Reactions of Octacarbonyldicobalt with Tetraphenyl Derivatives of Group 5A, including Tetraphenyldibismuthane. Synthesis and Crystal and Molecular Structure of Tricarbonyl(diphenylbismuthido)(triphenylphosphine)cobalt(I), $[Co(BiPh_2)(CO)_3(PPh_3)]$ †

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Tetraphenyldibismuthane reacts with $[Co_2(CO)_8]$ to give the product of oxidative addition, $[Co(BiPh_2)(CO)_4]$, which was isolated as its triphenylphosphine adduct, $[Co(BiPh_2)(CO)_3(PPh_3)]$. $[Co(BiPh_2)(CO)_3(PPh_3)]$ crystallises in the orthorhombic space group *Pbca*, with $a = 26.105(13)$, $b = 21.066(10)$, $c = 10.845(3)$ Å, $Z = 8$, $R = 0.0522$, and $R' = 0.0497$. The molecular structure consists of discrete $[Co(BiPh_2)(CO)_3(PPh_3)]$ units, the geometry around cobalt being that of a distorted trigonal bipyramid with three equatorial carbonyl groups and the $BiPh_2$ and PPh_3 ligands occupying the axial positions. The reactivity of $[Co_2(CO)_8]$ towards E_2Ph_4 was compared along the series from E = arsenic to bismuth. Oxidative addition (E = Bi) and substitutive oxidative addition (E = As or Sb) reactivity patterns were encountered. No tendency of terminal $BiPh_2$ to become bridging with CO substitution was observed. The unique behaviour of $BiPh_2$ as a ligand is explained in terms of the low availability of the second lone pair on bismuth for bonding, in spite of the considerable σ-donation from bismuth to cobalt suggested for terminal $BiPh_2$ by the i.r. spectra.

Earlier work has shown that the d^6 manganese(I) and rhenium(I) complexes $[M_2X_2(CO)_6(thf)_2]$ (X = halogen, thf = tetrahydrofuran) react with E_2Ph_4 (M = Mn, E = P[1a,b] or As;[1b] M = Re, E = P,[1c,d] As,[1d] or Sb[1d]) by substitutive (of co-ordinated thf) co-ordinative addition (s.c.a.) to form the halogeno- and E_2Ph_4-bridged complexes $[M_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}E_2Ph_4)]$. Substitutive (of carbon monoxide) co-ordinative additions of E_2R_4 are known for the d^6 systems of chromium(0), molybdenum(0), and tungsten(0),[2a-d] d^8 iron(0) $[Fe(CO)_5]$,[2a,e-g] d^{10} $[Ni(CO)_4]$,[2h] d^6 $[V(CO)_6]^-$,[2i] and d^4 $[V(\eta^5\text{-}C_5H_5)(CO)_4]$.[2i] With other systems {*e.g.*, d^9 $[Co_2(CO)_8]$} or with the same systems under more drastic conditions, a substitutive oxidative addition (s.o.a.) pattern may be followed,[3,‡] as illustrated by the formation of $[\{Co(\mu\text{-}PPh_2)(CO)_3\}_n]$[3a,f] $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$,[3e] and $[Mo_2(\mu\text{-}ER_2)_2(CO)_8]$ (E = P, As, or Sb; R = alkyl or aryl).[2a] Formation of metal–metal bonds will be dictated essentially by the 18 e inert-gas rule. A simple oxidative addition (o.a.) pattern, *i.e.* cleavage of the E–E bond with increase of the metal oxidation state without CO substitution, is not normally encountered, in view of the competing Lewis basicity of the resulting terminally bonded ER_2 group.

The patterns of reactivity of E_2R_4 with low-valent carbonyl derivatives of transition metals, ML_n, can be summarized as shown below.

$$\text{(s.c.a.)}\begin{cases}[ML_n] \longrightarrow [ML_{n-1}(\mu\text{-}E_2R_4)]\\ 2[ML_n] \longrightarrow [(ML_{n-1})_2(\mu\text{-}E_2R_4)]\end{cases}$$

$$\text{(s.o.a.)}\begin{cases}2[ML_n] \longrightarrow [(ML_{n-2})_2(\mu\text{-}ER_2)_2]\ \text{(M–M bond)}\\ [L_nM\text{–}ML_n] \longrightarrow [(ML_{n-1})_2(\mu\text{-}ER_2)_2]\\ [L_nM\text{–}ML_n] \longrightarrow [(ML_{n-2})_2(\mu\text{-}ER_2)_2]\ \text{(M=M bond)}\end{cases}$$

