Synthetic Studies on Cobalt Carbonyl Complexes containing Antimony and Bismuth. Crystal Structures of $[SbO(OH)\{Co(CO)_3L\}_2]$ [L = PPh_3 or $P(C_6H_4Me\text{-}p)_3$]†

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The reaction between $BiCl_3$ and 3 equivalents of $K[Co(CO)_3(PPh_3)]$ affords the complex $[Bi\{Co(CO)_3(PPh_3)\}_3]$ (**5**). This complex is also formed initially in the corresponding 1:2 reaction, although after longer reaction times $[BiCl\{Co(CO)_3(PPh_3)\}_2]$ (**6**) is the major product. The reaction between complex (**5**) and 0.5 equivalents of $BiCl_3$ also affords (**6**) demonstrating that (**5**) is an intermediate in the formation of (**6**). In addition, (**6**) and $K[Co(CO)_3(PPh_3)]$ afford (**5**). These data indicate that, in the reaction with a Co:Bi ratio of 2:1, initially formed (**6**) rapidly reacts with $K[Co(CO)_3(PPh_3)]$ to give (**5**) which then slowly undergoes a redistribution reaction with $BiCl_3$ to give (**6**). The corresponding 1:1 reaction affords two products, *viz.* $[Bi_2Co_2(CO)_4(PPh_3)_2]$ (**13**), and $[BiCl_2\{Co(CO)_3(PPh_3)\}]$ (**14**). All these reactions are discussed and compared with related work in the literature. The reactions between $BiCl_3$ and $K[Co(CO)_4]$ and also between bismuth metal and $[Co_2(CO)_8]$ are also discussed and compared with relevant literature material. Both reactions afford $[Bi\{Co(CO)_4\}_3]$ (**1**), and $[Bi\{Co(CO)_4\}_4]^-$ (**2**). The reaction between $SbCl_3$ and 1, 2, or 3 equivalents of $K[Co(CO)_3(PPh_3)]$ affords the complex $[Sb_2Co_2(CO)_4(PPh_3)_2]$ (**21**), analogous to the dibismuth complex (**13**), *via* the intermediate $[Sb\{Co(CO)_3(PPh_3)\}_3]$ (**20**). These reactions are also compared to previous work and a discussion presented of apparent similarities and differences. Oxidation of reaction solutions containing (**21**) afford the stibinic acid complex $[SbO(OH)\{Co(CO)_3(PPh_3)\}_2]$ (**23**), which has been characterised by *X*-ray crystallography. The tri-*p*-tolylphosphine derivatives of (**21**) and (**23**) have also been prepared and the latter, $[SbO(OH)\{Co(CO)_3[P(C_6H_4Me\text{-}p)_3]\}_2]$ (**24**), also characterised by *X*-ray crystallography. The results described for bismuth and antimony are compared with the corresponding chemistry known for arsenic and phosphorus.

Cobalt carbonyl complexes containing either antimony or bismuth atoms have been known for a number of years but have recently attracted significant attention from a number of groups. We will briefly review the complexes which are known and then refer to the reactions of most relevance to this work in the next section. An early report by Cullen *et al.*[1] described the synthesis of $[Bi\{Co(CO)_3(PPh_3)\}_3]$ and this compound was subsequently reported by Schmid and co-workers,[2] together with $AsPh_3$ and $SbPh_3$ derivatives, along with the parent carbonyl complex, $[Bi\{Co(CO)_4\}_3]$, which was characterised by *X*-ray diffraction.[2,3] More recent work by Whitmire *et al.*[4] has shown that the *closo* tetrahedral complex $[BiCo_3(CO)_6(\mu\text{-}CO)_3]$ is formed by thermolysis of $[Bi\{Co(CO)_4\}_3]$ and this cluster has also been described by Martinengo[5] as one of the products formed in the reaction between $BiCl_3$ and $[Co(CO)_4]^-$. In addition, Martinengo[5] has also described the synthesis of $[Bi\{Co(CO)_4\}_4]^-$ and $[Bi_2Co_4(CO)_{11}]^-$ both of which are also formed in the reaction between $BiCl_3$ and $[Co(CO)_4]^-$ depending on the reaction conditions (see later). The structure of $[Bi\{Co(CO)_4\}_4]^-$, which contains a bismuth atom bonded to four $Co(CO)_4$ fragments in a tetrahedral configuration, was later described by Leigh and Whitmire[6] and also by Martinengo *et al.*[7] Prolonged pyrolysis of $[Bi\{Co(CO)_4\}_3]$ affords the cubic cluster $[Bi_4Co_4(CO)_{12}]$[8] and the mixed-metal species $[Bi_2Fe_2Co(CO)_{10}]^-$ has been reported by Whitmire *et al.*[9]

Much less is known about antimony-containing complexes. An early report by Foust and Dahl[10] described the synthesis and structure of $[Sb_4Co_4(CO)_{12}]$ which is isostructural with the above-mentioned bismuth analogue, and recent work by Whitmire and co-workers[11] described two anionic complexes, $[Sb_2Co_4(CO)_{11}]^{n-}$ (n = 1 or 2), the monoanion of which is also known for bismuth.[5] Both anionic complexes were formed from the reaction between $SbCl_3$ and $[Co(CO)_4]^-$. We note also that a tetracobalt stibonium cation, $[Sb\{Co(CO)_3(PPh_3)\}_4]^+$, has been reported[1] and structurally characterised[12] which is interesting with regard to $[Bi\{Co(CO)_4\}_4]^-$ in that it contains two less valence electrons but is structurally similar.

Herein we report details of our own work on the reactions between $K[Co(CO)_3(PPh_3)]$ and $SbCl_3$ and $BiCl_3$ and compare our results with those reported in the literature for analogous reactions involving $[Co(CO)_4]^-$. Comparisons are also made between these various systems and the corresponding chemistry observed for phosphorus and arsenic.

Results and Discussion

(*a*) *Bismuth*.—It will be instructive before we describe our own results on the reactions between $BiCl_3$ and $K[Co(CO)_3(PPh_3)]$ to review in detail what is known about the corresponding reaction with $[Co(CO)_4]^-$. Schmid and co-workers[2] reported that the reaction between $BiCl_3$ and 3 equivalents of $Na[Co(CO)_4]$ afforded $[Bi\{Co(CO)_4\}_3]$ (**1**), quantitatively. No other bismuth-containing compounds were

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† Hexacarbonyl-1κ^3C,3κ^3C-hydroxo-2κ-oxo-2κ-bis(triphenylphosphine)-1κP,3κP-2-antimonydicobalt(2*Co–Sb*) and the corresponding bis(tri-*p*-tolyl)phosphine derivative.

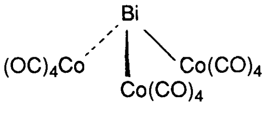
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical,[a] physical, and spectroscopic data for the complexes

Compound	Yield (%)	ν(CO)[b]/cm^{-1}	^{31}P N.m.r. (δ)[c]	Analysis (%) C	H
(5) $[Bi\{Co(CO)_3(PPh_3)\}_3]$	63	1 996m, 1 961s, 1 948s,	64.6	53.8	3.5
		1 994m, 1 958s, 1 947s[d]		(53.1)	(3.2)
(6) $[BiCl\{Co(CO)_3(PPh_3)\}_2]$	48	2 007w, 1 996m, 1 961s, 1 948s	90.3	48.5	3.2
		2 010w, 1 995w, 1 963s, 1 949m, 1 924w[d]		(47.8)	(2.9)
(13) $[Bi_2Co_2(CO)_4(PPh_3)_2]$	9	2 007w, 1 996w, 1 977 (sh), 1 961s, 1 950m, 1 920w	55.9		
(14) $[BiCl_2\{Co(CO)_3(PPh_3)\}]$	45	2 033w, 2 007w, 1 978s, 1 961s[e]	105.6[f]	36.9	2.1
			103.8—122.8	(36.8)	(2.2)
(21) $[Sb_2Co_2(CO)_4(PPh_3)_2]$	34	2 017w, 1 968s, 1 954m	56.5	49.3	3.3
				(48.1)	(3.0)[g]
(22) $[Sb_2Co_2(CO)_4\{P(C_6H_4Me\text{-}p)_3\}_2]$		2 017w, 1 966s, 1 952m	54.0	50.6	3.8
				(51.1)	(3.9)
(23) $[SbO(OH)\{Co(CO)_3(PPh_3)\}_2]$		1 983s, 1 966s	58.3		
(24) $[SbO(OH)\{Co(CO)_3[P(C_6H_4Me\text{-}p)_3]\}_2]$		1 984s, 1 964s			

[a] Calculated values are given in parentheses. [b] Measured in thf solution unless otherwise stated. [c] Chemical shifts in p.p.m., measurements at room temperature, in CD_2Cl_2 solution unless otherwise stated. Proton decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4. [d] Measured in CH_2Cl_2 solution. [e] A shoulder peak occurs at 1 922 cm^{-1} which varies in intensity depending on the sample. [f] Measured in $(CD_3)_2CO$. [g] P 5.9 (6.2), Co 11.1 (11.8), Sb 21.9 (24.4%); ratio P:Co:Sb = 1.02:1.00:0.96.

described but the reaction was carried out in water and presumably proceeds *via* $Bi(OH)_3$. A report has also appeared which describes the synthesis of **(1)** from the reaction between BiI_3 and $Na[Co(CO)_4]$.[13] More recent work by Martinengo and Ciani[5] described the reaction between $BiCl_3$ and 4 equivalents of $Na[Co(CO)_4]$ (tetrahydrofuran, room temperature) which afforded $[Bi\{Co(CO)_4\}_4]^-$ **(2)**. Traces of **(1)** were also formed and this complex is presumably an intermediate in the formation of **(2)** since a separate reaction between **(1)** and $[Co(CO)_4]^-$ also afforded **(2)**.[5,6] When the molar ratio of $BiCl_3$ to $[Co(CO)_4]^-$ was increased from 1:4 to 1:6 only **(2)** and unreacted $[Co(CO)_4]^-$ were observed. Mild heating of solutions of **(2)** afforded $[BiCo_3(CO)_6(\mu\text{-}CO)_3]$ **(3)**, and prolonged heating yielded $[Bi_2Co_4(CO)_{11}]^-$ **(4)**. We will return to some of these reactions again at the end of this section.



