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[2+3]CYCLOADDITION REACTION OF A KINETICALLY STABILIZED DISTIBENE WITH A NITRILE OXIDE LEADING TO THE FORMATION OF A UNIQUE HETEROCYCLIC COMPOUND

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The synthesis of a 1-oxa-5-aza-2,3-distibacyclopent-4-ene derivative by the [2+3]cycloaddition reaction of a kinetically stabilized distibene, BbtSb=SbBbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl), with MesCNO (Mes = mesityl) has been performed.

Keywords: distibene, nitrile oxide, 1-oxa-5-aza-2,3-distibacylopent-4-ene, cycloaddition, X-ray crystallographic analysis.

The chemistry of low-coordinated compounds of heavier group 15 elements has been one of the most attractive areas of main group element chemistry [1-4] since the first isolation of a diphosphene, Mes*P = PMes* (Mes* = 2,4,6-tri-*t*-butylphenyl), by taking advantage of kinetic stabilization [5]. The doubly bonded systems of heavier group 15 elements (dipnictenes) are no more imaginary species even in the case of the heaviest elements, bismuth, since our successful isolation of the first stable distibene (TbtSb=SbTbt, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) [6] and dibismuthene (TbtBi=BiTbt) [6, 7]. Recently, much more attention has been paid to the elucidation of their reactivity. Above all, the cycloaddition reactions of such heavier π-bond systems were found to be convenient routes to novel heterocyclic systems. For example, Yoshifuji et al. reported that the sulfurization and selenization reactions of Mes*P = PMes* afforded the corresponding chalcogenadiphosphiranes (three-membered ring compounds) as the final products [8-12]. In addition, many examples have been reported for the [2+4]cycloaddition reactions of diphosphenes with dienes giving the corresponding six-membered ring compounds containing a P–P bond [1–4]. On the other hand, we have reported the synthesis and properties of stable diphosphenes, distibenes, and dibismuthenes bearing efficient steric protection groups (Tbt and Bbt) [6, 7, 13]. The Bbt-substituted heterocyclic compounds containing two pnictogen and chalcogen (S, Se, or Te) atoms, such as thiadiphosphirane [13], selenadiphosphirane [13], 1,2,4,3,5-trithiadistibolane [14], 1,2,3,5,4,6-tetrathiadistibinane [14], selenadisti-birane [15], telluradistibirane [16], and telluradibismirane [16], were synthesized by the sulfurization, selenization, and tellurization of BbtE=EBbt (E = P, Sb, and Bi). Thus, dipnictenes should be good precursors for the corresponding heterocyclic compounds.

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* Dedicated to Prof. Dr. E. Lukevics on the occasion of his 70th birthday

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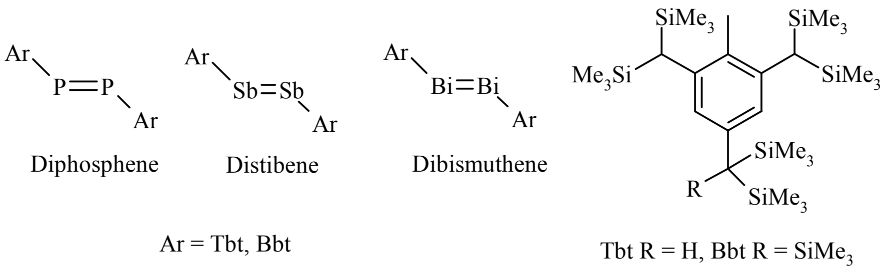
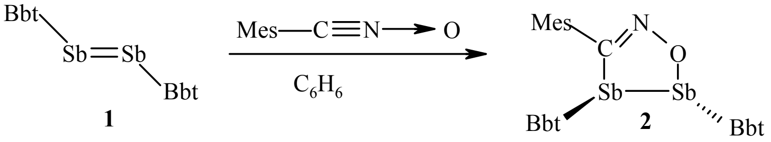
Scheme 1