$$\text{(o.a.)}\quad [L_nM\text{–}ML_n] \longrightarrow 2[ML_n(ER_2)]$$

The availability of the recently reported[4] tetraphenyldibismuthane, Bi_2Ph_4, offered the possibility of studying its reactivity towards transition-metal complexes, for cations of both d^n and d^{n+1} electronic configurations. We now report the results of the reaction of Bi_2Ph_4 with $[Co_2(CO)_8]$, including comparisons of the reactions of $[Co_2(CO)_8]$ with other E_2Ph_4 molecules. A further point of interest is that terminally bonded ER_2 groups are less frequently encountered than bridging ones (see later), the reasons for the bridging *versus* the terminal bonding arrangement not being completely clarified as yet. The availability of the $BiPh_2$ ligand from Bi_2Ph_4 was anticipated to contribute to a better understanding of this problem, in view of the drastic change in electronic situation at bismuth, as compared with other elements of the same Group.

Experimental

Unless otherwise stated, all operations were carried out under an atmosphere of prepurified nitrogen. Solvents were dried by conventional methods prior to use. Tetraphenyldibismuthane[4a] was prepared from $BiPh_2I$ and the stoicheiometric amount of sodium in liquid ammonia, followed by extraction with toluene and recrystallization from anhydrous ethanol, as previously described.[4b] Tetraphenyldiphosphane,[5,6] tetraphenyldiarsane,[7] and tetraphenyldistibane[8] were prepared according to literature methods. Octacarbonyldicobalt was purified by vacuum sublimation. Triphenylphosphine was recrystallized from ethanol. The complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ was prepared from $[Co_2(CO)_8]$ and P_2Ph_4 in toluene, as previously reported.[3a,e-f]

Reaction of $[Co_2(CO)_8]$ *with* Bi_2Ph_4: *Preparation of* $[Co(BiPh_2)(CO)_4]$.—Octacarbonyldicobalt (0.120 g, 0.351 mmol) was treated with Bi_2Ph_4 (0.289 g, 0.398 mmol) in toluene (10 cm³) at room temperature. A red-brown solution showing i.r. bands at 2 074s, 2 011m, and 1 991vs cm⁻¹ was promptly obtained within 5 min after mixing the reagents. (A parallel gas-volumetric experiment carried out at 19.7 °C under an atmosphere of carbon monoxide showed that no significant gas evolution accompanied the reaction.) Evaporation of the solvent left a red viscous oil, which was soluble in saturated

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† *Supplementary data available* (No. SUP 56031, 2 pp.): thermal parameters. See instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ References for the s.o.a. reactivity pattern also include refs. 2*a*, *c*, *e*, *g*, *i*, and *j*.

Table 1. Analytical and i.r. spectroscopic data of carbonyl complexes of cobalt(I) with terminal EPh_2 groups (E = As, Sb, or Bi)

Compound	Elemental analysis [a] (%)		$\nu(CO)^b/cm^{-1}$
	C	H	
$[Co(AsPh_2)(CO)_3(PPh_3)]$	63.0 (62.5)	4.2 (4.0)	2 030vw, 1 967s
$[Co(SbPh_2)(CO)_3(PPh_3)]$	58.3 (58.2)	3.7 (3.7)	2 026vw, 1 959s
$[Co(BiPh_2)(CO)_3(PPh_3)]$	51.6 (51.6)	3.3 (3.3)	2 013vw, 1 957s, 1 948s

[a] Calculated values in parentheses. [b] n-Heptane solution.

hydrocarbons. From the n-pentane solution, a red crystalline solid was obtained at *ca.* −80 °C: this solid could not be filtered because of melting near room temperature. No further attempts to isolate the compound were made, its formula as $[Co(BiPh_2)(CO)_4]$ being inferred from the gas-volumetric data, from its further reaction with PPh_3 (see later), and from its i.r. spectrum [n-hexane, ν(CO) at 2 077s, 2 017m, 1 998vs, and 1 993vs cm^{-1}]. A solution of $[Co(BiPh_2)(CO)_4]$ thus obtained was irradiated with a mercury lamp both under carbon monoxide and under nitrogen at 19.7 °C: no appreciable evolution of gas was observed and the i.r. spectrum remained unchanged.

Reaction of $[Co(BiPh_2)(CO)_4]$ *with* PPh_3: *Preparation of* $[Co(BiPh_2)(CO)_3(PPh_3)]$.—A solution of $[Co(BiPh_2)(CO)_4]$ (*ca.* 0.07 mol dm^{-3}) obtained as described above was treated with a standardized solution of PPh_3 in toluene, in a gas-volumetric apparatus at 14.1 °C. One mole of CO per cobalt atom was evolved upon addition of one equivalent of PPh_3 and no further evolution was observed with excess PPh_3. The resulting solution was filtered and a red-brown product was precipitated by adding double the volume of n-heptane and cooling to dry-ice temperature. The product was collected by filtration, dried *in vacuo* (65% yield), and recrystallized from n-heptane. Analytical and spectroscopic data are given in Table 1.