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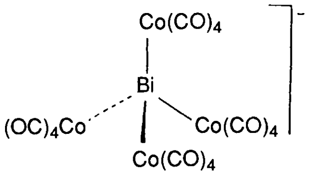

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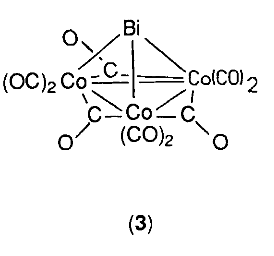

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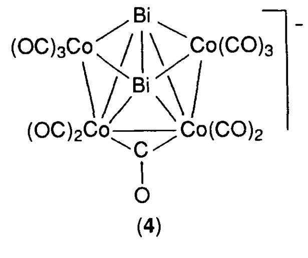
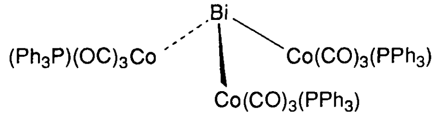


(4)

Treatment of $BiCl_3$ with 3 equivalents of $K[Co(CO)_3(PPh_3)]$, in which the $BiCl_3$ is added to a solution of the cobalt anion, afforded, after work-up, dark red crystals of $[Bi\{Co(CO)_3(PPh_3)\}_3]$ **(5)**. Spectroscopic and analytical data are presented in Table 1 and were in accord with the anticipated structure. Crystals of **(5)**, although well formed, were not suitable for *X*-ray crystallography since no diffraction patterns could be observed. However, this compound has been previously described by Schmid and co-workers[2] and Cullen *et al.*[1] The former report gave details of the synthesis of complex **(5)** from **(1)** and 3 equivalents of PPh_3, whilst in the latter **(5)** was prepared from the reaction between $BiCl_3$ and 2.3 equivalents of $Na[Co(CO)_3(PPh_3)]$. We will refer to the latter reaction in more detail later.



(5)

Treatment of $BiCl_3$ with 2 equivalents of $K[Co(CO)_3(PPh_3)]$ in tetrahydrofuran (thf) solution, in which the cobalt anion was added to the $BiCl_3$, led initially to a dark red solution which changed to dark green after stirring overnight. After work up a dark green powder was isolated and spectroscopic and analytical data (Table 1) were in accord with the dicobalt-bismuth species, $[BiCl\{Co(CO)_3(PPh_3)\}_2]$ **(6)**. Two additional reactions provide further support for the proposed structures of **(5)** and **(6)**. Thus the reaction between **(5)** and 0.5 equivalents of $BiCl_3$ afforded **(6)** quantitatively as evidenced by i.r. spectroscopy and in accordance with equation (1). Moreover

$$\underset{\textbf{(5)}}{2[Bi\{Co(CO)_3(PPh_3)\}_3]} + BiCl_3 \longrightarrow \underset{\textbf{(6)}}{3[BiCl\{Co(CO)_3(PPh_3)\}_2]} \quad (1)$$

the addition of 1 equivalent of $K[Co(CO)_3(PPh_3)]$ to complex **(6)** resulted in **(5)** [equation (2)]. Precisely these same types of

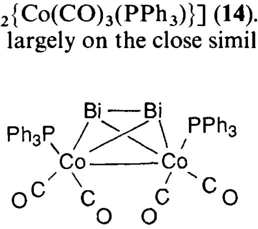
$$\underset{\textbf{(6)}}{[BiCl\{Co(CO)_3(PPh_3)\}_2]} + K[Co(CO)_3(PPh_3)] \longrightarrow \underset{\textbf{(5)}}{[Bi\{Co(CO)_3(PPh_3)\}_3]} + KCl \quad (2)$$

reaction have been observed in the related molybdenum[14] and manganese/rhenium[15] systems: $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ **(7)**, and $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **(8)**; and $[Bi\{M(CO)_5\}_3]$ [M = Mn, **(9a)**; or Re, **(9b)**] and $[BiCl\{M(CO)_5\}_2]$ [M = Mn, (**10a**); or Re, (**10b**)]. Unfortunately, suitable crystals of (**6**) could not be obtained and so the precise structure in the solid state is not known. We suspect, however, that some form of oligomeric structure involving Bi–Cl–Bi bridging is likely since most previously reported structures of [BiCl(ML$_n$)$_2$] compounds exhibit this type of intermolecular association[14–17] resulting from the Lewis acidity of the bismuth centre.

We mentioned previously that Cullen *et al.*[1] had reported a reaction between $BiCl_3$ and 2.3 equivalents of Na[Co(CO)$_3$(PPh$_3$)] from which the tricobaltbismuth complex (**5**) was obtained. Their reaction conditions were essentially the same as ours (thf solution, room temperature, order of addition of reactants) except for the reaction time, which was given as 0.5 h. This would appear to be all important since our own observations, based on colour changes, suggested that (**6**) was not the initial product in the reaction between $BiCl_3$ and 2 equivalents of K[Co(CO)$_3$(PPh$_3$)]. Rather, a dark red intermediate was formed first which then slowly reacted to give (**6**). It was anticipated that this intermediate was (**5**) based on its colour [(**5**) is dark red] and the results of Cullen wherein (**5**) was isolated after a short reaction time. This was confirmed in a separate experiment. The reaction between $BiCl_3$ and 2 equivalents of K[Co(CO)$_3$(PPh$_3$)] was carried out exactly as before except that work-up took place after 0.5 h. Analysis, by i.r. spectroscopy, of the dark red solid obtained showed it to be complex (**5**).

Nevertheless, these observations are somewhat curious in terms of the order of addition of the reactants. The anion [Co(CO)$_3$(PPh$_3$)]$^-$ is added to the $BiCl_3$ such that the latter is in excess in the early stages of the reaction and clearly the ratio of Co:Bi at no time exceeds 2:1. Since the initial product is (**5**), this suggests that chlorine substitution by cobalt at the bismuth centre occurs more readily as the degree of cobalt substitition increases. Thus the reaction proceeds initially to (**5**) and excess of $BiCl_3$ and then a slower redistribution reaction occurs to yield (**6**). Support for this proposal is again provided by the two reactions represented in equations (1) and (2). The former clearly demonstrates that complex (**5**) can be converted into (**6**) by addition of $BiCl_3$, but reaction times of the order of 12 h are required if high yields of (**6**) are to be obtained. The latter reaction occurs immediately upon addition of the reactants as judged by the observed colour changes. Moreover, it is possible that this type of reaction sequence is general but often goes unnoticed. Thus, for example, in the reactions between $BiCl_3$ and 2 equivalents of either [Fe(CO)$_2$(η-C$_5$H$_4$Me)]$^-$ [16] or [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$ [14] the 2:1 products [BiCl{Fe(CO)$_2$(η-C$_5$H$_4$Me)}$_2$] (**11**) and (**8**), are formed immediately upon addition of the reactants but separate experiments revealed that their formation from either [Bi{Fe(CO)$_2$(η-C$_5$H$_4$Me)}$_3$] (**12**) or (**7**), respectively and 0.5 equivalents of $BiCl_3$ [*cf.* equation (1)] is very rapid. The intermediacy of (**12**) and (**7**) in the formation of complexes (**11**) and (**8**) would, therefore, not be readily observed. These observations, while initially unexpected, are in fact characteristic of substitution chemistry at bismuth. This is illustrated in the reaction between BiX_3 ($X = Cl$ or Br) and LiPh which, rather than affording only $BiPhX_2$, gives a mixture of BiX_3, $BiPhX_2$, $BiPh_2X$, and $BiPh_3$. The compound $BiPhBr_2$, for example, is best prepared from the reaction between $2BiBr_3$ and $BiPh_3$ in Et_2O in which solvent it is insoluble and thus out of which it precipitates.[18]

The reaction between $BiCl_3$ and 1 equivalent of K[Co(CO)$_3$(PPh$_3$)] gives rise to two other products. If reaction times are short (*i.e.* a few hours or less) spectroscopic assay shows the presence of complexes (**5**) and (**6**) presumably for reasons which have just been discussed with regard to the formation of (**6**). However, work-up after a reaction time of 24 h affords a green product (**13**) and a dark red product (**14**). Both of these compounds are also obtained from the overnight reactions between (**5**) and 2 equivalents of $BiCl_3$ and between (**6**) and 1 equivalent of $BiCl_3$ although the relative proportions of the two products are always variable. In reality, the three reactions mentioned above probably just represent different starting points in a complex equilibrium, but for this reason it is important that prolonged reaction times are maintained. We cannot be certain as to the nature of (**13**) or (**14**) since *X*-ray-quality crystals could not be obtained, but the following structures are proposed: [Bi$_2$Co$_2$(CO)$_4$(PPh$_3$)$_2$] (**13**), and [BiCl$_2${Co(CO)$_3$(PPh$_3$)}] (**14**). The assignment of the former is based largely on the close similarity of the i.r. spectrum and the



