Journal of Organometallic Chemistry, 430 (1992) 205–219
Elsevier Sequoia S.A., Lausanne
JOM 22508

Further synthetic and structural studies on cobalt carbonyl containing antimony complexes

Nicholas C. Norman, Peter M. Webster
Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU (UK)

and Louis J. Farrugia
Department of Chemistry, The University, Glasgow, G12 8QQ (UK)

(Received October 24, 1991)

Abstract

The reaction between $SbCl_3$ and three equivalents of $K[Co(CO)_3(PR_3)]$ affords the tricobalt-antimony complexes $[Sb\{Co(CO)_3(PR_3)\}_3]$ (**5**, R = OPh; **6**, R = OMe; **7**, $R_3 = Ph_2Me$; **8**, R = Ph; **9**, R = *p*-tolyl). Complexes **5** and **6** have been characterised by X-ray crystallography; both contain antimony in a trigonal pyramidal coordination geometry bonded to three $Co(CO)_3(PR_3)$ fragments *via* unsupported Sb–Co bonds. Thermolysis of **5** in THF leads to CO loss and formation of the *closo* cluster species $[SbCo_3(CO)_3(P(OPh)_3)_3(\mu\text{-}CO)_3]$ (**10**) characterised by analytical and spectroscopic methods. The reaction between $SbCl_3$ and one equivalent of $K[Co(CO)_3(P(OR)_3)]$ affords the yellow crystalline complexes $[SbCl_2\{Co(CO)_2(P(OR)_3)_2\}]$ (**11**, R = Me; **12**, R = Ph), both of which have been characterised by X-ray crystallography. Complexes **11** and **12** are monomeric and each contains a $SbCl_2$ group bonded to a $Co(CO)_2(P(OR)_3)_2$ fragment. The geometry around the cobalt centre is trigonal bipyramidal, with the $SbCl_2$ group and one phosphite ligand in axial sites and the two carbonyls and remaining phosphite ligand in equatorial sites.

Introduction

We recently [1] presented the results of studies on some cobalt carbonyl containing antimony and bismuth compounds, with reference to previous work. The introduction and discussion presented [1] also provides an appropriate preface for the present paper, and is not duplicated here, but it will be useful briefly to summarize the results we obtained for antimony since it is a continuation of those studies which forms the basis of this paper. From the reactions between $SbCl_3$ and $K[Co(CO)_3(PR_3)]$ (R = Ph or *p*-tolyl) in tetrahydrofuran (THF) solution we were able to isolate, for the range of reaction stoichiometries 1:1, 1:2 and 1:3 (Sb:Co), a brown crystalline complex which we formulated, on the basis of spectroscopic and analytical data, as the dicobalt-diantimony species $[Co_2Sb_2(CO)_4(PR_3)_2]$ (R =

Correspondence to: Dr. N.C. Norman, The University of Newcastle, Department of Chemistry, Newcastle upon Tyne, NE1 7RU, UK.

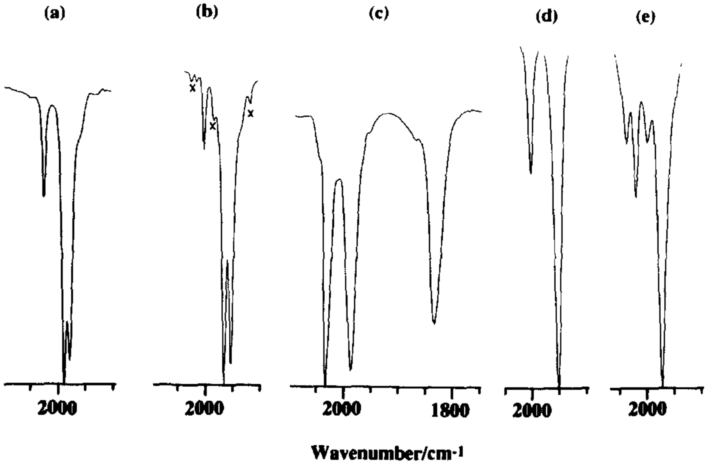


Fig. 1. Infrared spectra in the carbonyl stretching region measured in THF solution for (a) **5**, (b) **8** (× denotes impurities), (c) **10**, (d) **11**, (e) **12**.

Ph, **1**; R = *p*-tolyl, **2** [1]). It appeared from the colour changes during the reactions, however, that the formation of **1** and **2** occurred *via* green intermediates which we suggested to be the tricobalt-antimony complexes $[Sb\{Co(CO)_3(PR_3)\}_3]$. These were apparently unstable in THF solution, except at low temperature, rearranging to **1**/**2** with concomitant evolution of CO as the temperature was raised. A report by Whitmire and coworkers [2] concerning the instability of the green complex $[Sb\{Co(CO)_4\}_3]$ **3** in THF solution provided support for this view; complex **3** was observed to undergo rearrangement to the cluster species $[Sb_2Co_4(CO)_{11}]^{n-}$ ($n = 1, 2$), a full report of which has now appeared [3].

We have now found that the complexes $[Sb\{Co(CO)_3(PR_3)\}_3]$ can be readily isolated when PR_3 is a phosphite ligand, $P(OR)_3$, and so can other complexes of this general type. Moreover, when PR_3 is a phosphine, the tricobalt-antimony complexes can also be isolated, albeit with some difficulty and in much lower yields. These studies form the basis of most of the work reported here.

Results and discussion

The reaction between $SbCl_3$ and three equivalents of $K[Co(CO)_3(P(OPh)_3)]$ in THF, in which the $SbCl_3$ solution is added to the solution of the cobalt carbonylate anion, resulted in the immediate formation of a deep green solution from which dark green crystals were isolated after work-up and crystallisation from THF-hexane mixtures. The IR spectrum of a THF solution of this material (Fig. 1(a), Table 1) was very similar to that of the bismuth complex $[Bi\{Co(CO)_3(PPh_3)\}_3]$ **4** [1] and this, together with the analytical data (Table 1), was consistent with the formulation $[Sb\{Co(CO)_3(P(OPh)_3)\}_3]$ **5**. This formulation was confirmed by a subsequent X-ray diffraction study, the results of which are shown in Fig. 2; selected bond distance and angle data are given in Table 2 and atomic positional parameters are presented in Table 3. The molecule resides on a crystallographic three-fold axis and has a trigonal pyramidal antimony centre bonded to three

