Synthesis, Reactivity, and Crystal and Molecular Structure of Tetraphenyldibismuth, Bi_2Ph_4 †

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Tetraphenyldibismuth, Bi_2Ph_4, is best prepared by the reaction of $BiPh_2I$ with 1 equivalent of sodium in liquid ammonia, followed by extraction with toluene and recrystallization from anhydrous ethanol. It is sensitive to air and slightly thermochromic. The crystal and molecular structure was solved by *X*-ray diffraction methods: triclinic, space group $P\bar{1}$, with $a = 7.865(4)$, $b = 11.444(5)$, $c = 6.257(3)$ Å, $\alpha = 105.24(4)$, $\beta = 94.20(7)$, $\gamma = 96.52(6)°$, and $Z = 1$; $R = 0.0560$ for 1 097 absorption-corrected reflections having $I \geqslant 3\sigma(I)$. The molecule has a staggered *trans* conformation, with a bismuth–bismuth distance of 2.990(2) Å. Tetraphenyldibismuth reacts promptly with di-iodine to give $BiPh_2I$, and with *p*-benzoquinone, elemental sulphur, and diazomethane to give the corresponding products of bismuth(III) resulting from oxidative insertion into the bismuth–bismuth bond.

Almost 50 years ago Paneth and Loleit[1] reported the first experimental evidence of the existence of 'bisdimethylbismuth,' formed by the reaction of methyl radicals, generated[2] by heating tetramethyl-lead, with elemental bismuth. The existence of tetramethyldibismuth was recently[3] confirmed by its isolation as a thermally unstable thermochromic compound. The tetraethyl derivative, Bi_2Et_4, has also recently been synthesized[4] by the reaction of $BiEt_3$ with sodium in liquid ammonia followed by treatment with 1,2-dichloroethane. In view of the general tendency of metals, both transition and non-transition, to form more stable bonds with phenyl groups with respect to saturated alkyl ones,[5] it is perhaps intriguing that some attempts to isolate Bi_2Ph_4 failed.[6-8]

In this paper we report the preparation, isolation, and crystal and molecular structure of Bi_2Ph_4. The preparation of relatively large quantities of tetraphenyldibismuth and its relative stability have allowed the reactivity of the bismuth–bismuth bond to be studied in some detail for the first time. Preliminary results of the crystal and molecular structure were published earlier;[9a] other research groups have also reported the preparation of this compound.[9b-d]

Experimental

Unless stated otherwise, all the operations involving the preparation of Bi_2Ph_4 and its reactions were carried out under an atmosphere of prepurified nitrogen or argon. The i.r. spectra were recorded with a Perkin-Elmer model 283 instrument equipped with a grating. Magnetic susceptibilities were measured with a magnetic balance equipped for the Faraday method, using $CuSO_4 \cdot 5H_2O$ as calibrant. E.s.r. spectra were recorded with a Varian E-112 Century Series spectrometer and the mass spectra with a VG-MM 16 F instrument at 20 eV and 120 °C.

Liquid ammonia was dehydrated by condensation over sodium metal at about −80 °C. Commercial $BiPh_3$ was purified by vacuum sublimation and $BiPh_2Cl$ was prepared according to the literature method[10] and recrystallized from toluene. Iododiphenylbismuth was prepared by a slightly modified literature procedure:[6] chlorodiphenylbismuth and sodium iodide in equimolar amounts were allowed to react in acetone as solvent at room temperature; after filtration from NaCl, the solution was treated with water to precipitate the iodo-derivative, which was filtered off, washed with water, and after drying over P_4O_{10} was found to be analytically pure (95% yield). The compound was found to be monomeric by cryoscopy in benzene.

