b**) with **1a** or **1b** in the presence of base (triethylamine or butyllithium) affords bicyclic anionic intermediates (**Aa**-**c**: 10-Sb-4 type hypervalent species),6) suffering electrophilic attack by another aryldichloroantimony (**2a**,**b**) to produce the corresponding pentacoordinated stiboranes (**3a**-**c**), respectively. The formal oxidative addition of the amide and the electrophile is ascribable to both transannular participation of the amino group to the antimony atom and the more facile elimination of proton from the secondary amino group to afford **A** in the present heterocyclic cyclooctadiene system.



Scheme 2.



6a,b



7a,b

	R^1	R^2	Ar	R,H	Mp θ_m/°C
6 a	Me	H	C_6H_5	H	152.5-153.0
6 b	^{t}Bu	^{t}Bu	C_6H_5	H	(unstable)
7 a	Me	H	C_6H_5	Et	97.5-99.0
7 b	^{t}Bu	^{t}Bu	C_6H_5	Me	202.5-203.5

The assumed intermediate anion (**Aa**) was trapped with additional p-anisyldichloroantimony (**2b**) to give **3d** in 14% yield. The same trapping experiments of **Aa**,**b** by methyl iodide furnished methyltolylantimony derivatives (**5a**; 57% and **5b**; mp 120 °C dec., 18%), respectively.

On the other hand, treatment of dichlorophenylphosphine with the tridentate 2,2'-diphenolamine ligand (**1a**) in the presence of 2 equiv. triethylamine afforded pentacoordinate phosphorane (**6a**, 64%) in one step which is regarded as an oxidative addition product of the amino group to the phosphorus atom.[2] In this reaction, any trace of diphenyl compounds corresponding to **3a** was not obtained at all. An anion (10-P-4) prepared from **6a** with butyllithium in THF reacted with ethyl iodide to give the expected ethylphenylphosphorane derivative (**7a**) in 65% yield. The same reactions were realized starting with **1b** to afford **6b** and **7b**.

Different chemical behaviors of the antimony compounds from the phosphorus compounds may be attributed to several factors (higher acidity of "R$_4$SbH", larger atomic radius of Sb, and more softness of central antimony atom compared with phosphorus).

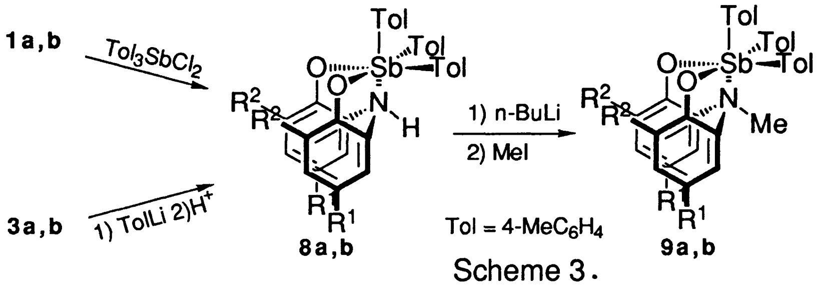
Table 1. Selected ^{1}H NMR Spectral Data of **3** and **5-9**[a]

	^{1}H NMR (δ, CDCl$_3$) Ar and R
3a	2.33 (s, 6H), 7.27 (d, *J*=8.1 Hz, 4H), 7.85 (d, *J*=8.1 Hz, 4H)
3b	2.35 (s, 6H), 7.29 (d, *J*=8.1 Hz, 4H), 7.89 (d, *J*=8.1 Hz, 4H)
3c	3.80 (s, 6H), 6.9-7.1 (m, 4H), 7.90 (d, *J*=8.8 Hz, 4H)
3d	2.39 (s, 3H), 3.82 (s, 3H), 7.32 (d, *J*=7.8 Hz, 2H), 7.55 (d, *J*=7.9 Hz, 2H), 7.89 (d, *J*=7.9 Hz, 2H), 7.95 (d, *J*=7.8 Hz, 2H)
5a	1.94 (s, 3H), 2.39 (s, 3H), 7.33 (d, *J*=8.1 Hz, 2H), 7.82 (d, *J*=8.1 Hz, 2H)
5b	1.80 (s, 3H), 2.38 (s, 3H), 7.32 (d, *J*=8.1 Hz, 2H), 7.86 (d, *J*=8.1 Hz, 2H)
6a	7.2-7.3 (m, 3H), 7.3-7.8 (m, 2H), 8.83 (d, *J*=766.9 Hz, 1H)
6b	7.2-7.6 (m, 5H), 8.80 (d, *J*=777.8 Hz, 1H)
7a	1.31 (dt, *J*=24.0 and 7.3 Hz, 3H), 2.1-2.8 (m, 2H), 7.2-7.4 (m, 5H)
7b	2.23 (d, *J*=15.2 Hz, 3H), 7.5-7.9 (m, 5H)
8a	2.25 (s, 6H), 2.37 (s, 3H), 6.69 (d, *J*=7.9 Hz, 2H), 6.85 (d, *J*=7.9 Hz, 2H), 6.8-7.7 (m, 2H), 7.1-7.3 (m, 4H), 7.90 (d, *J*=7.9 Hz, 2H), 5.25 (s, 1H; NH)
8b	2.23 (s, 6H), 2.39 (s, 3H), 6.94 (d, *J*=8.1 Hz, 6H), 7.25 (d, *J*=8.1 Hz, 4H), 7.90 (d, *J*=8.1 Hz, 2H), 5.42 (s, 1H; NH)
9a	2.31 (s, 6H), 2.39 (s, 3H), 6.7-7.1 (m, 6H), 7.45 (d, *J*=7.9 Hz, 4H), 7.88 (d, J=7.9 Hz, 2H), 3.20 (s, 3H; NMe)
9b	2.25 (s, 6H), 2.36 (s, 3H), 6.96 (d, *J*=8.1 Hz, 6H), 7.32 (d, *J*=8.1 Hz, 4H), 7.83 (d, *J*=8.1 Hz, 2H), 3.12 (s, 3H; NMe)

