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# Sterically crowded $\text{PhCCo}_3(\text{CO})_9$ derivatives: X-ray structures of the mono- and bis-diphenylphosphinomethane substitution products

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## Abstract

The bidentate phosphine ligand 1,1-bis(diphenylphosphinomethane) (dppm) forms both mono- and bis-substituted complexes with the tricobalt-carbon cluster  $\text{PhCCo}_3(\text{CO})_9$ . The crystal and molecular structures of  $\text{PhCCo}_3(\text{CO})_7(\text{dppm})$  and  $\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2$  have been determined from X-ray data collected at 123(5) K. The results provide a detailed characterization of these related complexes and reveal that the dppm ligand coordinates by bridging Co–Co bonds in both molecules.

## 1. Introduction

The chemistry of multidentate phosphine derivatives of the trinuclear carbyne clusters  $\text{RCCo}_3(\text{CO})_9$  ( $\text{R} \equiv \text{H}$ , alkyl aryl etc.) [1] has been the subject of a number of recent reports [2–6]. Work in this field is motivated by the expectation that bridging a metal–metal bond in the cluster system will bolster the metal–metal interaction and significantly reduce the tendency for fragmentation of the cluster units under the conditions experienced in catalytic processes. Our work on the redox and electron transfer chemistry of these cobalt complexes [7] has revealed an additional feature of substitution chemistry, namely that replacement of CO by ligands with poorer  $\pi$ -acceptor properties can transform the cluster moiety from a readily reducible to a readily oxidizable centre [8]. Clearly, this reflects the changes in electron density carried by the cluster core and has interesting implications when designing molecules with multiple redox centres [9,10].

Substitution at the periphery of a  $\text{Co}_3\text{C}$  cluster is generally limited; the degree of substitution reduces along the series  $\text{RNC} > (\text{RO})_3\text{P} > \text{R}_3\text{P}$  for monodentate

ligands [11]. Bidentate phosphines, such as 1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dimethylphosphino)ethane (dmpe), provide a more extensive range of coordination possibilities [2], and recent reports have identified both bridging and the less usual chelating ligation in complexes with dmpe [5,6]. In this paper, we describe the crystal and molecular structures of both the mono- and bis-dppm derivatives of the cluster  $\text{PhCCo}_3(\text{CO})_9$ .

## 2. Results and discussion

Both compounds consist of well-separated monomeric molecules in the solid state. No unusual intermolecular contacts are found in either structure with the closest contacts (not involving H atoms) being 3.174 Å between O(112) and C(254) for 1 and 3.109 Å between O(33) and C(102) for 2.

Figure 1 shows a general view of the two unique molecules in the asymmetric unit and defines the atom numbering scheme for 1. Selected bond lengths and angles for 1 are given in Table 1. Unless otherwise specified, molecular parameters for molecule 1 of 1 will be used in this discussion; small differences in bond lengths and angles between the two independent

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molecules can best be ascribed to crystal packing effects. Figure 2 shows the structure and numbering scheme for **2** and the bond lengths and angles for this molecule are collected in Table 2.

The pyramidal  $\text{CCo}_3$  core, topped by a phenyl ring, is a common feature in the structures of both **1** and **2**, and this feature of the structures is closely similar to that observed in the parent nonacarbonyl complex [12]. In **1**, the phenyl ring plane approximately bisects the  $\text{Co}(11)\text{--Co}(12)\text{--Co}(13)$  bond and is essentially orthogonal to the  $\text{Co}_3$  triangle (interplanar angle  $91.3(2)^\circ$ ). However, the  $\text{C}(11)\text{--C}(21)$  bond bends away from the coordinated dppm ligand such that it subtends an angle of  $3.8(2)^\circ$  with the  $\text{Co}_3$  plane. These orientations coupled with the displacement of the capping  $\text{C}(11)$  atom towards the dppm-bridged  $\text{Co}(11)\text{--Co}(12)$  bond (*vide infra*) serve to minimize the non-bonded interactions between the ligands and the apical phenyl substituent.

In **1**, the dppm ligand bridges one  $\text{Co}\text{--Co}$  bond with the P donor atoms coordinating to equatorial sites. The  $\text{P}(11)$ ,  $\text{P}(12)$  and central  $\text{C}(110)$  atom of the dppm ligand combine with the two ligated Co atoms and the apical C atom of the cluster to form a six-membered ring with a classical boat conformation (Figs. 3(a) and 3(b)). This appears to be the norm for  $\text{Co}_3\text{C}$  cluster molecules with a single dppm substituent [2–4] and may orient the ligand so as to minimize the non-bonded contacts between the apical substituent and the phenyl rings on P. One equatorial and one axial carbonyl ligands remain on each P-substituted Co atom. The additional Co atom carries two equatorial and one axial carbonyl ligands.  $\text{Co}\text{--P}$  and  $\text{Co}\text{--C}$  bond lengths, and other bond distances and angles within the dppm

and CO ligands are unremarkable and will not be discussed further.

The bridging di-equatorial mode of coordination is common for  $\text{RCCo}_3(\text{CO})_7(\text{L-L})$  complexes of bidentate phosphine ligands and is found for  $\text{R} = \text{Me}$ ,  $\text{Ph}$  and  $\text{Cl}$  and  $\text{L-L} = \text{dppm}$  [2–4],  $\text{dmpe}$  [5,6] and  $\text{dppe}$  [2,13] derivatives. Alternative bridging di-axial isomers of the complexes  $\text{RCCo}_3(\text{CO})_7\text{dppm}$  have been identified in solution by IR and nuclear magnetic resonance (NMR) techniques [2,13], but no solid state structures have been obtained. A further coordination possibility involves chelation of the bidentate phosphine ligand to an individual Co centre. Such binding has been observed previously in a bis-dmpe-substituted derivative of  $\text{PhCCo}_3(\text{CO})_9$  (*vide infra*) [5], and in reactions of the more rigid ligand  $\text{Ph}_2\text{PCH} = \text{CPh}_2$  (dppt) with tetracobalt clusters [14].