Preparation of Bi_2Ph_4.—Iododiphenylbismuth (8.65 g, 17.65 mmol) was suspended in liquid ammonia (*ca.* 100 cm^3) and sodium sand (0.419 g, 18.22 mmol) was added in portions (about 30 min), while the temperature was maintained between −80 and −50 °C. At the end of the addition, a green solid precipitated out and was filtered off. The solid, which turned grey during the drying procedure *in vacuo*, was extracted with portions of toluene (total about 100 cm^3) at room temperature and the resulting red-orange solution was filtered. Evaporation of the solvent to dryness under reduced pressure left tetraphenyldibismuth as a red-orange residue, which was recrystallized from hot absolute ethanol (400 cm^3). Fine red-orange crystals were obtained, which were filtered off and dried *in vacuo* (3.87 g, 60.4% yield) (Found: C, 40.0; H, 2.7. $C_{24}H_{20}Bi_2$ requires C, 39.7; H, 2.8%). The compound turns reversibly yellow on cooling to liquid-nitrogen temperature. It is soluble in toluene, tetrahydrofuran, acetone, diethyl ether, slightly soluble in n-heptane, decomposes in CCl_4, and is practically insoluble in liquid ammonia. It is sensitive to air in solution, but moderately stable as a solid. At room temperature over long periods of time (several days in normal daylight) it turned black even under an inert atmosphere, and rapidly darkened without melting at about 100 °C. It is indefinitely stable under nitrogen at about −30 °C. A solution of Bi_2Ph_4 (0.195 g, 0.268 mmol) in toluene (25 cm^3) was treated with dry oxygen and the volume of gas absorbed was measured. Within 25 min, 0.65 mol of O_2 was absorbed per mol of Bi_2Ph_4. I.r. [Nujol and $(C_2ClF_3)_n$ mulls] of Bi_2Ph_4: 3 055w, 3 040w, 3 005w, 1 565m, 1 470m, 1 425m, 1 325w, 1 300w, 1 260vw, 1 190vw, 1 155vw, 1 055w-m, 1 010w-m, 995m, 900vw, 850vw, 725s, 690m, 640w, 600w, 445m, and 435m cm^{-1}. Mass spectrum (*m*/*e*, relative abundance, fragment): 726, <1, M^+; 649, 1.5, $[M - Ph]^+$; 572, <1, $[M - 2Ph]^+$; 495, 0.1, $[M - 3Ph]^+$; 440, 2.5, $[M - BiPh]^+$; 363, 4.3, $[M - BiPh_2]^+$; 286, 100, $[M - BiPh_3]^+$; and 209.84, Bi^+. Both in solution (toluene) and in the solid state, no e.s.r. signals could be observed at room temperature. Magnetic sus-

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† *Supplementary data available* (No. SUP 23967, 12 pp.): thermal parameters, complete structural parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

ceptibility: $\chi^{M}_{corr.} = 49 \times 10^{-6}$ c.g.s. units (6.1×10^{-10} m^3 mol^{-1}); diamagnetic correction = -209×10^{-6} c.g.s. units (-2.6×10^{-9} m^3 mol^{-1}).

Collection and Reduction of X-*Ray Data for* Bi_2Ph_4.—Cell dimensions and intensity data were obtained on a computer-controlled Philips PW 1100 diffractometer using Mo-K_α radiation (λ = 0.710 69 Å) using a crystal (0.13 × 0.31 × 0.52 mm) sealed in a glass capillary.

Crystal data. $C_{24}H_{20}Bi_2$, M = 726.38, triclinic, a = 7.865(4), b = 11.444(5), c = 6.257(3) Å, α = 105.24(4), β = 94.20(7), γ = 96.52(6)°, U = 536.7(5) Å^3, Z = 1, D_c = 2.247 g cm^{-3}, $F(000)$ = 330, space group $P\bar{1}$, μ(Mo-K_α) = 163.27 cm^{-1}.

A total of 1 788 unique reflections with $6.0 < 2\theta < 49.0°$ was collected (scan speed 0.075° s^{-1}, scan width 1.2°, and scan type θ—2θ). Of these, 1 097 were considered observed, having $I > 3\sigma(I)$, and retained for refinement. There was no evidence of crystal decay. Corrections were applied for Lorentz, polarization, and absorption effects.

Since there is only one Bi_2Ph_4 molecule per unit cell, the asymmetric unit contains half a molecule, with the centre of gravity of the Bi–Bi bond constrained to lie on a crystallographic centre of symmetry. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with all atoms given anisotropic thermal parameters; the phenyl carbon atoms were allowed to refine freely. The hydrogen atoms were neglected. In the final cycles the weighting scheme $w = 1.2132/[\sigma^2(F_o) + 0.001\ 305(F_o)^2]$ was introduced and refinement converged to R = 0.0560 and R' = 0.0555. The largest peak on a final ΔF map, 2.4 e Å^{-3}, was close to the Bi atom. The ratio of observations to variables was 1 097 : 118 = 9.3 : 1. Calculations were made on a 7 600 C.D.C. computer using the SHELX 76 set of programs.[11] The final atomic co-ordinates are given in Table 1, bond distances and angles in Table 2.

