

# Thermochromic Effect in Distibines. The Role of Conjugation

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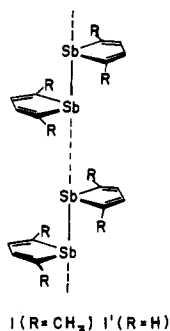
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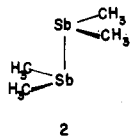
The thermochromic 2,2',5,5'-tetrakis(methylene)bistibolane (3) and 2,2',5,5'-tetrakis(methylene)bibismolane (4) were prepared by multistep syntheses from 2,5-dibromohexa-1,5-diene. The band structure of 3 and the related 2,2',5,5'-tetrakis(methylene)bistibolene (5) were calculated by using the tight-binding model based on extended Hückel calculations. The valence band is independent of the nature of the ring since it is localized on the Sb atoms. The conduction band is almost entirely localized on the carbon  $\pi$ -orbitals, and its energy is lowered by increasing the degree of conjugation of the carbon skeleton.

The distibine 2,2',5,5'-tetramethylbistibole (1) displays a dramatic thermochromic effect.<sup>1</sup> Crystals of 1 are intensely colored purple-blue plates ( $\lambda_{\max} = 605$  nm by diffuse reflectance)<sup>1b</sup> that melt reversibly at 99 °C to a pale yellow oil. Similarly, solutions of 1 in toluene are pale yellow (UV;  $\lambda_{\max}$  346 nm). Thus, crystallization of 1 brings about a red shift of approximately 1.5 eV.



The crystal structure of 1<sup>1</sup> and those of several related compounds<sup>2-4</sup> show that the antimony atoms are arrayed in a colinear chain with alternative short (2.83 Å) and long (3.63 Å) Sb-Sb separations. Since the "intermolecular" Sb...Sb separation is well below the van der Waals radius separation (4.4 Å), there is likely to be extended bonding along the Sb-Sb...Sb-Sb chain.

An extended Hückel calculation of 1 has indicated that the solid color is due to a transition between the HOMO which is largely an Sb-Sb  $\sigma$  band and the LUMO which is largely a diene  $\pi^*$  orbital (see Figure 1).<sup>5</sup> The thermochromic tetramethylbistibine 2 shows a crystal packing which is virtually identical with that of 1, but its solid-phase color ( $\lambda_{\max}$  530 nm) is blue-shifted relative to 1. The 0.3 eV larger band gap is consistent with this model since 2 is not expected to have low-lying  $\pi^*$  orbitals.



(1) (a) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* 1981, 103, 207. (b) A thin film of crystals of 1 shows an absorption band centered at 520 nm, while the absorption band measured by diffuse reflectance is centered at 605 nm.

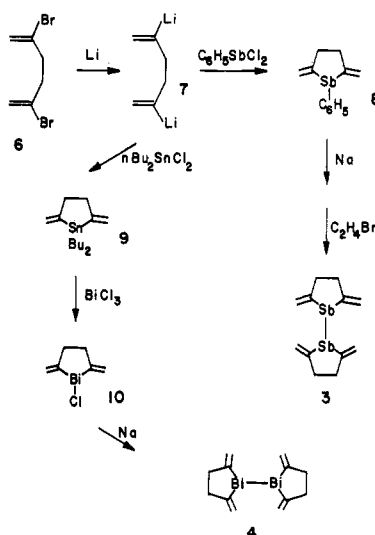
(2) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* 1982, 492, 37.

(3) Ashe, A. J., III; Ludwig, E. G., Jr.; Oleksyszyn, J.; Huffman, J. C. *Organometallics* 1984, 3, 337. Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1984, 39B, 317.

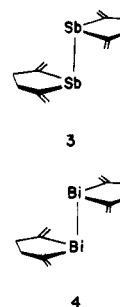
(4) Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* 1983, 506, 42.

(5) Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* 1982, 104, 3876.

