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Reactivity of Molecules Containing Element-Element Bonds. 1. Nontransition Elements

Fausto Calderazzo,*[†] Antonino Morvillo,[‡] Giancarlo Pelizzi,[§] Rinaldo Poli,^{†,||} and Fausto Ungari[†]

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A new method for preparing Bi_2Ph_4 consists of reducing BiPh_2I with bis(cyclopentadienyl)cobalt(II) in tetrahydrofuran as solvent, with yields as high as 80%. The mixed products Ph_2BiEPH (E = S, Se, Te) were obtained by reacting Bi_2Ph_4 with E_2Ph_2 in toluene as solvent at room temperature. The crystal and molecular structure of BiSePh_3 has been solved. Crystal data: $\text{C}_{18}\text{H}_{15}\text{BiSe}$, $M_r = 519.3$, orthorhombic, space group $P2_12_12_1$, $a = 15.936$ (3) Å, $b = 11.550$ (3) Å, $c = 8.855$ (2) Å, $Z = 4$, $d(\text{calcd}) = 2.116$ g cm^{-3} . The structure consists of tricoordinated and bicoordinated bismuth and selenium, respectively, paired by a Bi-Se bond 2.704 (3) Å long. The tellurium and selenium mixed species undergo diazomethane insertion with formation of the $\text{Ph}_2\text{Bi-CH}_2\text{-EPH}$ species. Tetraphenyldibismuthine is oxidized by elemental selenium, giving $(\text{BiPh}_2)_2\text{Se}$.

Introduction

The properties and reactivity of systems containing homonuclear element-element bonds are of considerable interest for both transition¹ and nontransition elements. Particularly weak E-E bonds could be expected for elements such as antimony, tellurium, and iodine, resulting in easy cleavage. The chemistry of main-group elements containing E-E bonds has been developed in this laboratory, especially concerning the exchange reaction between P_2Ph_4 and As_2Ph_4 ² and the recent synthesis of Bi_2Ph_4 .³ The latter contains an E-E bond accompanied by a lone pair on each atom. Thus, Bi_2Ph_4 should have a particularly high tendency to (a) break the Bi-Bi bond and (b) undergo electron-transfer processes prior or subsequent to the Bi-Bi bond cleavage.

In this paper we report a new synthesis of Bi_2Ph_4 that represents a considerable improvement with respect to the earlier method, a number of exchange processes involving Bi_2Ph_4 and some molecules containing E-E bonds (with E being a chalcogen atom), and carbene insertion into Bi-E bonds.

Experimental Section

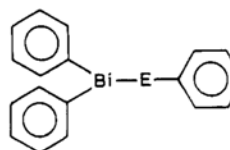
The following compounds were prepared according to literature methods: BiPh_2I ,³ BiPh_2Cl ,⁴ Te_2Ph_2 ,⁵ Sb_2Ph_4 .⁶ Bis(cyclopentadienyl)cobalt(II), CoCp_2 , was prepared by sodium reduction of CoCp_2I in tetrahydrofuran, followed by sublimation (70% yield).⁷ Commercial products purified before use were S_2Ph_2 (Fluka) and Se_2Ph_2 (Aldrich). Elemental selenium and tellurium were commercial (Fluka) products used without further purification. Solvents were carefully purified by conventional methods immediately before use.

The IR spectra were recorded with a Perkin-Elmer Model 283 instrument equipped with grating. ¹H and ¹³C NMR spectra were measured with Varian T60 and Bruker WP200 instruments, respectively. Mass spectra were measured with a VG-MM 16F instrument operating at 70 eV with a direct-insertion system and a source temperature of 200 °C. Elemental analyses (C, H) were performed by the microanalytical laboratory of the Istituto Chimica Organica, Facoltà di Farmacia, Università di Pisa. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified dinitrogen with exclusion of light.