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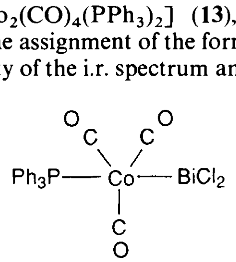


(14)

^{31}P n.m.r. chemical shift to those of the related diantimony complex [Sb$_2$Co$_2$(CO)$_4$(PPh$_3$)$_2$] which will be discussed in the next section. The assignment of the latter is more tenuous but two pieces of evidence are consistent with this structure. First, the i.r. spectrum of complex (**14**) has a similar pattern to those observed for (**5**) and (**6**) (Figure 1) both of which contain the Co(CO)$_3$(PPh$_3$) fragment, and secondly the ^{31}P n.m.r. chemical shift continues the observed trend to higher frequency as the number of chlorines attached to the bismuth centre increases [*i.e.* 64.6 for (**5**), 90.3 for (**6**), and 103.8—122.8 p.p.m. for (**14**)]. The structure is almost certainly not monomeric in the solid state; some degree of oligomerisation involving Bi–Cl–Bi bridging is likely and is consistent with the low solubility of (**14**) in all common solvents. Moreover the ^{31}P n.m.r. chemical shift is both solvent and concentration dependent which factor may reflect varying degrees of association in solution (Table 1). The ^1H n.m.r. spectrum of complex (**14**) in [$^2H_6$]acetone shows the presence of thf which is presumably associated with the bismuth centre and/or incorporated in the crystal structure. However, ^1H n.m.r. spectra obtained after prolonged pumping on solid (**14**) show that only traces of thf remain. Microanalytical data obtained on this material are also consistent with the proposed structure (Table 1). A comparison with the complex [BiPh$_2${Co(CO)$_3$(PPh$_3$)}] (**15**), is appropriate[19] as the only other example of a BiR$_2$ group co-ordinated to the Co(CO)$_3$(PPh$_3$) fragment of which we are aware.

We will now return to some of the reactions involving [Co(CO)$_4$]$^-$ mentioned at the beginning of this section. Both Schmid and co-workers[2] and Brill and Miller[13] describe the preparation of complex (**1**) from reactions involving a bismuth trihalide and 3 equivalents of Na[Co(CO)$_4$]. The nature of (**1**) is

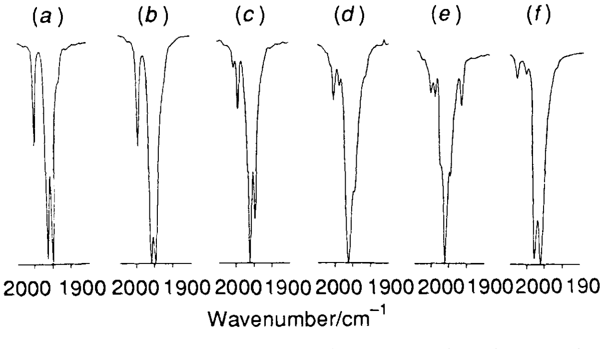


Figure 1. Solution i.r. spectra for the bismuth complexes in the carbonyl region: (*a*) (**5**) in thf, (*b*) (**5**) in CH_2Cl_2, (*c*) (**6**) in thf, (*d*) (**6**) in CH_2Cl_2, (*e*) (**13**) in thf, and (*f*) (**14**) in thf

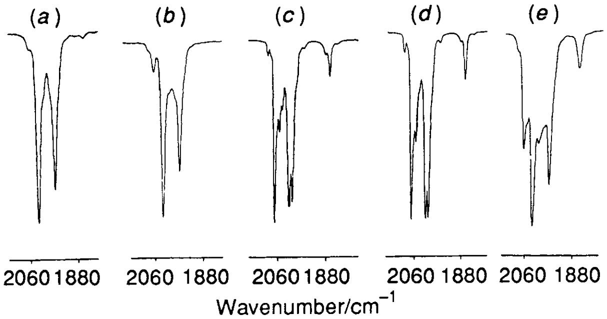


Figure 2. Solution i.r. spectra of the bismuth complexes (**1**) and (**2**) obtained from the reactions described in the text: (*a*) $BiCl_3$ + $3[Co(CO)_4]^-$, thf, 2 067w, 2 033s, and 1 970s; (*b*) $BiCl_3$ + $2[Co(CO)_4]^-$, thf, 2 069w, 2 033s, and 1 970s; (*c*) $BiCl_3$ + $3[Co(CO)_4]^-$, hexane, 2 098w, 2 072s, 2 055m, 2 044m, 2 018s, 2 007s, 1 882w, and 1 867m; (*d*) $[Co_2(CO)_8]$ + Bi metal, hexane, 2 098w, 2 072s, 2 055m, 2 018s, 2 007s, 1 963w, and 1 867m; (*e*) $[Co_2(CO)_8]$ + Bi metal, thf, 2 067m, 2 032s, 2 010m, 1 971s, and 1 859w cm^{-1}. The absorptions at 2 067 and 2 010 cm^{-1} are attributed to (**1**), those at 2 032 and 1 971 cm^{-1} to (**2**). The nature of the species which gives rise to the absorptions at around 1 860 cm^{-1} in (*c*)—(*e*) is not known but may be small amounts of $[Co_4(CO)_{12}]$ which is readily formed from $[Co_2(CO)_8]$ under ambient conditions

not at issue since it was characterised by *X*-ray diffraction[2] and both reports[2,13] present good analytical data. The reported solution i.r. data are, however, quite different. Brill and Miller report the values 2 071s, 2 016m, 2 004m, and 199w (sh) in hexane (the latter value is presumably a misprint) whilst the values presented by Schmid and co-workers are 2 115w, 2 083vs, 2 060w, 2 033vs, 2 020vw, 2 015vs, and 1 995 (sh) in light petroleum. Clearly these data cast some doubt on the nature of the species present in solution. Accordingly, we decided to reinvestigate this reaction.

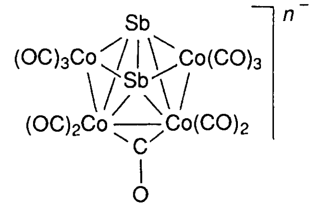
When a thf solution of $BiCl_3$ was added to a thf solution of 3 equivalents of $K[Co(CO)_4]$ a dark purple black solid was isolated after work-up, the thf solution i.r. spectrum of which is shown in Figure 2(*a*). Comparison with an i.r. spectrum reported by Martinengo *et al.*[7] clearly indicates that the compound present is $[Bi\{Co(CO)_4\}_4]^-$ (**2**). Moreover, (**2**) is also the major product from the reaction between $BiCl_3$ and 2 equivalents of $K[Co(CO)_4]$ [Figure 2(*b*)]. These results suggest, therefore, that maximal substitution at bismuth occurs regardless of the reaction stoicheiometry, a similar situation having been observed for reactions involving $K[Co(CO)_3(PPh_3)]$, although in this case tri- rather than tetra-substitution would appear to be the limit. We note, however, that even after reaction times of 48 h, (**2**) is the major product and that redistribution with excess of $BiCl_3$ to give less highly substituted compounds does not occur. Interestingly, however, i.r. spectra recorded in hexane solution for the products from both of the above reactions are quite different to those obtained in thf [Figure 2(*c*)]. These, we suggest, are certainly due to complex (**1**) and they agree with the data reported by Brill and Miller.[13]

Thus it would appear that the reactions between $BiCl_3$ and 2 or 3 equivalents of $K[Co(CO)_4]$ afford mainly complex (**2**) as judged by the thf solution i.r. spectra obtained on the products after work-up. The spectra recorded in hexane, however, indicate the presence of (**1**). We suggest that the explanation for these observations lies in the fact that while complex (**1**) is soluble in hexane, ionic (**2**) is only slightly soluble in this solvent. Whether hexane merely extracts some (**1**) already present or promotes dissociation of (**2**) into (**1**) and $[Co(CO)_4]^-$ with concomitant dissolution of (**1**) is unclear. Thus, returning to the literature values for complex (**1**), it would seem that those reported by Brill and Miller[13] are correct for pure (**1**) whereas those described by Schmid and co-workers[2] are probably the result of a mixture of (**1**) and (**2**).

A further interesting point concerns the reaction of $[Co_2(CO)_8]$ with bismuth metal in Et_2O which affords (**1**) also reported by Schmid and co-workers.[2] We have also re-examined this reaction and find that a black crystalline product may be isolated in agreement with the above report.[2] A hexane solution i.r. spectrum [Figure 2(*d*)] shows the presence of complex (**1**) whereas a thf solution spectrum [Figure 2(*e*)] clearly reveals the presence of (**2**). The observation of an ionic compound from this reaction was initially surprising but a report by Edgell and Lyford[20] indicates that $[Co_2(CO)_8]$ disproportionates in ether solvents affording $[Co(CO)_4]^-$ as the anionic product. Thus our results may be accounted for by assuming that bismuth metal reacts with $[Co_2(CO)_8]$ to give (**1**) some of which then reacts with any $[Co(CO)_4]^-$ present to give (**2**).