Reactions of $[Co_2(CO)_8]$ *with* E_2Ph_4 (E = As *or* Sb) *followed by* PPh_3: *Preparation of* $[Co(EPh_2)(CO)_3(PPh_3)]$.—(*a*) Octacarbonyldicobalt (0.236 g, 0.690 mmol) in benzene (10 cm^3) was reacted at room temperature with As_2Ph_4 (0.347 g, 0.757 mmol) under an initial atmosphere of dinitrogen. Gas evolution and precipitation of a red solid were observed. To the resulting suspension, which had been stirred overnight, n-heptane (100 cm^3) was added and the red solid was then collected by filtration and dried *in vacuo* (0.426 g, 83% yield as $[\{Co(\mu-AsPh_2)(CO)_3\}_n]$). The solid was purified by dissolution in benzene and precipitation with n-pentane (Found: C, 48.1; H, 3.0. Calc. for $C_{15}H_{10}AsCoO_3$: C, 48.4; H, 2.7%). A cryoscopic measurement in benzene gave an apparent molecular weight corresponding to $n = 3$. The i.r. spectrum (CH_2Cl_2) showed broad bands at *ca.* 2 015w, 1 995vs, and 1 965(sh) cm^{-1}. The solid was soluble in aromatic hydrocarbons, but the resulting solutions on standing for several hours were not stable and a solid of the same colour and very similar i.r. spectrum separated out. This phenomenon was observed both under nitrogen and under carbon monoxide.

A control gas-volumetric experiment carried out in toluene at 14.3 °C under CO showed that the reaction of $[Co_2(CO)_8]$ with As_2Ph_4 was accompanied by the evolution of approximately one mole of CO per cobalt atom within 15 min after mixing the reagents, and that no further CO displacement occurred.

The compound $[\{Co(\mu-AsPh_2)(CO)_2\}_n]$ (0.157 g, 0.211 mmol) was then reacted with PPh_3(0.133 g, 0.507 mmol) in benzene (10 cm^3) at room temperature for 24 h. (No CO evolution was observed in a gas-volumetric experiment carried out at 14.3 °C in toluene under CO.) The solution was evaporated almost to dryness under reduced pressure and n-heptane (10 cm^3) added; the orange solid which precipitated out was dissolved again by warming and the resulting solution cooled to room temperature. The red-orange crystals of $[Co(AsPh_2)(CO)_3(PPh_3)]$ so obtained (21% yield) had the analytical and spectroscopic properties reported in Table 1.

(*b*) The compound $[\{Co(\mu-SbPh_2)(CO)_3\}_n]$ [ν(CO) (CH_2Cl_2) at 1 990vs and 1 960(sh) cm^{-1}, broad bands] was similarly obtained as a red microcrystalline compound in 94% yield by reacting $[Co_2(CO)_8]$ (0.547 g, 1.60 mmol) with Sb_2Ph_4 (0.889 g, 1.61 mmol) in benzene (25 cm^3) for 12 h at room temperature. The compound was purified by dissolution in dichloromethane and precipitation with n-heptane (Found: C, 42.8; H, 2.5. Calc. for $C_{15}H_{10}CoO_3Sb$: C, 43.0; H, 2.4%). A parallel gas-volumetric experiment carried out in toluene at 14.2 °C under CO showed that one mole of CO was evolved within 2 h after mixing the reagents and that no further evolution was observed. The compound is soluble in aromatic hydrocarbons, but, similar to the diphenylarsenido-derivative, these solutions were unstable upon long standing, even under an atmosphere of carbon monoxide. Cryoscopic measurements in benzene carried out both under nitrogen and CO gave an apparent molecular weight corresponding to n slightly above 2, between 2 and 2.3, depending on the concentration used for the measurement.

The red crystalline compound $[Co(SbPh_2)(CO)_3(PPh_3)]$ (see Table 1) was obtained in 70% yield by the reaction of $[\{Co(\mu-SbPh_2)(CO)_3\}_n]$ (0.477 g, 0.569 mmol) with PPh_3 (0.312 g, 1.19 mmol) in benzene (15 cm^3), by a procedure similar to that described for the corresponding arsenic derivative.