Preparation of Bi_2Ph_4 . In a 1-L flask BiPh_2I (8.806 g; 17.97 mmol) was dissolved in thf (250 mL). A solution of CoCp_2 (3.368 g; 17.83 mmol) in thf was added dropwise at room temperature in 5 min. After about 10 min of stirring, the precipitate of CoCp_2I was filtered off and the orange solution was evaporated to dryness under reduced pressure at room temperature. The solid was recrystallized from hot dry ethanol (600 mL) as described earlier.³ The orange needles of Bi_2Ph_4 so obtained were collected by filtration and dried in vacuo (80% yield). The product had an IR spectrum superimposable on that reported in the literature³ and gave satisfactory elemental analysis.

Tetraphenyldibismuthine was also prepared from BiPh_2Cl in the presence of NaI in tetrahydrofuran without isolating the intermediate BiPh_2I . Into a 100-mL flask were introduced 0.443 g (1.11 mmol) of

Table I. ¹³C NMR Data for Ph_2BiEPH (E = S, Se, Te) and Bi_2Ph_4



compd	δ^a					
	2,6-C		3,5-C		4-C	
	E	Bi	E	Bi	E	Bi
$\text{Ph}_2\text{BiSPh}^b$	137.1	134.6	131.3	128.4	128.2	126.3
$\text{Ph}_2\text{BiSePh}^b$	137.7	136.4	131.2	128.6	128.1	126.8
Ph_2BiTePh	139.0 ^b	141.3 ^b	131.1 ^b	128.8 ^b	127.8 ^b	127.5 ^b
	140.2 ^c	142.6 ^c	132.1 ^c	129.8 ^c	128.7 ^c	128.4 ^c
$\text{Ph}_2\text{BiBiPh}_2^c$	141.5		131.8		128.2	

^a From TMS. The chemical shifts were actually measured by making reference to the ¹³C values of the solvent. Similar values for the chalcogen-bonded phenyl group were observed in the mixed compounds $\text{Me}_2\text{Bi-EPH}$ (E = S, Se, Te): Wieber, M.; Sauer, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1668. The homonuclear species, S_2Ph_2 , Se_2Ph_2 , and Te_2Ph_2 , have the following resonances (Me_2SO) for the 1-C, 2,6-C, 3,5-C, and 4-C atoms, respectively. S: 137.0, 129.0, 127.5, 127.1. Se: 130.9, 131.5, 129.1, 127.6. Te: 108.0, 137.6, 129.2, 128.0. See: Forchioni, A.; Galasso, V.; Irgolic, K. J.; Pappalardo, G. C. *J. Organomet. Chem.* **1977**, *135*, 327. The resonance due to 1-C was not observed for the bismuth-containing compounds because of unfavorable relaxation time. ^b CDCl_3 . ^c C_6D_6 .

BiPh_2Cl and 15 mL of tetrahydrofuran. To the resulting solution was added 0.17 g (1.15 mmol) of NaI. After about 4 h of stirring at room temperature, the resulting suspension was filtered to eliminate NaCl. The yellow solution of BiPh_2I was treated with the equivalent amount of CoCp_2 as described above, and Bi_2Ph_4 was obtained in 54% yield.

Reaction of Bi_2Ph_4 with E_2Ph_2 (E = S, Se, Te). Preparation of Ph_2BiSPh . To a 100-mL flask containing 0.18 g (0.82 mmol) of S_2Ph_2 in 25 mL of toluene was added Bi_2Ph_4 (0.62 g; 0.85 mmol) at room temperature. The initially orange solution became yellow. After about 45 min, it was filtered to eliminate a small quantity of a dark solid, and then solvent was removed up to the first appearance of crystals. Addition of *n*-heptane (30 mL) caused the yellow BiPh_2SPh to precipitate. The product was collected by filtration and dried in vacuo (0.36 g; 46% yield). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{BiS}$: C, 45.8; H, 3.2. Found: C, 45.8; H, 2.9. The IR spectrum (Nujol) has bands at 3070 (w), 3050 (w), 3020 (w), 1570 (m), 1432 (s), 1325 (vw), 1295 (vw), 1260 (vw), 1190 (vw), 1180 (vw), 1162 (vw), 1157 (vw), 1076 (w), 1060 (w), 1050 (m), 1020 (w), 1010 (m), 990 (m), 912 (vw), 897 (vw), 733 (vs), 718 (vs), 684 (s), 476

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(w), 446 (w), and 436 (m-s) cm^{-1} . The ^{13}C NMR data are presented in Table I.

