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

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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: $C_{18}H_{15}BiSe$, $M_r = 519.3$, orthorhombic, space group $P2_12_12_1$, $a = 15.936$ (3) Å, $b = 11.550$ (3) Å, $c = 8.855$ (2) Å, $Z = 4$, $d$(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 $Ph_2Bi{-}CH_2{-}EPh$ species. Tetraphenyldibismuthine is oxidized by elemental selenium, giving $(BiPh_2)_2Se$.

## Introduction

The properties and reactivity of systems containing homonuclear element–element bonds are of considerable interest for both transition[1] 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

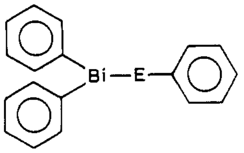
The following compounds were prepared according to literature methods: $BiPh_2I$,[3] $BiPh_2Cl$,[4] $Te_2Ph_2$,[5] $Sb_2Ph_4$.[6] Bis(cyclopentadienyl)cobalt(II), $CoCp_2$, was prepared by sodium reduction of $CoCp_2I$ in tetrahydrofuran, followed by sublimation (70% yield).[7] Commercial products purified 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 $^{13}C$ 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, Facoltá di Farmacia, Universitá 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 literature[3] 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 $BiPh_2Cl$ 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.

**Table I.** $^{13}C$ NMR Data for $Ph_2BiEPh$ (E = S, Se, Te) and $Bi_2Ph_4$



| | $\delta^a$ | | | | | |
|---|---|---|---|---|---|---|
| | 2,6-C | | 3,5-C | | 4-C | |
| compd | E | Bi | E | Bi | E | Bi |
| $Ph_2BiSPh^b$ | 137.1 | 134.6 | 131.3 | 128.4 | 128.2 | 126.3 |
| $Ph_2BiSePh^b$ | 137.7 | 136.4 | 131.2 | 128.6 | 128.1 | 126.8 |
| $Ph_2BiTePh$ | $139.0^b$ | $141.3^b$ | $131.1^b$ | $128.8^b$ | $127.8^b$ | $127.5^b$ |
| | $140.2^c$ | $142.6^c$ | $132.1^c$ | $129.8^c$ | $128.7^c$ | $128.4^c$ |
| $Ph_2BiBiPh_2^c$ | 141.5 | | 131.8 | | 128.2 | |

[a] From TMS. The chemical shifts were actually measured by making reference to the $^{13}C$ values of the solvent. Similar values for the chalcogen-bonded phenyl group were observed in the mixed compounds $Me_2Bi{-}EPh$ (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] $C_6D_6$.

**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 $C_{18}H_{15}BiS$: 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 $C_{18}H_{15}BiSe$: 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 × 0.23 × 0.38, sealed in a Lindemann glass capillary under dinitrogen. The $2\theta$ 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**: $C_{18}H_{15}BiSe$, $M_r = 519.3$, 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) Å$^3$, $Z = 4$, $d$(calcd) = 2.116 g cm$^{-3}$, Mo K$\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu$(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 $\omega$–$2\theta$ step–scan technique, with a scan rate of 0.075° s$^{-1}$ and a scan width of 1.2°. One octant of reciprocal space was surveyed with $3.0 < \theta < 25.0°$. 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 procedure[8] 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 $\chi$ value near 90° at different $\psi$ 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 nonhydrogen 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 [$R = \sum \Delta F/\sum F_o$; $R' = \sum(\Delta F)w^{1/2}/\sum F_o w^{1/2}$; $R_g = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$]. 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 e 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 programs[10] 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. Anal. Calcd for $C_{18}H_{15}BiTe$: 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 (M$^+$ – TePh), 5%; 286 (M$^+$ – TePh$_2$), 96%; 284 (M$^+$ – BiPh), 24%; 209 (M$^+$ – TePh$_3$), 98%; 207 (M$^+$ – BiPh$_2$), 11%; 154 (M$^+$ – BiTePh), 100%; 77 (M$^+$ – BiTePh$_2$), 77%.