Reactions of Bi_2Ph_4.—*With di-iodine.* To a suspension of tetraphenyldibismuth (0.300 g, 0.413 mmol) in acetone (25 cm^3) was slowly added a solution of di-iodine (0.107 g, 0.422 mmol) in the same solvent (10 cm^3). The colour of the solution turned from orange to yellow and at the end of the addition the reaction mixture was filtered and the resulting solution concentrated to a small volume; water (20 cm^3) was added, with consequent precipitation of analytically pure $BiPh_2I$, which was filtered off and dried *in vacuo* over P_4O_{10} (0.102 g, 25.2% yield) (Found: C, 29.8; H, 2.1. $C_{12}H_{10}BiI$ requires C, 29.4; H, 2.1%). The reaction was also carried out in toluene as solvent; in this case, however, several iodinated products were observed and no pure $BiPh_2I$ could be isolated.

Table 1. Fractional atomic co-ordinates (× 10^4 for Bi and × 10^3 for C) of Bi_2Ph_4 with estimated standard deviations in parentheses

Atom	X/a	Y/a	Z/a
Bi	8 195(1)	5 173(3)	−636(2)
C(1)	710(3)	370(2)	91(3)
C(2)	637(3)	392(2)	285(3)
C(3)	566(3)	298(2)	374(4)
C(4)	572(3)	177(2)	253(4)
C(5)	650(4)	153(2)	54(4)
C(6)	726(3)	247(2)	−28(4)
C(7)	834(2)	680(2)	237(3)
C(8)	755(3)	774(2)	201(4)
C(9)	769(4)	885(3)	378(7)
C(10)	852(4)	890(2)	574(7)
C(11)	923(3)	789(2)	625(5)
C(12)	908(3)	684(2)	442(4)

With p-*benzoquinone: preparation of* 1,4-$C_6H_4(OBiPh_2)_2$. To a solution of tetraphenyldibismuth (0.288 g, 0.396 mmol) in toluene (25 cm^3) was slowly added a solution of *p*-benzoquinone (0.044 g, 0.407 mmol) in 25 cm^3 of the same solvent at room temperature. This caused instantaneous precipitation of the product as a pale yellow solid. After filtration and washing with toluene, the product was dried *in vacuo* (0.275 g, 83% yield). A pure sample was obtained by recrystallization from toluene and drying *in vacuo* for several hours at room temperature to remove lattice toluene (Found: C, 43.0; H, 2.9. $C_{30}H_{24}Bi_2O_2$ requires C, 43.2; H, 2.9%). I.r. spectrum (Nujol mull): 3 060w, 3 040w, 3 005w, 1 995vw, 1 870vw, 1 600vw, 1 570w, 1 430m, 1 330vw, 1 300vw, 1 280vw, 1 260vw, 1 230w, 1 205w, 1 185s, 1 155w, 1 085w, 1 055w, 1 030vw, 1 015w, 995w, 840m, 770s, 730(sh), 720s, 690m-s, 640w, 600w, 480w, 450m, and 360w cm^{-1}. The product is only sparingly soluble in common organic solvents at room temperature and the n.m.r. spectrum could not therefore be recorded.

With octasulphur: preparation of $(Ph_2Bi)_2S$. Tetraphenyldibismuth (0.705 g, 0.971 mmol) was dissolved in toluene (15 cm^3) and to the resulting solution was added octasulphur (0.034 g, 0.133 mmol) recrystallized from carbon disulphide. In about 5 min at room temperature the colour of the solution turned from orange to yellow. By cooling to −30 °C, the pale yellow sulphide crystallized out: it was filtered off, dried *in vacuo*, and rapidly stored at −30 °C (0.352 g, 47.8% yield) (Found: C, 37.9; H, 2.6; S, 4.6. $C_{24}H_{20}Bi_2S$ requires C, 38.0; H, 2.7; S, 4.2%). I.r. spectrum (Nujol mull): 3 060w-m, 3 040w, 3 010w, 1 570w-m, 1 556(sh), 1 430m, 1 330w, 1 260w, 1 185w, 1 175w, 1 155vw, 1 150w, 1 060w-m, 1 010w-m, 910w, 905w, 860vw, 850w, 725s, 720s, 690m, 640m, 600w, 445m, and 435w cm^{-1}. At room temperature under an inert atmosphere the compound slowly turned brown.