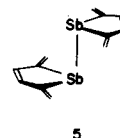
Scheme I. Preparation of 2,2',5,5'-Tetrakis(methylene)bistibolane (3) and 2,2',5,5'-Tetrakis(methylene)bibismolane (4)

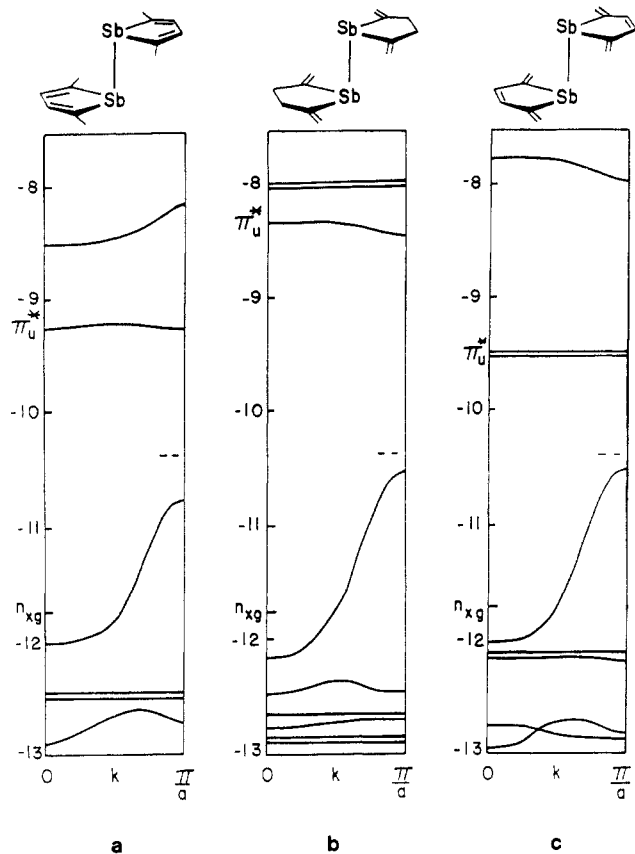


We have decided to probe the question of ordering of the MO's of thermochromic distibines by using a combined synthetic and theoretical approach. We have prepared 2,2',5,5'-tetrakis(methylene)bistibolane (3) and its dibismuthine analogue 4. It was felt that the  $\sigma_g$  orbital of



3 should be approximately the same energy as that of 1; on the other hand, the cross-conjugated 3 would likely have a higher  $\pi^*$  orbital. These qualitative expectations have been confirmed by performing band calculations of 3. Finally, our calculations suggest that related distibine 5 may be a particularly attractive future synthetic goal.





**Figure 1.** Band structure of (a) 1', (b) 3, and (c) 5. The dashed line indicates the highest occupied band. Some lower and higher bands have been omitted for clarity.

## Results and Discussion

**Synthesis.** 2,2',5,5'-Tetrakis(methylene)bistibolane (**3**) and 2,2',5,5'-tetrakis(methylene)bibismolane (**4**) could be prepared from 2,5-dibromohexa-1,5-diene<sup>6</sup> (**6**) by the routes outlined in Scheme I.

Lithiation of **6** followed by reaction with dichlorophenylstibine gave 20% of 1-phenyl-2,5-bis(methylene)stibolane (**8**). Reaction of **8** with sodium in liquid ammonia takes place with preferential cleavage of the phenyl rather than the ring vinyl groups. Subsequent coupling afforded 85% of orange crystals of the distibine **3**.

Dibismuthine **4** was prepared by an analogous but less direct route. Reaction of dilithio compound **7** with dibutyltin dichloride gave 38% of the bis(methylene)stannolane **9**. The stannolane undergoes an efficient exchange reaction with  $\text{BiCl}_3$  in tetrahydrofuran to afford 1-chloro-2,5-bis(methylene)bismolane (**10**) as yellow crystals. Although **10** is rather thermally sensitive, it is less so than 1-phenyl-2,5-dimethylbismole.<sup>7</sup> Reaction of **10** with sodium in liquid ammonia gave violet crystals of the bibismolane **4**.