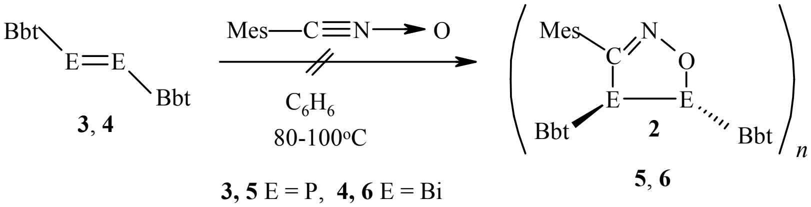
Although the thermal reaction of BbtSb=SbBbt with 2,3-dimethyl-1,3-butadiene in the expectation of generating a 1,2-distibacyclohex-4-ene derivative *via* [2+4]cycloaddition failed, we have preliminarily reported the trapping reaction of TbtSb=SbTbt using MesCNO as a 1,3-dipole to afford the corresponding five-membered ring system *via* [2+3]cycloaddition. In this case, however, the reaction requires severe reaction conditions due to the extremely low solubility of TbtSb=SbTbt in organic solvents. Recently, it was demonstrated by the chalcogenation reaction of dipnictenes (*vide supra*) that the Bbt-substituted dipnictenes (BbtE=EBbt, E = P, Sb, Bi) should be appropriate compounds for the investigation of the reactivity of dipnictenes due to their higher solubility in organic solvents [6, 13–18]. We report here the details for the synthesis of a novel heterocyclic system containing a five-membered ring of –Sb–Sb–C=N–O–, i. e., 1-oxa-5-aza-2,3-distibacyclopent-4-ene, *via* [2+3]cycloaddition reaction of the kinetically stabilized distibene (**1**, BbtSb=SbBbt) with MesCNO.

When MesCNO (1.0 eq) was added to the benzene solution of BbtSb=SbBbt (**1**) at room temperature, the reaction proceeded smoothly as judged by the color change from orange to yellow. The reaction mixture was purified by GPLC to afford the corresponding 1-oxa-5-aza-2,3-distibacyclopent-4-ene derivative **2** in 60% yield (Scheme 2). Unfortunately, the reactions of BbtP=PBbt (**3**) and BbtBi=BiBbt (**4**) with MesCNO in the expectation of generating the corresponding [2+3]cycloadducts, **5** and **6**, did not proceed even at 80-100ºC in a sealed tube (benzene-d_6) (Scheme 3). Although the reason why diphosphene **3** and dibismuthene **4** are inert toward MesCNO even under such severe conditions is unclear at present, the steric reason should be dominant in the case of the diphosphene and the long Bi–Bi bond might be structurally inappropriate for the [2+3] cycloaddition with MesCNO. In the theoretical calculations (comparison of SCF energies without ZPE corrections) for the H-substituted model compounds, such as HCNO, HP=PH, HSb=SbH, and HBi=BiH, the [2+3]cycloaddition reactions of HP=PH and HSb=SbH with HCNO were found to be highly exothermic reactions (48.3 and 34.4 kcal/mol, respectively), while that of HBi=BiH with HCNO was calculated to be slightly exothermic (only 0.05 kcal/mol).

Scheme 2



Scheme 3



The structure of the novel heterocyclic system, 1-oxa-5-aza-2,3-distibacyclopent-4-ene derivative **2**, was definitively confirmed by the X-ray crystallographic analysis (Fig. 1). The two Bbt groups on the Sb atoms are in *trans* configuration. The five-membered ring of the 1-oxa-5-aza-2,3-distibacyclopent-4-ene moiety is not planar, as shown in Fig. 1, *b*, probably due to the steric congestion, although the theoretically optimized structure of the H-substituted model compound **7** exhibits planar geometry. In addition, the structural parameters obtained by the theoretical calculations for Dmp-substituted (Dmp = 2,6-dimethylphenyl) model compound **8**, which is less hindered as compared with **2**, are in good agreement with those observed for compound **2** as shown Fig. 2. The Sb–Sb bond length of **2** is 2.8459(3) Å, which is longer than that of BbtSb=SbBbt (**1**) and within the range of typical Sb–Sb bond lengths [ex. Ph_2Sb–$SbPh_2$: 2.837 Å] [19]. All the bond angles around the Sb atoms are close to 90º (Sb–Sb–C(Mes): 79.50(9), Sb–Sb–C(Bbt): 100.76(9) and 111.83(9), Sb–Sb–O: 82.39(7), C(Bbt)–Sb–C(Mes): 99.17(13), C(Bbt)–Sb–O: 103.48(11)º), reflecting the intrinsic nature of an antimony atom, that is, a lower tendency to form a hybridized orbital and preference to maintain $5s^25p^3$ valence electron configuration [20-22].