Finally, we note that photolysis of complex (**2**) afforded (**4**) but that attempted solution thermolysis or photolysis (thf) of (**5**) did not result in any isolable new complexes in contrast to the situation with cluster complex (**3**), which is reportedly produced by thermolysis[4] or photolysis[5] of (**1**). Thermal gravimetric analysis measurements on (**5**) do indicate, however, that CO loss occurs at about 175 °C and PPh_3 loss at about 240 °C.

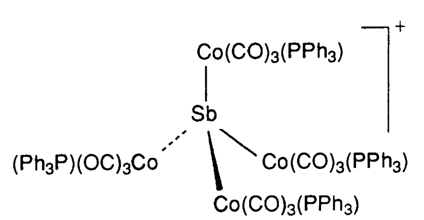
(*b*) *Antimony.*—As we mentioned in the introduction, Whitmire and co-workers[11] have recently reported details of the reaction between $SbCl_3$ and $3Na[Co(CO)_4]$ which affords the cluster complexes $[Sb_2Co_4(CO)_{11}]^{n-}$ [n = 1, (**16**); or 2, (**17**)]. The reaction apparently proceeds *via* the unstable complex $[Sb\{Co(CO)_4\}_3]$ (**18**), which can be isolated as a dark green powder from aqueous HCl but which decomposes immediately in thf solution. The observed instability of (**18**) when compared with the bismuth analogue (**1**), is interesting and we will return to this point later although it is worth noting that (**18**) has been mentioned in a review by Schmid[21] without reference to any instability.



(**16**), n = 1 ; (**17**), n = 2

Of more relevance to the present work, however, is a report by Cullen *et al.*[1] which describes the reaction between $SbCl_3$ and 0.94 equivalents of $Na[Co(CO)_3(PPh_3)]$, derived from sodium amalgam reduction of $[Co_2(CO)_6(PPh_3)_2]$, in thf at 20 °C for 1 h. The dark red crystalline product obtained after work-up was formulated as $[Sb\{Co(CO)_3(PPh_3)\}_4]_3[Sb_2Cl_9]$ (**19a**), on the basis of analytical and i.r. data and the same product was also obtained when a ratio of $Na[Co(CO)_3(PPh_3)]$:$SbCl_3$ 10:6 was employed. A similar product, $[Sb\{Co(CO)_3(PPh_3)\}_4]_3[Sb_5Br_{18}]$ (**19b**), was obtained from the reaction between $SbBr_3$ and 5 equivalents of $Na[Co(CO)_3(PPh_3)]$. Moreover, the same tetracobalt stibonium complex, as a chloroantimonate salt, is apparently formed in the reaction between 2 equivalents of $[Co_2(CO)_6(PPh_3)_2]$ and 1.47 equivalents of $SbCl_3$ in refluxing 1,2-dichloroethane after 4 h.

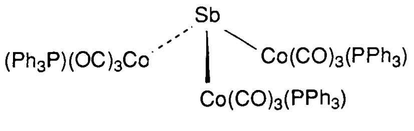
Our own results involving the reaction between $SbCl_3$ and $K[Co(CO)_3(PPh_3)]$ appear to take a different course. When 1 equivalent of $SbCl_3$ in thf was added to a cold (−78 °C) solution of 3 equivalents of $K[Co(CO)_3(PPh_3)]$ an intense



(19)

green colour developed immediately. On warming to room temperature the colour changed to dark brown and dark brown crystals were obtained after work-up. We observed similar behaviour in the reactions between $SbCl_3$ and 1 or 2 equivalents of $K[Co(CO)_3(PPh_3)]$. In these cases the cobalt anion was added to a solution of $SbCl_3$ and as each drop of the solution of the cobalt anion mixed with the $SbCl_3$ solution a green colour was observed which rapidly changed to brown. Moreover, after complete addition and on warming to room temperature, gas evolution (presumably CO) was observed. Both the latter reactions afforded brown crystals after work-up and i.r. spectroscopy revealed that all three products from the above reactions were the same material.

We propose that the initial product formed in all these reactions is the green tricobaltantimony complex $[Sb\{Co(CO)_3(PPh_3)\}_3]$ **(20)**. This would be the expected product from the 3:1 reaction but, in line with the previously discussed bismuth chemistry, is probably also formed even when smaller Co:Sb ratios are employed, *i.e.* in the 2:1 and 1:1 reactions. We have not been able to isolate **(20)** but further support for its formulation is its colour, green, which is the same as that of the unstable intermediate **(18)** reported by Whitmire and co-workers.[11] Moreover, **(20)** is clearly unstable in thf solution at room temperature, as is **(18)**, and rearranges with apparent loss of CO to a brown product, **(21)**. We were unable to obtain *X*-ray-quality crystals of **(21)**, but spectroscopic and analytical data (Table 1) are consistent with a dicobaltdiantimony complex as represented in the diagram. Two other lines of evidence support the structure of **(21)** as drawn. Firstly, **(18)** readily rearranges to the cluster species **(16)** and **(17)** as previously discussed. Although **(21)** is structurally different to **(16)**/**(17)**, the presence of bulky phosphine ligands may inhibit larger cluster formation such that, whilst **(18)** gives the Co_4Sb_2 clusters, **(20)** yields the smaller Co_2Sb_2 complex **(21)**. Secondly, analogues of complex **(21)** containing P_2 and As_2 ligands are also formed in reactions between PCl_3 and $AsCl_3$ respectively and cobalt carbonylate anions as will be described in section (*c*). All things considered, the proposed structure for **(21)** is quite reasonable but the absence of a crystal structure prompted us to make an analogue containing the tri-*p*-tolylphosphine ligand, $P(C_6H_4Me\text{-}p)_3$. Reactions between $SbCl_3$ and 3, 2, or 1 equivalent of $K[Co(CO)_3\{P(C_6H_4Me\text{-}p)_3\}]$ all afforded, after work-up, brown crystals of $[Sb_2Co_2(CO)_4\{P(C_6H_4Me\text{-}p)_3\}_2]$ **(22)**. Spectroscopic data (Table 1), particularly the solution i.r. spectra (Figure 3), indicated a similar structure for **(21)** but unfortunately no diffraction-quality crystals could be obtained.



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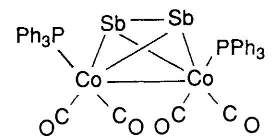
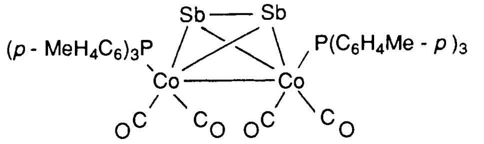


(21)



(22)

A lack of suitable crystals of the dibismuth complex **(13)** had, as previously mentioned, also prevented characterisation by *X*-ray crystallography, but the similarity between the solution i.r. and ^{31}P n.m.r. spectra [Figures 1(*e*), 3(*a*),(*b*), Table 1] of **(13)** and **(21)**/**(22)** is apparent.

When dealing with molecules such as **(21)** the lack of structural data from *X*-ray crystallography is always bothersome since spectroscopic and analytical methods cannot be used unambiguously to assign a structure. However, in this particular case the problem was even more acute in view of the results reported by Cullen *et al.*[1] outlined at the beginning of this section. Thus, in an apparently very similar reaction between $SbCl_3$ and $Na[Co(CO)_3(PPh_3)]$, the product reported is the tetracobalt stibonium complex **(19)**. The i.r. spectra reported for **(19)** were quite different from those which we obtained for **(21)** and the postulated structure of **(19)** was subsequently confirmed by an *X*-ray study[12] on the $[BPh_4]^-$ salt, $[Sb\{Co(CO)_3(PPh_3)\}_4][BPh_4]$ **(19c)**. Nevertheless, we decided to repeat the Cullen work exactly as they described in ref. 1, p. 869. As reported, a dark red crystalline material was obtained, the i.r. spectrum of which is shown in Figure 3(*c*). This spectrum is in excellent agreement with that reported by Cullen *et al.*[1] but clearly different from that obtained for **(21)**.* In summary, the reaction between $SbCl_3$ and $K[Co(CO)_3(PPh_3)]$

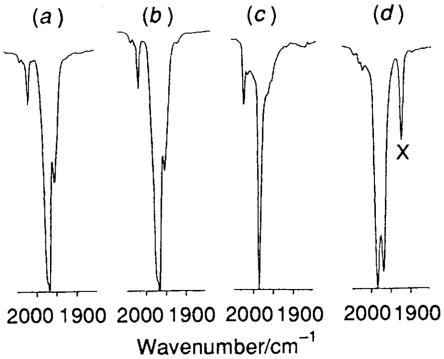


Figure 3. Solution i.r. spectra (thf) for the antimony complexes in the carbonyl region: (*a*) **(21)**; (*b*) **(22)**; (*c*) **(19)** prepared as in ref. 1, 2 026w and 1 987s cm^{-1} (corresponding values in CH_2Cl_2 are 2 028w, and 1 987s which compare with those reported[1] in this solvent of 2 028m, and 1 985vs cm^{-1}); (*d*) **(23)**, × denotes an impurity at 1 920 cm^{-1}

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* The spectrum shown in Figure 3(*c*) is of the major product from the Cullen reaction and, as stated in the text, agrees with that reported.[1] There is, however, a second product which generally occurs in low yield although on one occasion it was present in significant amounts. The i.r. spectrum (CH_2Cl_2 solution) has carbonyl absorptions at 2 066w, 2 045w, and 2 003s cm^{-1}, but the nature and structure of this compound are not known. Other materials are also observed in smaller amounts. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the crude product from the Cullen reaction shows signals at δ 55.8, 54.6, and 52.7 p.p.m. None of these corresponds to complex **(21)**, but we are not sure which signal is due to **(19)**. On some occasions we observed the signal at δ 52.7 p.p.m. in spectra obtained on impure samples of **(21)**.