**UV-Visible Spectra.** Like most distibines, solutions of **3** are light yellow.<sup>8</sup> The structureless UV maximum at 300 nm is quite similar to that shown by its acyclic analogue tetraisopropenyldistibine **11** (290 nm).<sup>9</sup> Like **11**, crystals of **3** are orange. The diffuse reflectance spectrum of solid **3** shows a broad absorption band centered at 475 nm. Thus, there is a red shift of 175 nm on crystallization.

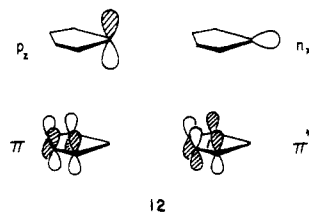
On the other hand, this absorption is considerably blue-shifted from the maximum of solid **1** at 605 nm.

The spectral properties of dibismuthine **4** are completely analogous. The solution UV spectrum of **4** shows a maximum at 330 nm with end absorption to about 700 nm. The solid-phase diffuse reflectance maximum is at 570 nm.<sup>9</sup>

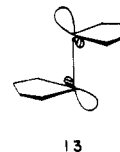
Unfortunately, we have been unable to obtain crystals of either **3** or **4**, which were of suitable quality for a single-crystal X-ray diffraction study. However, we note that crystal structures are now available for three thermochromic distibines: **1**, **2**, and tetrakis(trimethylsilyl)distibine and for the thermochromic tetrakis(trimethylsilyl)dibismuthine. Although these four compounds have rather diverse molecular structures, they all display crystal structures in which the metal atoms are arranged in chains with alternating long and short separations (M-M...M-M). We regard this crystal packing arrangement essential for the thermochromism of organodipnictogen compounds. Since the molecular dimensions of **3** must be similar to those of its isomer **1**, we have used the solid-phase structures of **1** to approximate that of **3** in our subsequent discussions.

**Band Calculations.** The band structures of compounds 1' (R = H) and **3** are shown in Figure 1. They have been calculated by using the tight-binding method based on extended Hückel calculations.<sup>10</sup> Structural parameters for 1' were taken from experimental values for **1**,<sup>1</sup> and those for **3** were adapted from **1**. Atomic parameters are given in the Experimental Section.

The electronic structure of 1' has already been discussed in detail. However, for the sake of comparison with the band structure of **3** we need to recall some of the salient features. The important orbitals of the unit cell are all easily derived from the molecular orbitals of the  $\text{SbC}_4\text{H}_4$  fragment shown in **12**. The lower and higher energy or-



bitals are neglected in that scheme. The HOMO of the distibine results from a mixing of  $p_z$  and  $n_x$  and is the in-phase combination of the two Sb lone pairs **13** ( $n_{xg}$ ). The band made from that HOMO is the valence band and has a significant dispersion since **13** is mostly localized on Sb.



The LUMO of distibine is made from out-of-phase combination of the  $\pi^*$  orbital stabilized by  $\sigma^*_{\text{Sb-Sb}}$  (**14**),  $\pi^*_u$ . The in-phase combination  $\pi_g$  lies higher since it is destabilized by the  $\sigma_{\text{Sb-Sb}}$ . In any event, **14** is mostly localized on the diene which results in an essentially flat conduction band. In a similar manner, **15** gives way to a higher rather flat band.

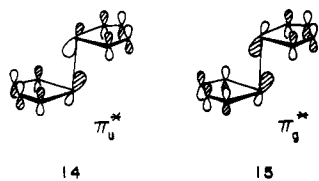
(6) Shehan, D. Ph.D. Dissertation, Yale University, 1964.

(7) Ashe, A. J., III; Drone, F. J. *Organometallics* 1984, 3, 495.

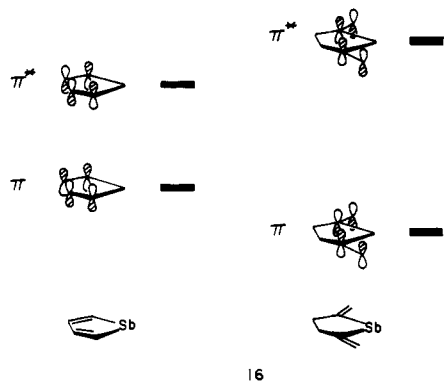
(8) Ashe, A. J., III; Ludwig, E. G., Jr.; Pommerening, H. *Organometallics* 1983, 2, 1573.