The effect of di-equatorial substitution on the  $\text{CCo}_3$  core of the cluster molecule has been the subject of some speculation. The observation [2,4] that the  $\text{Co}\text{--Co}$  bond is lengthened on dppm bridging is not supported here and the results for the known structures of  $\text{CCo}_3$  clusters bridged by bidentate phosphine ligands (Table 3) clearly show that significant lengthening is not necessarily the norm. A common factor does emerge from the data presented in Table 3, however; namely, that there is a significant variation in the  $\text{Co}\text{--C}_{\text{apical}}$  bond lengths, such that the  $\text{Co}\text{--C}$  bond opposite the phosphine-bridged  $\text{Co}\text{--Co}$  bond is lengthened significantly. This has the effect of displacing the apical C atom towards the substituted Co atoms. This semi-capping orientation of the carbyne ligand with respect to the  $\text{Co}_3$  triangle has been noted previously and was as-

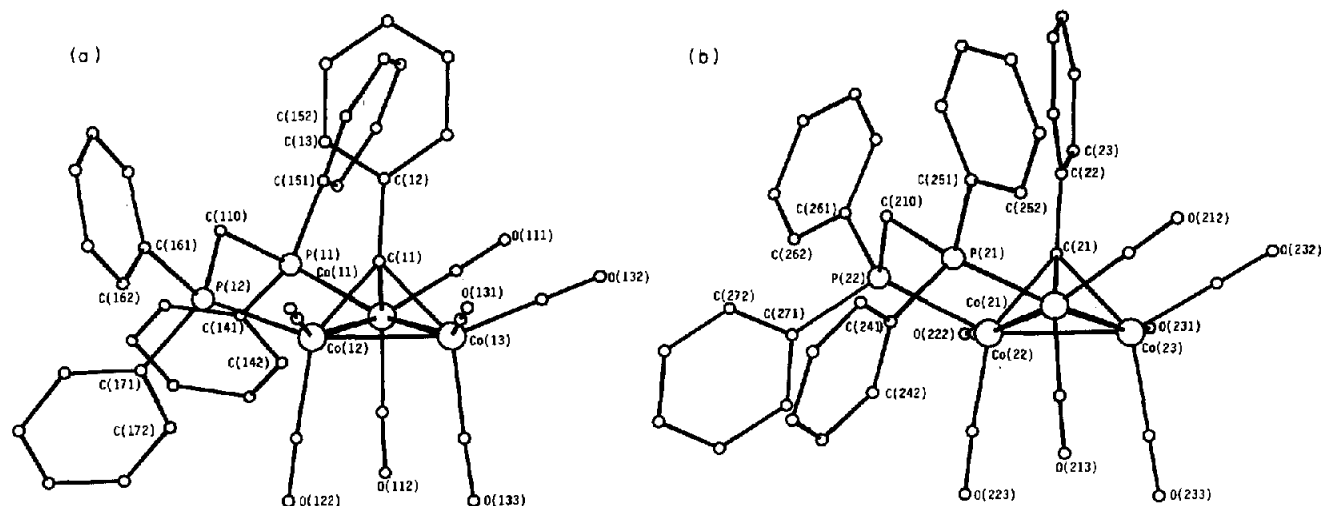


Fig. 1. Perspective view of the two unique molecules of  $\text{PhCCo}_3(\text{CO})_7\text{dppm}$  (**1**), showing the atom numbering scheme: (a) molecule **1**; (b) molecule **2**. For clarity the H atoms have been omitted and only the first two atoms of consecutively numbered phenyl rings have been labelled.

TABLE 1. Selected bond lengths and angles for PhCCo<sub>3</sub>(CO)<sub>7</sub>(dppm) (1)