Table 1

Spectroscopic and analytical data for the complexes

Compound	ν(CO) (cm^{-1}) [b]	^{31}P NMR [c]	Analysis [a]	
			C	H
[Sb{Co(CO)$_3$(P(OPh)$_3$)}$_3$] **(5)**	2024m, 1989s, 1978s	147.4	52.6 (51.1)	3.7 (3.1)
[Sb{Co(CO)$_3$(P(OMe)$_3$)}$_3$] **(6)**	2040w, 2013m, 1976s, 1965s	158.3	23.3 (23.4)	2.9 (2.9)
[Sb{Co(CO)$_3$(PPh$_2$Me)}$_3$] **(7)**	2002m, 1963s, 1950s	33.3	49.9 (50.1)	3.3 (3.4)
[Sb{Co(CO)$_3$(PPh$_3$)}$_3$] **(8)**	2004m, 1966s, 1953s			
[Sb{Co(CO)$_3$(P(*p*-tolyl)$_3$)}$_3$] **(9)**	2003m, 1965s, 1953s	48.2 [d]	58.0 (59.1)	4.2 (4.3)
[SbCo$_3$(CO)$_3$(P(OPh)$_3$)$_3$(μ-CO)$_3$] **(10)**	2034s, 1987s, 1834s	147.7	51.1 (51.6)	3.5 (3.3)
[SbCl$_2${Co(CO)$_2$(P(OMe)$_3$)$_2$}] **(11)**	2002m, 1952s	163.9	16.9 (17.3)	3.2 (3.3)
[SbCl$_2${Co(CO)$_2$(P(OPh)$_3$)$_2$}] **(12)**	2035w, 2019m, 1996w, 1970s	151.0	49.9 (49.2)	3.7 (3.3)

[a] Calculated values in parentheses. [b] Measured in THF solution. [c] Measured in CD_2Cl_2 unless otherwise stated, ^{1}H decoupled, referenced to 85% H_3PO_4 (ext). [d] Measured in acetone-d_6.

Co(CO)$_3$(P(OPh)$_3$) fragments by unsupported Co–Sb bonds. The geometry around each cobalt centre is trigonal bipyramidal, with the three carbonyls occupying the equatorial positions and the triphenylphosphite ligand *trans* to the antimony centre in the remaining axial site. The Co–Sb bond distance (2.667(2) Å) is

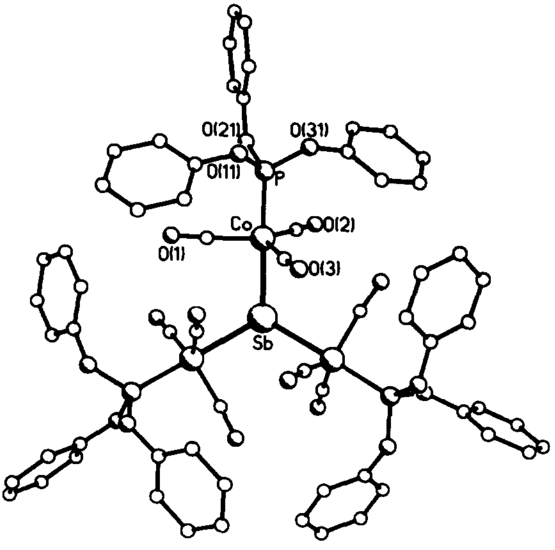


Fig. 2. Molecular structure of **5** indicating the atom numbering scheme. Hydrogen atoms omitted for clarity.

Table 2

Selected bond distances (Å) and angles (deg) for complexes **5** and **6**

5		**6**	
Bond distances			
Sb–Co	2.667(2)	Sb–Co(1)	2.690(1)
		Sb–Co(2)	2.664(1)
		Sb–Co(3)	2.665(1)
Bond angles			
Co–Sb–Co	108.5(1)	Co(1)–Sb–Co(2)	106.8(1)
		Co(1)–Sb–Co(3)	106.5(1)
		Co(2)–Sb–Co(3)	108.0(1)

comparable to, although slightly longer than, those found in the cobalt-stibinic acid complexes $[SbO(OH)\{Co(CO)_3(PR_3)\}_2]$ (R = Ph, *p*-tolyl) [1], where the mean Co–Sb bond length is 2.618 Å, whilst the Co–Sb–Co bond angle at antimony (108.5(1)°)

Table 3

Atom coordinates and equivalent isotropic displacement parameters (Å^2) for $[Sb\{Co(CO)_3(P(OPh)_3)\}_3]$ (**5**) [a]

Atom	*x*	*y*	*z*	U_{eq}
Sb	0.66667	0.33333	0.33371(5)	0.037
Co	0.60123(9)	0.18013(9)	0.37174(6)	0.041
P	0.54554(19)	0.05541(19)	0.39936(12)	0.045
O(1)	0.7580(6)	0.1901(6)	0.3501(5)	0.087
O(2)	0.4956(7)	0.1405(6)	0.2749(4)	0.083
O(3)	0.5656(7)	0.2329(6)	0.4750(4)	0.090
O(11)	0.5762(5)	0.0339(5)	0.4549(3)	0.054
O(21)	0.5530(5)	−0.0012(5)	0.3537(3)	0.058
O(31)	0.4526(5)	0.0069(5)	0.4189(3)	0.054
C(1)	0.6983(8)	0.1894(8)	0.3587(6)	0.058
C(2)	0.5356(8)	0.1567(7)	0.3125(6)	0.054
C(3)	0.5815(8)	0.2162(8)	0.4345(5)	0.057
C(111)	0.6566(8)	0.0623(11)	0.4665(5)	0.058
C(112)	0.6970(11)	0.0234(9)	0.4449(5)	0.072
C(113)	0.7784(8)	0.0501(6)	0.4594(7)	0.097
C(114)	0.8193(7)	0.1158(9)	0.4956(5)	0.096
C(115)	0.7789(10)	0.1548(7)	0.5172(5)	0.087
C(116)	0.6975(8)	0.1280(8)	0.5027(7)	0.072
C(211)	0.5221(9)	−0.0845(4)	0.3518(6)	0.051
C(212)	0.4893(10)	−0.1374(6)	0.3965(5)	0.061
C(213)	0.4616(6)	−0.2211(6)	0.3902(3)	0.063
C(214)	0.4667(7)	−0.2519(4)	0.3393(5)	0.075
C(215)	0.4994(8)	−0.1990(6)	0.2946(4)	0.088
C(216)	0.5272(5)	−0.1152(6)	0.3009(4)	0.075
C(311)	0.3895(9)	0.0053(13)	0.3891(6)	0.053
C(312)	0.3562(8)	−0.0467(8)	0.3441(8)	0.083
C(313)	0.2898(10)	−0.0503(8)	0.3159(5)	0.109
C(314)	0.2568(8)	−0.0019(10)	0.3328(5)	0.103
C(315)	0.2901(8)	0.0501(6)	0.3779(7)	0.101
C(316)	0.3564(11)	0.0537(10)	0.4061(5)	0.074

---

[a] Esd's are in parentheses. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$ in this and in all subsequent Tables.