Preparation of Ph_2BiSePh . By an experimental procedure similar to that reported above for Ph_2BiSPh , 0.646 g (2.07 mmol) of Se_2Ph_2 dissolved in 30 mL of toluene was reacted with Bi_2Ph_4 (1.541 g; 2.12 mmol). After filtration of the yellow solution, concentration to small volume, and addition of *n*-heptane, 1.15 g of Ph_2BiSePh was obtained in 54% yield. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{BiSe}$: C, 41.6; H, 2.9. Found: C, 41.5; H, 2.8. The IR spectrum (Nujol) has bands at 3060 (w), 3045 (w), 3020 (w), 1575 (w), 1570 (m), 1436 (m), 1430 (m-s), 1330 (vw), 1295 (w), 1260 (vw), 1185 (vw), 1175 (vw), 1155 (w), 1052 (m), 1020 (m), 1013 (m), 995 (m), 902 (w), 850 (w), 838 (w), 740 (m), 733 (s), 720 (vs), 690 (s), 662 (w), 465 (w), 445 (m), and 435 (m) cm^{-1} . The ^{13}C NMR data are presented in Table I. The filtrate from the preparation was kept in a refrigerator at about 5 °C, and crystals suitable for the X-ray diffractometric study were obtained.

Collection and Reduction of X-ray Data for Ph_2BiSePh . A Philips PW 1100 computer-controlled diffractometer was used for the X-ray analysis of a crystal of approximate dimensions (mm) $0.23 \times 0.23 \times 0.38$, sealed in a Lindemann glass capillary under dinitrogen. The 2θ angles of 20 intense reflections, accurately measured, were employed to determine, by least-squares analysis, the lattice parameters and their estimated standard deviations.

Crystal Data: $\text{C}_{18}\text{H}_{15}\text{BiSe}$, $M_r = 519.3$, orthorhombic, space group $P2_12_12_1$, $a = 15.936$ (3) Å, $b = 11.550$ (3) Å, $c = 8.855$ (2) Å, $V = 1629.9$ (6) Å³, $Z = 4$, $d(\text{calcd}) = 2.116$ g cm^{-3} , Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 129.84$ cm^{-1} , $F(000) = 960$.

Systematic extinctions in $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd uniquely determined the space group to be $P2_12_12_1$.

The intensities were measured at room temperature with Mo $K\alpha$ radiation (graphite crystal monochromator) by using an ω - 2θ step-scan technique, with a scan rate of $0.075^\circ \text{ s}^{-1}$ and a scan width of 1.2° . One octant of reciprocal space was surveyed with $3.0 < \theta < 25.0^\circ$. Of the 1681 independent reflections measured, 1121 were observed to have $I \geq 3\sigma(I)$ and were subsequently utilized throughout the analysis. A modification of the Lehman and Larsen procedure⁸ was used to analyze the reflection diffraction profiles. A standard reflection was measured periodically as a check on the centering and stability of the crystal and diffractometer system and found to show no systematic variation in intensity. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was made by measuring one reflection with a χ value near 90° at different ψ values (0 – 180° , in steps of 10°).