Table 2. Selected bond lengths (Å) and angles (°) for complex (**23**)*

Sb–Co	2.547(2)	Sb–O(4)	1.914(4)
Sb–Co′	2.652(2)	Sb–O(4′)	2.417(4)
Co–Sb–O(4)	120.8(2)	Co–Sb–Co′	107.9(1)
O(4)–Sb–Co′	111.2(1)	Co–Sb–O(4′)	99.5(1)
O(4)–Sb–O(4′)	114.7(2)	Co′–Sb–O(4′)	100.2(1)

* Numbers in parentheses are the estimated standard deviations of the least significant digit in this and all subsequent tables.

Table 3. Atomic co-ordinates ($\times 10^4$) for complex (**23**)

Atom	*x*	*y*	*z*
Sb	20(1)	3 053(1)	2 671(1)
Co	−846(1)	1 678(1)	2 480(1)
P	−1 552(1)	406(1)	2 444(1)
C(1)	−325(2)	694(4)	3 118(4)
O(1)	−11(2)	38(4)	3 533(3)
C(2)	−1 121(2)	2 922(4)	2 838(4)
O(2)	−1 323(2)	3 715(3)	3 066(3)
C(3)	−1 029(2)	1 617(4)	1 480(3)
O(3)	−1 155(1)	1 578(4)	841(2)
O(4)	314(1)	4 106(2)	3 540(2)
C(11)	−1 349(2)	−1 202(3)	2 449(3)
C(12)	−1 080(2)	−1 566(4)	1 963(4)
C(13)	−890(2)	−2 749(4)	1 962(5)
C(14)	−977(3)	−3 579(5)	2 441(5)
C(15)	−1 258(2)	−3 261(5)	2 914(4)
C(16)	−1 440(2)	−2 074(5)	2 913(4)
C(21)	−2 216(2)	537(4)	1 618(3)
C(22)	−2 554(2)	−463(5)	1 294(3)
C(23)	−3 050(2)	−301(7)	666(4)
C(24)	−3 208(2)	827(8)	355(4)
C(25)	−2 884(2)	1 817(7)	650(4)
C(26)	−2 387(2)	1 701(5)	1 280(3)
C(31)	−1 778(2)	534(4)	3 249(4)
C(32)	−2 344(2)	478(6)	3 184(4)
C(33)	−2 484(3)	581(10)	3 826(5)
C(34)	−2 073(3)	729(7)	4 515(5)
C(35)	−1 511(3)	781(8)	4 587(5)
C(36)	−1 367(3)	703(7)	3 973(4)
C(41)	−170(6)	4 484(32)	9 909(16)
C(42)	239(8)	3 299(25)	9 869(13)
C(43)	−110(13)	2 223(35)	9 813(16)

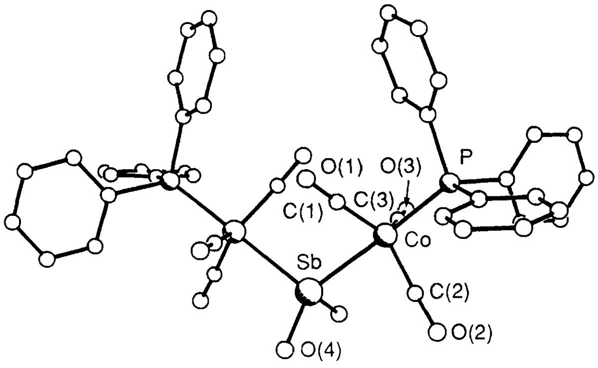


Figure 4. A view of the molecular structure of complex (**23**) showing the atom numbering scheme adopted. Hydrogen atoms omitted for clarity

Table 4. Selected bond lengths (Å) and angles (°) for complex (**24**)

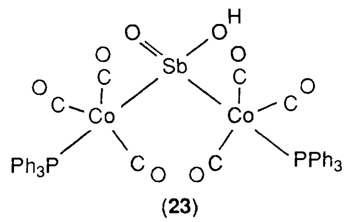
Sb–O(7)	2.420(3)	Sb–O(8)	1.741(7)
Sb–Co(1)	2.606(1)	Sb–Co(2)	2.610(1)
Sb′–O(7)	1.706(3)	Sb′–O(8)	2.403(7)
Sb′–Co(1)	2.692(2)	Sb′–Co(2)	2.602(2)
O(7)–Sb–O(8)	97.8(2)	O(7)–Sb–Co(1)	98.8(1)
O(7)–Sb–Co(2)	100.9(1)	O(8)–Sb–Co(1)	122.1(2)
O(8)–Sb–Co(2)	121.1(2)	Co(1)–Sb–Co(2)	109.5(1)
O(7)–Sb′–O(8)	99.4(2)	O(7)–Sb′–Co(1)	118.8(1)
O(8)–Sb′–Co(1)	97.2(2)	O(7)–Sb′–Co(2)	127.2(1)
O(8)–Sb′–Co(2)	99.2(2)	Co(1)–Sb′–Co(2)	107.1(1)

affords complex (**21**) whereas that between $SbCl_3$ and $Na[Co(CO)_3(PPh_3)]$ affords (**19a**), the reasons for which are not at all obvious. The only important difference between the above reactions is the nature of the cobalt starting complex. It is unlikely that a change in the counter cation from potassium to sodium is responsible for these observations; rather, we suspect that the method of preparation is the important factor. The potassium salt which we have used in our studies is prepared in a two-step process, first involving the formation of $K[Co(CO)_4]$ from $[Co_2(CO)_8]$ and KOH (Edgell and Lyford[20]) and secondly the reaction of $K[Co(CO)_4]$ with PPh_3 (Ungvary and Wojcicki[22]). In contrast, Cullen prepared $Na[Co(CO)_3(PPh_3)]$ directly from sodium amalgam reduction of $[Co_2(CO)_6(PPh_3)_2]$. However, it is known from early work by Hieber and Freyer[23] and Vohler[24] that $[Co_2(CO)_6(PPh_3)_2]$ readily disproportionates to give $[Co(CO)_3(PPh_3)_2]^+$ and $[Co(CO)_4]^-$. It is therefore possible that, in Cullen's work, (**20**) is the initial product resulting from the reaction between $SbCl_3$ and $[Co(CO)_3(PPh_3)]^-$ and that this then reacts with some $[Co(CO)_3(PPh_3)_2]^+$ which is present according to equation (3)

$$\underset{\textbf{(20)}}{[Sb\{Co(CO)_3(PPh_3)\}_3]} + [Co(CO)_3(PPh_3)_2]^+ \longrightarrow \underset{\textbf{(19)}}{[Sb\{Co(CO)_3(PPh_3)\}_4]^+} + PPh_3 \quad (3)$$

to give (**19**). The absence of such a trapping reagent in our reactions allows (**20**) to rearrange to (**21**). These are speculative ideas but we have no better explanation to offer at this time.

Finally in this section we report an oxidation product obtained from the reactions between $SbCl_3$ and $K[Co(CO)_3(PPh_3)]$. If air is admitted to the brown reaction solution containing (**21**), before work-up, an intense purple colour quickly develops. Filtration and crystallisation affords a heterogeneous partially crystalline solid embedded within which are small, well formed purple crystals. Spectroscopic data gave little indication as to the nature of the product although the i.r. spectrum [Figure 3(*d*)] was indicative of the presence of $Co(CO)_3(PPh_3)$ fragments. Accordingly, we undertook an *X*-ray diffraction study the results of which are shown in Tables 2 and 3 and Figure 4. The molecule (**23**) may best be described as a dimetallastibinic acid comprising a central antimony atom in a tetrahedral co-ordination environment bonded to two $Co(CO)_3(PPh_3)$ fragments and two oxygen atoms. Electron-counting arguments require that the bonding to one oxygen be represented either as Sb=O or Sb→O whilst the other is singly bonded and therefore attached, by a further single bond, to some other group. We suggest that this is a hydrogen atom such that the latter oxygen is part of a hydroxide function but this



(23)

Table 5. Atomic co-ordinates (× 10^4) for complex (**24**)