**Table II.** Fractional Atomic Coordinates (×10$^5$ for Bi; ×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) |

**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, $Ph_2BiCH_2TePh$, was identified by $^1$H NMR and mass spectra. The following data were obtained. (a) For the oily residue left after evaporation to dryness: $^1$H NMR ($CCl_4$) [$\delta$ 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 (M$^+$ – CH$_2$), <0.5%; 507 (M$^+$ – Ph), <0.5%; 493 (M$^+$ – CH$_2$Ph), <0.5%; 430 (M$^+$ – Ph$_2$), <0.5%; 416 (M$^+$ – CH$_2$Ph$_2$), <0.5%; 363 (M$^+$ – CH$_2$TePh), 3%; 298 (M$^+$ – BiPh), 1%; 286 (M$^+$ – CH$_2$TePh$_2$), 31%; 284 (M$^+$ – CH$_2$BiPh), 5%; 221 (M$^+$ – BiPh$_2$), 6%; 209 (M$^+$ – CH$_2$TePh$_3$), 28%; 207 (M$^+$ – CH$_2$BiPh$_2$), 3%; 154 (M$^+$ – BiCH$_2$TePh), 15%; 91 (M$^+$ – BiTePh$_2$), 100%; 77 (M$^+$ – BiCH$_2$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 $Ph_2BiSeBiPh_2$. Anal. Calcd for $C_{24}H_{20}Bi_2Se$: 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 time[3] by sodium reduction of $BiPh_2X$ (X = Cl, 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

$$2BiPh_2I + 2CoCp_2 \xrightarrow{\text{thf}} 2CoCp_2I + Bi_2Ph_4 \qquad (1)$$

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

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titanium(II) complexes have been prepared[12] 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 $E_2Ph_2$ (E = S, Se, Te) to give the corresponding mixed species, according to eq 2. The reactions were

$$Bi_2Ph_4 + E_2Ph_2 \rightarrow 2\ Ph_2Bi\text{-}EPh \qquad (2)$$

$$E = S, Se, Te$$

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 $\delta$ 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 $\delta$ 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 $R_2E\text{-}E'R$[13-16] have been prepared. These were obtained by exchange reactions of the type shown in eq 2 for $E_2R_4$ and $E'_2R_2$. In addition, other mixed chalcogen–bismuth molecules are known, namely $Et_2BiSPh$[17] and $Ph_2BiSR$[18] (R = 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 ourselves[2] and other workers[19] showing exchange reactions between alkyl and aryl derivatives of group V. These give mixed $R_2E\text{-}E'R_2$ products in equilibrium with starting materials, as shown in eq 3.

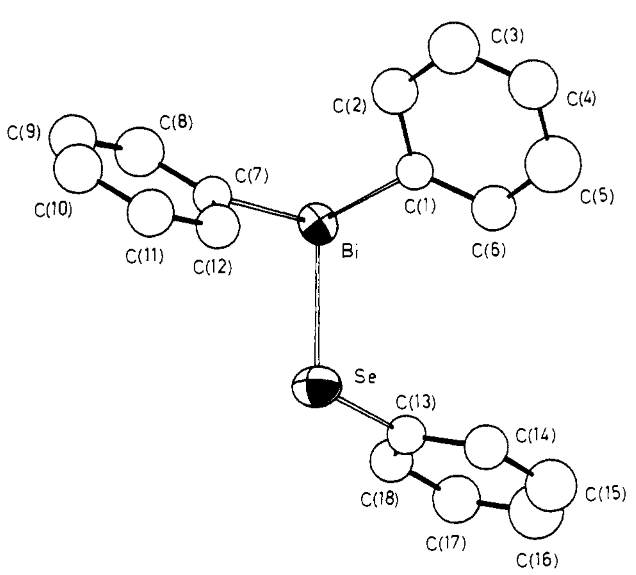

**Figure 1.** ORTEP diagram and numbering scheme for $Ph_2Bi\text{-}SePh$. Anisotropic parameters were used only for shaded atoms. Thermal ellipsoids are drawn at the 50% probability level.

$$E_2R_4 + E'_2R_4 \rightleftarrows 2\ EE'R_4 \qquad (3)$$

$$\begin{array}{l} R = Ph, E = P, E' = As^{2} \\ R = Me, E = P, E' = As^{19a} \\ R = Me, E = Bi, E' = Sb^{19a} \\ R = Me, E = Sb, E' = As^{19a} \\ R = Me, E = Bi, E' = As^{19a} \end{array}$$