Structure Solution and Refinement. The structure was solved by conventional heavy-atom and electron density difference methods. A Patterson function gave vectors that uniquely determined the position of both the bismuth and selenium atoms, while the remainder of the non-hydrogen atoms were derived from a difference Fourier calculation phased on the heavy-atom contributions. The atomic coordinates were refined by full-matrix least squares with minimization of $\sum w|\Delta F|^2$, where w is given as $1.1464/[\sigma^2(F_o) + 0.00002F_o^2]$. The Bi and Se atoms were refined anisotropically; the C atoms, isotropically. The phenyl rings were treated as rigid groups. As the space group $P2_12_12_1$ is free of reflective elements, it was necessary to determine the absolute configuration of the crystal. The transmission coefficient range was 1.0044 – 1.1809 . Final refinement of the correct configuration resulted in $R = 0.0437$, $R' = 0.0403$, and $R_g = 0.0439$, respectively [$R = \sum \Delta F / \sum F_o$; $R' = \sum (\Delta F)w^{1/2} / \sum F_o w^{1/2}$; $R_g = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$]. The corresponding values obtained by refinement of the inverted structure are $R = 0.0569$, $R' = 0.0574$, and $R_g = 0.0673$. Seven suspect reflections were not included in the last refinement cycle. The reflection:parameter ratio was 20:1. The two largest peaks in the final difference Fourier map had a magnitude of ca. $1.05 \text{ e } \text{Å}^{-3}$ and were observed around the bismuth position. Atomic scattering factors were corrected for anomalous dispersion of bismuth and selenium.⁹ Calculations were carried out by using the SHELX system of programs¹⁰ on the CDC Cyber 76 computer of CINECA (Casalecchio, Bologna). The final atomic coordinates are listed in Table II.

Preparation of Ph_2BiTePh . By an experimental procedure similar to that described for Ph_2BiSePh , Bi_2Ph_4 (2.83 g; 3.90 mmol) dissolved in 100 mL of toluene was reacted with Te_2Ph_2 (1.59 g; 3.90 mmol). After about 30 min of stirring at room temperature, filtration, and usual workup, Ph_2BiTePh (3.06 g; 69% yield) was recovered as an orange solid.

Table II. Fractional Atomic Coordinates ($\times 10^5$ for Bi; $\times 10^4$ for Se and C) for Ph_2BiSePh with Esd's in Parentheses

atom	x/a	y/b	z/c
Bi	76496 (5)	3726 (8)	3626 (10)
Se	8078 (2)	1962 (2)	-1743 (3)
C(1)	8723 (7)	701 (12)	1965 (13)
C(2)	9089 (7)	-294 (12)	2567 (13)
C(3)	9688 (7)	-201 (12)	3710 (13)
C(4)	9921 (7)	887 (12)	4249 (13)
C(5)	9555 (7)	1882 (12)	3647 (13)
C(6)	8956 (7)	1789 (12)	2505 (13)
C(7)	8431 (8)	-913 (12)	-939 (15)
C(8)	8113 (8)	-2007 (12)	-1278 (15)
C(9)	8586 (8)	-2778 (12)	-2142 (15)
C(10)	9378 (8)	-2455 (12)	-2666 (15)
C(11)	9696 (8)	-1360 (12)	-2326 (15)
C(12)	9223 (8)	-589 (12)	-1462 (15)
C(13)	7486 (8)	3289 (9)	-975 (15)
C(14)	7942 (8)	4133 (9)	-200 (15)
C(15)	7542 (8)	5133 (9)	311 (15)
C(16)	6687 (8)	5290 (9)	47 (15)
C(17)	6231 (8)	4447 (9)	-728 (15)
C(18)	6631 (8)	3447 (9)	-1239 (15)

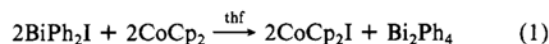
Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{BiTe}$: C, 38.1; H, 2.7. Found: C, 38.0; H, 2.7. IR bands (Nujol) were observed at 3065 (w), 3040 (w), 3020 (w), 1570 (m), 1435 (m), 1430 (m), 1380 (m), 1370 (w), 1227 (vw), 1295 (w), 1263 (w), 1175 (vw), 1155 (w), 1053 (m), 1015 (m), 995 (m), 900 (w), 850 (w), 840 (w), 733 (s), 720 (vs), 690 (s), 650 (w), 455 (w), 445 (m), and 435 (m) cm^{-1} . The ^{13}C NMR data are given in Table I. The mass spectrum showed the molecular ion and the following fragmentation (m/e): 570 (M^+), <0.5%; 363 ($\text{M}^+ - \text{TePh}$), 5%; 286 ($\text{M}^+ - \text{TePh}_2$), 96%; 284 ($\text{M}^+ - \text{BiPh}$), 24%; 209 ($\text{M}^+ - \text{TePh}_3$), 98%; 207 ($\text{M}^+ - \text{BiPh}_2$), 11%; 154 ($\text{M}^+ - \text{BiTePh}$), 100%; 77 ($\text{M}^+ - \text{BiTePh}_2$), 77%.

