employed to increase kinetic stability toward external reagents, may be the key to suppressing germasilene and digermene isomerizations as well.

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Synthesis of Thermochromic Dibismuthines with Nonthermochromic Distibine Analogs

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Summary: Octamethylbistibole (**4a**), octamethylbibismole (**4b**), 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbistibole (**5a**), and 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbibismole (**5b**) have been prepared by the reductive coupling of their respective precursor phenyl- or bromopnictoles. The bibismoles are thermochromic, while the bistiboles are not. This is the first observation of differing behavior between analogous distibines and dibismuthines with regard to thermochromicity.

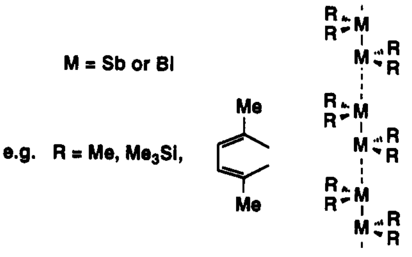
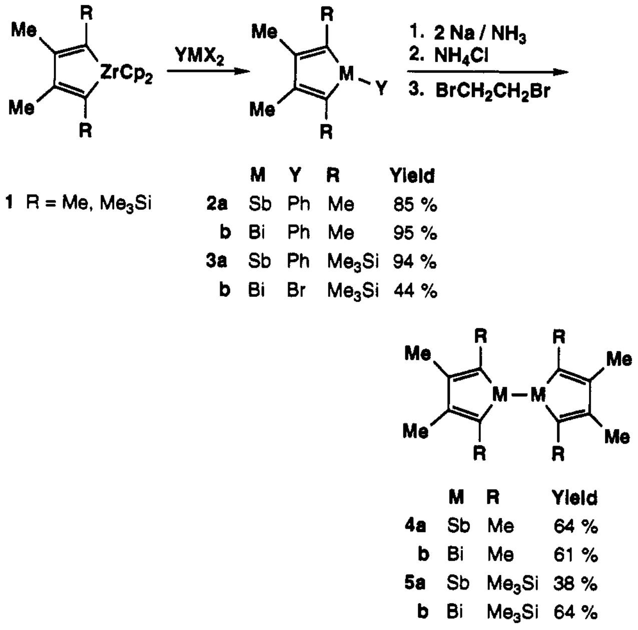


Figure 1.

Scheme I



1 R = Me, Me$_3$Si

	M	Y	R	Yield
2a	Sb	Ph	Me	85 %
b	Bi	Ph	Me	95 %
3a	Sb	Ph	Me$_3$Si	94 %
b	Bi	Br	Me$_3$Si	44 %

	M	R	Yield
4a	Sb	Me	64 %
b	Bi	Me	61 %
5a	Sb	Me$_3$Si	38 %
b	Bi	Me$_3$Si	64 %

Certain distibines and dibismuthines display a dramatic color change upon melting.[1,2] This change has been labeled thermochromic, although it is associated with a phase change.[2] The thermochromic compounds also show color changes on solvation. To date, when a dibismuthine has been thermochromic, its antimony analog has also displayed the same behavior and vice versa.[2,3] However, there are no reasons to anticipate that this should always be the case. The crystal structures[4-10] of these thermochromic species, when available, reveal the pnictogen centers to be ordered in a stacked linear arrangement with short intermolecular pnictogen–pnictogen contacts (Figure 1[11,12]). This packing arrangement is not observed in nonthermochromic dipnictines[13] and is believed to be responsible for the thermochromic behavior.[2,14] Since the van der Waals radius of bismuth (2.3 Å)[10] is considerably greater than that of antimony (2.2 Å),[10] it seems likely that

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dibismuthines might more readily achieve the intermolecular contacts necessary for thermochromicity. Continuing our interest into the synthesis and unusual structural properties of main-group heterocycles,[15] we report here the first thermochromic dibismuthines which have nonthermochromic distibine analogs.