Attempts to react the diphenylphosphido-complex $[\{Co(\mu-PPh_2)(CO)_3\}_n]$ with PPh_3 in benzene failed. The solid present in the suspension after stirring for 10 d at room temperature had an i.r. spectrum very similar to that of the starting material with no bands attributable to the expected PPh_3 adduct.

Collection and Reduction of X-*Ray Data for* $[Co(BiPh_2)(CO)_3(PPh_3)]$.—A single crystal for *X*-ray diffraction analysis was obtained by recrystallization from n-heptane. A crystal of approximate dimensions 0.10 × 0.25 × 0.34 mm was chosen in air and then sealed in a glass capillary for protection against possible air oxidation. Symmetry information, unit-cell, and crystal orientation data were obtained by using the search and index routines on a Philips PW 1 100 automatic diffractometer. Accurate lattice parameters, with estimated standard deviations, were determined by least-squares refinement using the θ values for 21 automatically centred reflections.

Crystal data. $C_{33}H_{25}BiCoO_3P$, $M = 786.45$, orthorhombic, space group *Pbca*, $a = 26.105(13)$, $b = 21.066(10)$, $c = 10.845(3)$ Å, $U = 5\,964(4)$ Å^3, $D_c = 1.712$ g cm^{-3}, $Z = 8$, $F(000) = 2\,976$, $\mu(Mo-K_\alpha) = 65.13$ cm^{-1}.

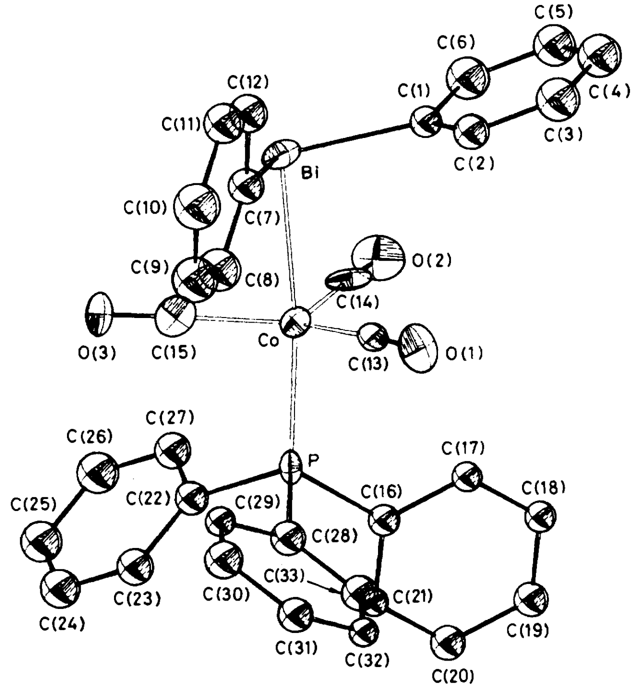
Intensities were recorded by the ω scan technique (scan speed, 0.075° s^{-1}), using Mo-K_α radiation ($\lambda = 0.710\,69$ Å). One octant of the reciprocal space was surveyed with 6.0 <

Table 2. Fractional atomic co-ordinates (× 10^4) of [$Co(BiPh_2)(CO)_3(PPh_3)$] with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Bi	2 879(1)	362(1)	5 659(1)	C(12)	2 928(9)	1 077(11)	8 186(15)
Co	3 550(2)	−560(2)	5 071(4)	C(16)	4 545(7)	−1 398(10)	3 630(15)
P	4 108(3)	−1 347(4)	4 963(7)	C(17)	4 637(7)	−849(10)	2 947(15)
O(1)	4 322(9)	320(10)	5 902(20)	C(18)	4 989(7)	−859(10)	1 982(15)
O(2)	3 283(11)	−440(14)	2 475(22)	C(19)	5 249(7)	−1 418(10)	1 700(15)
O(3)	2 870(11)	−1 314(12)	6 629(22)	C(20)	5 157(7)	−1 966(10)	2 382(15)
C(13)	4 017(13)	−13(13)	5 523(32)	C(21)	4 805(7)	−1 956(10)	3 347(15)
C(14)	3 375(12)	−466(16)	3 436(33)	C(22)	3 794(8)	−2 121(7)	4 983(20)
C(15)	3 131(13)	−1 013(18)	6 034(27)	C(23)	3 946(8)	−2 597(7)	5 796(20)
C(1)	3 272(8)	1 217(8)	4 850(20)	C(24)	3 702(8)	−3 185(7)	5 778(20)
C(2)	3 605(8)	1 624(8)	5 467(20)	C(25)	3 305(8)	−3 297(7)	4 948(20)
C(3)	3 774(8)	2 178(8)	4 897(20)	C(26)	3 153(8)	−2 822(7)	4 135(20)
C(4)	3 608(8)	2 326(8)	3 709(20)	C(27)	3 397(8)	−2 234(7)	4 153(20)
C(5)	3 275(8)	1 919(8)	3 093(20)	C(28)	4 573(8)	−1 353(9)	6 265(16)
C(6)	3 106(8)	1 365(8)	3 663(20)	C(29)	4 373(8)	−1 359(9)	7 456(16)
C(7)	3 140(9)	540(11)	7 636(15)	C(30)	4 692(8)	−1 246(9)	8 462(16)
C(8)	3 461(9)	143(11)	8 315(15)	C(31)	5 212(8)	−1 126(9)	8 276(16)
C(9)	3 568(9)	283(11)	9 544(15)	C(32)	5 411(8)	−1 120(9)	7 085(16)
C(10)	3 356(9)	820(11)	10 093(15)	C(33)	5 092(8)	−1 234(9)	6 079(16)
C(11)	3 036(9)	1 216(11)	9 414(15)				

