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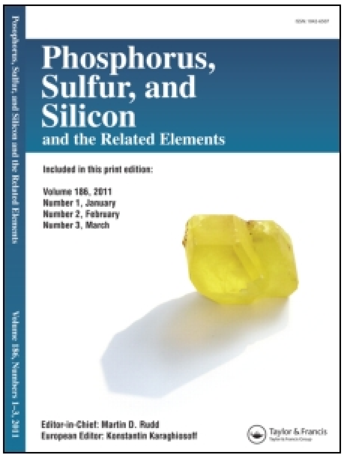

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SYSTEMATIC STUDIES ON HOMO- AND HETERONUCLEAR DOUBLY BONDED COMPOUNDS OF HEAVIER GROUP 15 ELEMENTS

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*The first stable phosphabismuthene (R^1—P═Bi—R^2) and stibabismuthene (R^1—Sb═Bi—R^2) were successfully synthesized by taking advantage of efficient steric protection groups, 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl (Tbt), 2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt), and 2,4,6-tri-*t*-butylphenyl (Mes*). Their spectroscopic properties and structural parameters were systematically compared with those of previously reported stable, homonuclear, doubly bonded systems, such as diphosphene, diarsene, distibene, and dibismuthene.*

Keywords: Diarsene; dibismuthene; diphosphene; distibene; heteronuclear doubly bonded systems; homonuclear doubly bonded systems; phosphabismuthene; steric protection; stibabismuthene

Since the first synthesis and isolation of a stable diphosphene,[1–5] many examples have been reported for stable homonuclear doubly bonded compounds of heavier group 15 elements such as diphosphenes and diarsenes.[6,7] We have also succeeded in the synthesis and isolation

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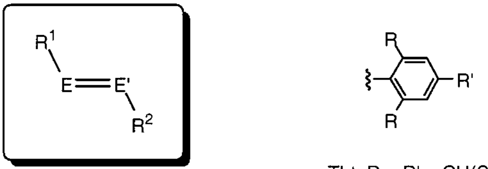

1a: E = E' = Sb, $R^1 = R^2$ = Tbt
1b: E = E' = Sb, $R^1 = R^2$ = Bbt
2a: E = E' = Bi, $R^1 = R^2$ = Tbt
2b: E = E' = Bi, $R^1 = R^2$ = Bbt
3: E = Sb, E' = Bi, $R^1 = R^2$ = Bbt
4: E = P, E' = Bi, R^1 = Mes*, R^2 = Bbt

Tbt: R = R' = $CH(SiMe_3)_2$
Bbt: R = $CH(SiMe_3)_2$, R' = $C(SiMe_3)_3$
Mes*: R = R' = CMe_3

FIGURE 1

of the first stable distibene **1**[8] and dibismuthene **2**[9] by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-tris(trimethylsilyl)methylphenyl (Bbt) (Figure 1). The successful isolation of these homonuclear doubly bonded systems naturally prompted us to examine the synthesis and isolation of the unprecedented heteronuclear double bonds between bismuth and other group 15 elements.

RESULTS AND DISCUSSION

Recently, we succeeded in the isolation of new members of doubly bonded systems of heavier group 15 elements: stibabismuthene **3**[10] and phosphabismuthene **4**,[11] the first examples of stable doubly bonded systems between bismuth and the other heavier group 15 elements. In this paper, a systematic comparison is made for these homo- and heteronuclear doubly bonded compounds of heavier group 15 elements from the viewpoints of their structural parameters and spectroscopic properties.

The synthesis of heteronuclear doubly bonded systems, that is, stibabismuthene **3** and phosphabismuthene **4**, was achieved by the condensation of an overcrowded dibromobismuthine [$Bbt\text{-}BiBr_2$ (**5**)] with the corresponding dihydrostibine [$BbtSbH_2$ (**6**)] and dihydrophosphine [Mes^*PH_2 (**7**)] in the presence of 1,8-diazabicylco[5.4.0]undec-7-ene (DBU) as a base (Figure 2).

The formation of **3** and **4** was fully confirmed by their nuclear magnetic resonance (NMR), ultraviolet–visible (UV-vis), Raman, and mass spectroscopic data, and finally determined by the crystallographic

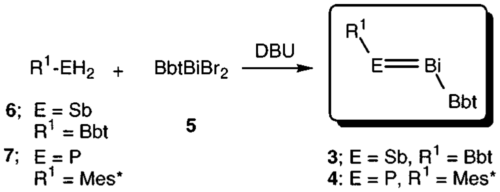

FIGURE 2

structural analysis. Unfortunately, we have not yet succeeded in obtaining the detailed structural parameters for stibabismuthene **3** due to the inevitable disorder between the two heavier central elements (Sb and Bi). However, such a problem has been solved for the nonsymmetrically substituted phosphabismuthene **4** to give us the well-refined structural parameters for this new P=Bi bonding system.

The synthesis and isolation of these two heteronuclear doubly bonded systems of heavier group 15 elements, **3** and **4**, are worthy of special note as the first stable examples of this class of double bonds. With these stable systems in hand, we can compare systematically the structural features of a variety of doubly bonded systems between heavier group 15 elements. Theoretical calculations were also performed for their model systems to reveal the intrinsic nature of the double bonds of heavier main group elements.

Interestingly, phosphabismuthene **4** showed three absorption maxima in its electronic spectra at 455, 540, and 670 nm in hexane, the former two maxima of which are assignable to the π–π^* and n–π^* transitions as in the cases of other homonuclear doubly bonded systems.[1–4] Stibabismuthene **3** also showed similar longer absorption maxima at 709 nm, although the second maximum for the n–π^* transition probably overlapped the strong π–π^* maxima at 516 nm.[5] The assignment of the longest absorption is not clear at present, and we are now examining the origin of this unique phenomenon for the heteronuclear doubly bonded systems by the use of theoretical calculations.

Studies on their thermal and photochemical stabilities revealed the unique reactivities of these doubly bonded systems. Thus, an interesting disproportionation reaction into the corresponding homonuclear double bond species **1b** and **2b** (Figure 3) via head-to-head dimerization was observed for the thermolysis and photolysis of stibabismuthene **3**, while the photolysis of **4** resulted in a ready intramolecular cyclization of the intermediary phosphinidene together with the formation of dibismuthene **2b**.

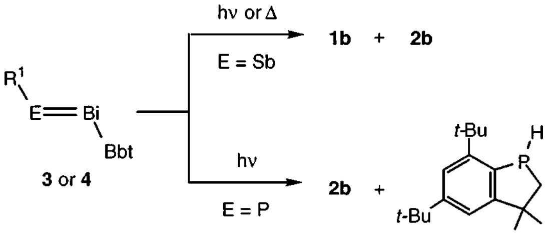

FIGURE 3

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