With diazomethane: formation of $(Ph_2Bi)_2CH_2$. Tetraphenyldibismuth (0.466 g, 0.642 mmol) dissolved in diethyl ether (75 cm^3) was treated at room temperature with a diethyl ether solution containing an excess of diazomethane, with careful exclusion of light. Within 5 min the reaction was complete as evidenced by the change in colour from orange to yellow. The solution was concentrated under reduced pressure almost to dryness, n-hexane (25 cm^3) was added, and further evaporation of the more volatile solvent under reduced pressure resulted in precipitation of the colourless product. Cooling to about −30 °C, filtration, and drying *in vacuo* gave 0.233 g (49% yield) of the product (Found: C, 40.3; H, 3.0. $C_{25}H_{22}Bi_2$ requires C, 40.6; H, 3.0%). I.r. spectrum (Nujol mull): 3 060w, 3 040w, 3 005w, 1 565w-m, 1 560(sh), 1 425m, 1 325w, 1 295w, 1 260w, 1 155w, 1 055m, 1 010m, 995m, 930vw, 905w, 840vw, 725s, 695m, 640m, 600m, 580(sh), 540m, 485w, 450m, 440m, and 415 cm^{-1}. The melting point and ^{1}H n.m.r.

Table 2. Selected bond distances (Å) and angles (°) in Bi_2Ph_4 with estimated standard deviations in parentheses *

Bi–Bi′	2.990(2)	C(1)–Bi–C(7)	98.3(8)	Bi–C(1)–C(2)	124(1)
Bi–C(1)	2.28(2)	C(7)–Bi–Bi′	90.9(5)	Bi–C(7)–C(12)	123(1)
Bi–C(7)	2.26(2)	C(1)–Bi–Bi′	91.6(5)	Bi–C(1)–C(6)	115(1)
				Bi–C(7)–C(8)	115(1)

* Primed atoms of position $2 - x$, $1 - y$, $- z$.