(9) For comparison see: Ashe, A. J., III; Ludwig, E. G., Jr.; Oleksyszyn, J. *Organometallics* 1983, 2, 1859.

(10) André, J.-M. *J. Chem. Phys.* 1969, 50, 1536. *Electronic Structure of Polymers and Molecular Crystals*: André, J.-M., Ladik, J., Eds.; Plenum: New York, 1972; p 1. Ladik, J. *Ibid.*, p 23.



The band structure of **3** can be accounted for in a similar manner, starting from the orbitals of the unit cell. Since the HOMO of the unit cell involves exclusively the Sb atoms, its energy is not affected by the nature of the ring and its energy is found equal to that in **1'**. The major difference between these two cyclic Sb fragments resides in the  $\pi$  and  $\pi^*$  energy level. The  $\pi$  and  $\pi^*$  orbitals of the more conjugated species are respectively higher and lower than those of the cross-conjugated ring (**16**). Thus, the frontier molecular orbitals of the unit cell of **3** are the in-phase combination of the Sb lone pairs (HOMO) and the out-of-phase combination of  $\pi^*$  stabilized by  $\sigma_{\text{Sb-Sb}}^*$  (LUMO).

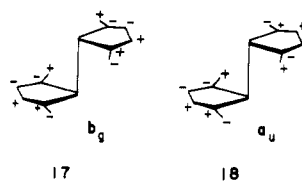


The relative energies of the bands of **1'** (Figure 1a) and **3** (Figure 1b) follow the order found in the unit cell. The valence band of **3** has a large dispersion since it consists of the Sb-Sb bond. It reaches a slightly higher energy at the zone edge ( $K = \pi/a$ ) than in **1'**. The conduction band forms an essentially flat band that lies significantly higher in energy than that in **1'**. If, as we have hypothesized beforehand, the color is due to the transition between the valence and conduction band, then there is a blue shift from **1'** to **3**.

Calculations were not attempted on dibismuthine **4** both because we lack structural data on **4** or analogous compounds and good parameters for bismuth atoms are lacking. Nonetheless, the qualitative features of the band structure of **4** can be anticipated. The substitution of Bi for Sb in **3** is unlikely to greatly affect the ring  $\pi^*$  orbitals. On the other hand, the  $\sigma_g$  orbitals of **4** will likely be raised to reflect the weaker metal-metal bonding of the dibismuthine.<sup>7</sup> Thus, a smaller band gap is predicted in agreement with observation.

From the comparison of **1'** and **3**, it is clear that increased conjunction results in a red shift since it lowers the energy of the empty  $\pi^*$  orbital without strongly affecting the valence band which derives essentially from the Sb  $\sigma$  bond. We can thus propose that the transition in **5** (if this compound stacks) should be red-shifted relative to **1**. The band structure shown in Figure 1c confirms this. The band structure of **5** is closely related to that of **1'** and **3** with the exception of the symmetry of the lowest empty bands. There are two, almost degenerate empty bands derived from the LUMO of the hexatriene moiety of the ring. Since the LUMO of hexatriene is antisymmetric with respect to the mirror plane, it does not mix with the Sb-Sb bond orbitals. The lowest empty orbitals of the chemical

unit are thus the in-phase  $b_g$  (**17**) and out-of-phase  $a_u$  (**18**)



combination of the LUMO of the hexatriene part. They are almost degenerate and create flat bands since there is no interaction between two hexatriene fragments. The transition from the HOMO to  $a_u$  is allowed in the isolated molecule. It should also be allowed in the solid.

## Experimental Section

**General Remarks.** The NMR spectra were recorded with a Bruker AM 300 NMR spectrometer. Tetramethylsilane was used as an internal reference. UV-visible spectra were obtained on a Varian Associates Cary 219 spectrophotometer, and solid reflectance data were determined on the same instrument using a Varian Associates in-cell space diffuse reflectance accessory. This was accomplished by placing the sample on a microscope slide topped with a coverslip, and the sample was frozen by clamping a piece of dry ice against it. Mass spectral determinations were made by using a Finnigan 4023 GC/MS with an electron-ionization energy of 70 eV. Elemental analyses were performed by the Spang Microanalytical Laboratory, Eagle Harbor, MI. Because of their lability, it was not possible to obtain microanalyses of the bismuth compounds. All operations were performed under argon or nitrogen.