The bipnictoles **4** and **5** were prepared according to Scheme I. By use of the procedures of Fagan and Nugent,[16] reaction of zirconacycles **1**[17] with $PhSbCl_2$,[18] $PhBiBr_2$,[19] or $BiBr_3$ in benzene or ether (**3b**), gave the known phenylpnictoles **2a**,[16] **2b**,[16] and **3a**[20] and the bromobismole **3b**.[20,21] After removal of solvent, the products were isolated simply by extraction with hexane or ether (**3b**), filtration to remove zirconocene dihalide, and concentration in vacuo (**3b** was recrystallized from ether). Compounds **2** and **3** were then coupled using standard procedures[3,21,22] to give octamethylbistibole (**4a**), octamethylbibismole (**4b**), 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbistibole (**5a**),[21] and 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbibismole (**5b**)[21] in reasonable yield.

Bistiboles **4a** and **5a** both show the colors and behavior typical of nonthermochromic distibines.[2] They form orange solids that melt[23] to identically colored liquids and give orange/yellow solutions. In contrast, bibismoles **4b** and **5b** are thermochromic, forming lustrous deep green crystalline solids that melt[23] reversibly to orange and red oils, respectively. Furthermore, compound **4b** gives yellow/orange solutions, while **5b** appears red in hexane and benzene.

The bipnictoles **4** and **5** have been characterized by spectroscopy (^1H and ^{13}C NMR and IR) and by elemental analysis. It is noteworthy that bibismole **5b** gives a single sharp signal in the ^1H NMR spectrum for the protons of the trimethylsilyl groups, while its antimony analog **5a** gives a very broad peak, indicative of restricted rotation.[21] This differing spectral feature of **5a** and **5b** is likely a consequence of the shorter pnictogen–pnictogen bond (Sb–Sb = 2.84–2.88 Å; cf. Bi–Bi = 2.99–3.12 Å)[4-10,13] in the distibine forcing the trimethylsilyl groups of the two stibole rings into close proximity. Preliminary X-ray crystallographic information[24] suggests that, in the solid state, compound **4b** displays a linear construction of bismuth atoms, as observed in other thermochromic compounds.[4-10]

Ashe has prepared the antimony and bismuth 2,2′,5,5′-tetramethylbipnictoles and found them to be thermochromic.[5,8] Addition of further methyl groups to the 3- and 4-positions of the bipnictoles, as in compounds **4**, is apparently a great enough change to prevent thermochromicity in the bistibole **4a** but not in the bibismole **4b**.

Compounds **4** and **5** importantly demonstrate, for the first time, that antimony and bismuth dipnictogen analogs can behave differently with regard to thermochromicity. Further results, from our laboratories, on distibine and dibismuthine compounds will be reported in due course.

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Supplementary Material Available: Text giving full experimental details for the preparation of compounds 2 and 4 and NMR, elemental analysis, and IR characterization data for compounds 4 (3 pages). Ordering information is given on any current masthead page.