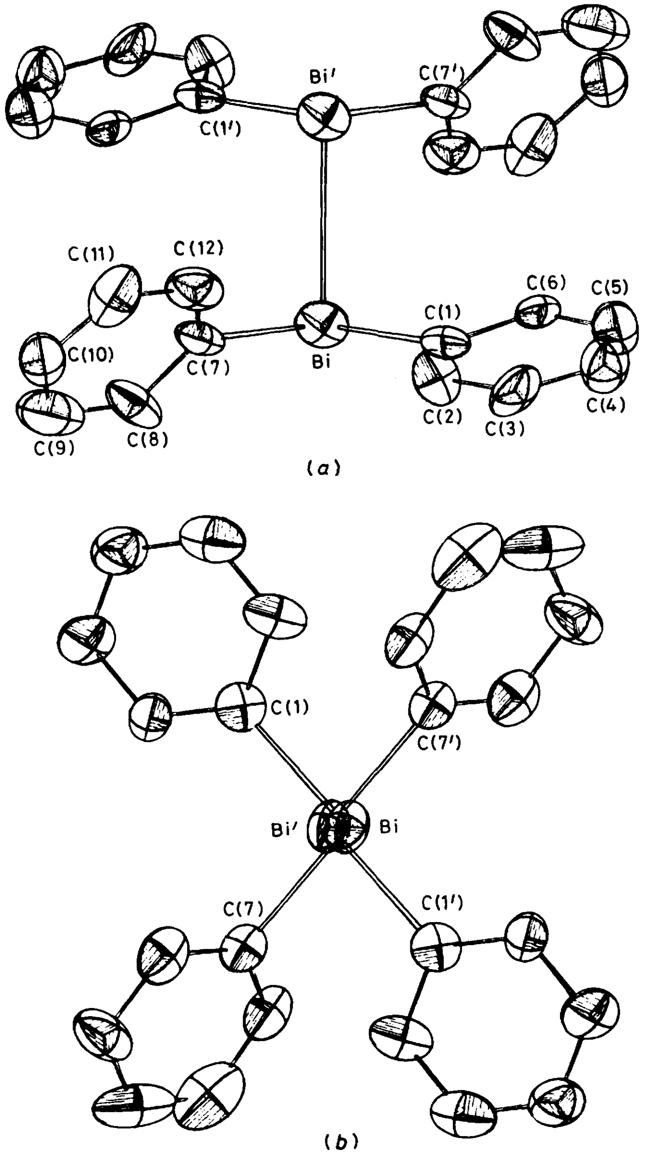


Figure 1. ORTEP views of Bi_2Ph_4 showing the atom labelling used: (*a*) almost perpendicular to the Bi–Bi bond, and (*b*) almost parallel to the Bi–Bi bond

spectrum agree with those reported in the literature,[12] within experimental error.

Results and Discussion

Tetraphenyldibismuth was obtained by sodium reduction of $BiPh_2X$ ($X = Cl$ or I) [equation (1)]. The use of $BiPh_2I$ was

$$2\ BiPh_2X + 2\ Na \xrightarrow{NH_3(l)} Bi_2Ph_4 + 2\ NaX \qquad (1)$$

found to improve the yields up to about 60%. This is presumably due to the fact that the iodo-derivative is much less reactive than $BiPh_2Cl$ [8] towards ammonia, thus decreasing the tendency to form secondary products. Tetraphenyldibismuth is a reasonably stable substance, under an inert atmosphere and with the exclusion of light, at room temperature. A qualitative indication of its stability is given by the observation that the compound can be recrystallized from hot ethanol (recrystallization time about 20 min).