Reaction of Ph_2BiTePh with Diazomethane. The tellurium derivative (0.83 g; 1.46 mmol) dissolved in 25 mL of tetrahydrofuran was treated with 7.7 mL of a 0.2 M solution of diazomethane in diethyl ether. After a few minutes of stirring at room temperature and then filtration, the yellow solution was evaporated to a small volume under reduced pressure and 20 mL of *n*-heptane was added. Cooling at -30°C caused precipitation of a yellow solid that, however, dissolved again and/or melted upon attempts to filter it out. The product of the reaction, $\text{Ph}_2\text{BiCH}_2\text{TePh}$, was identified by ^1H NMR and mass spectra. The following data were obtained. (a) For the oily residue left after evaporation to dryness: ^1H NMR (CCl_4) [δ 3.2 (CH_2)] and IR (neat between KBr windows) [3065 (m), 3050 (m), 3015 (w), 2985 (w), 2920 (w), 1574 (m), 1476 (m), 1430 (m-s), 1325 (w), 1295 (w), 1260 (w), 1185 (w), 1155 (w), 1055 (m), 1013 (m), 995 (m), 795 (w), 720 (vs), 690 (s), 445 (m) cm^{-1}]. (b) For a concentrated thf solution from the reaction as described above: mass spectrum [m/e : 584 (M^+), <0.5%; 570 ($\text{M}^+ - \text{CH}_2$), <0.5%; 507 ($\text{M}^+ - \text{Ph}$), <0.5%; 493 ($\text{M}^+ - \text{CH}_2\text{Ph}$), <0.5%; 430 ($\text{M}^+ - \text{Ph}_2$), <0.5%; 416 ($\text{M}^+ - \text{CH}_2\text{Ph}_2$), <0.5%; 363 ($\text{M}^+ - \text{CH}_2\text{TePh}$), 3%; 298 ($\text{M}^+ - \text{BiPh}$), 1%; 286 ($\text{M}^+ - \text{CH}_2\text{TePh}_2$), 31%; 284 ($\text{M}^+ - \text{CH}_2\text{BiPh}$), 5%; 221 ($\text{M}^+ - \text{BiPh}_2$), 6%; 209 ($\text{M}^+ - \text{CH}_2\text{TePh}_3$), 28%; 207 ($\text{M}^+ - \text{CH}_2\text{BiPh}_2$), 3%; 154 ($\text{M}^+ - \text{BiCH}_2\text{TePh}$), 15%; 91 ($\text{M}^+ - \text{BiTePh}_2$), 100%; 77 ($\text{M}^+ - \text{BiCH}_2\text{TePh}_2$), 23%].

Reaction of Bi_2Ph_4 with Elemental Selenium. In a 100 mL flask, Bi_2Ph_4 (0.24 g; 0.32 mmol) was dissolved in 25 mL of toluene. After addition of finely divided selenium (0.03 g; 0.38 mmol), the mixture was stirred at room temperature with exclusion of light. After 1 h the initially suspended selenium had disappeared and the solution was yellow. Evaporation to small volume, addition of *n*-heptane, filtration of the solid, and drying in vacuo gave a 33% yield of $\text{Ph}_2\text{BiSeBiPh}_2$. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Bi}_2\text{Se}$: C, 35.8; H, 2.5. Found: C, 35.7; H, 2.1. The IR spectrum (Nujol) had bands at 3060 (w), 3040 (w), 3010 (w), 1566 (m), 1429 (m-s), 1328 (vw), 1300 (vw), 1260 (vw), 1060 (w), 1055 (m), 1010 (m), 995 (m), 910 (vw), 848 (vw), 725 (vs), 720 (vs), 690 (s), 445 (m-s), and 435 (m) cm^{-1} .