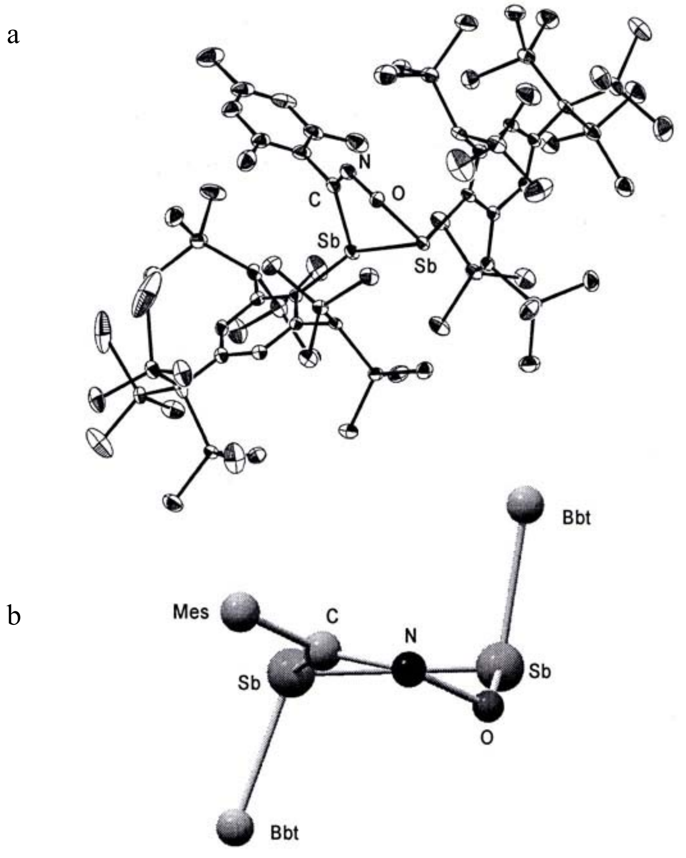


Fig. 1. ORTEP drawing of **2** (thermal ellipsoid plots, 50% probability). The hexane molecule and the hydrogen atoms are omitted for clarity (*a*). Top view of the 1-oxa-5-aza-2,3-distibacyclopent-4-ene ring of **2** (ball & stick model) (*b*).

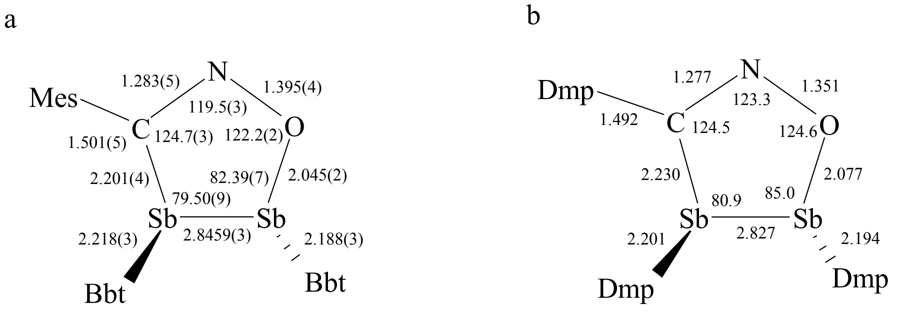


Fig. 2. Selected bond lengths (Å) and angles (deg) of **2** (*a*). Theoretically optimized structural parameters of model compound **8** (*b*).

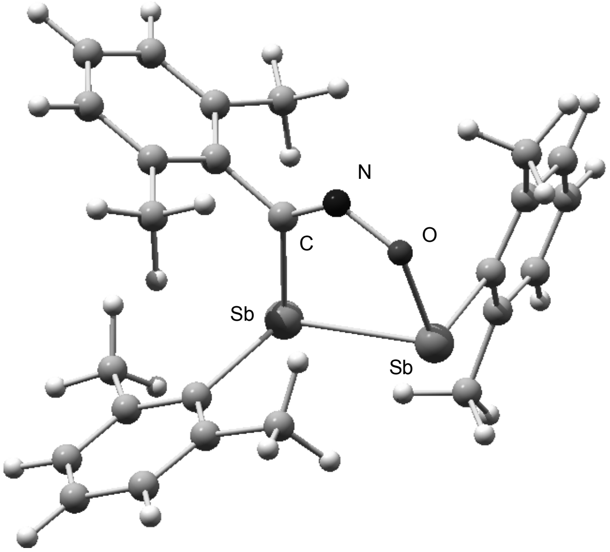
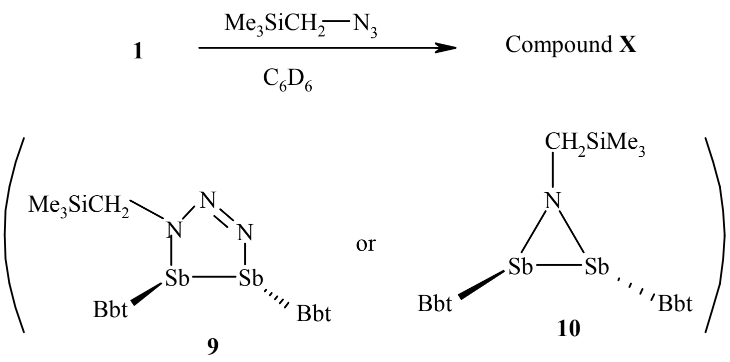