Table 3. Selected bond distances (Å) and angles (°) for [$Co(BiPh_2)(CO)_3(PPh_3)$] with estimated standard deviations in parentheses

Bi–Co	2.692(5)	Co–C(13)	1.75(3)
Bi–C(1)	2.25(2)	Co–C(14)	1.84(3)
Bi–C(7)	2.28(2)	Co–C(15)	1.79(3)
Co–P	2.210(9)	C(13)–O(1)	1.14(4)
P–C(16)	1.84(2)	C(14)–O(2)	1.07(4)
P–C(22)	1.83(2)	C(15)–O(3)	1.13(4)
P–C(28)	1.86(2)		
Co–Bi–C(1)	100.9(5)	C(13)–Co–C(15)	128(1)
Co–Bi–C(7)	98.5(5)	C(14)–Co–C(15)	118(1)
C(1)–Bi–C(7)	95.7(8)	Co–P–C(16)	119.5(7)
Bi–Co–P	169.3(3)	Co–P–C(22)	111.9(8)
Bi–Co–C(13)	85(1)	Co–P–C(28)	113.2(7)
Bi–Co–C(14)	89(1)	C(16)–P–C(22)	103.6(9)
Bi–Co–C(15)	81(1)	C(16)–P–C(28)	101.0(9)
P–Co–C(13)	93(1)	C(22)–P–C(28)	106.1(9)
P–Co–C(14)	101(1)	Co–C(13)–O(1)	175(3)
P–Co–C(15)	92(1)	Co–C(14)–O(2)	176(3)
C(13)–Co–C(14)	112(1)	Co–C(15)–O(3)	178(3)



$2\theta < 48.0°$. Of the 5 245 reflections measured, 552 were systematically extinct and 1 672 were considered observed having $I \geqslant 2\sigma(I)$. Examination of the data set revealed systematic absences (*hk*0 absent with *h* odd, 0*kl* absent with *k* odd, and *h*0*l* absent with *l* odd) consistent with the *Pbca* space group.

No significant change was observed in the measured intensity of a standard reflection monitored every 75 reflections to check crystal and instrumental stability. The intensities were corrected for Lorentz and polarization factors and for absorption.

Solution of the structure was achieved by the standard heavy-atom technique. A Patterson map, computed with all measured data, was used to obtain the positional parameters of the bismuth atom; these parameters were refined before a Fourier synthesis (based upon the phases assigned from this refinement) was employed to establish the positions of the cobalt and phosphorus atoms. Subsequent refinements and difference-Fourier syntheses revealed all of the remaining non-hydrogen atoms. Full-matrix least-squares refinement of their co-ordinates, using isotropic thermal parameters, gave convergence to a conventional *R* index of 0.1198 for the observed reflections only. Because of the low number of observed data and of the large number of independent atoms to be refined, all the phenyl rings were treated as rigid groups. The use of anisotropic thermal parameters for all the non-hydrogen atoms other than the carbon atoms of the phenyl rings led to convergence with $R = 0.0950$. At this point of the refinement, with all the expected atoms contributing, the *R* value was rather high. From an examination of the data set, it was noted that a large number of weak reflections were at the limit of observation; accordingly, 452 reflections giving $F_o < 6\sigma(F_o)$ were removed from the final cycles of refinement, together with 44 other reflections showing bad agreement with the calculated values. This procedure reduced the *R* factor considerably (final residuals $R = 0.0522$ and $R' = 0.0497$), yielding a ratio between observations (1 176) and parameters (142) of 8.3 : 1. The quantity minimized was $\Sigma w|\Delta F^2|$; in the early stages of the refinement unit weights were used and in the last cycles the weighting scheme $w = 0.825/[\sigma^2(F_o) + 0.00058\, F_o^2]$ was employed. A final ΔF map contained areas of residual electron density of intensity *ca.* 0.9 e Å^{-3}, in the vicinity of the bismuth atom. Computations were carried out on a Cyber 76 computer using the SHELX 76 crystallographic programs,[9] while the atomic scattering factors used were those for neutral atoms. Real and imaginary dispersion corrections were applied to the calculated structure factors. The final atomic positional parameters are listed in Table 2 and selected bond distances and angles are in Table 3. Because of the dominating effect of the bismuth atom on the scattering of the *X*-rays, the standard deviations for the light atoms are high and little significance should be attached to bond distances and angles involving these atoms. An ORTEP drawing of the molecule together with the atom labelling used is shown in the Figure.