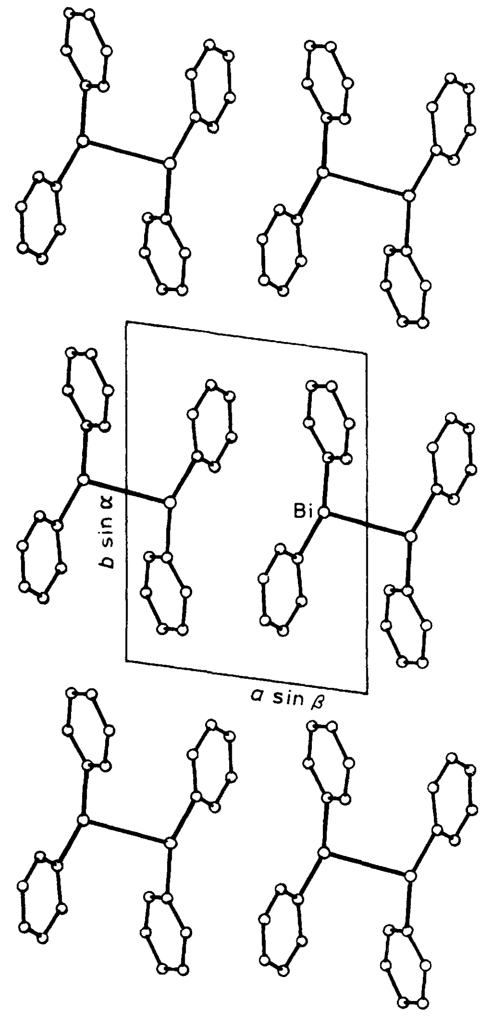


Figure 2. Crystal packing of Bi_2Ph_4

The molecular structure of Bi_2Ph_4 is shown in Figure 1, which also gives the atom labelling used. The molecule has a staggered *trans* conformation, as has also been found in Sb_2Ph_4.[13] The environment of the bismuth atom is approximately pyramidal, the Bi being displaced 1.31 Å from the plane defined by C(1), C(7), and Bi' ($2 - x$, $1 - y$, $-z$). The Bi–Bi' distance is 2.990(2) Å, which is slightly longer than the 2.936(2) and 2.941(2) Å reported for the Bi_4^{2-} anion.[14] It is interesting that this distance is only slightly shorter than the nearest-neighbour distance in elemental bismuth [15] [3.071(1) Å] and that in Sb_2Ph_4 [13] the Sb–Sb distance [2.837(1) Å] is also slightly shorter than that in elemental antimony (2.86 Å).[16] The angles around bismuth, especially the two [C(1)–Bi–Bi' 91.6(5) and C(7)–Bi–Bi', 90.9(5)°] not involving possible steric repulsion between the aromatic rings, are very close to 90°, thus suggesting that the lone pair at bismuth has essentially *s* character, and no important *s–p* hybridization is therefore envisaged to explain the bonding in Bi_2Ph_4. This is a further aspect of the so-called 'inert-pair effect' [17] for post-transition elements, which is also evidenced by the relative stability of the oxidation state III for bismuth. The electronic properties of bismuth should have important consequences for the ligand properties of Bi_2Ph_4 [18] and Bi_2R_4 in general. A similar situation concerning bond angles around the central element can be found in Sb_2Ph_4,[13] the corresponding angles at antimony being 96.5 and 93.8°, *i.e.* considerably smaller than the tetrahedral value but larger than 90°. It is interesting that in P_2Me_4, for which an electron-diffraction study is available,[19] the angle at phosphorus (average) is 101.1(7)°, *i.e.* even closer to the tetrahedral value.

Tetraphenyldibismuth is the first crystallographically studied tetraorganyl of bismuth(II) to be reported; there are therefore no data with which to compare it. The two bismuth–carbon bond distances are 2.28(2) and 2.26(2) Å and an indirect estimate of a bond of this type may be obtained by considering the distances found in the four crystallographically characterized phenylbismuth(III) derivatives, namely 2.42(2) Å in $BiPh_3$,[20] 2.26(2) Å in bis(1-oxopyridine-2-thiolato)-phenylbismuth(III),[21] 2.216(8) Å (average) in $[Cr(CO)_5(BiPh_3)]$,[22] and 2.25(1) Å in (*O*-isopropyl dithiocarbonato)-diphenylbismuth(III).[23] The phenyl rings are inclined at angles of 49.6 and 75.5° with respect to the C(1)–C(7)–Bi plane. The angles formed by the normals to the phenyl planes and the Bi–Bi′ bond are 126.9 and 49.3°. The dihedral angle formed by the least-squares phenyl planes is 122.6°. The C–C bond lengths as well as the C–C–C angles in the phenyl rings are equivalent and normal within experimental error. The crystal packing is shown in Figure 2. The molecules are packed by van der Waals interactions, the shortest contacts being C(4) ··· C(10) $(1-x, 1-y, 1-z)$ 3.65 Å and C(10) ··· C(10) $(2-x, 2-y, 1-z)$ 3.58 Å.

By e.s.r. measurements both in solution (toluene) and in the solid state, it has been ascertained that homolytic cleavage of Bi_2Ph_4, see equation (2), does not proceed to any appreciable extent. Moreover, the compound is substantially diamagnetic. On the other hand, cleavage of the bismuth–bismuth bond is the dominant feature of Bi_2Ph_4 chemistry, and bismuth(III) derivatives are formed, with some differences depending on the reagent used. With di-iodine, $BiPh_2I$ was the product [equation (3)], whereas in other cases the prevailing reaction path was ' oxidative insertion', see equations (4)—(6).

$$Bi_2Ph_4 \rightleftharpoons 2\ BiPh_2 \qquad (2)$$

$$Bi_2Ph_4 + I_2 \longrightarrow 2\ BiPh_2I \qquad (3)$$

$$Bi_2Ph_4 + p\text{-}C_6H_4O_2 \longrightarrow Ph_2Bi\text{–}OC_6H_4O\text{–}BiPh_2 \qquad (4)$$

$$Bi_2Ph_4 + \tfrac{1}{8}S_8 \longrightarrow (Ph_2Bi)_2S \qquad (5)$$

$$Bi_2Ph_4 + CH_2N_2 \longrightarrow (Ph_2Bi)_2CH_2 + N_2 \qquad (6)$$

No reaction was observed with nitrogen oxide NO, *NN′*-ethylenebis(salicylideneiminato)cobalt(II), carbon monoxide, or ethylene. With the last two reagents, high pressures and temperatures above ambient were used, and decomposition of Bi_2Ph_4 was observed.