Molecule 1	Bond length (Å)	Molecule 2	Bond length (Å)
Co(11)–Co(12)	2.470(1)	Co(21)–Co(22)	2.472(1)
Co(11)–Co(13)	2.471(1)	Co(21)–Co(23)	2.483(1)
Co(12)–Co(13)	2.467(1)	Co(22)–Co(23)	2.471(1)
Co(11)–C(11)	1.892(7)	Co(21)–C(21)	1.885(7)
Co(12)–C(11)	1.877(7)	Co(22)–C(21)	1.908(6)
Co(13)–C(11)	1.938(7)	Co(23)–C(21)	1.939(7)
C(11)–C(12)	1.50(1)	C(21)–C(22)	1.46(1)
C(12)–C(13)	1.38(1)	C(22)–C(23)	1.41(1)
C(12)–C(17)	1.40(1)	C(22)–C(27)	1.402(9)
C(13)–C(14)	1.38(1)	C(23)–C(24)	1.37(1)
C(14)–C(15)	1.39(1)	C(24)–C(25)	1.39(1)
C(15)–C(16)	1.38(1)	C(25)–C(26)	1.39(1)
C(16)–C(17)	1.38(1)	C(26)–C(27)	1.37(1)
Co(11)–C(112)	1.774(7)	Co(21)–C(212)	1.781(7)
C(112)–O(112)	1.141(9)	C(212)–O(212)	1.142(9)
Co(11)–C(113)	1.814(8)	Co(21)–C(213)	1.812(8)
C(113)–O(113)	1.13(1)	C(213)–O(213)	1.14(1)
Co(11)–P(11)	2.204(2)	Co(21)–P(21)	2.201(2)
P(11)–C(141)	1.829(8)	P(21)–C(241)	1.833(8)
P(11)–C(151)	1.831(7)	P(21)–C(251)	1.823(7)
P(11)–C(110)	1.788(5)	P(21)–C(210)	1.841(7)
C(110)–P(12)	1.839(4)	C(210)–P(22)	1.826(6)
Co(12)–P(12)	2.200(2)	Co(22)–P(22)	2.194(2)
P(12)–C(161)	1.831(7)	P(22)–C(261)	1.826(7)
P(12)–C(171)	1.824(7)	P(22)–C(271)	1.836(8)
Co(12)–C(122)	1.772(8)	Co(22)–C(222)	1.762(7)
C(122)–O(122)	1.13(1)	C(222)–O(222)	1.143(9)
Co(12)–C(123)	1.804(8)	Co(22)–C(223)	1.794(8)
C(123)–O(123)	1.128(9)	C(223)–O(223)	1.14(1)
Co(13)–C(131)	1.775(8)	Co(23)–C(231)	1.783(8)
C(131)–O(131)	1.14(1)	C(231)–O(231)	1.132(9)
Co(13)–C(132)	1.789(9)	Co(23)–C(232)	1.780(7)
C(132)–O(132)	1.15(1)	C(232)–O(232)	1.147(9)
Co(13)–C(133)	1.831(8)	Co(23)–C(233)	1.90(1)
C(133)–O(133)	1.13(1)	C(233)–O(233)	1.09(1)
Molecule 1	Bond angle (°)	Molecule 2	Bond angle (°)
Co(12)–Co(11)–Co(13)	59.90(1)	Co(22)–Co(21)–Co(23)	59.90(1)
Co(12)–Co(11)–C(11)	48.8(2)	Co(22)–Co(21)–C(21)	49.7(2)
Co(12)–Co(11)–P(11)	98.6(1)	Co(22)–Co(21)–P(21)	94.9(1)
Co(12)–Co(11)–C(112)	149.1(3)	Co(22)–Co(21)–C(212)	146.7(2)
Co(12)–Co(11)–C(113)	98.7(2)	Co(22)–Co(21)–C(213)	104.6(2)
Co(13)–Co(11)–C(11)	50.6(2)	Co(23)–Co(21)–C(21)	50.5(2)
Co(13)–Co(11)–P(11)	151.6(1)	Co(23)–Co(21)–P(21)	150.5(1)
Co(13)–Co(11)–C(112)	96.8(3)	Co(23)–Co(21)–C(212)	96.1(2)
Co(13)–Co(11)–C(113)	98.4(2)	Co(23)–Co(21)–C(213)	101.2(2)
C(11)–Co(11)–P(11)	101.6(2)	C(21)–Co(21)–P(21)	102.4(2)
C(11)–Co(11)–C(112)	101.2(3)	C(21)–Co(21)–C(212)	97.6(3)
C(11)–Co(11)–C(113)	141.6(3)	C(21)–Co(21)–C(213)	147.2(3)
P(11)–Co(11)–C(112)	94.8(3)	P(21)–Co(21)–C(212)	99.4(2)
P(11)–Co(11)–C(113)	103.4(3)	P(21)–Co(21)–C(213)	99.8(2)
C(112)–Co(11)–C(113)	105.1(3)	C(212)–Co(21)–C(213)	102.5(3)
Co(11)–Co(12)–Co(13)	60.10(1)	Co(21)–Co(22)–Co(23)	60.30(1)
Co(11)–Co(12)–C(11)	49.3(2)	Co(21)–Co(22)–C(21)	48.9(2)
Co(11)–Co(12)–P(12)	94.7(1)	Co(21)–Co(22)–P(22)	98.8(1)
Co(11)–Co(12)–C(122)	150.8(3)	Co(21)–Co(22)–C(222)	156.4(2)
Co(11)–Co(12)–C(123)	102.2(2)	Co(21)–Co(22)–C(223)	93.7(2)
Co(13)–Co(12)–C(11)	50.8(2)	Co(23)–Co(22)–C(21)	50.6(2)
Co(13)–Co(12)–P(12)	151.0(1)	Co(23)–Co(22)–P(22)	149.2(1)

TABLE 1 (continued)

Molecule 1	Bond angle (°)	Molecule 2	Bond angle (°)
Co(13)–Co(12)–C(122)	98.6(3)	Co(23)–Co(22)–C(222)	99.6(3)
Co(13)–Co(12)–C(123)	98.8(3)	Co(23)–Co(22)–C(223)	98.8(2)
C(11)–Co(12)–P(12)	102.7(2)	C(21)–Co(22)–P(22)	98.8(2)
C(11)–Co(12)–C(122)	102.1(3)	C(21)–Co(22)–C(222)	109.6(3)
C(11)–Co(12)–C(123)	144.3(3)	C(21)–Co(22)–C(223)	138.5(3)
P(12)–Co(12)–C(122)	98.8(3)	P(22)–Co(22)–C(222)	93.9(3)
P(12)–Co(12)–C(123)	100.5(3)	P(22)–Co(22)–C(223)	105.3(2)
C(122)–Co(12)–C(123)	100.7(3)	C(222)–Co(22)–C(223)	102.0(3)
Co(11)–Co(13)–Co(12)	60.00(1)	Co(21)–Co(23)–Co(22)	59.90(1)
Co(11)–Co(13)–C(11)	49.0(2)	Co(21)–Co(23)–C(21)	48.6(2)
Co(11)–Co(13)–C(131)	148.9(2)	Co(21)–Co(23)–C(231)	151.1(3)
Co(11)–Co(13)–C(132)	98.8(3)	Co(21)–Co(23)–C(232)	98.4(2)
Co(11)–Co(13)–C(133)	97.5(3)	Co(21)–Co(23)–C(233)	95.6(2)
Co(12)–Co(13)–C(11)	48.6(2)	Co(22)–Co(23)–C(21)	49.5(2)
Co(12)–Co(13)–C(131)	95.1(3)	Co(22)–Co(23)–C(231)	94.7(2)
Co(12)–Co(13)–C(132)	152.9(3)	Co(22)–Co(23)–C(232)	148.0(3)
Co(12)–Co(13)–C(133)	97.1(3)	Co(22)–Co(23)–C(233)	99.9(2)
C(11)–Co(13)–C(131)	101.1(3)	C(21)–Co(23)–C(231)	105.3(3)
C(11)–Co(13)–C(132)	105.2(3)	C(21)–Co(23)–C(232)	98.7(3)
C(11)–Co(13)–C(133)	139.0(4)	C(21)–Co(23)–C(233)	139.5(3)
C(131)–Co(13)–C(132)	97.6(4)	C(231)–Co(23)–C(232)	97.9(3)
C(131)–Co(13)–C(133)	104.4(3)	C(231)–Co(23)–C(233)	102.7(3)
C(132)–Co(13)–C(133)	102.7(4)	C(232)–Co(23)–C(233)	105.7(4)
Co(11)–C(11)–Co(12)	81.9(3)	Co(21)–C(21)–Co(22)	81.3(3)
Co(11)–C(11)–Co(13)	80.4(3)	Co(21)–C(21)–Co(23)	80.9(3)
Co(11)–C(11)–C(12)	133.2(5)	Co(21)–C(21)–C(22)	134.3(5)
Co(12)–C(11)–Co(13)	80.6(3)	Co(22)–C(21)–Co(23)	79.9(3)
Co(12)–C(11)–C(12)	134.0(5)	Co(22)–C(21)–C(22)	132.9(4)
Co(13)–C(11)–C(12)	126.7(5)	Co(23)–C(21)–C(22)	127.2(5)
Co(11)–P(11)–C(141)	120.8(2)	Co(21)–P(21)–C(241)	118.0(2)
Co(11)–P(11)–C(151)	112.4(2)	Co(21)–P(21)–C(251)	116.2(2)
Co(11)–P(11)–C(110)	108.7(2)	Co(21)–P(21)–C(210)	111.1(2)
C(141)–P(11)–C(151)	101.5(3)	C(241)–P(21)–C(251)	103.0(3)
C(141)–P(11)–C(110)	107.0(3)	C(241)–P(21)–C(210)	103.5(3)
C(151)–P(11)–C(110)	105.4(3)	C(251)–P(21)–C(210)	103.3(3)
P(11)–C(110)–P(12)	110.7(2)	P(21)–C(210)–P(22)	110.4(4)
Co(12)–P(12)–C(110)	109.5(2)	Co(22)–P(22)–C(210)	110.9(2)
Co(12)–P(12)–C(161)	115.0(2)	Co(22)–P(22)–C(261)	115.6(2)
Co(12)–P(12)–C(171)	115.8(2)	Co(22)–P(22)–C(271)	119.2(3)
C(110)–P(12)–C(161)	103.6(3)	C(210)–P(22)–C(261)	103.0(3)
C(110)–P(12)–C(171)	106.9(3)	C(210)–P(22)–C(271)	105.8(3)
C(161)–P(12)–C(171)	105.1(3)	C(261)–P(22)–C(271)	100.6(3)
Co(11)–C(112)–O(112)	178.1(7)	Co(21)–C(212)–O(212)	176.9(6)
Co(11)–C(113)–O(113)	177.1(7)	Co(21)–C(213)–O(213)	177.9(6)
Co(12)–C(122)–O(122)	176.7(8)	Co(22)–C(222)–O(222)	179.3(7)
Co(12)–C(123)–O(123)	178.3(7)	Co(22)–C(223)–O(223)	177.5(7)
Co(13)–C(131)–O(131)	178.4(8)	Co(23)–C(231)–O(231)	179.5(7)
Co(13)–C(132)–O(132)	178.0(7)	Co(23)–C(232)–O(232)	177.7(7)
Co(13)–C(133)–O(133)	178.9(7)	Co(23)–C(233)–O(233)	178.3(7)