Atom	*x*	*y*	*z*
Sb	806(1)	117(1)	1 525(1)
Sb′	1 560(1)	132(1)	1 694(1)
O(7)	2 525(2)	−441(1)	1 985(1)
O(8)	−5(6)	−567(3)	1 290(3)
Co(1)	169(1)	810(1)	2 375(1)
C(1)	−305(8)	1 398(4)	1 859(3)
O(1)	−627(8)	1 786(3)	1 546(2)
C(2)	−782(8)	118(4)	2 469(3)
O(2)	−1 377(7)	−316(3)	2 551(3)
C(3)	1 672(8)	825(4)	2 666(3)
O(3)	2 651(6)	861(4)	2 873(3)
P(1)	−535(1)	1 376(1)	3 085(1)
C(11)	−1 848(6)	1 889(3)	2 874(2)
C(12)	−1 865(6)	2 547(3)	2 948(3)
C(13)	−2 891(7)	2 904(3)	2 778(3)
C(14)	−3 893(6)	2 619(4)	2 526(3)
C(15)	−3 865(7)	1 951(4)	2 459(3)
C(16)	−2 884(7)	1 597(4)	2 628(3)
C(17)	−5 021(9)	3 018(5)	2 339(4)
C(21)	546(6)	1 943(3)	3 436(3)
C(22)	600(6)	2 014(3)	4 023(3)
C(23)	1 399(7)	2 461(4)	4 273(3)
C(24)	2 130(6)	2 851(3)	3 969(3)
C(25)	2 053(7)	2 769(3)	3 380(3)
C(26)	1 274(7)	2 326(3)	3 128(3)
C(27)	2 972(10)	3 353(4)	4 243(5)
C(31)	−1 043(6)	872(3)	3 661(2)
C(32)	−411(8)	331(3)	3 815(3)
C(33)	−763(10)	−44(4)	4 259(4)
C(34)	−1 775(9)	87(5)	4 536(4)
C(35)	−2 405(9)	663(6)	4 386(4)
C(36)	−2 037(8)	1 031(4)	3 961(4)
C(37)	−2 183(16)	−370(7)	4 989(6)
Co(2)	1 884(1)	860(1)	821(1)
C(4)	2 866(6)	196(3)	680(3)
O(4)	3 512(6)	−203(3)	567(3)
C(5)	400(6)	857(3)	518(3)
O(5)	−566(5)	839(4)	309(3)
C(6)	2 359(8)	1 418(4)	1 366(3)
O(6)	2 706(8)	1 783(3)	1 696(2)
P(2)	2 594(1)	1 467(1)	140(1)
C(41)	3 943(6)	1 931(3)	385(2)
C(42)	3 970(6)	2 593(3)	400(3)
C(43)	5 004(8)	2 915(4)	628(4)
C(44)	6 018(6)	2 580(4)	832(3)
C(45)	5 984(7)	1 905(4)	805(3)
C(46)	4 962(6)	1 589(3)	590(3)
C(47)	7 135(8)	2 920(5)	1 061(4)
C(51)	1 547(5)	2 087(2)	−160(2)
C(52)	1 438(6)	2 207(3)	−734(2)
C(53)	661(7)	2 684(4)	−951(3)
C(54)	6(6)	3 068(3)	−601(3)
C(55)	103(7)	2 940(3)	−38(3)
C(56)	855(6)	2 448(3)	187(3)
C(57)	−813(8)	3 602(4)	−848(4)
C(61)	3 078(5)	1 025(2)	−472(2)
C(62)	4 009(5)	1 241(3)	−778(3)
C(63)	4 374(6)	883(3)	−1 231(3)
C(64)	3 818(6)	300(4)	−1 386(3)
C(65)	2 881(7)	101(4)	−1 092(3)
C(66)	2 519(7)	447(3)	−636(3)
C(67)	4 280(10)	−98(6)	−1 857(5)
C(91)	275(29)	3 701(10)	1 837(13)
C(92)	8(57)	4 308(15)	1 538(19)
C(93)	758(42)	4 433(16)	1 143(15)
C(94)	2 081(54)	4 021(17)	1 317(22)
C(95)	1 487(33)	3 548(14)	1 666(14)

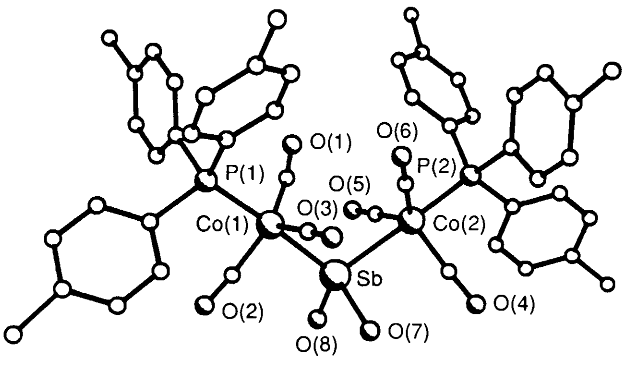


Figure 5. A view of the molecular structure of complex (**24**) showing the atom numbering scheme adopted. Hydrogen atoms omitted for clarity

was difficult to confirm from the diffraction data since the molecule resides on a C_2 axis such that the SbO_2 fragment is disordered and both O atoms appear equivalent. It was possible to resolve two distinct sites only for the Sb atom and the hydrogen atom could not be located on either oxygen atom. The presence of a hydroxide hydrogen was indicated, however, from the i.r. spectrum which showed a broad absorption around 3 500 cm^{-1} (KBr disc) and from the ^1H n.m.r. spectrum which contained a low-field signal at δ +13.8 (CD_2Cl_2 solution). The crystal structure also contains n-hexane molecules derived from the crystallisation procedure; there are no significant intermolecular interactions.

In an attempt to obtain a better crystal structure, the $P(C_6H_4Me\text{-}p)_3$ derivative was synthesised in an analogous manner. The resulting purple crystals of the thf solvate of $[SbO(OH)\{Co(CO)_3[P(C_6H_4Me\text{-}p)_3]\}_2]$ (**24**) were also examined by *X*-ray crystallography the results of which are shown in Tables 4 and 5 and Figure 5. However, although there is no crystallographically imposed symmetry, the O and OH sites in the structure of (**24**) are clearly disordered which is again reflected in a two-site disorder of the antimony atom; disorder components could not be resolved for any other atoms. The thf is not co-ordinated in any way.

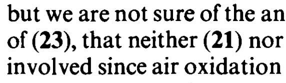
Although it has not been possible unambiguously to characterise the O and OH groups in either (**23**) or (**24**), a number of points are worthy of mention. In neither case are there any short intermolecular contacts involving antimony or oxygen and therefore both stibinic acid complexes may be described as monomeric. This is in contrast to organostibinic acids which are high-molecular-weight amorphous materials[25] presumably involving Sb–O–Sb bridging interactions. Similar structural units are not generally found for phosphorus and arsenic analogues which are usually monomeric, a factor which reflects the greater size and Lewis acidity of antimony. This is, in fact, a general observation since while isolated P=O and As=O units are often observed, analogous Sb=O groups are extremely uncommon. Doak and co-workers[26] have presented a comprehensive and interesting report on the nature of triphenylstibine oxide which is either dimeric or polymeric but not monomeric. Moreover, they state that at the time of publication (1986) 'evidence for the existence of any antimony compound containing the Sb=O (or Sb→O) group is questionable,' although a recent report has appeared[27] describing the crystal structure of $Sb(C_6H_2Me_3\text{-}2,4,6)_3O\cdot$

HO_3SPh in which the oxygen atom in trimesitylantimony oxide is hydrogen bonded to a hydroxide hydrogen in benzenesulphonic acid. The novelty of (**23**) and (**24**) is thus two-fold in that they are monomeric stibinic acids and contain non-bridging Sb=O (or Sb→O) groups. It is unfortunate that neither crystal structure has provided reliable bond-length and -angle data for the SbO(OH) fragment but attempts are in progress to form stibinate ester complexes from which to obtain better structural data.

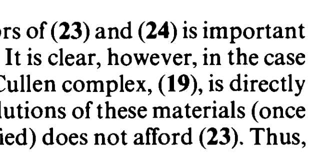
The question as to the precursors of (**23**) and (**24**) is important but we are not sure of the answer. It is clear, however, in the case of (**23**), that neither (**21**) nor the Cullen complex, (**19**), is directly involved since air oxidation of solutions of these materials (once they have been isolated and purified) does not afford (**23**). Thus, the precursor is presumably some as yet uncharacterised material present in small amounts in the crude reaction solution. Isolated yields of complex (**21**) are low and other materials are probably present in the reaction mixture. Moreover, i.r. spectra obtained on the crude oxidised reaction solution indicate that many products are present and the isolation of (**23**) was only possible as a result of fortuitous crystallisation.

We have seen no evidence for a bismuth analogue of (**23**).

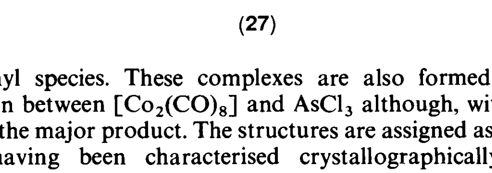
(*c*) *Arsenic and Phosphorus.*—In concluding this paper it will be useful to compare the results presented above with what is known for reactions involving cobalt carbonylate anions and arsenic and phosphorus trihalides. Markó and co-workers[28a] have described the reaction between AsX_3 (X = Cl, Br, or I) and 3—4 equivalents $Na[Co(CO)_4]$ which affords three complexes, $[Co_2As_2(CO)_6]$ (**25**), $[Co_3As(CO)_9]$ (**26**), and $[Co_9As_3(CO)_{24}]$ (**27**), plus a further unidentified arsenic cobalt carbonyl species. These complexes are also formed in the reaction between $[Co_2(CO)_8]$ and $AsCl_3$ although, with AsI_3, (**26**) is the major product. The structures are assigned as shown, (**27**) having been characterised crystallographically.[28b] A triarsenic compound, $[CoAs_3(CO)_3]$, has been reported and structurally characterised by Dahl and co-workers[29] from the reaction between $[Co_2(CO)_8]$ and $(AsMe)_5$ and reports have also appeared describing the structures of $[Co_2As_2(CO)_5(PPh_3)]$ (**28**)[30,31] and $[Co_2As_2(CO)_4(PPh_3)_2]$ (**29**).[31,*] Although neither complex (**28**) nor (**29**) was synthesised by routes involving cobalt carbonylate anions, (**29**) is noteworthy as the arsenic analogue of (**21**).