Fig. 3. Optimized structure of model compound **8**.

The successful result of the reaction of distibene **1** with MesCNO leading to the formation of [2+3]-adduct **2** prompted us to attempt the reaction of **2** with other 1,3-dipoles. Although distibene **1** and dibismuthene **2** did not react with $MesN_3$ as a 1,3-dipole even at 80°C in benzene (in a sealed tube) or under photo-irradiation (100 W high-pressure Hg lamp) conditions probably due to the steric reason, the reaction of distibene **1** with $Me_3SiCH_2N_3$ in C_6D_6 at room temperature afforded a novel compound. The product (compound **X**) should be the corresponding [2+3]cycloadduct **9** or the azadistibirane **10**. However, the extremely high sensitivity of compound **X** toward air, moisture, and/or light prevented us from executing further analytical procedures.

Thus, it was found that the kinetically stabilized distibene, BbtSb=SbBbt (**1**), can undergo facile [2+3] cycloaddition reaction with MesCNO leading to the formation of the corresponding [2+3]cycloadduct, 1-oxa-5-aza-2,3-distibacyclopent-4-ene **2**. This reaction should be important from the viewpoints of not only the synthesis of a novel heterocyclic compound but also the novel reactivity of the Sb=Sb double-bond compound. We hope that the unique reactivities of dipnictenes reported here will lead to further progress in main group element chemistry and novel application of heterocyclic compounds.

Scheme 4



EXPERIMENTAL

All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods prior to use. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in C_6D_6 with a JEOL JNM AL-300 spectrometer. Signals due to C_6D_5H (7.15 ppm) and C_6D_6 (128 ppm) were used as an internal standard in ^1H and ^{13}C NMR, respectively. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. GPLC (gel permeation liquid chromatography) was performed on an LC-908 or LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene or chloroform). All melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. BbtP=PBbt (**3**) [13], BbtSb=SbBbt (**1**) [6], BbtBi=BiBbt (**4**) [6], and MesCNO [23] were prepared according to the reported procedures.

Reaction of distibene 1 with MesCNO. To a benzene solution (1 ml) of BbtSb=SbBbt (45.0 mg, 0.03 mmol) was added MesCNO (4.8 mg, 0.03 mmol) at room temperature. After stirring the solution for 2 h at the same temperature, the solvent of the reaction mixture was removed under reduced pressure. Purification of the residue by GPLC afforded 1-oxa-5-aza-2,3-distibacyclopent-4-ene derivative **2** (30 mg, 60%) as yellow crystals, mp. 115ºC (hexane, decomp.). ^1H NMR (60 ºC, C_6D_6), δ ppm: 6.92 (2H, br.s, Bbt-*m*-CH); 6.91 (2H, s, Bbt-*m*-CH); 6.67 (2H, s, Mes-*m*-CH); 3.24 (1H, br.s, Bbt-*o*-CH); 2.56 (1H, br.s, Bbt-*o*-CH); 2.20 (6H, s, Mes-*o*-CH_3); 2.04 (3H, s, Mes-*p*-CH_3); 2.01 (1H, s, Bbt-*o*-CH); 1.98 (1H, s, Bbt-*o*-CH); 0.51 (9H, s, Bbt–TMS); 0.44 (9H, s, Bbt–TMS); 0.41 (9H, s, Bbt–TMS); 0.40 (9H, s, Bbt-TMS); 0.36 (27H, s, Bbt–TMS); 0.35 (27H, s, Bbt–TMS); 0.32 (18H, s, Bbt–TMS); 0.29 (9H, s, Bbt–TMS); -0.07 (9H, s, Bbt–TMS). The ^{13}C NMR spectrum of compound **2** is too complicated to be assigned even at high temperature probably due to the restricted rotation caused by the severe steric congestions between the Bbt groups and the Mes group. HRMS (FAB), Found: *m/z* 1654.6292 $[M]^+$. $C_{70}H_{146}NO^{123}Sb_2Si_{14}$. Calculated: M = 1654.6258. Found, %: C 50.24; H 8.88; N 0.82. $C_{70}H_{146}NOSb_2Si_{14}$. Calculated, %: C 50.84; H 8.84; N 0.85.