Results and Discussion

Octacarbonyldicobalt reacts rapidly with Bi_2Ph_4 by cleavage of the bismuth–bismuth bond and formation of the tetracarbonyl derivative of cobalt(I), according to the stoicheiometry of equation (1). The product of reaction (1) is likely to be a low

$$[Co_2(CO)_8] + Bi_2Ph_4 \longrightarrow 2[Co(BiPh_2)(CO)_4] \qquad (1)$$

melting-point solid and its isolation in a pure state was not possible. However, its formulation as a monomeric tetracarbonyl derivative is based on the following points. (*a*) The reaction was shown to occur without CO evolution, thus the compound has four CO groups per cobalt atom. (*b*) The i.r. spectrum (n-hexane) shows terminal and no bridging CO groups: a CO-bridged dimeric structure is therefore excluded and a $BiPh_2$-bridged structure is unlikely for the considerations that follow and because this would give a 20 e count for cobalt. Four intense carbonyl stretching vibrations are present in the i.r. spectrum, including the lowest energy band which is split into two bands, separated by *ca.* 5 cm^{-1}. By assuming a trigonal bipyramidal geometry with the $BiPh_2$ group in the axial position, due to the orientation of the $BiPh_2$ group, the molecule has C_s symmetry at most, for which four stretching vibrations ($3A' + A''$) are expected. Moreover, the i.r. spectra of complexes of general formula $[CoX(CO)_4]$ [10] have i.r. patterns similar to that of $[Co(BiPh_2)(CO)_4]$. It has already been pointed out [10b] that, when X has less than three-fold symmetry ($GeMe_2Cl$, $GePh_2Cl$, *etc.*), the i.r. spectrum is characterized by four intense bands. (*c*) Treatment of $[Co(BiPh_2)(CO)_4]$ with PPh_3 led to the formation of the substitution product with evolution of one mole of CO, according to equation (2). The PPh_3-substituted compound has been fully

$$[Co(BiPh_2)(CO)_4] + PPh_3 \longrightarrow CO + [Co(BiPh_2)(CO)_3(PPh_3)] \qquad (2)$$

characterized and an *X*-ray diffraction study (see later) confirms that three equatorial groups are present in the parent compound.

The crystal structure of $[Co(BiPh_2)(CO)_3(PPh_3)]$ consists of distinct, well separated monomers, occupying general positions in the space group *Pbca*. The geometry around cobalt is that of a distorted trigonal bipyramid with three equatorial carbonyl groups slightly oriented towards the $BiPh_2$ group which occupies an axial position. The cobalt atom is 0.16 Å below the plane of the three carbonyl carbon atoms, and two of the equatorial C–Co–C angles (see Table 3) and the axial Bi–Co–P angle are considerably different from the 120 and 180°, respectively, expected for a trigonal bipyramid.

This is the first *X*-ray crystal structure reported for a compound containing a bismuth–cobalt bond. The Bi–Co distance of 2.692(5) Å may be compared with the values of 2.593(3)—2.602(2) Å found [11] for the cobalt–antimony distances in $[\{Co(CO)_3(PPh_3)\}_4Sb]BPh_4{\cdot}CH_2Cl_2$. By taking into account the observed distances in Sb_2Ph_4[12] [Sb–Sb, 2.837(1) Å] and Bi_2Ph_4 [Bi–Bi, 2.990(2) Å] [4a] and the covalent radii reported [13] for Group 5A elements, the cobalt–bismuth distance observed in our compound is in line with the *ca.* 0.1 Å increase in the covalent radius observed on going from antimony to bismuth.