Molecular oxygen was found to react promptly with tetraphenyldibismuth, the amount of dioxygen absorbed being close to that required for the formation of the μ-oxo-species $(Ph_2Bi)_2O$. However, no pure product could be obtained in this case, presumably due to the ligand-redistribution reaction (7) (X = O or S). This reaction probably occurs to some

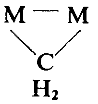
$$3\ (Ph_2Bi)_2X \longrightarrow Bi_2X_3 + 4\ BiPh_3 \qquad (7)$$

extent also with elemental sulphur, but in the latter case the pure μ-sulphido-compound could be isolated, although in small yields (see below). The reaction with dioxygen presumably occurs *via* the intermediate formation of the superoxo- and μ-peroxo-compounds $Ph_2Bi\text{–}OO^{\cdot}$ and $Ph_2Bi\text{–}O_2\text{–}BiPh_2$, which were not isolated. A peroxo-like compound was obtained in the case of *p*-benzoquinone, see reaction (4). In this product the $BiPh_2$ moieties are bridged by a hydroquinone dianion, in agreement with the fact that the i.r. spectrum does not show any intense band in the 1600—1 700 cm^{-1} region, the CO stretching vibrations of *p*-benzoquinone being reported[24] to be at 1 674 and 1 662 cm^{-1} ($CHCl_3$).

The i.r. spectrum of the μ-sulphido-compound in the 250—470 cm^{-1} region (usually associated with transition metal–sulphur stretching vibrations[25]) does not show any band attributable to a Bi–S vibration, presumably because of coincidence with one of the bands of the $BiPh_2$ core.

The reaction of diazomethane with Bi_2Ph_4 gives bis(diphenylbismuthino)methane directly, according to equation (6). This compound has been reported in the literature only recently,[12] being obtained by the reaction of $NaBiPh_2$ with dichloromethane in an unspecified solvent. The reaction of Bi_2Ph_4 with diazomethane occurs in the dark, is very fast, and the product arising from a single insertion of CH_2 into the Bi–Bi bond has been observed in spite of the fact that the reaction was carried out with an excess of CH_2N_2. This observation is of some relevance, in view of the finding that polymethylene, resulting from multiple attachment to the metal, is sometimes observed when diazomethane is treated with transition-metal complexes, *e.g.* $[Ni(\eta\text{-}C_5H_5)_2]$.[26]

Transition-metal complexes of the types $(ML_n)C_6H_4O_2$ and $(ML_n)_2S$ have been prepared predominantly by the reaction of mononuclear ML_n species with *p*-benzoquinone[27] and with elemental sulphur,[28] respectively. Concerning reaction (6), diazomethane is known[29] to react with organic disulphides, diselenides, and ditellurides, giving the corresponding insertion products. Also the tin–tin bond of $R_3Sn\text{–}SnR_3$ undergoes insertion of dichlorocarbene.[30] Transition-metal complexes containing double metal–metal bonds undergo reaction with diazomethane[31] to give dimetallacyclopropane compounds.



A rare case of insertion of diazomethane into a transition-metal complex containing a single metal–metal bond is that of the d^9 platinum(I) derivative $[Pt_2Cl_2(L\text{–}L)_2]$ (L–L = bidentate tertiary phosphine ligand).[32]

We believe that diazomethane attacks the bismuth–bismuth bond of Bi_2Ph_4 directly, a relatively low-energy empty orbital (6*d* or 5*f*) of bismuth being possibly involved in the preliminary transient association with the carbon lone pair of CH_2N_2.

Attempts have been made to generate stable solutions of $BiPh_2^-$ by the sodium reduction of Bi_2Ph_4 in tetrahydrofuran as solvent. Our results are in agreement with those of the electrochemical experiments published earlier:[7,33] we find that the red solutions obtained by treatment of Bi_2Ph_4 with 2 equivalents of sodium are unstable at room temperature and blackish solids are rapidly formed. At lower temperatures (solid-CO_2 temperature) the reduction appears to stop at an earlier stage with formation of blue-green solutions.