**1-Phenyl-2,5-bis(methylene)stibolane.** A solution of 2,5-dilithio-1,5-hexadiene, prepared from 2.4 g (10 mmol) of 2,5-dibromo-1,5-hexadiene<sup>6</sup> and excess lithium-2% sodium in 40 mL of diethyl ether at 0 °C, was added dropwise to a suspension of 2.7 g (9 mmol) of dichlorophenylstibine in 100 mL of diethyl ether at 25 °C and allowed to stir for 12 h. The solution was filtered after which the solvent was removed. The residue was extracted with pentane. Removal of the solvent left a yellow oil that was purified by Kugelrohr distillation (100 °C at 0.005 torr) to give 0.51 g (20%) of 1-phenyl-2,5-bis(methylene)stibolane.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.65 (s, 4 H), 5.65 (br s, 2 H), 6.10 (br s, 2 H), 7.60 (m, 3 H), 7.80 (m, 2 H). MS:  $m/z$  (relative intensity) 280 (2, M<sup>+</sup> for C<sub>12</sub>H<sub>13</sub><sup>123</sup>Sb), 77 (100, C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>12</sub>H<sub>13</sub>Sb: C, 51.65; H, 4.70. Found: C, 51.72; H, 4.60.

**2,2',5,5'-Tetrakis(methylene)bistibolane.** Sodium metal (0.035 g, 1.5 mmol) was added piecewise to 0.2 g (0.7 mmol) of 1-phenyl-2,5-bis(methylene)stibolane in 40 mL of liquid ammonia. After the solution had stirred for 30 min, ammonium chloride (0.037 g, 0.7 mmol) was added in one portion. Then 0.068 g (0.36 mol) of 1,2-dibromoethane was added over 30 min. After the ammonia had evaporated, the yellow residue was taken up in 25 mL of pentane. After the mixture was filtered and cooled to -78 °C, 0.12 g (83%) of orange crystals (dec 45 °C) of product were isolated.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.83 (s, 4 H), 5.30 (s, 4 H), 2.64 (s, 8 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  157, 122, 45. MS:  $m/z$  (relative intensity) 406 (0.1 M<sup>+</sup> for C<sub>12</sub>H<sub>16</sub><sup>123</sup>Sb), 246 (2, <sup>123</sup>Sb<sub>2</sub>), 79 (100, C<sub>6</sub>H<sub>7</sub>). UV (pentane):  $\lambda_{\text{max}}$  300 nm (43 000); diffuse reflectance, maximum absorbance 475 nm. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>Sb<sub>2</sub>: C, 35.59; H, 3.99. Found: C, 35.72; H, 4.08.

**1,1-Dibutyl-2,5-bis(methylene)stannolane.** A solution of 2,5-dilithio-1,5-hexadiene, prepared from 2.4 g (10 mmol) of 2,5-dibromo-1,5-hexadiene and excess lithium-2% sodium in 40 mL of ether at 0 °C, was added to a solution of dibutyltin dichloride (3.04 g, 10 mmol) in 50 mL of ether at 25 °C. The reaction mixture was allowed to stir for 12 h, after which it was filtered and the solvent evaporated. The residue was extracted with pentane. On filtration followed by evaporation of the solvent, a yellow oil was isolated that could be distilled at 60 °C (0.005 torr) to give 1.20 g (38%) of product.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.82 (d,  $J = 2.9$ , Hz, <sup>3</sup>J<sub>119</sub>SnH = 54 Hz, 2 H), 5.22 (d,  $J = 3.0$  Hz, <sup>3</sup>J<sub>119</sub>SnH = 24 Hz, 2 H), 2.39 (s, <sup>2</sup>J<sub>119</sub>SnH = 19 Hz, 4 H), 1.55 (m, 4 H), 1.31 (m, 4 H), 1.02 (t,  $J = 7.6$  Hz, 4 H), 0.88 (t,  $J = 7.2$  Hz, 6 H). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>Sn: C, 53.71;

H, 8.37. Found: C, 53.86; H, 8.24.