The cobalt–phosphorus distance of 2.210(9) Å agrees well with the corresponding average distance of 2.217 Å found in the above mentioned $[\{Co(CO)_3(PPh_3)\}_4Sb]BPh_4{\cdot}CH_2Cl_2$[11] and with 2.19(1) Å found [14] in $[Co_2(CO)_6(PBu_3)_2]$ and $[Hg\{Co_2(CO)_6(PEt_3)_2\}]$. The geometry around phosphorus is distorted tetrahedral with the mean Co–P–C angle increasing to 115°, the mean C–P–C angle being 104°.

The pyramidal geometry around bismuth is essentially the same as that in Bi_2Ph_4.[4a] The three angles at bismuth (100.9, 98.5, and 95.7°), although far from the tetrahedral value, are considerably larger than those found [4a] in Bi_2Ph_4, especially those [C(1)–Bi–Bi′, 91.6° and C(7)–Bi–Bi′, 90.9°] not involving possible steric repulsions between the phenyl rings. We believe that, in the case of the cobalt complex, the increase of the angles at bismuth with respect to Bi_2Ph_4 is at least partly due to steric repulsion between the carbonyl and phenyl groups. On the other hand, the structural parameters suggest that the residual lone pair at bismuth has considerable *s* character. The bismuth–carbon bond distances are 2.25(2) and 2.28(2) Å, virtually identical to those found in Bi_2Ph_4.[4a]

The molecular packing is dominated by van der Waals interactions. Short intermolecular contacts occur between an oxygen atom and three phenyl carbon atoms: O(1) ··· C(17′), 3.19(3); O(1) ··· C(18′), 3.13(3); and O(1) ··· C(33′), 3.27(3) Å (primed atoms indicate the position $1 - x, \bar{y}, 1 - z$).

The essentially *s* character of the lone pair at bismuth, suggested by the geometrical parameters of $[Co(BiPh_2)(CO)_3(PPh_3)]$, and therefore its low availability for bonding is confirmed by the failure to convert the tetracarbonyl derivative into the corresponding $BiPh_2$-bridged complex, even under ultraviolet irradiation [equation (3)]. Apparently $BiPh_2$ preferentially acts towards cobalt(I) as a two-electron

$$[Co(BiPh_2)(CO)_4] \longrightarrow CO + \frac{1}{n}[\{Co(\mu\text{-}BiPh_2)(CO)_3\}_n] \qquad (3)$$

terminal ligand. It is interesting to note that stable monomeric tetracarbonyl derivatives of cobalt(I), $[CoX(CO)_4]$, could be isolated only when the group X attached to cobalt had no residual lone pairs [10] ($GeCl_3$, $GePh_3$, $SnPh_3$, *etc.*). It has also been pointed out that $[CoI(CO)_4]$ [15] [ν(CO) [15a] at 2 115, 2 050, and 2 046 cm^{-1}] is stable at *ca.* −40 °C in saturated hydrocarbons. Moreover, the terminal dimethylarsenido-complex $[Co(AsMe_2)(CO)_4]$,[16] as obtained from $[Co(SiMe_3)(CO)_4]$ and $AsMe_2Cl$, could not be isolated because of decomposition at room temperature.

The present investigation has allowed a comparison to be made of the reactivity of $[Co_2(CO)_8]$ with E_2Ph_4 along the Group from phosphorus to bismuth, and of the ligand behaviour of EPh_2 with respect to cobalt(I). Octacarbonyldicobalt was found to react promptly with As_2Ph_4 and Sb_2Ph_4 with formation of the corresponding EPh_2-bridged species of d^8 cobalt(I) [equation (4); E = P,[3a,e,f,17] As, or Sb]. The PPh_2-bridged compound shows broad ν(CO) bands (in CH_2Cl_2) at 2 054w, 2 033w, 1 998vs, and 1 975(sh) cm^{-1}, which are very

$$[Co_2(CO)_8] + E_2Ph_4 \longrightarrow 2\,CO + \frac{2}{n}[\{Co(\mu\text{-}EPh_2)(CO)_3\}_n] \qquad (4)$$

similar to those of the corresponding arsenic and antimony derivatives and to that reported [3e,f] for the oligomeric [$\{Co(\mu\text{-}PPh_2)(CO)_3\}_n$] by Geoffroy and co-workers. In the course of reaction (4) we did not observe any clear evidence of the [$Co(EPh_2)(CO)_4$] complexes, which, on the basis of the present results with Bi_2Ph_4, were expected to be the primary products of the [$Co_2(CO)_8$]–E_2Ph_4 interaction.