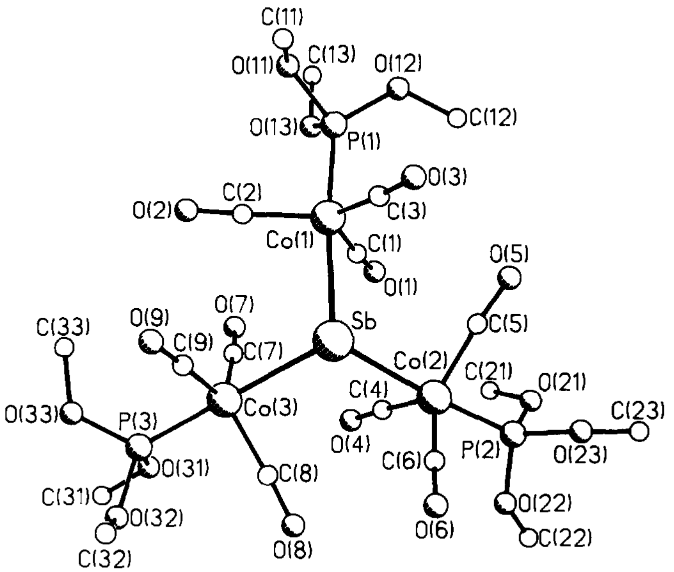
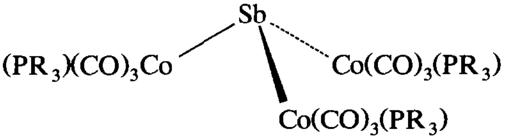


Fig. 3. Molecular structure of **6** indicating the atom numbering scheme. Hydrogen atoms omitted for clarity.

gives a sum of angles of 325.5° as a measure of the pyramidality. By way of comparison, the sum of angles in the related tricobaltbismuth complex $[Bi\{Co(CO)_4\}_3]$ [4] is 320.3°, *i.e.* the bismuth centre is more pyramidal. This is in line with the expected trend of increasing pyramidality as group 15 is descended although the larger steric bulk of the phosphite ligand in **5** should not be ignored. In the only other trimetallastibine complex to have been structurally characterised, namely $[Sb\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]$ [5], the sum of angles around antimony is 330.9°.



5, R = OPh; **6**, R = OMe; **7**, R_3 = Ph_2Me; **8**, R = Ph; **9**, R = *p*-tolyl

The $P(OMe)_3$ derivative, $[Sb\{Co(CO)_3(P(OMe)_3)\}_3]$ **6**, was prepared in a similar manner and also characterised by X-ray crystallography and the results are shown in Fig. 3. Bond distances and angles are given in Table 2 and atom coordinates in Table 4. The structure is similar in all respects to that of **5** although slightly more pyramidal; the sum of the angles is 321.3°. Spectroscopic and analytical data for **6** are listed in Table 1. We note, in particular, that the IR spectrum is very similar to that of **5** and apparently quite characteristic of the $[E\{Co(CO)_3(L)\}_3]$ structure since, as we have seen, the same basic spectrum is also observed for the bismuth complex **4** (see Fig. 1(a) in ref. [1]).

Having established that complexes of the general type $[Sb\{Co(CO)_3(L)\}_3]$ were stable for L = phosphite, we turned our attention to phosphine-substituted derivatives. The reaction between $SbCl_3$ and three equivalents of $K[Co(CO)_3(PPh_2Me)]$ afforded, after work up and crystallisation, dark green crystals of the complex

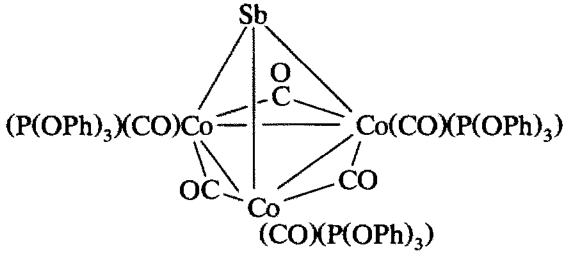
Table 4

Atom coordinates and equivalent isotropic displacement parameters (Å^2) for $[Sb\{Co(CO)_3(P(OMe)_3)\}_3]$ (**6**)

Atom	x	y	z	U_{eq}
Sb	0.12001(5)	0.07331(4)	0.14259(3)	0.044
Co(1)	0.19782(9)	−0.07125(9)	0.20603(7)	0.051
Co(2)	0.33579(9)	0.27412(9)	0.16540(7)	0.052
Co(3)	0.00609(9)	0.15490(9)	0.28147(7)	0.051
P(1)	0.2754(2)	−0.1800(2)	0.2509(2)	0.068
P(2)	0.5157(2)	0.4277(2)	0.1828(2)	0.068
P(3)	−0.0950(2)	0.2160(2)	0.3853(2)	0.059
O(1)	0.4266(6)	0.1611(5)	0.3625(4)	0.086
O(2)	−0.0351(6)	−0.1729(6)	0.2666(5)	0.102
O(3)	0.1677(8)	−0.1973(7)	−0.0208(5)	0.123
O(4)	0.3587(6)	0.3952(6)	0.3905(5)	0.103
O(5)	0.4241(6)	0.0936(6)	0.0629(5)	0.106
O(6)	0.1695(6)	0.3124(6)	0.0192(5)	0.095
O(7)	0.1883(6)	0.1730(6)	0.4578(4)	0.092
O(8)	0.0787(7)	0.3784(6)	0.2394(5)	0.112
O(9)	−0.2263(6)	−0.0877(6)	0.1443(5)	0.089
O(11)	0.1754(7)	−0.3207(6)	0.2319(6)	0.124
O(12)	0.3739(8)	−0.2072(8)	0.2001(6)	0.177
O(13)	0.3375(6)	−0.1276(6)	0.3748(4)	0.107
O(21)	0.6460(6)	0.4584(6)	0.2594(5)	0.100
O(22)	0.5145(7)	0.5559(5)	0.2176(6)	0.129
O(23)	0.5520(7)	0.4055(7)	0.0748(5)	0.127
O(31)	0.0001(6)	0.3334(5)	0.4941(4)	0.086
O(32)	−0.1813(7)	0.2733(7)	0.3483(5)	0.133
O(33)	−0.1988(6)	0.1194(6)	0.4143(5)	0.113
C(1)	0.3342(8)	0.0728(7)	0.2990(6)	0.061
C(2)	0.0548(8)	−0.1319(7)	0.2417(6)	0.065
C(3)	0.1778(8)	−0.1455(8)	0.0667(7)	0.073
C(4)	0.3482(8)	0.3433(8)	0.3008(7)	0.074
C(5)	0.3866(8)	0.1619(7)	0.1048(6)	0.063
C(6)	0.2339(8)	0.2958(7)	0.0765(6)	0.063
C(7)	0.1187(8)	0.1641(7)	0.3847(6)	0.058
C(8)	0.0518(8)	0.2891(8)	0.2534(6)	0.068
C(9)	−0.1340(8)	0.0061(8)	0.1951(6)	0.067
C(11)	0.0880(12)	−0.4134(9)	0.1360(8)	0.116
C(12)	0.4740(11)	−0.1201(12)	0.1785(13)	0.178
C(13)	0.3986(11)	−0.1813(12)	0.4256(9)	0.141
C(21)	0.6671(11)	0.4859(11)	0.3692(9)	0.122
C(22)	0.589(3)	0.663(2)	0.247(2)	0.396
C(23)	0.668(2)	0.458(2)	0.061(1)	0.271
C(31)	−0.0431(12)	0.3914(9)	0.5801(8)	0.125
C(32)	−0.2751(10)	0.2134(11)	0.2493(9)	0.119
C(33)	−0.1744(11)	0.0334(9)	0.4472(7)	0.112