cribed to a response by the molecule to the increase in electron density on the cluster core as a result of carbonyl substitution by the poorer  $\pi$ -acceptor phosphine ligands [2]. The more traditional response to additional electron density on the cluster core is to form carbonyl bridges, but di-equatorial substitution by

the phosphine ligands precludes this response. It is noteworthy that the most significant carbyne displacement occurs in the dmpe-bridged cluster unit [6]. The  $\sigma$ -donor ability of the P atoms in this ligand is likely to be significantly greater than that for dpmm owing to the inductive effect of the Me substituents. This would

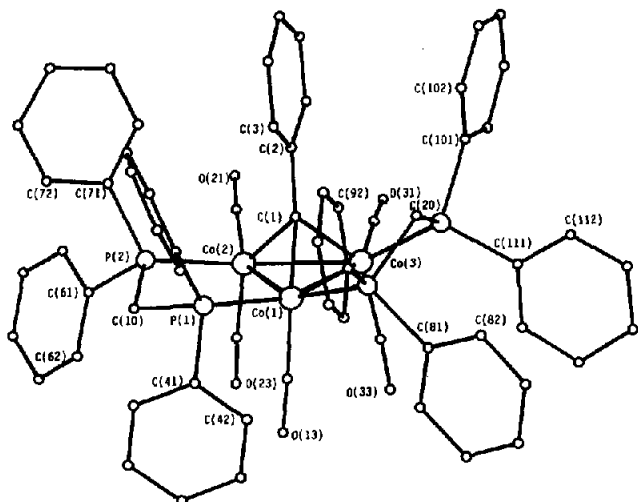


Fig. 2. Perspective view of  $\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2$  (**2**) showing the atom numbering scheme. For clarity the H atoms have been omitted and only the first two atoms of consecutively numbered phenyl rings have been labelled.

translate to an additional build-up of electron density on the cluster core which may be dissipated, at least partially, by the displacement of the capping C atom.

Compound **2** confirms the preference of the dppm ligand for the bridging coordination mode and the occupancy of equatorial sites on the  $\text{Co}_3$  triangle. Both dppm ligands are coordinated to the unique Co(1) atom and the ligands respectively bridge the Co(1)–Co(2) and Co(1)–Co(3) edges of the metal triangle. The remaining CO ligand on Co(1) is axially coordinated, while Co(2) and Co(3) each carry one equatorial and one axial CO ligand.

To our knowledge, the only previously reported structural determination on a  $\text{Co}_3\text{C}$  cluster with two bidentate phosphine substituents is for the molecule  $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$  [**5**]. This molecule exhibits unusual features in coordinating the phosphine ligands with one dmpe chelating a unique Co atom and the second adopting a singular bridging di-axial conformation. Differences in both the steric requirements of an ethane compared to a methane derivative and in the  $\sigma$ -donor ability of the dimethyl- *vs.* diphenyl-substituted phosphine ligands account for the considerable differences in the low energy conformations of these related molecular systems.