(**25**)



(**26**)



(**27**)

The P_2 complex $[Co_2P_2(CO)_6]$ (**30**), is reportedly formed[32] from the reaction between PCl_3 or PBr_3 and $Na[Co(CO)_4]$ although later reports[28a,33] indicate that $[Co_3P(CO)_9]$ (**31**), $[CoP_3(CO)_3]$ (**32**), and $[Co_9P_3(CO)_{24}]$ (**33**) are also formed in these reactions. The relative yields of the various products depend upon the Co:P ratio in the reaction but (**30**) is apparently the most stable compound in this series. The crystal structure of $[Co_2P_2(CO)_5(PPh_3)]$ (**34**), has also been described.[34]

Several points are noteworthy. For neither phosporus nor arsenic are any of the following species observed: $[E\{Co(CO)_4\}_3]$, $[EX\{Co(CO)_4\}_2]$, or $[EX_2\{Co(CO)_4\}]$ (E = P or As; X = Cl, Br, or I). These results are similar to our own observations for antimony and probably for much the same reasons. Thus one possibility is that, while the latter two halogen-containing species may be present as intermediates, the reactions quickly proceed to give the tricobalt species $[E\{Co(CO)_4\}_3]$ which are unstable in solution and rearrange with CO loss to give the observed clusters. The fact that the As_2- and P_2-containing clusters, (**25**) and (**30**), are formed provides further support for our proposed structure for (**21**). [Although (**25**) and (**30**) have not been structurally characterised, the PPh_3 derivatives (**28**), (**29**), and (**34**) have; (**28**) and (**29**) were synthesised directly from (**25**) and 1 or 2 equivalents of PPh_3 and (**34**) likewise from (**30**).]

It is interesting that the tricobaltbismuth species (**1**) and (**5**) are stable whereas the lighter congeners are not. We have no good reason for this except possibly one involving a steric argument such that the larger the main-group element the more easily accommodated are three $Co(CO)_4$ or $Co(CO)_3(PPh_3)$ fragments. If the main-group element is too small the resulting steric crowding leads to CO loss and cluster formation. While this is undoubtedly not the whole truth, there is evidence that the trend is general[35] for $[E(ML_n)_3]$ species, a matter which we will address in a future publication.

Experimental

General Considerations.—All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use (sodium–benzophenone for all solvents except CH_2Cl_2 for which CaH_2 was used). Proton and ^{13}C n.m.r. spectra were recorded in dried and degassed deuteriated solvents on a Bruker WP 200 spectrometer operating at 200.13 and 50.324 MHz, respectively. Chemical shifts are referenced to solvent peaks in all cases with values taken from ref. 36. The ^{31}P n.m.r. spectra were recorded on a Bruker WM300 spectrometer operating at 121.49 MHz; further details are given in Table 1. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer. Microanalytical data were obtained either at the University of Newcastle or from Malissa and Reuter Analytische Laboratorien, West Germany. Bismuth trichloride, antimony trichloride (both 99%+), $[Co_2(CO)_8]$, and PPh_3 were procured commercially and used without further purification; $K[Co(CO)_3(PPh_3)]$ was prepared according to literature procedures.[20,22] Analytical, i.r., ^{31}P n.m.r., and other relevant data for all new compounds are presented in Table 1.

Preparations.—$[Bi\{Co(CO)_3(PPh_3)\}_3]$ (**5**). A solution of

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[*] The i.r. data reported by Dahl and co-workers[31] for complex (**29**) are 2 010, 1 970, and 1 955 cm^{-1} (KBr disc). The KBr-disc spectrum for (**21**) showed peaks at 2 015, 1 964, 1 948, with additional shoulders at 2 035 and 1 918 cm^{-1}. The similarity between the main peaks observed for (**21**) and those reported for (**29**) provides further support for the proposed structure.

$K[Co(CO)_3(PPh_3)]$ (2.01 g, 3.99 mmol) in thf (30 cm^3) was cooled to -78 °C. Dropwise addition of a solution of $BiCl_3$ (0.419 g, 1.33 mmol, Co:Bi 3:1) in thf (20 cm^3) led to an initial red colouration, which darkened to deep red-brown on complete addition. The solution was allowed to warm to room temperature and stirred for a further 2 h, after which time it was filtered through Celite. Removal of all volatiles *in vacuo* afforded a dark red-brown solid which was redissolved in the minimum of fresh thf (8 cm^3) over which was layered hexane (*ca.* 40 cm^3). Solvent diffusion over a period of 72 h at -30 °C afforded complex (**5**) as a dark red-brown powder (1.192 g, 63% yield). A second crystallisation from CH_2Cl_2–hexane mixtures produced a crystalline sample although the crystals were not suitable for *X*-ray diffraction. N.m.r. (CD_2Cl_2): ^1H, δ 7.44 (m, 45 H, C_6H_5); ^{13}C-$\{^1H\}$, δ 199.2 (br s, CO), 135.2 (d, *ipso*-C_6H_5, $^1J_{PC}$ = 44.2), 133.9 (d, *o*-C_6H_5, $^2J_{PC}$ = 11.4), 130.8 (s, *p*-C_6H_5), and 128.9 p.p.m. (d, *m*-C_6H_5, $^3J_{PC}$ = 10.2 Hz).

$[BiCl\{Co(CO)_3(PPh_3)\}_2]$ (**6**). *Method* (*a*). A sample of $BiCl_3$ (0.249 g, 0.79 mmol) was dissolved in thf (15 cm^3) and stirred at 0 °C. To this a solution of 2 equivalents of $K[Co(CO)_3(PPh_3)]$ (0.795 g, 1.58 mmol) in thf (30 cm^3) was added with constant stirring over 10 min. This caused an initial green colouration which darkened to red-brown on complete addition. The solution was allowed to warm to room temperature and stirred for a further 24 h, over which time the initial green colour returned. The resulting mixture was filtered through Celite, to remove dispersed KCl, and after removal of all volatiles *in vacuo* a dark green solid remained. The crude solid was redissolved in thf (10 cm^3), over which hexane (50 cm^3) was layered. Solvent diffusion over 72 h at -30 °C afforded complex (**6**) as a dark green powder (0.398 g, 48%). Further crystallisations failed to result in suitable *X*-ray-quality crystals.

As described in the text, if the same work-up is performed after 0.5 h when the solution is dark red brown in colour the product isolated is (**5**).

Method (*b*). To a solution of $[Bi\{Co(CO)_3(PPh_3)\}_3]$ (0.096 g, 0.067 mmol) in thf (15 cm^3) was added $BiCl_3$ (0.011 g, 0.033 mmol) in thf (5 cm^3). Over a period of 15 h the initial deep red solution changed to green-brown. Following filtration through Celite, the solvent volume was reduced to approximately 3 cm^3 over which hexane (20 cm^3) was layered. Solvent diffusion at -30 °C over 72 h afforded complex (**6**) as a dark green powder. N.m.r. ($[^2H_8]$thf): ^1H, δ 7.47 (m, 30 H, C_6H_5); ^{13}C-$\{^1H\}$, δ 135.9 (d, *ipso*-C_6H_5, $^1J_{PC}$ = 43.8), 134.5 (d, *o*-C_6H_5, $^2J_{PC}$ = 11.2), 131.6 (s, *p*-C_6H_5), and 129.5 p.p.m. (d, *m*-C_6H_5, $^3J_{PC}$ = 10.5 Hz).

$[Bi_2Co_2(CO)_4(PPh_3)_2]$ (**13**), *and* $[BiCl_2\{Co(CO)_3(PPh_3)\}]$ (**14**). *Method* (*a*). To a cooled solution of $BiCl_3$ (0.564 g, 1.79 mmol) in thf (20 cm^3) was added 1 equivalent of $K[Co(CO)_3(PPh_3)]$ (0.795 g, 1.79 mmol) in thf (20 cm^3). This caused an initial green colour which quickly darkened to green-brown. The resultant solution was stirred for a further 48 h at room temperature.

Method (*b*). To a solution of $[Bi\{Co(CO)_3(PPh_3)\}_3]$, (**5**) (0.626 g, 0.44 mmol), in thf (30 cm^3) was added a solution containing 2 equivalents of $BiCl_3$ (0.277 g, 0.88 mmol) in thf (20 cm^3). The initial red solution was stirred at room temperature and slowly turned dark green over a period of 24 h.

Method (*c*). To a sample of $[BiCl\{Co(CO)_3(PPh_3)\}_2]$, (**6**) (0.091 g, 0.086 mmol), dissolved in thf (15 cm^3) was added $BiCl_3$ (0.027 g, 0.086 mmol) in thf (5 cm^3). The initial green colouration persisted throughout the addition. The resultant reaction mixture was stirred for 15 h over which time the solution remained green.

For the three methods described above the work-up procedure was essentially the same. In each case filtration of the resulting solution through Celite followed by removal of all volatiles *in vacuo* afforded a dark green-brown solid. Extraction into CH_2Cl_2 resulted in a green solution and a dark red solid residue. Filtration of the green solution through Celite followed by recrystallisation from CH_2Cl_2–hexane mixtures at -30 °C afforded complex (**13**) as an emerald-green powder (*ca.* 9%). The red residue was washed with hexane then redissolved in thf and refiltered through Celite. The solvent volume was reduced to approximately 10 cm^3 over which hexane (40 cm^3) was layered. Solvent diffusion at -30 °C over a period of days afforded complex (**14**) as a dark red powder (*ca.* 45%). Further recrystallisation of both (**13**) and (**14**) failed to result in suitable *X*-ray-quality crystals. Each of the reactions was accompanied by a considerable degree of decomposition.