$[Sb\{Co(CO)_3(PPh_2Me)\}_3]$ (**7**), analytical and spectroscopic data for which are shown in Table 1. Of more interest, however, were the results for complexes containing PPh_3 and P(*p*-tolyl)$_3$. We reported previously [1] that although dark green solutions were obtained during the initial stages of the reactions between $SbCl_3$ and $K[Co(CO)_3(PR_3)]$ (R = Ph, *p*-tolyl), we were unable to isolate green complexes. Rather it appeared that these complexes were unstable in solution and rearranged at close to room temperature to give the dicobalt-diantimony compounds $[Co_2Sb_2(CO)_4(PR_3)_2]$ which were subsequently isolated and characterised. What we have since found, however, is that if the reaction stoichiometry is precisely controlled (at 3 : 1) and if the product mixture is worked up quickly, the dark green complexes $[Sb\{Co(CO)_3(PPh_3)\}_3]$ (**8**) and $[Sb\{Co(CO)_3(P(p\text{-tolyl})_3)\}_3]$ (**9**) can be isolated as stable materials. Spectroscopic and analytical data for **8** and **9** are presented in Table 1 and the solution IR spectrum of **8** is shown in Fig. 1(b). Recrystallised yields were low and the compounds were difficult to isolate in pure form but it is clear from IR experiments that, in the pure form, they are quite stable in THF solution and show no signs of any rearrangement to **1**/**2** or any other material. These observations therefore lead us to modify our original statements regarding the formation of **1** and **2**. It is clear that **8** and **9** are not the direct precursors in any thermal rearrangement although they may well react, under the reaction conditions, with other, as yet unidentified, species present in solution to give **1** and **2**. Nevertheless, having access to a range of complexes of the type $[Sb\{Co(CO)_3(PR_3)\}_3]$ enabled us to explore their reactivity in more detail.

The easiest compound to make and isolate in high yield is **5** and it was this compound that we studied further. Photolysis in THF solution led only to intractable mixtures from which no characterisable products could be isolated. Thermolysis in THF led, however, to a clean reaction from which a complex characterised as $[SbCo_3(CO)_3(P(OPh)_3)_3(\mu\text{-}CO)_3]$ (**10**) was isolated, a structure for which is proposed below. Support for this formulation comes primarily from the IR spectrum (Table 1, Fig. 1(c)), which shows two strong terminal CO absorptions and one characteristic of bridging carbonyls consistent with the proposed C_{3v} symmetry, and the analytical data (Table 1). We note the similarity between the transformation of **5** into **10** by CO thermolysis and the formation of the structurally similar cluster $[BiCo_3(CO)_6(\mu\text{-}CO)_3]$ from $[Bi\{Co(CO)_4\}_3]$ reported by Whitmire *et al.* [6]. Thermolysis of **6** under similar conditions did not lead to the isolation of any products.



10

As stated above and in ref. [1], the reaction between $SbCl_3$ and one or two equivalents of $K[Co(CO)_3(PR_3)]$ (R = Ph, *p*-tolyl) affords the dicobalt-diantimony complexes **1** and **2**. With the phosphite ligands $P(OPh)_3$ and $P(OMe)_3$, we found that the reactions took a different course. Thus the reaction between $SbCl_3$ and one equivalent of $K[Co(CO)_3(P(OMe)_3)]$ afforded, after work up and crystallisation from THF-hexane, yellow crystals of the complex $[SbCl_2\{Co(CO)_2(P(OMe)_3)_2\}]$ (**11**) whose structure was established by X-ray crystallography, the results of which are shown in Fig. 4. Selected bond distances and angles and atomic positional

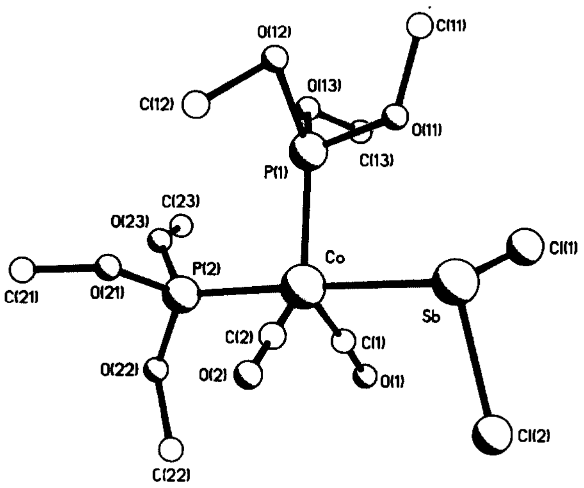


Fig. 4. Molecular structure of **11** indicating the atom numbering scheme. Hydrogen atoms omitted for clarity.

parameters are presented in Tables 5 and 6. Compound **11** is monomeric with no short intermolecular contacts and consists of a central cobalt atom bonded to a $SbCl_2$ fragment, two carbonyls and two $P(OMe)_3$ ligands. The geometry around the cobalt centre is trigonal bipyramidal with the $SbCl_2$ group occupying an axial site, the carbonyls occupying equatorial sites and the phosphite ligands occupying the remaining axial and equatorial positions. The antimony centre is trigonal pyramidal (sum of angles 295.1°). The infrared spectrum of **11** (Table 1, Fig. 1(d)) shows two terminal carbonyl absorptions consistent with the solid state structure being maintained in solution although the presence of only one signal in the ^{31}P NMR spectrum (Table 1) implies that the molecule is fluxional on this time scale.