Results and Discussion

Synthesis and Reactivity. Tetraphenyldibismuthine, which was previously obtained for the first time³ by sodium reduction of BiPh_2X ($\text{X} = \text{Cl}, \text{I}$) in liquid ammonia, can be more easily prepared by reducing BiPh_2I with bis(cyclopentadienyl)cobalt(II), CoCp_2 , in tetrahydrofuran as solvent (see eq 1). CoCp_2 has been



used earlier as a reducing agent.¹¹ Recently, titanium(III) and

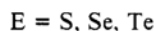
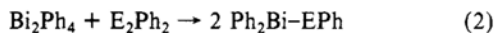
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titanium(II) complexes have been prepared¹² from the corresponding titanium(IV) compounds. Reaction 1 occurs at room temperature, the product being obtained as analytically pure solid by recrystallization after elimination of the substantially insoluble CoCp_2I by filtration. The successful synthesis of Bi_2Ph_4 by this route should be attributed to the good leaving capacity of bismuth-bonded iodide, presumably associated with a particularly weak Bi-halogen bond. In fact, when BiPh_2Cl was used for the same purpose, no straightforward reaction was obtained. Reaction 1 is particularly interesting also because CoCp_2I can be reduced back to CoCp_2 by sodium in tetrahydrofuran.⁷

Bi_2Ph_4 reacts with E_2Ph_2 ($\text{E} = \text{S}, \text{Se}, \text{Te}$) to give the corresponding mixed species, according to eq 2. The reactions were



usually fast and complete within a few hours of the mixing of the reagents. The nature of the products was established mainly by ^{13}C NMR spectra, since the mixed products have ^{13}C resonances distinct from those of the starting materials; see Table I. The table compares the chemical shifts of the individual starting materials with those of the mixed compounds. Although the spectrum of Bi_2Ph_4 could not be measured in CDCl_3 due to its low stability in this solvent, it is evident from the data in the table that formation of the mixed compound results in a decrease of the δ values for the 2,6-carbon atoms of the bismuth-bonded phenyl group with respect to Bi_2Ph_4 , while for the chalcogen-bonded phenyl group the opposite effect is observed. This can be attributed simply to the effect of the oxidation state being averaged to 1.5 in the mixed compound. On the other hand, both in the homonuclear species and in the mixed ones there is a general trend toward an increase of the 2,6-C δ values on descending the vertical sequence of the chalcogen. It is interesting to note that molecules containing group V and group VI element-element bonds of the type $\text{R}_2\text{E-E}'\text{R}_2$ ¹³⁻¹⁶ have been prepared. These were obtained by exchange reactions of the type shown in eq 2 for E_2R_4 and $\text{E}'_2\text{R}_2$. In addition, other mixed chalcogen-bismuth molecules are known, namely Et_2BiSPh ¹⁷ and Ph_2BiSR ¹⁸ ($\text{R} = \text{alkyl, aryl}$) obtained by reactions different from the exchange.

Comparison with Group V Mixed Dimers. The exchange reaction (2) giving a mixed group V-group VI species contrasts with the recent findings by ourselves² and other workers¹⁹ showing exchange reactions between alkyl and aryl derivatives of group

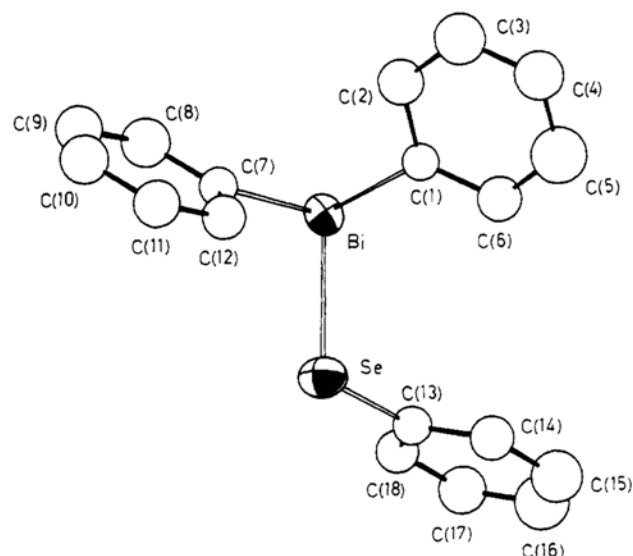
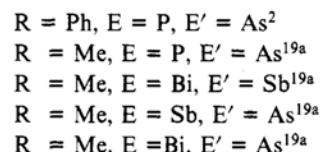


Figure 1. ORTEP diagram and numbering scheme for $\text{Ph}_2\text{Bi-SePh}$. Anisotropic parameters were used only for shaded atoms. Thermal ellipsoids are drawn at the 50% probability level.