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 finding[3] that diazomethane will add across the bismuth–bismuth bond of $Bi_2Ph_4$, we attempted the reaction of $CH_2N_2$ with $Ph_2Bi\text{-}TePh$ and obtained the product corresponding to the insertion into the heteronuclear bond, (see eq 4). The product of

$$Ph_2Bi\text{-}TePh + CH_2N_2 \rightarrow N_2 + Ph_2BiCH_2TePh \qquad (4)$$

reaction 4 has a low melting point, and it is difficult to recrystallize. Its identification came from the $^1H$ NMR spectra ($Ph_2BiCH_2TePh$ $\delta$ 3.2) excluding the presence of the $CH_2$-inserted homonuclear compounds ($Ph_2BiCH_2BiPh_2$ $\delta$ 2.65; $PhTeCH_2TePh$ $\delta$ 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, $\delta$ ($CH_2$) 3.4, is available for the product of carbene insertion into the element–element bond of $Ph_2Bi\text{-}SePh$ to give $Ph_2BiCH_2SePh$. For comparison, the corresponding values for the $CH_2$-inserted homonuclear species are $\delta$ 2.65 for $Ph_2BiCH_2BiPh_2$ and $\delta$ 4.0 for $PhSeCH_2SePh$.[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 believed[21] to occur via a

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**Table III.** Selected Bond Distances (Å) and Angles (deg) for $Ph_2Bi-SePh$

| | | | |
|---|---|---|---|
| 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 $CH_2N_2$ into the tellurium-tellurium bond of $Te_2Ph_2$[22] 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 $Bi_2Ph_4$ by several reagents such as $O_2$, $S_8$, *p*-benzoquinone, and $I_2$.[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

$$Bi_2Ph_4 + (1/n)Se_n \rightarrow Ph_2Bi-Se-BiPh_2 \qquad (5)$$

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 $Bi_2(p\text{-}C_6H_4Me)_4$, which is also unreactive toward tellurium.[15b]

**Structure Study.** The crystal of $Ph_2BiSePh$, obtained by slow crystallization at about +5 °C, belongs to the enantiomeric space group $P2_12_12_1$. 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 $Ph_2Bi-SePh$ 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 $Bi_2Ph_4$[3] and in $[Co(BiPh_2)(CO)_3(PPh_3)]$.[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 $BaBiSe_3$[25] and is slightly shorter than the strongest bonds (2.82-2.85 Å) in $Bi_2Se_3$.[26] However, if we consider the Bi-Bi distance in $Bi_2Ph_4$[3] (2.990 (2) Å) and the Se-Se distance in $Se_2Ph_2$[27] (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 $Se_2Ph_2$,[27] 1.92 (4) Å in di-*p*-tolyl selenide,[28] 1.936 (9), 1.960 (12), and 1.962 (12) Å in $\eta^7\text{-}C_7H_7Mo(\mu\text{-}SePh)_3Mo(CO)_3$,[29] and 1.92 (2) Å in $Mn_2Br_2(CO)_6Se_2Ph_2$[30]). 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.** $BiPh_2I$, 95825-92-6; $CoCp_2$, 1277-43-6; $Bi_2Ph_4$, 7065-21-6; $BiPh_2Cl$, 5153-28-6; $S_2Ph_2$, 882-33-7; $BiPh_2SPh$, 115419-47-1; $Se_2Ph_2$, 1666-13-3; $Ph_2BiSePh$, 115419-48-2; $Te_2Ph_2$, 32294-60-3; $Ph_2BiTePh$, 115464-56-7; $Ph_2BiCH_2TePh$, 115464-57-8; Se, 7782-49-2; $Ph_2BiSeBiPh_2$, 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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# Reactivity of Pentacoordinate Ferrous Porphyrins with Exo-Bidentate Nitrogenous Bases. Mononuclear and Binuclear Complexes in Dynamic Equilibrium

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The reaction of several exo-bidentate nitrogenous bases with thiocarbonyl(5,10,15,20-tetraphenylporphinato)iron(II) afforded six-coordinate mononuclear and binuclear porphyrin complexes in dynamic equilibrium. This reaction was carried out in halocarbon solvents and monitored both spectrally and electrochemically. Within the potential limits of the solvent/supporting electrolyte system, each complex underwent at least four separate electron-transfer reactions with retention of the thiocarbonyl ligand. An electron-transfer pathway is presented and supported by the combined results of infrared and electronic absorption spectra, variable-temperature proton NMR, variable-temperature electrochemical, and spectroelectrochemical experiments.

## Introduction

The preparation and properties of binuclear metalloporphyrin complexes have been actively pursued since the structural characterization of hematin was reported.[1] Three general classes of binuclear metalloporphyrins have been prepared: porphyrins linked at their periphery[2] by either covalent bonds[3,4] or ionic interactions,[5]

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