The corresponding reaction between $SbCl_3$ and $K[Co(CO)_3(P(OPh)_3)]$ afforded the analogous yellow crystalline complex $[SbCl_2\{Co(CO)_2(P(OPh)_3)_2\}]$ (**12**) which was also characterised by X-ray crystallography. The results are shown in Fig. 5; selected bond distances and angles and atomic positional parameters are given in Tables 5 and 7. The structure of **12** is substantially similar to that of **11** in terms of

Table 5

Selected bond distances (Å) and angles (deg) for complexes **11** and **12**

11		**12**	
Bond distances			
Sb–Co	2.523(1)	Sb–Co	2.538(2)
Sb–Cl(1)	2.397(2)	Sb–Cl(1)	2.369(3)
Sb–Cl(2)	2.425(2)	Sb–Cl(2)	2.378(3)
Bond angles			
Co–Sb–Cl(1)	102.3(1)	Co–Sb–Cl(1)	103.7(1)
Co–Sb–Cl(2)	99.7(1)	Co–Sb–Cl(2)	98.0(1)
Cl(1)–Sb–Cl(2)	93.1(1)	Cl(1)–Sb–Cl(2)	95.4(1)

Table 6

Atom coordinates and equivalent isotropic displacement parameters (Å^2) for [$SbCl_2\{Co(CO)_2(P(OMe)_3)_2\}$] (11)

Atom	x	y	z	U_{eq}
Sb	0.06081(4)	0.07537(4)	0.32007(2)	0.045
Co	0.28502(7)	0.20016(7)	0.35003(3)	0.038
Cl(1)	0.0591(2)	−0.0829(2)	0.4088(1)	0.077
Cl(2)	0.1263(2)	−0.1102(2)	0.2517(1)	0.074
P(1)	0.19080(15)	0.31750(16)	0.41872(7)	0.047
P(2)	0.47742(17)	0.30644(17)	0.37123(9)	0.057
O(1)	0.4072(6)	−0.0756(5)	0.3815(3)	0.087
O(2)	0.2421(6)	0.3070(6)	0.2193(2)	0.080
O(11)	0.0329(4)	0.2798(4)	0.4083(2)	0.057
O(12)	0.1957(5)	0.4866(4)	0.4205(2)	0.063
O(13)	0.2387(5)	0.3013(5)	0.4940(2)	0.065
O(21)	0.4748(5)	0.4611(5)	0.3476(3)	0.087
O(22)	0.6028(7)	0.2371(8)	0.3540(7)	0.214
O(23)	0.5417(10)	0.3380(13)	0.4418(4)	0.200
C(1)	0.3564(7)	0.0324(7)	0.3700(3)	0.057
C(2)	0.2556(6)	0.2659(6)	0.2710(3)	0.052
C(11)	−0.0628(8)	0.3418(10)	0.4454(4)	0.096
C(12)	0.1672(9)	0.5683(7)	0.3626(4)	0.083
C(13)	0.2491(8)	0.1646(10)	0.5231(3)	0.084
C(21)	0.5904(10)	0.5521(9)	0.3542(5)	0.099
C(22)	0.6233(10)	0.1528(12)	0.3040(6)	0.120
C(23)	0.5797(10)	0.2785(14)	0.4930(4)	0.118

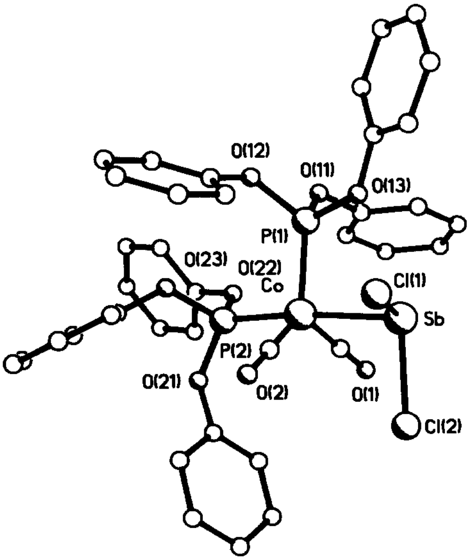


Fig. 5. Molecular structure of **12** indicating the atom numbering scheme. Hydrogen atoms omitted for clarity.

Table 7

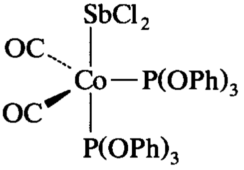
Atom coordinates and equivalent isotropic displacement parameters (Å^2) for [SbCl$_2${Co(CO)$_2$(P(OPh)$_3$)$_2$}]·1/2C$_4$H$_8$O **12**. For solvent atoms *U* is the isotropic displacement parameter