The presumably oligomeric EPh_2-bridged complexes (E = As or Sb) react with PPh_3 to give the corresponding monomeric complexes with terminal EPh_2 groups, see equation (5), while the PPh_2 compound was unaffected by PPh_3 under the same conditions [equation (6)]. Based on the molecular

$$\frac{1}{n}[\{Co(\mu\text{-}EPh_2)(CO)_3\}_n] + PPh_3 \longrightarrow [Co(EPh_2)(CO)_3(PPh_3)]\ (E = As\ or\ Sb) \quad (5)$$

$$\frac{1}{n}[\{Co(\mu\text{-}PPh_2)(CO)_3\}_n] + PPh_3 \longrightarrow [Co(PPh_2)(CO)_3(PPh_3)] \quad (6)$$

structure of the bismuth derivative [$Co(BiPh_2)(CO)_3(PPh_3)$] there is no difficulty in assigning the same geometry to the monomeric complexes of equation (5), with the three carbonyl groups in the equatorial positions of a trigonal bipyramid. The solution spectra, see Table 1, are consistent with this assignment. The arsenic and antimony derivatives have two CO stretching vibrations in agreement with the C_{3v} symmetry ($A_1 + E$) of the carbonyl groups clearly not being severely disturbed by the EPh_2 group lying on the three-fold axis. Only at bismuth, due to either the bulkiness of the heteroatom or probably to the closer approach of the phenyl groups to the equatorial ligands (the 'inert lone pair' is particularly effective at bismuth, as discussed earlier), does the third CO stretching vibration become observable.

Comparison of the three complexes [$Co(EPh_2)(CO)_3(PPh_3)$] as a function of E shows, see Table 1, that the ν(CO) bands change drastically with E from arsenic to bismuth. Contrary to what happens with *tertiary* alkyl and aryl derivatives of Group 5, ER_3,[18] and with E_2Ph_4,[1a–e] for which the effect of changing the heteroatom is generally small, the values of ν(CO) in these complexes containing terminal EPh_2 groups decrease in the sequence As > Sb > Bi. A similar effect has been found [19] for terminal phosphole, arsole, and stibole complexes of manganese, molybdenum, and tungsten. It therefore appears that terminal ER_2 ligands of Group 5 behave similarly to the isoelectronic terminal ER_2 or bridging ER ligands of Group 6 (E = S, Se, or Te), which also cause a decrease in ν(CO) from the lighter to the heavier donor atom.[20,21]

Earlier work on manganese(I) and rhenium(I) complexes of E_2Ph_2 ligands (E = S, Se, or Te) had indicated that a stronger σ-component for bond formation to the transition element was a plausible assumption for the heavier chalcogens. Increased electron density flowing into the metal from diaryl derivatives of Group 5 donor atoms may be operative, although no data are available as yet to establish the corresponding effect on the bond strength.

The present investigation has indicated that although $BiPh_2$ is presumably a good σ-donor, the availability of the second lone pair is low, which explains why complexes of cobalt(I) with bridging $BiPh_2$ groups are not easily accessible.

We believe that σ- and π-effects of both the Group 5 donor and the carbonyl ligands are operative in these systems and that the resulting stability of a given system depends on a delicate, difficult to predict, balance of these factors. However, two trends of relative stabilities for the cobalt(I)–ER_2 systems are suggested by the present results, one pertaining to terminally bonded ER_2 groups (P, As, Sb ≪ Bi) and the other to the bridging ones (P, As, Sb ≫ Bi). We also think that the first lone pair σ-donation is the dominating factor in the former sequence, whereas the inertness of the second lone pair, being large at bismuth, plays an important role in the latter effect. Back donation from the metal to CO increases the overall stability, in phase with σ-donation to the metal from the Group 5 donor.

In view of the preceding observations, low-valent metal complexes containing terminal BiR_2 groups should be the most easily obtained and work to verify this is now in progress in these laboratories, by using Bi_2Ph_4 as a starting material. On the other hand, several examples [22] are known in the literature of transition-metal complexes containing terminal ER_2 groups for phosphorus, arsenic, and antimony, although, as mentioned earlier, the most common bonding mode with these elements is a bridging one. Terminal BiR_2 groups have been reported for molybdenum(II) and tungsten(II),[22e] for iron(II),[22l] and for rhenium(I).[22m]

Acknowledgements

The authors wish to thank the National Research Council (C.N.R., Roma) and the Ministry of Education for support of this work, Dr. R. Zamboni for elemental analyses, Dr. G. Bor for helpful discussions, and Mr. A. Barbati for technical assistance. We also thank Professor A. J. Ashe for sending a copy of his paper (ref. 4*d*) prior to publication.

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Received 4*th January* 1984; *Paper* 4/017