X-Ray crystallographic analysis. Single crystals of compound **2** suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane at room temperature. The prismatic crystal was mounted on a glass fiber. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71070$ Å) at -170ºC to $2\theta_{max} = 50.0º$. The structure was solved by a direct method (SHELXS-97) [24, 25] and refined by full-matrix least squares procedures on F^2 for all reflections (SHELXL-97) [25]. The solvated hexane was disordered and their occupancies were refined (0.55:0.45). The trimethylsilyl groups of $C(SiMe_3)_3$ at the *para* position of one of the Bbt groups were disordered, and the occupancies were refined (0.55:0.45). All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. Crystal data: formula, $C_{76}H_{159}NOSb_2Si_{14}$; formula weight, 1739.80; habit, yellow, prismatic; crystal dimensions (mm), 0.30 × 0.20 × 0.10; temperature –170ºC; monoclinic, $P2_1/c$ (14); $a = 17.9504(7)$, $b = 33.5625(11)$, $c = 18.0515(8)$ Å, $\beta = 113.8363(13)^{\circ}$, $V = 9947.7(7)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.162$ g•cm^{-3}, independent reflections/parameters = 17489/993, R_1 ($I > 2\sigma(I)$) = 0.0466, wR_2 ($I > 2\sigma(I)$) = 0.0986, R_1 (all data) = 0.0521, wR_2 (all data) = 0.1010, GOF = 1.163, largest difference peak and hole 2.313 and -0.998 eÅ^{-3} (around the Sb atoms). CCDC-622802 (**2**) contains the supplementary crystallographic data for this paper. These can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic data Centre.

Reaction of distibene 1 with $Me_3SiCH_2N_3$. A benzene-d_6 solution (0.6 ml) of BbtSb=SbBbt (29.0 mg, 0.02 mmol) and $Me_3SiCH_2N_3$ (4 µl, 0.03 mmol) was degassed and sealed in an NMR tube. The signals of distibene **1** disappeared and those of the unidentified compound (compound **X**) were observed as a sole product as judged by the ^{1}H NMR spectrum. Compound **X**: ^{1}H NMR (room temperature, C_6D_6), δ, ppm: 6.93 (4H, s); 2.97 (2H, s); 2.25 (4H, s); 0.39 (36H, s); 0.37 (36H, s); 0.35 (54H, s); 0.25 (9H, s); 6.91 (2H, s, Bbt-*m*-CH); 6.67 (2H, s, Mes-*m*-CH); 3.24 (1H, br.s, Bbt-*o*-CH); 2.56 (1H, br.s, Bbt-*o*-CH); 2.20 (6H, s, Mes-*o*-CH_3); 2.04 (3H, s, Mes-*p*-CH_3); 2.01 (1H, s, Bbt-*o*-CH); 1.98 (1H, s, Bbt-*o*-CH); 0.51 (9H, s, Bbt–TMS); 0.44 (9H, s, Bbt–TMS); 0.41 (9H, s, Bbt–TMS); 0.40 (9H, s, Bbt–TMS); 0.36 (27H, s, Bbt–TMS); 0.35 (27H, s, Bbt-TMS); 0.32 (18H, s, Bbt–TMS); 0.29 (9H, s, Bbt–TMS); -0.07 (9H, s, Bbt–TMS).

Theoretical calculations. All calculations were conducted using the Gaussian 03 series of electronic structure programs [26]. It was confirmed by frequency calculations that the optimized structures have minimum energies. The triple zeta basis set ([3*s*3*p*]) [27] augmented by two sets of *d*-polarization functions and diffuse functions [28] for *P* (*d*-exponents 0.537 and 0.153, *sp*-exponents 0.0298), Sb (*d*-exponents 0.277 and 0.088, *sp*-exponents 0.0219), and Bi (*d*-exponents 0.229 and 0.069, *sp*-exponents 0.0204) were used with an effective core potential. The 6-31+G(d) basis sets were used for C and H.

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