a) All of the compounds showed the NMR signals of the corresponding tridentate ligand part in addition to the above, respectively.

In order to inquire into the interesting chemical behaviors of **3a,b** and to confirm the assigned structure chemically, reaction of the stiboranes (**3a,b**) with a lithium reagent was examined. Treatment of **3a,b** with p-tolyllithium gave tritolyl derivatives (**8a**, 93%; **8b**, 71%), respectively, which were also prepared by reaction of tritolylantimony dichloride with **1a,b** as shown in Scheme 3. ^{1}H NMR spectra of **8a** and **8b** indicated the presence of two kinds of tolyl group (**8a**: δ 2.25, 2.37 and **8b**: δ 2.23, 2.39 for the methyl hydrogens, the ratio being 2 : 1). According to the spectral characteristics, **8a** and **8b** were assigned to pseudooctahedral structure as shown in

Scheme 3. Deprotonation of **8a,b** with butyllithium, followed by methylation by methyl iodide, gave rise to *N*-methyl derivatives (**9a,b**), respectively. Selected ^{1}H NMR spectral data of stiboranes and their related compounds are summarized in Table 1.7) **8a,b** and **9a,b** show unique structure and are rare examples of hexacoordinate antimony compounds which are stable for usual handling in the air. In this communication, the existence of 10-Sb-4 and 10-P-4 species with tridentate ligand was verified and the isolation of 12-Sb-6 compounds has been stimulating further study.



Scheme 3.

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2) R. Contreras, A. Murillo, G. Uribe, and Klaebe, *Heterocycles*, **23**, 2187 (1985).
3) C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *J. Am. Chem. Soc.*, **88**, 2727 (1966). For **1a**; mp 120-125.5 °C; ^{1}H NMR (δ, CDCl$_3$) 2.22 (s, 6H), 5.22 (brs, 3H), 6.6-6.9 (m, 6H).
4) A. Y. Girgis and A. L. Balch, *Inorg. Chem.*, **14**, 2774 (1975).
5) Experimental procedure for preparation of **1b**: to a solution of the zinc complex (0.1 mmol) in ethanol (10 ml) was added hydrazine hydrate (0.5 mmol) and the reaction mixture was heated in the reflux temperature for 4 h. After concentration of the mixture, the residue was purified with column chromatography over silica gel (hexane/ethyl acetate; 5:1) to give **1b** in 90% yield. Due to instability of **1b** under the air, the product was converted into diacetyl derivative for identification; mp 199-201 °C; MS: m/z 510 (M^+); ^{1}H NMR (δ, CDCl$_3$); 1.26 (s, 18H), 1.37 (s, 18H), 2.29 (s, 6H), 7.00 (d, J = 2.2 Hz, 2H), 7.25 (d, J = 2.2 Hz, 2H).
6) The N-X-L designation was proposed by J. C. Martin et al.: X, central atom; N, formal valence-shell electrons about an X; L, the number of ligands. C. W. Perkins, J. C. Martin, A. J. Arduengo, A. Algeria, and J. K. Kochi, *J. Am. Chem. Soc.*, **102**, 7753 (1980).
7) Elemental analyses (C, H, N) for new compounds (**3a,b**, **6a**, **7a**, **8a,b**, and **9a,b**) were fully compatible with the given assignments.
8) Partial support of this work was provided by Grant-in Aids for Scientific Research (Nos. 63470017 and 01540427) administered by the Ministry of Education, Science and Culture of the Japanese Government.

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