Despite the retention of bridging di-equatorial coordination with the second dppm substitution, the transition from mono- to bis-dppm substitution has significant implications for both the steric and electronic environment of the cluster moiety in **2**. Indeed, the minimum energy solid state structure of **2** represents a delicate balance of steric and electronic forces within the molecular unit. Hence, the dppm ligand coordi-

nated through P(1) and P(2) forms a six-membered ring [C(1)Co(1)P(1)C(10)P(2)Co(2)] with a distorted chair conformation in contrast to the more usual boat form found for the [C(1)Co(1)P(3)C(20)P(4)Co(3)] unit (Fig. 3(c)). This variation may serve to minimize the interaction between the phenyl rings of the phosphines and that of the apical substituent. Figure 2 shows that the P-bound rings C(51)–C(56), C(91)–C(96) and C(101)–C(106), and the C(2)–C(7) ring at the cluster apex adopt roughly parallel orientations which will minimize non-bonded interactions involving the apical group. This effect of achieving parallel ring configurations has been noted previously in derivatives of this cluster moiety [**2**]. The steric effect of additional substitution on the apical substituent is also signalled by the displacement of the C(2)–C(6) ring (inclination  $94.0(3)^\circ$ ) and the C(1)–C(2) bond (inclination  $97.6(7)^\circ$ ) with respect to the  $\text{Co}_3$  triangle. The net effect is to tilt the apical substituent towards the P(1)P(2) ligand. The adoption of a chair conformation in this chelate system should minimize steric interactions between the apical substituent and the methylene H atoms of the dppm ligand.

The electronic consequences of the substitution of four equatorial CO groups by P atoms are also manifest. Thus, the Co–C bonds of the remaining CO ligands in **2** are perceptibly shortened (mean Co–C  $1.76(1) \text{ \AA}$  *cf.*  $1.80(3) \text{ \AA}$  for **1**) and the C–O bonds lengthened (mean C–O  $1.16(1) \text{ \AA}$  *cf.*  $1.13(1) \text{ \AA}$  for **1**) in comparison with those for **1**. This is a predictable response to the increase in the electron density on the cluster core occasioned by substitution of the four equatorial CO groups with poorer  $\pi$ -acceptor ligands. The formation of carbonyl bridges is again precluded by the bridging bidentate ligands. The variation of the Co–C<sub>apical</sub> bond lengths in this molecule indicates a displacement of the apical C atom towards Co(1), the most highly substituted Co atom. This too would assist removal of the additional electron density via an increased interaction between the carbyne  $p_\pi$  orbital and an orbital of appropriate symmetry on Co(1) [**2**].

### 2.1. Structural analysis of **1** and **2**

Samples of both compounds were prepared from the cluster  $\text{PhCCo}_3(\text{CO})_9$  and dppm as described previously [**2**]. Crystals of **1** were grown as substantial needles from ethanol– $\text{CHCl}_3$ , while **2** crystallized as plates from hexane– $\text{CH}_2\text{Cl}_2$ . Precession photography (Cu  $K\alpha$  radiation) indicated a triclinic unit cell for **1** and a unique monoclinic cell for **2**. The structure of **1** was successfully solved in the centrosymmetric alternative  $P\bar{1}$  [**15**] with two unique molecules in the asymmetric unit. Data from both crystals were collected at low temperature on a Nicolet R3M fully automated diffrac-

TABLE 2. Selected bond lengths and angles for  $\text{PhCCo}_3(\text{CO})_5$  ( $\text{dppm}$ )<sub>2</sub>, 2

	Bond length (Å)		Bond length (Å)
Co(1)–Co(2)	2.464(3)	Co(2)–P(2)	2.180(5)
Co(1)–Co(3)	2.486(3)	P(2)–C(61)	1.84(2)
Co(2)–Co(3)	2.456(3)	P(2)–C(71)	1.84(2)
Co(1)–C(1)	1.91(1)	Co(2)–C(21)	1.76(2)
Co(2)–C(1)	1.95(1)	C(21)–O(21)	1.13(2)
Co(3)–C(1)	1.94(1)	Co(2)–C(23)	1.79(2)
C(1)–C(2)	1.47(2)	C(23)–O(23)	1.15(2)
C(2)–C(3)	1.38(2)	Co(1)–P(3)	2.199(5)
C(2)–C(7)	1.39(2)	P(3)–C(81)	1.84(1)
C(3)–C(4)	1.39(2)	P(3)–C(91)	1.83(2)
C(4)–C(5)	1.35(2)	P(3)–C(20)	1.84(1)
C(5)–C(6)	1.39(2)	C(20)–P(4)	1.83(1)
C(6)–C(7)	1.38(2)	Co(3)–P(4)	2.206(5)
Co(1)–C(13)	1.75(2)	P(4)–C(101)	1.85(2)
C(13)–O(13)	1.18(2)	P(4)–C(111)	1.83(2)
Co(1)–P(1)	2.211(5)	Co(3)–C(31)	1.75(2)
P(1)–C(41)	1.84(2)	C(31)–O(31)	1.17(2)
P(1)–C(51)	1.85(2)	Co(3)–C(33)	1.77(2)
P(1)–C(10)	1.85(1)	C(33)–O(33)	1.16(2)
C(10)–P(2)	1.84(1)	Cl(1)–C(120)	2.47(3)
		C(120)–Cl(2)	2.17(4)

