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**The Synthesis of Thermochromic Dibismuthines with Non-thermochromic Distibine  
Analogues**

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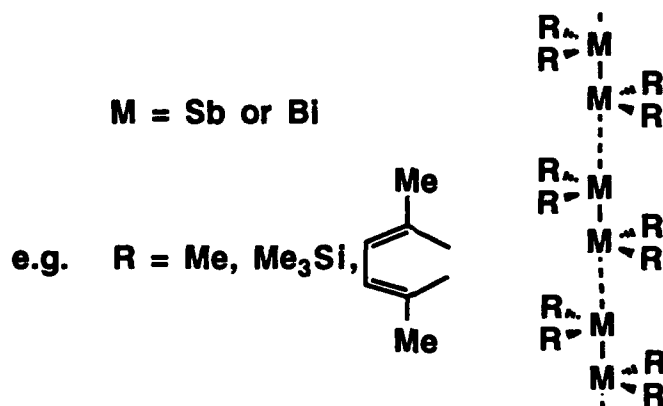
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**Abstract.**

Octamethylbistibole (**4a**), octamethylbibismole (**4b**), 2,2',5,5'-tetra(trimethylsilyl)-3,3',4,4'-tetramethylbistibole (**5a**) and 2,2',5,5'-tetra(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.

Certain distibines and dibismuthines display a dramatic color change upon melting.<sup>1,2</sup> This change has been labeled thermochromic, although it is associated with a phase change.<sup>2</sup> 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.<sup>2,3</sup> However, there are no reasons to anticipate that this should always be the case. The crystal structures<sup>4-10</sup> 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<sup>11,12</sup>). This packing arrangement is not observed in non-thermochromic dipnictines<sup>13</sup> and is believed to be responsible for the thermochromic behavior.<sup>2,14</sup> Since the van der Waals radius of bismuth (2.3 Å)<sup>10</sup> is considerably greater than that of antimony (2.2 Å),<sup>10</sup> it seems likely that 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,<sup>15</sup> we report here the first thermochromic dibismuthines which have non-thermochromic distibine analogs.

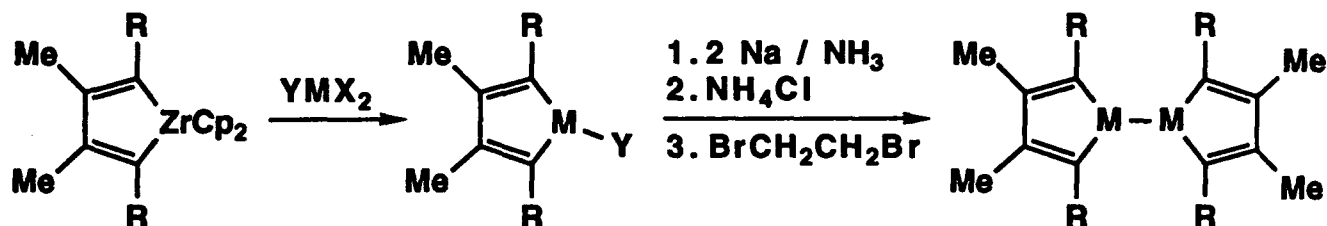
Figure 1



The bipnictoles **4** and **5** were prepared according to Scheme 1. Utilizing the transmetallation procedures of Fagan and Nugent,<sup>16</sup> reaction of zirconacycles **11**<sup>7</sup> with  $\text{PhSbCl}_2$ ,<sup>18</sup>  $\text{PhBiBr}_2$ <sup>19</sup> or  $\text{BiBr}_3$  in benzene or ether (**3b**), gave the known phenylpnictoles **2a**,<sup>16</sup> **2b**<sup>16</sup> and **3a**<sup>20</sup> and the bromobismole **3b**.<sup>20</sup> 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<sup>3,21</sup> to give octamethylbistibole (**4a**), octamethylbibismole (**4b**), 2,2',5,5'-tetra(trimethylsilyl)-3,3',4,4'-tetramethylbistibole (**5a**), and 2,2',5,5'-tetra(trimethylsilyl)-3,3',4,4'-tetramethylbibismole (**5b**) in reasonable yield.

**Scheme 1**



|                                     |            | M  | Y  | R                  | Yield |
|-------------------------------------|------------|----|----|--------------------|-------|
| <b>1</b> R = Me, Me <sub>3</sub> Si | <b>2 a</b> | Sb | Ph | Me                 | 85 %  |
|                                     | <b>b</b>   | Bi | Ph | Me                 | 95 %  |
|                                     | <b>3 a</b> | Sb | Ph | Me <sub>3</sub> Si | 94 %  |
|                                     | <b>b</b>   | Bi | Br | Me <sub>3</sub> Si | 44 %  |

|     | M  | R                  | Yield |
|-----|----|--------------------|-------|
| 4 a | Sb | Me                 | 64 %  |
| b   | Bi | Me                 | 61 %  |
| 5 a | Sb | Me <sub>3</sub> Si | 38 %  |
| b   | Bi | Me <sub>3</sub> Si | 64 %  |

Bistiboles **4a** and **5a** both show the colors and behavior typical of non-thermochromic distibines.<sup>2</sup> They form orange solids that melt<sup>22</sup> 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<sup>22</sup> 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 spectroscopically (<sup>1</sup>H and <sup>13</sup>C NMR and IR) and by elemental analysis. It is noteworthy that bibismole **5b** gives a single sharp signal in the <sup>1</sup>H NMR spectrum for the protons of the trimethylsilyl groups, while its antimony analog, **5a**, gives a very broad peak, indicative of restricted rotation.<sup>23</sup> 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)<sup>4-10,13</sup> in the distibine forcing the trimethylsilyl groups of the two stibole rings into close proximity. Preliminary X-ray crystallographic information suggests that, in the solid state, compound **4b** displays a linear construction of bismuth atoms, as observed in other thermochromic compounds.<sup>4-10</sup>

Ashe has prepared the antimony and bismuth 2,2',5,5'-tetramethylbipnictoles and found them to be thermochromic.<sup>5,8</sup> 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:** Full experimental details to the preparation of compounds **2**, **3**, **4** and **5**. NMR, elemental analysis and IR characterization of compounds **3**, **4** and **5**. Ordering information is given on any current masthead page.

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21.  $\text{NH}_4\text{Cl}$ , used to remove phenylsodium, was not necessary in the coupling of **3b**.
22. Melting points: **4a**, 84-85 °C; **4b**, 128-129 °C; **5a**, 95-100 °C; **5b**, 121-122 °C.
23.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) data: **5a**,  $\delta$  2.07 (s, 12H), 0.29 (v. br., 36H); **5b**,  $\delta$  2.03 (s, 12H), 0.30 (s, 36H). The signal for the protons of the trimethylsilyl groups in **5a** sharpened considerably when the spectrum was obtained at 65 °C.