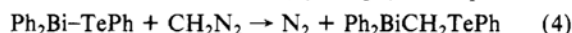
V. These give mixed $\text{R}_2\text{E-E}'\text{R}_2$ products in equilibrium with starting materials, as shown in eq 3.



The stronger tendency of formation of group V-group VI alkyl and aryl dimers from homonuclear starting materials must originate from an enthalpic contribution much more favorable than in the case of the exchange between molecules within group V.

On the other hand, it is to be noted that the attempted exchange between Bi_2Ph_4 and Pb_2Ph_6 failed. The reasons might be kinetic, due to the absence of lone pairs on lead, thus making the attack on bismuth less likely.

Insertion into Element-Element Bonds. Following our earlier finding³ that diazomethane will add across the bismuth-bismuth bond of Bi_2Ph_4 , we attempted the reaction of CH_2N_2 with $\text{Ph}_2\text{Bi-TePh}$ and obtained the product corresponding to the insertion into the heteronuclear bond, (see eq 4). The product of



reaction 4 has a low melting point, and it is difficult to recrystallize. Its identification came from the ^1H NMR spectra ($\text{Ph}_2\text{BiCH}_2\text{TePh}$ δ 3.2) excluding the presence of the CH_2 -inserted homonuclear compounds ($\text{Ph}_2\text{BiCH}_2\text{BiPh}_2$ δ 2.65; $\text{PhTeCH}_2\text{TePh}$ δ 3.8); the mass spectral data for a tetrahydrofuran solution confirmed the nature of the product, as evidenced by the observation of the molecular ion, although of low intensity.

^1H NMR spectral evidence, δ (CH_2) 3.4, is available for the product of carbene insertion into the element-element bond of $\text{Ph}_2\text{Bi-SePh}$ to give $\text{Ph}_2\text{BiCH}_2\text{SePh}$. For comparison, the corresponding values for the CH_2 -inserted homonuclear species are δ 2.65 for $\text{Ph}_2\text{BiCH}_2\text{BiPh}_2$ and δ 4.0 for $\text{PhSeCH}_2\text{SePh}$.²⁰

On the other hand, no CH_2 insertion was observed with Ph_2BiSPh . An increasingly difficult reaction with CH_2N_2 can be related to a stronger E-E bond on decreasing the atomic number of the chalcogen.

As far as the mechanism of the CH_2N_2 reaction is concerned, some information may come from the literature. Insertions of diazomethane into Ge-Cl bonds are believed²¹ to occur via a

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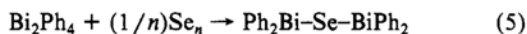
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Table III. Selected Bond Distances (Å) and Angles (deg) for Ph₂Bi–SePh

Bi–Se	2.704 (3)	Bi–C(1)	2.25 (1)
Se–C(13)	1.92 (1)	Bi–C(7)	2.25 (1)
Se–Bi–C(1)	97.4 (3)	Bi–C(7)–C(8)	120.4 (9)
Se–Bi–C(7)	87.4 (3)	Bi–C(7)–C(12)	119.5 (10)
C(1)–Bi–C(7)	90.8 (4)	Bi–Se–C(13)	100.0 (4)
Bi–C(1)–C(2)	114.8 (9)	Se–C(13)–C(14)	118.3 (9)
Bi–C(1)–C(6)	124.7 (9)	Se–C(13)–C(18)	121.6 (8)

nucleophilic attack at the *metal*. On the other hand, insertion of carbene from CH₂N₂ into the tellurium–tellurium bond of Te₂Ph₂²² has been found to occur at room temperature, whereas the insertion into Se–Se and S–S bonds required the use of visible light.