Atom	*x*	*y*	*z*	U_{eq}
Sb	0.47621(5)	0.00260(3)	0.63302(3)	0.049
Co	0.45577(10)	−0.07716(5)	0.73643(5)	0.042
Cl(1)	0.6766(2)	0.0358(1)	0.6549(1)	0.077
Cl(2)	0.5007(3)	−0.0829(1)	0.5468(1)	0.089
P(1)	0.44425(19)	0.00974(10)	0.80398(10)	0.043
P(2)	0.4322(2)	−0.1525(1)	0.8147(1)	0.046
O(1)	0.2334(6)	−0.1131(3)	0.6485(3)	0.085
O(2)	0.6852(6)	−0.1283(3)	0.7164(3)	0.088
O(11)	0.3216(4)	0.0283(3)	0.8290(3)	0.053
O(12)	0.5122(4)	0.0157(2)	0.8842(2)	0.050
O(13)	0.4815(5)	0.0795(2)	0.7668(2)	0.048
O(21)	0.4266(5)	−0.2318(2)	0.7941(2)	0.057
O(22)	0.3114(5)	−0.1424(2)	0.8425(3)	0.056
O(23)	0.5199(5)	−0.1544(2)	0.8882(2)	0.054
C(1)	0.3214(8)	−0.0993(4)	0.6836(5)	0.055
C(2)	0.5938(9)	−0.1080(4)	0.7241(5)	0.057
C(111)	0.2179(7)	0.0302(7)	0.7818(5)	0.059
C(112)	0.1984(7)	0.0800(5)	0.7283(3)	0.077
C(113)	0.0906(4)	0.0827(4)	0.6830(4)	0.119
C(114)	0.0024(6)	0.0355(6)	0.6913(4)	0.146
C(115)	0.0219(6)	−0.0143(4)	0.7448(3)	0.130
C(116)	0.1296(5)	−0.0170(5)	0.7901(5)	0.091
C(121)	0.6296(5)	0.0016(5)	0.9057(5)	0.050
C(122)	0.6601(5)	−0.0251(3)	0.9744(4)	0.062
C(123)	0.7772(6)	−0.0407(3)	1.0006(3)	0.079
C(124)	0.8638(4)	−0.0295(4)	0.9579(5)	0.099
C(125)	0.8333(5)	−0.0027(2)	0.8892(3)	0.090
C(126)	0.7162(6)	0.0128(4)	0.8631(4)	0.066
C(131)	0.4978(9)	0.1457(3)	0.7929(4)	0.047
C(132)	0.5691(9)	0.1874(2)	0.7577(5)	0.069
C(133)	0.5875(4)	0.2560(2)	0.7778(3)	0.093
C(134)	0.5347(8)	0.2831(3)	0.8331(4)	0.097
C(135)	0.4634(7)	0.2414(2)	0.8684(4)	0.081
C(136)	0.4450(5)	0.1728(2)	0.8482(2)	0.069
C(211)	0.4532(11)	−0.2618(3)	0.7331(4)	0.055
C(212)	0.3673(7)	−0.2677(4)	0.6728(6)	0.075
C(213)	0.3927(7)	−0.3019(5)	0.6123(4)	0.094
C(214)	0.5040(9)	−0.3303(3)	0.6122(4)	0.107
C(215)	0.5898(5)	−0.3244(4)	0.6726(5)	0.106
C(216)	0.5645(9)	−0.2901(5)	0.7330(3)	0.075
C(221)	0.2702(5)	−0.1827(3)	0.8928(3)	0.058
C(222)	0.1976(9)	−0.2387(5)	0.8711(3)	0.084
C(223)	0.1525(9)	−0.2784(5)	0.9218(3)	0.118
C(224)	0.1799(4)	−0.2622(3)	0.9942(3)	0.115
C(225)	0.2525(9)	−0.2062(5)	1.0159(3)	0.118
C(226)	0.2976(8)	−0.1664(4)	0.9652(3)	0.088
C(231)	0.6120(6)	−0.2003(5)	0.9048(6)	0.052
C(232)	0.5973(5)	−0.2632(4)	0.9377(4)	0.079
C(233)	0.6929(6)	−0.3074(2)	0.9552(3)	0.111
C(234)	0.8032(6)	−0.2886(4)	0.9399(5)	0.105

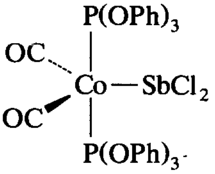
Table 7 (continued)

Atom	x	y	z	U_{eq}
C(235)	0.8179(5)	−0.2257(3)	0.9070(3)	0.088
C(236)	0.7223(7)	−0.1815(3)	0.8895(4)	0.067
O(S1)	0.021(3)	−0.010(1)	0.506(1)	0.27(1)
C(S1)	0.152(2)	−0.002(2)	0.511(3)	0.151(9)
C(S2)	0.177(2)	0.069(2)	0.488(2)	0.103(7)
C(S3)	0.061(3)	0.106(1)	0.468(2)	0.35(3)
C(S4)	−0.035(2)	0.057(2)	0.480(3)	0.27(2)

the coordination geometries around the cobalt and antimony centres (sum of angles at Sb = 297.1°). The only apparent difference between the two complexes is in THF solution where the IR spectrum for **12** (Table 1, Fig. 1(e)) shows four absorptions which is indicative of the presence of two isomers. We cannot be sure as to the exact nature of the species present in solution but suggest that one isomer is likely to be that observed in the solid state (**12a**) whilst the other probably has the sterically bulky $P(OPh)_3$ ligand *trans* in axial sites (**12b**). As with **11**, however, the singlet observed in the ^{31}P NMR spectrum (Table 1) shows that the molecule is fluxional on the NMR time scale. Clearly, the formation of **11** and **12** is not straightforward since these products have two phosphite ligands per cobalt atom rather than the one present in the starting cobalt carbonylate anion. We have previously observed, however, that in reactions of $K[Co(CO)_3(PPh_3)]$ with $InCl_3$, phosphine transfer reactions are facile under the reaction conditions [7].



12a



12b

Compounds **11** and **12** are unusual in containing a $SbCl_2$ fragment bonded to only one transition metal although we are aware of the related bromo analogue $[SbBr_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ [8]. There are, however, a number of complexes of the type $[L_nMSbX_2(M'L_n)]$ where $M'L_n$ is a 16 electron fragment and the L_nMSbX_2 unit acts as a two-electron donor through the antimony lone pair. Details of these complexes are available [9a–e]. The SbX_2 group can also act as a Lewis acid and accept an electron pair as seen in the complex $[SbBr_2(PMe_3)\{Fe(CO)(PMe_3)(\eta\text{-}C_5H_5)\}]$ [9f].

The results reported here show that complexes with a 3:1 and a 1:1 Co:Sb ratio can be isolated from reactions between $K[Co(CO)_3(PR_3)]$ and $SbCl_3$ of the appropriate stoichiometry particularly where PR_3 is a phosphite ligand, although the 3:1 compounds can also be obtained for phosphines as well albeit in rather low yield. However, whilst our understanding of the compounds obtainable from this general reaction system has increased, in terms of isolable crystalline complexes, the nature of the reactions occurring in solution is still not clear.

Experimental

General considerations

All experiments were performed under dry, oxygen-free dinitrogen by standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. IR spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle. ^{31}P NMR spectra were measured on a Bruker WM 300 spectrometer operating at 121.49 MHz and referenced to 85% H_3PO_4; ^1H and ^{13}C NMR spectra were obtained on a Bruker WP 200 spectrometer operating at 200.13 and 50.324 MHz respectively and referenced to Me_4Si.

The cobalt salts $K[Co(CO)_3(PR_3)]$ were prepared in a two stage procedure. $K[Co(CO)_4]$ and the phosphine or phosphite substituted derivatives were prepared following literature methods ([10] and [11] respectively). All other starting materials were procured commercially.

Preparations

$[Sb\{Co(CO)_3(P(OPh)_3)\}_3]$ **(5)**. A solution of $SbCl_3$ (0.206 g, 0.903 mmol) in THF (10 cm^3) was added to a stirred solution of $K[Co(CO)_3(P(OPh)_3)]$ (2.709 mmol) in THF (30 cm^3) at −78°C (dry ice/ethanol), resulting in the immediate appearance of a deep green colour. The mixture was allowed to warm to room temperature during 4 h. The solution was then filtered through Celite and the volume of the filtrate reduced under vacuum to about 10 cm^3. Hexane (30 cm^3) was layered over this solution and cooling to −26°C for some days afforded dark green crystals of **5** (1.22 g, 90%). NMR data for **5**: ^1H (CD_2Cl_2) δ 7.05–7.39 (m, Ph); ^{13}C-$\{^1H\}$ δ 130.2 (o-C_6H_5), 125.8 (p-C_6H_5), 121.9 (m-C_6H_5).