**1-Chloro-2,5-bis(methylene)bismolane.** A solution of bismuth trichloride (0.2 g, 0.6 mmol) in 3 mL of dry tetrahydrofuran was added to 0.2 g (0.6 mmol) of 1,1-dibutyl-2,5-bis(methylene)stannolane at 0 °C. After the solvent was removed under vacuum at 0 °C, the residue was washed with 10 mL of pentane to remove the dibutyltin dichloride. The solid residue was dissolved in 10 mL of tetrahydrofuran and filtered. Evaporation of the solvent at 0 °C left (0.2 g, 99%) yellow crystals that could be stored at 0 °C but decomposed at 25 °C.

<sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>): δ 7.12 (s, 2 H), 6.12 (s, 2 H), 3.65 (s, 4 H). MS: *m/z* (relative intensity) 324 (5, M<sup>+</sup> for C<sub>6</sub>H<sub>8</sub><sup>35</sup>ClBi), 289 (50, M<sup>+</sup> - Cl), 80 (70, C<sub>6</sub>H<sub>8</sub>).

**2,2',5,5'-Tetrakis(methylene)bismolane.** Sodium metal (0.014 g, 0.6 mmol) was added to a solution of 0.2 g (0.62 mmol) of 1-chloro-2,5-bis(methylene)bismolane in 25 mL of liquid ammonia. A violet solid precipitated from the ammonia. After evaporation of the ammonia, the product was taken up in pentane. When the mixture was cooled to -78 °C, the product crystallized. The labile dibismuthine decomposed on warming >0 °C.

MS: *m/z* (relative intensity) 578 (5, M<sup>+</sup> for C<sub>12</sub>H<sub>16</sub>Bi<sub>2</sub>), 498 (3, M - C<sub>6</sub>H<sub>8</sub>), 418 (32, Bi<sub>2</sub>), 369 (15, M<sup>+</sup> - Bi), 289 (40, M<sup>+</sup> - C<sub>6</sub>H<sub>8</sub>Bi), 209 (100, Bi). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.6 (s, 4 H), 5.4 (s, 4 H), 3.2 (br d, *J* = 9.5 Hz, 4 H), 2.9 (br d, *J* = 9.5 Hz, 4 H). UV (pentane): λ<sub>max</sub> 330 nm (4200 sh).

**MO Calculations.** The following structural parameters were used in calculations:

Compound 1': intermolecular Sb-Sb, 3.625 Å; Sb<sub>1</sub>-Sb<sub>1'</sub>, 2.835 Å; Sb<sub>1</sub>-C<sub>1</sub>, 2.14 Å; C<sub>2</sub>-C<sub>3</sub>, 1.32 Å; C<sub>5</sub>-Sb<sub>1</sub>-C<sub>2</sub>, 81°; Sb<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>, 109°;

C-H, 1.08 Å. All H's are set in the bisector plane of the X-C-Y angle.

Compound 3: same Sb-Sb distances as in 1'; Sb<sub>1</sub>-C<sub>2</sub>, 2.14 Å; C<sub>2</sub>-C (exo methylene), 1.34 Å; C<sub>5</sub>-Sb<sub>1</sub>-C<sub>2</sub>, 81°; Sb<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>, 114.9°; Sb<sub>1</sub>-C<sub>2</sub>-C (exo methylene), 122.5°; C(sp<sup>2</sup>)-H, 1.08 Å; C(sp<sup>3</sup>)-H, 1.09 Å; H-C(sp<sup>3</sup>)-H, 104°.

Compound 5: same Sb-Sb distances as in 1'; Sb<sub>1</sub>-C<sub>2</sub>, 2.14 Å; C<sub>2</sub>-C (exo methylene), 1.34 Å; C<sub>2</sub>-C<sub>3</sub>, 1.46 Å; C<sub>5</sub>-Sb<sub>1</sub>-C<sub>2</sub>, 81°; Sb<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>, 109.95°; Sb<sub>1</sub>-C<sub>2</sub>-C (exo methylene), 125.03°.