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(21) **Representative Experimental Procedures. Preparation of 3a.** To a solution of $PhSbCl_2$ (5 mmol) in benzene (15 mL) was added 1 equiv of the metallacycle 1 (R = Me_3Si) in benzene (15 mL). After the mixture was stirred for 10 min, the volatiles were removed in vacuo and the product was extracted with hexane (25 mL) and cannula-filtered from the residues. The hexane extracts were cooled to −80 °C, and a small amount of precipitate formed. The solution was again filtered and the solid discarded. Removal of the solvent gave **3a**, a known compound,[20] as a tan solid: yield 1.997 g, 4.72 mmol, 94%. **Preparation of 3b.** Zirconacycle 1 (R = Me_3Si) was generated in situ from the sequential addition of *n*-BuLi (24.8 mL, 1.61 M, 40 mmol) and 1-(trimethylsilyl)-1-propyne (7 mL, 47 mmol) to Cp_2ZrCl_2 (5.842 g, 20 mmol) at −78 °C in THF and subsequent heating of the reaction mixture to 50 °C for 20 min. The volatiles were removed in vacuo and ether (60 mL) was added to give a red solution and white precipitate. To the zirconacycle reaction mixture was added a solution of $BiBr_3$ (8.974 g, 20 mmol; ether 60 mL), and after 10 min the solution was cannulated from the precipitate. The ether was removed, the solid residues were washed with hexane (40 mL), and the product was again dissolved in ether (160 mL). Cannula filtration to remove insoluble material and cooling (−80 °C) of the ether solution gave the product as an orange crystalline solid: yield 4.536 g, 8.8 mmol, 44%. The material obtained showed small amounts (<5%, by ^1H NMR) of zirconium species but was suitable for the coupling reaction. Recrystallization from CH_2Cl_2 gave analytically pure material: mp 206–208 °C. ^1H NMR (C_6D_6): δ 1.63 (s, 6 H), 0.35 (s, 18 H). $^{13}C\{^1H\}$ NMR: δ 176.7, 174.7, 35.3, 2.9. IR: 2948, 2894, 1562, 1519, 1427, 1402, 1371, 1311, 1245, 1212, 1105, 1032, 994, 838, 778, 753, 731, 686, 629, 540 cm^{-1}. Anal. Calcd for $C_{12}H_{24}BrSi_2Bi$: C, 28.08; H, 4.71. Found: C, 27.92; H, 4.89. **Preparation of the Bipnictoles 5a,b.** To a suspension of finely ground 3 (**a**, 1.181 mmol; **b**, 2 mmol) in refluxing ammonia (ca. 75 mL) was added Na (2 equiv). Addition was completed over 10 min, and the reaction mixtures were vigorously stirred for a short time (**3a**, 60 min; **3b**, 5 min). In the case of **3a**, NH_4Cl (1 equiv) was then added to remove phenylsodium. Subsequent dropwise addition of 1,2-dibromoethane (1 equiv) over 2–5 min to the dark reaction solutions gave the dipnictoles as precipitates. The volatiles were then removed and the bipnictoles extracted with hexane (10–20 mL) followed by filtration. The products were purified by crystallization from hexane at −80 °C (**5b**) and sublimation (**5a** and **5b**). **5a**: yield 0.156 g, 0.23 mmol, 38%; ^1H NMR (C_6D_6) δ 2.07 (s, 12 H), 0.29 (v br, 36 H) (the signal at 0.29 ppm sharpened considerably when the spectrum was obtained at 65 °C); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 185.0, 163.9, 24.1, 1.7; IR 2988, 2947, 2897, 2846, 1539, 1483, 1429, 1401, 1374, 1312, 1245, 1113, 1029, 991, 850, 836, 751, 686, 631, 545 cm^{-1}. Anal. Calcd for $C_{24}H_{48}Si_4Sb_2$: C, 41.63; H, 6.99. Found: C, 41.62; H, 7.06. **5b**: yield 0.562 g, 0.64 mmol, 64% (pure by ^1H NMR); ^1H NMR (C_6D_6) δ 2.03 (s, 12 H), 0.30 (s, 36 H); $^{13}C\{^1H\}$ NMR δ 170.2, 32.4, 2.9 (carbon nuclei adjacent to bismuth centers are frequently not observed);[3] IR 2988, 2947, 2895, 2845, 1545, 1486, 1428, 1399, 1371, 1243, 1102, 1029, 990, 834, 780, 749, 684, 628, 542 cm^{-1}. Anal. Calcd for $C_{24}H_{48}Si_4Bi_2$ (sublimed): C, 33.25; H, 5.58. Found: C, 33.31; H, 5.72.

(22) NH_4Cl, used to remove phenylsodium, was not necessary in the coupling of **3b**.

(23) Melting points: **4a**, 84–85 °C; **4b**, 128–129 °C; **5a**, 95–100 °C; **5b**, 121–122 °C.

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