	Bond angle (°)		Bond angle (°)
Co(2)–Co(1)–Co(3)	59.5(1)	C(1)–Co(3)–C(33)	141.0(6)
Co(2)–Co(1)–C(1)	50.9(4)	P(4)–Co(3)–C(31)	100.0(5)
Co(2)–Co(1)–P(1)	100.4(1)	P(4)–Co(3)–C(33)	110.1(5)
Co(2)–Co(1)–P(3)	147.9(1)	C(31)–Co(3)–C(33)	97.7(7)
Co(2)–Co(1)–C(13)	92.2(5)	Co(1)–C(1)–Co(2)	79.5(5)
Co(3)–Co(1)–C(1)	50.3(4)	Co(1)–C(1)–Co(3)	80.5(5)
Co(3)–Co(1)–P(1)	157.9(1)	Co(1)–C(1)–C(2)	140(1)
Co(3)–Co(1)–P(3)	93.1(1)	Co(2)–C(1)–Co(3)	78.4(5)
Co(3)–Co(1)–C(13)	97.0(5)	Co(2)–C(1)–C(2)	126(1)
C(1)–Co(1)–P(1)	110.9(4)	Co(3)–C(1)–C(2)	128(1)
C(1)–Co(1)–P(3)	99.5(4)	Co(1)–P(1)–C(41)	113.6(5)
C(1)–Co(1)–C(13)	138.2(7)	Co(1)–P(1)–C(51)	128.9(5)
P(1)–Co(1)–P(3)	102.7(2)	Co(1)–P(1)–C(10)	107.6(5)
P(1)–Co(1)–C(13)	92.6(5)	C(41)–P(1)–C(51)	99.9(7)
P(3)–Co(1)–C(13)	108.6(5)	C(41)–P(1)–C(10)	100.3(6)
Co(1)–Co(2)–Co(3)	60.7(1)	C(51)–P(1)–C(10)	102.7(7)
Co(1)–Co(2)–C(1)	49.5(4)	P(1)–C(10)–P(2)	112.7(7)
Co(1)–Co(2)–P(2)	95.4(1)	Co(2)–P(2)–C(10)	112.1(5)
Co(1)–Co(2)–C(21)	152.0(5)	Co(2)–P(2)–C(61)	111.8(5)
Co(1)–Co(2)–C(23)	102.1(5)	Co(2)–P(2)–C(71)	121.4(5)
Co(3)–Co(2)–C(1)	50.7(4)	C(10)–P(2)–C(61)	105.1(7)
Co(3)–Co(2)–P(2)	153.6(2)	C(10)–P(2)–C(71)	104.7(7)
Co(3)–Co(2)–C(21)	99.4(5)	C(61)–P(2)–C(71)	100.0(7)
Co(3)–Co(2)–C(23)	98.5(5)	Co(1)–P(3)–C(81)	120.7(5)
C(1)–Co(2)–P(2)	106.1(4)	Co(1)–P(3)–C(91)	121.0(5)
C(1)–Co(2)–C(21)	103.0(7)	Co(1)–P(3)–C(20)	110.1(5)
C(1)–Co(2)–C(23)	143.9(7)	C(81)–P(3)–C(91)	99.6(7)
P(2)–Co(2)–C(21)	98.3(5)	C(81)–P(3)–C(20)	102.1(7)
P(2)–Co(2)–C(23)	97.3(6)	C(91)–P(3)–C(20)	100.2(7)
C(21)–Co(2)–C(23)	100.2(7)	P(3)–C(20)–P(4)	107.8(7)
Co(1)–Co(3)–Co(2)	59.8(1)	Co(3)–P(4)–C(20)	110.0(5)
Co(1)–Co(3)–C(1)	49.1(4)	Co(3)–P(4)–C(101)	116.1(5)
Co(1)–Co(3)–P(4)	98.5(1)	Co(3)–P(4)–C(111)	121.5(5)
Co(1)–Co(3)–C(31)	151.8(5)	C(20)–P(4)–C(101)	101.8(7)
Co(1)–Co(3)–C(33)	95.7(5)	C(20)–P(4)–C(111)	102.2(7)

TABLE 2 (continued)

	Bond angle (°)		Bond angle (°)
Co(2)–Co(3)–C(1)	50.9(4)	C(101)–P(4)–C(111)	102.6(7)
Co(2)–Co(3)–P(4)	144.6(2)	Co(1)–C(13)–O(13)	176(1)
Co(2)–Co(3)–C(31)	93.3(5)	Co(2)–C(21)–O(21)	176(2)
Co(2)–Co(3)–C(33)	100.2(5)	Co(2)–C(23)–O(23)	174(2)
C(1)–Co(3)–P(4)	93.7(4)	Co(3)–C(31)–O(31)	173(1)
C(1)–Co(3)–C(31)	108.3(7)	Co(3)–C(33)–O(33)	174(1)

tometer. Details of the crystal data collection and structure refinements are summarized in Table 4. Lorentz and polarization corrections were applied using the SHELXTL system [16] with analytical absorption corrections applied in SHELX-76 [17].

Both structures were solved by direct methods using the *EEES* option of SHELX-76. In each case, the optimum E-map revealed the  $\text{Co}_3$  triangles and the position of the ligated P atoms. The remaining non-hydrogen atoms were found in subsequent difference Fourier

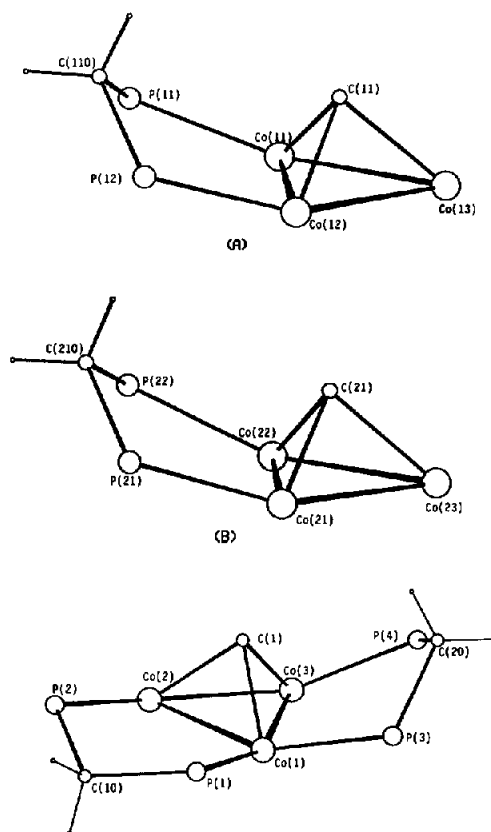


Fig. 3. Views of the detailed coordination geometry of the *dppm* ligand in compounds 1 and 2. All the carbonyl ligands and phenyl rings have been omitted: (A) for molecule 1 of 1; (B) for molecule 2 of 1; (C) for 2.

TABLE 3. Deformation of the cluster core in  $\text{RCCo}_3(\text{CO})_7(\text{L-L})$  complexes

Cluster		Co–Co	Mean Co–Co	$\text{C}_{\text{apical}}\text{–Co}$	Mean $\text{C}_{\text{apical}}\text{–Co}$	Reference
R	L-L	P-bridged	unbridged	unsubstituted	substituted	
Cl	dppm	2.492(1)	2.486(3)	1.901(5)	1.858(1)	[4]
Me	dppm	2.490(3)	2.472	1.945(3)	1.85(3)	[2]
Me	dppm	2.486(1)	2.468	1.954(1)	1.87(1)	[3]
Ph <sup>a</sup>	dppm	2.470(1)	2.472(2)	1.938(7)	1.884(7)	This work
Ph <sup>a</sup>	dppm	2.472(1)	2.477(5)	1.939(7)	1.90(1)	This work
Ph	dppm	2.481(3)	2.474(2)	1.99(1)	1.90(1)	[6]

<sup>a</sup> One of two unique molecules in the unit cell.