The complexes **6**, **7**, **8** and **9** were prepared analogously from the corresponding cobalt carbonylate anion. Typical yields for **6** were 70–80% and for **7**, 40%. Compounds **8** and **9** were obtained with isolated yields of about 20% only. For complex **8** the reaction solution was dark red although pure **8** is dark green in solution. On some occasions we also obtained a dark red solid, the THF solution IR spectrum for which (ν(CO) 2024w, 1985s, 1886m) is consistent with the formulation $[Sb\{Co(CO)_3(PPh_3)\}_4][Co(CO)_4]$. The low frequency absorption is due to the $[Co(CO)_4]^-$ anion whilst the two higher frequency absorptions are very similar to those reported for the $[Sb\{Co(CO)_3(PPh_3)\}_4]^+$ cation ([1] and refs. therein). NMR data for **6**: ^1H (CD_2Cl_2) δ 3.70 (d, $P(OMe)_3$, $^3J(PH) = 12.4$ Hz); ^{13}C-$\{^1H\}$ δ 200.0 (d, CO, $^2J(PC) \approx 50$ Hz), 53.3 (d, $P(OMe)_3$, $^2J(PC) \approx 50$ Hz). NMR data for **7**: ^1H (CD_2Cl_2) δ 7.40–7.68 (m, 30H, PPh_2Me), 2.10 (m, 9H, PPh_2Me); ^{13}C-$\{^1H\}$ δ 201 (bs, CO), 137 (d, *ipso*-C_6H_5, $^1J(PC) \approx 60$ Hz), 131.8 (d, o-C_6H_5, $^2J(PC) = 11.6$ Hz), 130.5 (s, p-C_6H_5), 128.8 (d, m-C_6H_5, $^4J(PC) = 9.6$ Hz).

$[SbCo_3(CO)_3(P(OPh)_3)_3(\mu\text{-}CO)_3]$ **(10)**. A solution of **5** (0.438 g, 0.296 mmol) in THF (30 cm^3) was refluxed for 6 h and then stirred at room temperature for 17 h during which the colour of the solution had changed from dark green to dark brown. The solution was filtered through Celite and the volume reduced by vacuum to about 5 cm^3. Hexane (30 cm^3) was layered over this solution and cooling to −26°C for some days afforded dark brown crystals of **10** (0.251 g, 55%).

[$SbCl_2\{Co(CO)_2(P(OMe)_3)_2\}$] (11). A solution of K[$Co(CO)_3(P(OMe)_3)$] (1.113 mmol) in THF (20 cm^3) was added to a stirred solution of $SbCl_3$ (0.254 g, 1.113 mmol) in THF (10 cm^3) at room temperature, resulting in a yellow colour. Stirring was continued for 1 h and the solution then filtered through Celite. The volume of the filtrate was reduced to about 5 cm^3 under vacuum and hexane (30 cm^3) was layered over this. Cooling to −26°C over a period of days afforded yellow crystals of **11** (30%). NMR data for **11**: ^1H (CD_2Cl_2) δ 3.66 (t, $P(OMe)_3$, $|J(PH)+J'(PH)| = 12$ Hz); $^{13}C\text{-}\{^1H\}$ δ 52.8 (s, $P(OMe)_3$).

Complex **12** was prepared similarly from K[$Co(CO)_3(P(OPh)_3)$] as yellow crystals in similar yield. NMR data for **12**: ^1H (CD_2Cl_2) δ 7.09–7.50 (m, $P(OPh)_3$); $^{13}C\text{-}\{^1H\}$ δ 151.6 (s, *ipso*-C_6H_5), 130.2 (s, *o*-C_6H_5), 125.8 (s, *p*-C_6H_5), 121.6 (s, *m*-C_6H_5).

X-ray crystallography

Compound 5. A crystal was mounted in a general position on a glass fibre and coated with acrylic resin. Data were collected at ambient temperature using the $\theta/2\theta$ scan mode on an Enraf–Nonius CAD4F automated diffractometer with graphite monochromated X-radiation. Unit cell parameters were determined by refinement of a number of setting angles given in Table 8. Standards were measured every 2 h and a linear correction was applied for any observed decay. Lorentz-polarisation and absorption/extinction (DIFABS [12]) corrections were also applied. The diffraction symmetry was inconsistent with the hexagonal Laue classes $6/mmm$ and $6/m$ and with the trigonal point group $\bar{3}1m$ but gave satisfactory merging statistics (R_{merge} for 9644 observations was 0.03) for the point group $\bar{3}m1$. From the systematic absences ($h\bar{h}0l$ and $000l$, $l = 2n+1$) and an examination of normalised structure factor statistics, the centrosymmetric space group $P\bar{3}c1$ was indicated. This was confirmed by successful solution and refinement of the structure. The structure was solved by direct methods (MITHRIL [13]) and subsequent electron density difference syntheses. Refinement was by full-matrix least squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with unit weights used. $\sigma(F_o)$ was estimated from counting statistics. The phenyl groups were refined as rigid groups with idealised geometry (C–C = 1.395, C–H = 1.0 Å), and with fixed isotropic thermal parameters (0.05 $Å^2$) for the H atoms. Refinement converged to give the R values given in Table 8. A final electron density difference synthesis showed several maxima in the region of ~1 e$Å^{-3}$ which are probably due to a disordered, partially occupied solvent molecule, but this could not be modelled by any chemically reasonable molecule. Remaining features were in the vicinity of the antimony atom. Neutral atom scattering factors were taken from ref. [14] with corrections applied for anomalous scattering. All calculations were carried out on a MicroVAX 3600 computer using the Glasgow GX suite of programs [15].