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References

1 F. A. Paneth and H. Loleit, *J. Chem. Soc.*, 1935, 366.
2 F. Paneth and W. Hofeditz, *Chem. Ber.*, 1929, **62**, 1335.
3 A. J. Ashe and E. G. Ludwig, *Organometallics*, 1982, **1**, 1408.

4 H. J. Breunig and D. Müller, *Angew. Chem. Int., Ed. Engl.*, 1982, **21**, 439.

5 H. A. Skinner, *Adv. Organomet. Chem.*, 1964, **2**, 49.

6 F. F. Blicke, U. O. Oakdale, and F. D. Smith, *J. Am. Chem. Soc.*, 1931, **53**, 1025.

7 R. E. Dessy, T. Chivers, and W. Kitching, *J. Am. Chem. Soc.*, 1966, **88**, 467.

8 L. D. Freedman and G. O. Doak, *Chem. Rev.*, 1982, **82**, 15 and refs. therein; H. Gilman and H. L. Yablunky, *J. Am. Chem. Soc.*, 1941, **63**, 212.

9 (*a*) F. Calderazzo, A. Morvillo, G. Pelizzi, and R. Poli, *J. Chem. Soc., Chem. Commun.*, 1983, 507; (*b*) H. J. Breunig and D. Müller, *J. Organomet. Chem.*, 1983, **253**, C21; (*c*) A. J. Ashe, E. C. Ludwig, and J. Oleksyszyn, *Organometallics*, 1983, **2**, 1859; (*d*) E. O. Fischer and R. Reitmeier, *Z. Naturforsch., Teil B*, 1983, **38**, 582.

10 F. Challenger and C. F. Allpress, *J. Chem. Soc.*, 1915, **107**, 16.

11 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.

12 F. Steinseifer and T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 723.

13 K. Deuten and D. Rehder, *Cryst. Struct. Commun.*, 1980, **9**, 617.

14 A. Cisar and J. D. Corbett, *Inorg. Chem.*, 1977, **16**, 2482.

15 P. Cucka and C. S. Barrett, *Acta Crystallogr.*, 1962, **15**, 865.

16 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1960, p. 225.

17 C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry,' The Clarendon Press, Oxford, 1965.

18 F. Calderazzo, R. Poli, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, in the press.

19 A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, 1970, **66**, 2732.

20 D. M. Hawley and G. Ferguson, *J. Chem. Soc. A*, 1968, 2059.

21 J. D. Curry and R. J. Jandacek, *J. Chem. Soc., Dalton Trans.*, 1972, 1120.

22 A. J. Carty, N. J. Taylor, A. W. Coleman, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1979, 639.

23 M. Wieber, H. G. Rüdling, and C. Burschka, *Z. Anorg. Allg. Chem.*, 1980, **470**, 171.

24 J. F. Bagli, *J. Am. Chem. Soc.*, 1962, **84**, 177.

25 A. Müller, W. Jaegermann, and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245; F. J. Farrell and T. G. Spiro, *Inorg. Chem.*, 1971, **10**, 1606; E. A. Pasek and D. K. Straub, *Inorg. Chim. Acta*, 1977, **21**, 29; D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1969, 1152; M. G. B. Drew, P. J. Baricelli, P. C. H. Mitchell, and A. R. Read, *J. Chem. Soc., Dalton Trans.*, 1983, 649.

26 H. Werner and J. H. Richards, *J. Am. Chem. Soc.*, 1968, **90**, 4976.

27 C. Floriani, G. Fachinetti, and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1973, 765; F. Calderazzo and G. Dell'Amico, *ibid.*, 1979, 1238.

28 C. Floriani and G. Fachinetti, *Gazz. Chim. Ital.*, 1973, **103**, 1317.

29 N. Petragnani and G. Schill, *Chem. Ber.*, 1970, **103**, 2271.

30 D. Seyferth and F. M. Armbrecht, *J. Am. Chem. Soc.*, 1967, **89**, 2790; D. Seyferth, F. M. Armbrecht, and B. Schneider, *ibid.*, 1969, **91**, 1954.

31 W. A. Herrmann, *Adv. Organomet. Chem.*, 1981, **20**, 159; *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 800 and refs. therein.

32 M. P. Brown, J. R. Fischer, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1979, **18**, 2808.

33 R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, 1966, **88**, 5117.

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