Reaction of $BiCl_3$ *with* 3 *equivalents of* $Na[Co(CO)_4]$. A sample of $[Co_2(CO)_8]$ (0.937 g, 2.74 mmol) was dissolved in thf (30 cm^3) and stirred over a sodium amalgam for 4 h. The resulting solution of $Na[Co(CO)_4]$ (5.48 mmol) was transferred to a separate nitrogen-filled flask, stirred, and cooled to 0 °C. Dropwise addition of a solution of $BiCl_3$ (0.576 g, 1.83 mmol) in thf (15 cm^3) led to an initial purple colouration, which rapidly became dark purple-black. The solution was stirred for a further 90 min after which time it was filtered through Celite. The solvent volume was reduced to approximately 10 cm^3, over which hexane (40 cm^3) was layered. Solvent diffusion at -30 °C over a period of days afforded a dark purple-black powder. The same product was obtained when $K[Co(CO)_4]$ was used (prepared by the method of Edgell and Lyford [20]) and a reaction time of 48 h.

Reaction of $BiCl_3$ *with* 2 *equivalents of* $Na[Co(CO)_4]$. A sample of $BiCl_3$ (0.776 g, 2.46 mmol) was dissolved in thf (20 cm^3) and stirred at 0 °C. To this, a solution of 2 equivalents of $Na[Co(CO)_4]$, prepared by sodium amalgam reduction of the dimer $[Co_2(CO)_8]$ (0.842 g, 2.46 mmol) in thf (30 cm^3), was added with constant stirring. This caused an immediate colour change to deep purple, the mixture was then allowed to warm to room temperature and stirred for a further 3 h. Filtration through Celite followed by removal of all volatiles *in vacuo* afforded a purple-black solid. The crude solid was redissolved in thf (10 cm^3), over which hexane (30 cm^3) was layered. Solvent diffusion at -30 °C over a period of days afforded a dark purple-black powder.

Reaction of $[Co_2(CO)_8]$ *with bismuth metal.* This reaction was performed in a manner analagous to that reported by Schmid and co-workers [2] but with a reaction time of 20 h.

$[Sb_2Co_2(CO)_4(PPh_3)_2]$ (**21**). A solution of $K[Co(CO)_3(PPh_3)]$ (0.88 mmol) in thf (20 cm^3) was added to a solution of $SbCl_3$ (0.200 g, 0.877 mmol) in thf (10 cm^3) at 0 °C. This resulted in an initial green colouration which quickly changed to yellow-brown and eventually to dark red-brown after complete addition of the reactants. On warming to room temperature, gas evolution (presumably CO) was observed and the reaction mixture was stirred for 2 h. Filtration through Celite afforded a dark red-brown solution for which the solvent volume was reduced, by vacuum pumping, to about 7 cm^3. Hexane (40 cm^3) was carefully layered over this reaction filtrate and solvent diffusion over a period of days at -26 °C afforded brown crystals of complex (**21**) (0.3 g, 34%).

A reaction involving 2 equivalents of $K[Co(CO)_3(PPh_3)]$ and 1 of $SbCl_3$ was performed and worked-up in exactly the same way. However, for the reaction between 3 equivalents $K[Co(CO)_3(PPh_3)]$ and $SbCl_3$ the thf solution of $SbCl_3$ was added to a thf solution of $K[Co(CO)_3(PPh_3)]$ at -78 °C. At this temperature the green colouration persisted throughout the addition of the reactants and the reaction solution remained green at this temperature. On warming to room temperature a colour change to dark brown occurred. Work-up was as described above and isolated yields of crystalline material in all cases were about 30%. N.m.r. (CD_2Cl_2): ^1H, δ 7.47 (m, 30 H, C_6H_5); ^{13}C-$\{^1H\}$, δ 199.2 (d, CO, $^2J_{PC}$ = 17), 133.7 (d, *o*-C_6H_5,

$^2J_{PC}$ = 11.3), 131.3 (s, p-C_6H_5), and 129.2 p.p.m. (d, m-C_6H_5, $^3J_{PC}$ = 11.1 Hz).

The $P(C_6H_4Me$-$p)_3$ derivative, **(22)** was prepared in an exactly analogous manner using $K[Co(CO)_3\{P(C_6H_4Me$-$p)_3\}]$. N.m.r. (CD_2Cl_2): ^1H, δ 7.29 (m, 24 H, C_6H_4Me) and 2.40 (s, 18 H, C_6H_4Me); ^{13}C-$\{^1H\}$, δ 141.7 (s, p-C_6H_4Me, *i.e.* CMe), 133.4 (d, o-C_6H_4Me, $^2J_{PC}$ = 11.3), 129.8 (d, m-C_6H_4Me, $^3J_{PC}$ = 10.8 Hz), and 21.5 p.p.m. (s, C_6H_4Me).

$[SbO(OH)\{Co(CO)_3(PPh_3)\}_2]$ **(23)**. A thf solution of complex **(21)** was prepared as described above. However, prior to filtration and subsequent work-up, air was admitted to the reaction flask leading to an immediate colour change from brown to dark red-purple. Filtration through Celite, reduction of the solvent volume to *ca.* 8 cm^3, and careful layering with hexane (45 cm^3) gave, after solvent diffusion at −26 °C over a period of days, a heterogeneous crystalline mass from which low yields of purple crystalline complex **(23)** were obtained. Complex **(24)** was prepared similarly from solutions of **(22)**.

All compounds are air sensitive in solution but as solids can be handled in air for short periods.

X-Ray Crystallographic Studies.—Crystal data for compound **(23)**. $C_{42}H_{31}Co_2O_8P_2Sb{\cdot}C_6H_{14}$, M_r = 1 051.4, monoclinic, space group $C2/c$, a = 25.003(4), b = 10.891(2), c = 18.899(4) Å, β = 111.61(2)°, U = 4 784.6 Å^3 (from 2θ values of 32 reflections in the range 22—25°), Z = 4, D_c = 1.362 g cm^{-3}, $F(000)$ = 2 128, μ(Mo-K_α) = 1.36 mm^{-1}, λ = 0.710 73 Å.

Data collection and reduction. Stoe-Siemens diffractometer with graphite monochromator, crystal size 0.72 × 0.44 × 0.28 mm, T = 295 K, $2\theta_{max.}$ = 50°. Index ranges: h −29 to 29, k 0—12, l 0—22, with equivalent reflections (k, l < 0), ω—θ scan mode, on-line profile fitting.[37] Of 14 703 reflections measured, 4 226 were unique and 3 509 with $F > 4\sigma_c(F)$ were used for structure determination (R_{int} = 0.021, σ_c from counting statistics only). Data were corrected for Lorentz and polarisation effects, crystal decay (*ca.* 30%), and absorption (semiempirically); transmission factors 0.54—0.61, extinction insignificant.

Structure solution and refinement.[38] Atom positions were determined from Patterson and difference syntheses and refined together with anisotropic thermal motion parameters to minimise $\Sigma w\Delta^2$; $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 171 - 372G + 699G^2 - 239S + 121S^2 - 355GS$ ($G = F_o/F_{max.}$, $S = \sin\theta/\sin\theta_{max.}$).[39] Molecule constrained on C_2 axis except for two-fold disorder of Sb atom; disorder components could not be resolved for other atoms. Hydrogen atoms constrained on ring-angle external bisectors with C–H 0.96 Å, U(H) = 1.2U_{eq}(C); O–H not located. No H atoms included for n-hexane molecule on centre of symmetry. For 281 refined parameters, R = 0.075, R' = 0.040, goodness of fit = 0.96. The largest features in the final difference synthesis were close to the heavy atoms. Scattering factors were taken from ref. 40.

Crystal data for compound **(24)**. $C_{48}H_{43}Co_2O_8P_2Sb{\cdot}C_4H_8O$, M_r = 1 121.5, monoclinic, space group $P2_1/n$, a = 11.063(1), b = 20.568(2), c = 23.752(2) Å, β = 93.73(1)°, U = 5 393.1 Å^3 (from 32 reflections in the range 2θ 20—25°), Z = 4, D_c = 1.333 g cm^{-3}, $F(000)$ = 2 280, μ(Mo-K_α) = 1.17 mm^{-1}.

Data collection and reduction. As for **(23)** except: crystal size 0.27 × 0.35 × 0.54 mm, index ranges h −13 to 13, k 0—24, l 0—28 with equivalent reflections, transmission 0.50—0.54, no significant decay. Of 29 990 data, 9 477 were unique and 6 625 had $F > 4\sigma_c(F)$, R_{int} = 0.035.

Structure solution and refinement. Atom positions determined by direct methods and difference syntheses and refined with anisotropic thermal motion parameters for all non-hydrogen atoms except O atoms attached to Sb; $w^{-1} = \sigma_c^2(F) + 57 + 785G - 387G^2 - 200S + 191S^2 - 1\,333GS$. Antimony atom two-fold disordered in ratio 70:30; disorder could not be resolved for other atoms. Tetrahydrofuran solvent molecule disordered and refined as five carbon atoms. Angle H–C–H 109.5° in constrained methyl groups, aromatic H as for **(23)**; hydrogens of thf and OH not located. For 614 refined parameters, R = 0.084, R' = 0.049, goodness of fit = 1.01. Largest features in final difference map next to Sb atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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