Compound 6. As for **5** except that the statistics of the normalised structure factors indicated the centrosymmetric space group $P\bar{1}$. The structure was solved by heavy atom methods. A weighting scheme $w = [\sigma^2(F_o)]^{-1}$ was used and judged satisfactory. All non-hydrogen atoms were allowed anisotropic thermal motion with fixed isotropic thermal parameters (0.08 $Å^2$) for all H atoms. The thermal parameters for C(22) and C(23) were much larger than for other corresponding C atoms and indicate the possibility of some disorder. However, no suitable disorder

Table 8

Crystallographic data for the complexes

	5	6	11	12
Formula	$C_{63}H_{45}Co_3$-$O_{18}P_3Sb$	$C_{18}H_{27}Co_3$-$O_{18}P_3Sb$	$C_8H_{18}CoCl_2$-O_8P_2Sb	$C_{38}H_{30}CoCl_2O_8$-$P_2Sb\cdot 1/2C_4H_8O$
M	1481.5	922.87	555.76	956.24
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{3}c1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	18.775(5)	11.786(1)	10.020(3)	11.516(2)
b (Å)		12.7481(9)	9.419(2)	19.438(4)
c (Å)	24.439(5)	13.866(1)	21.113(4)	18.950(5)
α (deg)		109.502(6)		
β (deg)		97.966(8)	99.38(2)	98.99(2)
γ (deg)		113.819(6)		
V (Å^3)	7460(3)	1703.9(3)	1966.0(8)	4190(2)
Z	4	2	4	4
D_c (g cm^{-3})	1.32	1.80	1.88	1.52
$F(000)$	2976	912	1088	1920
μ(Mo-K_α) (cm^{-1})	11.36	24.28	26.88	12.65
λ(Mo-K_α) (Å)	0.71069	0.71069	0.71069	0.71069
Cryst. size/mm	$0.4 \times 0.4 \times 0.8$	$0.6 \times 0.6 \times 0.4$	$0.8 \times 0.4 \times 0.6$	$0.4 \times 0.5 \times 0.5$
No. of reflections for unit cell	25 ($\theta \sim 12°$)	25 ($9 < \theta < 13°$)	25 ($11 < \theta < 13°$)	25 ($11 < \theta < 13°$)
Standards	$8\,2\,\bar{6}, \bar{5}\,0\,\overline{12}$	$3\,\bar{4}\,\bar{3}, 5\,\bar{6}\,\bar{1}$	$3\,\bar{5}\,\bar{1}, 2\,5\,1, \bar{1}\,\bar{5}\,\bar{5}$	$\bar{3}\,9\,4, \bar{3}\,\bar{6}\,\bar{7}$
Decay (%)	20	35	3	40
Absorption (max/min)	1.06/0.84	1.18/0.82	1.31/0.78	1.15/0.81
2θ range (deg)	4–45	4–50	4–50	4–45
Indices	$h\ -20 \Rightarrow +17$ $k\ 0 \Rightarrow +20$ $l\ 0 \Rightarrow +26$	$h\ 0 \Rightarrow 14$ $k\ -15 \Rightarrow +15$ $l\ -18 \Rightarrow +18$	$h\ 0 \Rightarrow +11$ $k\ 0 \Rightarrow +11$ $l\ -24 \Rightarrow +24$	$h\ 0 \Rightarrow +12$ $k\ 0 \Rightarrow +20$ $l\ -20 \Rightarrow +20$
No. reflections	10368	6301	3909	6042
Unique reflections	3258	5983	3450	5467
Observed reflections	2441	3558	2827	3580
Obs. criterion	$I > 3.0\sigma(I)$			
No. parameters	229	280	199	488
R	0.048	0.038	0.038	0.050
R_w	0.080	0.042	0.056	0.049
Δ/σ (mean/max)	0.009/0.045	0.01/0.13	0.0015/0.015	0.005/0.035
Max/min $\Delta\rho$	+0.48/−0.54	+0.91/−0.53	+1.16/−0.99	+0.8/−0.42
S	6.9	1.78	2.9	1.78

model could be satisfactorily refined and these two atoms were refined in the positions shown with 100% occupancy.

Compound 11. As for **5** except that the statistics of normalised structure factors and systematic absences uniquely indicated the centrosymmetric space group $P2_1/c$. A weighting scheme as for **6** was used. All non-hydrogen atoms were allowed anisotropic thermal motion; H atoms were included at calculated positions and allowed to ride on their attached C atom. There was some indication of a rotational disorder about the Co–P(2) bond in one $P(OMe)_3$ group, but this could not be satisfactorily modelled. The thermal parameters associated with this group are larger than the other.

Compound 12. As for **5** except that the statistics of normalised structure factors and systematic absences uniquely indicated the centrosymmetric space group $P2_1/n$. A weighting scheme as for **6** was used. All non-hydrogen atoms (apart from the solvent atoms) were allowed anisotropic thermal motion. The disordered molecule of THF (site occupancy 0.5) was close to a centre of inversion. This solvent molecule was refined as a rigid group.

References

1 W. Clegg, N.A. Compton, R.J. Errington, D.C.R. Hockless, N.C. Norman, M. Ramshaw and P.M. Webster, J. Chem. Soc., Dalton Trans., (1990) 2375.
2 J.S. Leigh, K.H. Whitmire, K.A. Yee and T.A. Albright, J. Am. Chem. Soc., 111 (1989) 2726.
3 T.A. Albright, K.A. Yee, J.-Y. Saillard, S. Kahlal, J.-F. Halet, J.S. Leigh and K.H. Whitmire, Inorg. Chem., 30 (1991) 1179.
4 G. Etzrodt, R. Boese and G. Schmid, Chem. Ber., 112 (1979) 2574.
5 A.M. Borr, M.D. Kerlogue, N.C. Norman, P.M. Webster and L.J. Farrugia, Polyhedron, 8 (1989) 2495.
6 K.H. Whitmire, J.S. Leigh and M.E. Gross, J. Chem. Soc., Chem. Commun., (1987) 926.
7 L.M. Clarkson, K. McKrudden, N.C. Norman and L.J. Farrugia, Polyhedron, 9 (1990) 2533.
8 L. Zsolnai, PhD Thesis, University of Konstanz, 1984.
9 (a) F.W.B. Einstein and R.D.G. Jones, Inorg. Chem., 12 (1973) 1690; (b) J. von Seyerl, L. Wohlfahrt and G. Huttner, Chem. Ber., 113 (1980) 2868; (c) A. Lombard, G. Huttner and L. Zsolnai, J. Organomet. Chem., 352 (1988) 295; (d) W. Malisch and P. Panster, Z. Naturforsch., 39B (1975) 229; (e) P. Panster and W. Malisch, Chem. Ber., 109 (1976) 692; (f) H.-A. Kaul, D. Greissinger, W. Malisch, H.-P. Klein and U. Thewalt, Angew. Chem., Int. Ed. Engl., 22 (1983) 60.
10 W.F. Edgell and J. Lyford, Inorg. Chem., 9 (1970) 1932. See also J.E. Ellis, P.T. Barger, M.L. Winzenburg and G.F. Warnock, J. Organomet. Chem., 383 (1990) 521.
11 F. Ungvary and A. Wojcicki, J. Am. Chem. Soc., 109 (1987) 6848.
12 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, A39 (1983) 158.
13 C.J. Gilmore, J. Appl. Crystallogr., 17 (1984) 42.
14 International Tables for X-ray Crystallography; Kynoch Press, Birmingham, 1974, vol. 4.
15 P.R. Mallinson and K.W. Muir, J. Appl. Crystallogr., 18 (1985) 51.