We have recently reported the oxidation of Bi₂Ph₄ by several reagents such as O₂, S₈, *p*-benzoquinone, and I₂.³ Elemental selenium gives the product resulting from the oxidative insertion into the Bi–Bi bond (see eq 5). No reaction was found to occur



with elemental tellurium, although this may be due simply to difficulties connected with the heterogeneous nature of the system.

While this work was in progress, similar results were found for Bi₂(*p*-C₆H₄Me)₄, which is also unreactive toward tellurium.^{15b}

Structure Study. The crystal of Ph₂BiSePh, obtained by slow crystallization at about +5 °C, belongs to the enantiomeric space group *P*2₁2₁2₁. This is a quite common case of enantiomeric enrichment during crystallization.²³

All intermolecular contacts in the structure conform to normal van der Waals interactions; the shortest contact is C(6)⋯C(8) (³/₂ – *x*, –*y*, ¹/₂ + *z*), i.e. 3.48 (2) Å.

The molecular unit of Ph₂Bi–SePh is illustrated by the ORTEP drawing of Figure 1, which also gives the adopted numbering scheme. The coordination geometry about the bismuth atom can be described as pyramidal with the metal displaced 1.327 Å from the plane defined by Se, C(1), and C(7). The bond angles around bismuth are all significantly less than the tetrahedral value, thus indicating that the lone pair has considerable *s* character. In this respect, the geometry around bismuth is virtually identical with those observed in Bi₂Ph₄³ and in [Co(BiPh₂)(CO)₃(PPh₃)].²⁴ The

two Bi–C bond distances, both of 2.25 (1) Å (see Table III), are practically the same as they are in the two aforementioned compounds, in which these values are 2.28 (2), 2.26 (2) and 2.25 (2), 2.28 (2) Å, respectively. The Bi–Se bond distance of 2.704 (3) Å compares fairly well with the 2.684 Å reported for BaBiSe₃²⁵ and is slightly shorter than the strongest bonds (2.82–2.85 Å) in Bi₂Se₃.²⁶ However, if we consider the Bi–Bi distance in Bi₂Ph₄³ (2.990 (2) Å) and the Se–Se distance in Se₂Ph₂²⁷ (2.29 (1) Å), we come to the conclusion that the observed Se–Bi distance of 2.704 (3) Å is somewhat longer than expected (2.64 (1) Å) on the basis of the distance in the homonuclear species.

The Bi–Se bond makes angles of 46.4 (3), 44.1 (3), and 16.6 (2)° with the normals to the C(1)⋯C(6), C(7)⋯C(12), and C(13)⋯C(18) planes, respectively.

The Se–C bond distance was found to be 1.92 (1) Å, which is very similar to the values previously observed for this bond (e.g. 1.93 (5) Å in Se₂Ph₂,²⁷ 1.92 (4) Å in di-*p*-tolyl selenide,²⁸ 1.936 (9), 1.960 (12), and 1.962 (12) Å in η⁷-C₇H₇Mo(μ-SePh)₃Mo(CO)₃,²⁹ and 1.92 (2) Å in Mn₂Br₂(CO)₆Se₂Ph₂³⁰). The angle at Se is 100.0 (4)°, and the displacement of this atom from the plane through the attached phenyl ring is 0.09 Å.

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Registry No. BiPh₂I, 95825-92-6; CoCp₂, 1277-43-6; Bi₂Ph₄, 7065-21-6; BiPh₂Cl, 5153-28-6; S₂Ph₂, 882-33-7; BiPh₂SPh, 115419-47-1; Se₂Ph₂, 1666-13-3; Ph₂BiSePh, 115419-48-2; Te₂Ph₂, 32294-60-3; Ph₂BiTePh, 115464-56-7; Ph₂BiCH₂TePh, 115464-57-8; Se, 7782-49-2; Ph₂BiSeBiPh₂, 115464-58-9.

Supplementary Material Available: A table of thermal parameters for bismuth, selenium, and carbon atoms (1 page); structure factors tables (9 pages). Ordering information is given on any current masthead page.

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