The assumption of identical Sb-Sb bond lengths in 1', 3, and 5 is consistent with the fact that Mulliken overlap populations are calculated to be essentially the same in all three systems. This fact also means that the short-long Sb-Sb band alternation observations should be present in 3 and 5.

Atomic parameters: reference previous paper.<sup>5</sup>

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**Registry No.** 1', 108036-04-0; 3, 108036-00-6; 4, 108036-03-9; 5, 108036-05-1; 6, 71566-70-6; 7, 108035-99-0; 8, 108035-98-9; 9, 108036-01-7; 10, 108036-02-8; dichlorophenylstibine, 5035-52-9; 1,2-dibromoethane, 106-93-4; dibutyltin dichloride, 683-18-1; bismuth trichloride, 7787-60-2.

## Agostic Bonds in (MCH<sub>3</sub>)<sup>+</sup> Fragments. Implications for M<sup>+</sup>-CH<sub>3</sub> Bond Dissociation Energies

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Available data for transition-metal fragments ML<sup>+</sup> show that M<sup>+</sup>-CH<sub>3</sub> bonds are stronger than M<sup>+</sup>-H bonds, in opposition to the trend observed for coordinatively saturated complexes, for which *D*(M-CH<sub>3</sub>) is significantly lower than *D*(M-H). Extended Hückel molecular orbital calculations on some MCH<sub>3</sub><sup>+</sup> systems indicate that strong agostic interactions may be responsible for that "reversed" trend.

The energetics of transition-metal-carbon and -hydrogen bonds in coordinatively saturated complexes and in organometallic fragments and ions has been the subject of many recent studies.<sup>1-3</sup> Available data for saturated

complexes show that M-H bond energies are higher (by ca. 60-100 kJ/mol)<sup>4</sup> than M-CH<sub>3</sub> bond energies, while an opposite conclusion is drawn for the unsaturated species MCH<sub>3</sub><sup>+</sup> and MH<sup>+</sup>: metal-hydrogen bonds are weaker (by ca. 2-75 kJ/mol)<sup>1a,3a,b</sup> than metal-methyl bonds. Data for neutral MCH<sub>3</sub> fragments are still rather scarce,<sup>5</sup> but the "reversed" trend may also hold. However, it is probably less pronounced than in the case of the ions.

The stability of MCH<sub>3</sub><sup>+</sup> fragments, as compared to MH<sup>+</sup>, was discussed by Mandich, Halle, and Beauchamp, the conclusion being that the resonant charge stabilization of the methyl cation, favored for the more polarizable, more easily ionized methyl ligand, was the main reason for the unexpectedly large bond dissociation energy.<sup>6</sup> This has recently been supported by a correlation showing that

(1) (a) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.*, to be submitted for publication. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79. (d) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1982; Chapter 2.

(2) Some recent examples from which the energetics of M-CH<sub>3</sub> and M-H bonds in coordinatively saturated complexes can be compared include (a) Alibrandi, G.; Minniti, D.; Romeo, R.; Cum, G.; Gallo, R. *J. Organomet. Chem.* **1985**, *291*, 133. (b) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (c) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *J. Organomet. Chem.* **1986**, *315*, 187. (d) Calhorda, M. J.; Dias, A. R.; Minas da Piedade, M. E.; Salema, M. S.; Martinho Simões, J. A. *Organometallics*, in press.

(3) Recent gas-phase results enabling comparisons between M<sup>+</sup>-CH<sub>3</sub> and M<sup>+</sup>-H (or between M-CH<sub>3</sub> and M-H) bond energies in MR<sup>+</sup> (or MR) species include: (a) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065. (b) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626. (c) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316. (d) Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379.

(4) A larger difference (228 kJ/mol, recalculated value) has been estimated for platinum complexes. See ref 2a.

(5) *D*(Co-H) is close to *D*(Co-CH<sub>3</sub>). See ref 1a.

(6) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.