TABLE 4. Crystal data, data collection and refinement of compounds 1 and 2

	$\text{PhCCo}_3(\text{CO})_7\text{dppm}$ (1)	$\text{PhCCo}_3(\text{CO})_5(\text{dppm})_2 \cdot \text{CH}_2\text{Cl}_2$ (2)
Empirical formula	$\text{C}_{39}\text{H}_{27}\text{O}_7\text{P}_2\text{Co}_3$	$\text{C}_{63}\text{H}_{51}\text{O}_5\text{P}_4\text{Cl}_2\text{Co}_3$
M (g mol <sup>-1</sup> )	846.4	1259.7
Crystal system	Triclinic	Monoclinic
Space group <sup>a</sup>	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14) <sup>b</sup>
a (Å)	12.832(2)	13.150(3)
b (Å)	14.933(4)	26.374(17)
c (Å)	19.249(4)	17.143(8)
$\alpha$ (°)	77.53(2)	90
$\beta$ (°)	89.07(2)	107.23(3)
$\gamma$ (°)	88.34(2)	90
V (Å <sup>3</sup> )	3600(1)	5682(5)
$D_c(D_m)$ (g cm <sup>-3</sup> )	1.56(1.58)	1.47
Z	4 <sup>c</sup>	4
Crystal size (mm)	0.88 × 0.28 × 0.24	0.62 × 0.30 × 0.12
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	15.0	17.4
F(000)	1712	2576
Diffractometer	Nicolet R3M	Nicolet R3M
Temperature (K)	123(5)	123(5)
Radiation	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)
Scan type	( $\theta - 2\theta$ )	( $\theta - 2\theta$ )
Scan speed (deg min <sup>-1</sup> )	4.88	4.88
Data limits (°)	3 < 2 $\theta$ < 45	4 < 2 $\theta$ < 40
Reflections measured	$h, \pm k, \pm l$	$h, k, \pm l$
Crystal decay <sup>d</sup>	< 4%	< 2%
Absorption correction	Analytical	Analytical
Transmission	0.881 (maximum) 0.646 (minimum)	0.940 (maximum) 0.839 (minimum)
Total reflections <sup>e</sup>	10302	5777
Unique data ( $I > 2\sigma I$ )	7405	3111
Method of solving	Direct	Direct
Number of variables	463 <sup>f</sup>	396
Treatment of protons	Calculated	Calculated
$R(\Sigma \Delta F / \Sigma  F_o )$	0.0600	0.0759
$R_w[\Sigma w^{1/2}(\Delta F) / \Sigma w^{1/2}F_o]$	0.0738	0.0818
Weight (w)	$[2.6846 / (\sigma^2 F + 0.000777 F^2)]$	$[1.5175 / (\sigma^2 F + 0.001121 F^2)]$
Residual density (e Å <sup>-3</sup> )	1.06	1.02

<sup>a</sup> After ref. 15. <sup>b</sup> A non-standard setting of  $P2_1/n$ . <sup>c</sup> Two unique molecules in the asymmetric unit. <sup>d</sup> Standard reflections (600)(080)(0010) for 1 and (-424)(060)(202) for 2 measured after every 100 reflections. <sup>e</sup> Lorentz and polarization corrections and empirical absorption corrections were applied using the SHELXTL system. <sup>f</sup> Individual molecules refined in alternating blocked matrix cycles.

TABLE 5. Final positional and equivalent thermal parameters for  $\text{PhCCo}_3(\text{CO})_7\text{dppm}$  (1)

Atom	x	y	z	$U_{\text{eq}}/U_{11}$
<i>Molecule 1</i>				
Co(11)	0.1616(1)	0.8224(1)	-0.0019(0)	0.019
Co(12)	0.2385(1)	0.6859(1)	0.0786(0)	0.021
Co(13)	0.0981(1)	0.6680(1)	-0.0029(1)	0.025
C(11)	0.2356(5)	0.7188(4)	-0.0211(4)	0.023
C(12)	0.3104(6)	0.7056(5)	-0.0791(4)	0.027
C(13)	0.4113(6)	0.6744(5)	-0.0635(4)	0.025
C(14)	0.4838(6)	0.6691(5)	-0.1165(5)	0.039
C(15)	0.4554(7)	0.6939(5)	-0.1874(4)	0.045
C(16)	0.3535(8)	0.7215(6)	-0.2036(4)	0.051
C(17)	0.2812(7)	0.7269(6)	-0.1506(4)	0.043
P(11)	0.2886(1)	0.9183(1)	-0.0005(1)	0.020
C(141)	0.2749(5)	1.0086(4)	0.0501(3)	0.022
C(142)	0.1801(7)	1.0527(5)	0.0507(4)	0.037
C(143)	0.1677(8)	1.1288(6)	0.0809(5)	0.057
C(144)	0.2530(8)	1.1572(6)	0.1136(5)	0.052
C(145)	0.3455(7)	1.1126(5)	0.1143(4)	0.040
C(146)	0.3582(6)	1.0391(5)	0.0825(4)	0.030
C(151)	0.3205(5)	0.9847(5)	-0.0894(4)	0.024
C(152)	0.3647(6)	0.9418(6)	-0.1400(4)	0.035
C(153)	0.3707(7)	0.9883(6)	-0.2104(4)	0.046
C(154)	0.3318(7)	1.0772(6)	-0.2320(4)	0.046
C(155)	0.2904(8)	1.1210(6)	-0.1814(4)	0.047
C(156)	0.2846(7)	1.0768(5)	-0.1103(4)	0.037
C(110)	0.4047(3)	0.8534(3)	0.0297(2)	0.020
P(12)	0.3756(1)	0.7574(1)	0.1043(1)	0.020
C(161)	0.4970(5)	0.6887(5)	0.1153(4)	0.022
C(162)	0.5004(6)	0.6085(5)	0.1672(4)	0.029
C(163)	0.5840(6)	0.5471(6)	0.1726(4)	0.037
C(164)	0.6652(7)	0.5659(7)	0.1244(5)	0.051
C(165)	0.6656(6)	0.6471(6)	0.0745(4)	0.041
C(166)	0.5818(6)	0.7084(5)	0.0695(4)	0.033
C(171)	0.3638(5)	0.8047(4)	0.1839(3)	0.021
C(172)	0.2720(6)	0.8523(5)	0.1969(4)	0.024
C(173)	0.2623(6)	0.8916(5)	0.2549(4)	0.027
C(174)	0.3413(6)	0.8816(5)	0.3034(4)	0.028
C(175)	0.4303(6)	0.8323(5)	0.2930(4)	0.037
C(176)	0.4428(6)	0.7962(5)	0.2332(4)	0.030
C(112)	0.1182(6)	0.8767(5)	-0.0882(4)	0.029
O(112)	0.0908(5)	0.9094(4)	-0.1443(3)	0.044
C(113)	0.0651(6)	0.8547(5)	0.0587(4)	0.027
O(113)	0.0024(4)	0.8720(4)	0.0960(3)	0.039
C(122)	0.2928(6)	0.5729(5)	0.0939(4)	0.036
O(122)	0.3227(5)	0.4995(4)	0.1035(4)	0.065
C(123)	0.1616(6)	0.6800(5)	0.1587(4)	0.025
O(123)	0.1118(4)	0.6750(4)	0.2082(3)	0.037
C(131)	0.1262(6)	0.5501(6)	0.0003(4)	0.033
O(131)	0.1440(5)	0.4749(4)	0.0008(4)	0.061
C(132)	0.0347(7)	0.6939(5)	-0.0873(5)	0.037
O(132)	-0.0062(5)	0.7077(4)	-0.1411(3)	0.058
C(133)	-0.0107(7)	0.6681(5)	0.0598(4)	0.033
O(133)	-0.0790(5)	0.6687(4)	0.0977(3)	0.049
<i>Molecule 2</i>				
Co(21)	0.2547(1)	0.1619(1)	0.4678(0)	0.018
Co(22)	0.2887(1)	0.3079(1)	0.3829(0)	0.019
Co(23)	0.4337(1)	0.1963(1)	0.4207(0)	0.021
C(21)	0.3408(5)	0.2591(4)	0.4761(3)	0.018
C(22)	0.3687(5)	0.3014(4)	0.5349(4)	0.022
C(23)	0.4486(6)	0.3654(5)	0.5278(4)	0.025

TABLE 5 (continued)

Atom	x	y	z	$U_{\text{eq}}/U_{11}$
<i>Molecule 2</i>				
C(24)	0.4711(6)	0.4084(5)	0.5817(4)	0.031
C(25)	0.4152(6)	0.3902(5)	0.6456(4)	0.026
C(26)	0.3384(6)	0.3248(5)	0.6550(4)	0.026
C(27)	0.3174(6)	0.2812(4)	0.6011(3)	0.021
P(21)	0.1020(1)	0.2074(1)	0.5031(1)	0.020
C(241)	-0.0141(6)	0.1854(4)	0.4557(4)	0.023
C(242)	-0.0113(6)	0.2024(5)	0.3810(4)	0.029
C(243)	-0.0995(6)	0.1919(5)	0.3446(4)	0.034
C(244)	-0.1896(7)	0.1610(5)	0.3797(4)	0.037
C(245)	-0.1922(6)	0.1417(5)	0.4522(4)	0.037
C(246)	-0.1048(6)	0.1553(5)	0.4906(4)	0.029
C(251)	0.0673(5)	0.1629(5)	0.5961(4)	0.022
C(252)	0.0653(6)	0.0681(5)	0.6210(4)	0.025
C(253)	0.0455(6)	0.0310(5)	0.6922(4)	0.030
C(254)	0.0289(6)	0.0876(6)	0.7396(4)	0.037
C(255)	0.0309(6)	0.1817(5)	0.7161(4)	0.035
C(256)	0.0499(6)	0.2192(5)	0.6449(4)	0.026
C(210)	0.0960(5)	0.3326(4)	0.4948(3)	0.021
P(22)	0.1568(1)	0.3902(1)	0.4113(1)	0.020
C(261)	0.1893(6)	0.5016(4)	0.4286(4)	0.024
C(262)	0.1820(7)	0.5790(5)	0.3738(4)	0.040
C(263)	0.2172(7)	0.6626(5)	0.3829(5)	0.048
C(264)	0.2569(6)	0.6705(5)	0.4464(5)	0.038
C(265)	0.2665(6)	0.5948(5)	0.5006(4)	0.035
C(266)	0.2333(6)	0.5107(5)	0.4917(4)	0.029
C(271)	0.0498(6)	0.4239(5)	0.3481(4)	0.032
C(272)	-0.0472(7)	0.4472(7)	0.3693(5)	0.055
C(273)	-0.1251(9)	0.4760(9)	0.3216(7)	0.096
C(274)	-0.103(1)	0.4879(8)	0.2484(7)	0.090
C(275)	-0.0066(9)	0.4667(6)	0.2261(5)	0.061
C(276)	0.0712(7)	0.4346(5)	0.2756(4)	0.038
C(212)	0.2935(5)	0.0839(5)	0.5474(4)	0.027
O(212)	0.3229(4)	0.0354(4)	0.5979(3)	0.034
C(213)	0.2126(6)	0.0856(5)	0.4128(4)	0.026
O(213)	0.1888(4)	0.0360(4)	0.3784(3)	0.038
C(222)	0.3606(6)	0.4044(5)	0.3424(4)	0.029
O(222)	0.4064(5)	0.4674(4)	0.3157(3)	0.044
C(223)	0.2461(6)	0.2668(5)	0.3074(4)	0.028
O(223)	0.2220(5)	0.2383(4)	0.2599(3)	0.048
C(231)	0.5334(6)	0.2758(5)	0.3880(4)	0.026
O(231)	0.5973(4)	0.3256(4)	0.3673(3)	0.035
C(232)	0.5046(6)	0.1260(5)	0.4918(4)	0.031
O(232)	0.5528(4)	0.0828(4)	0.5372(3)	0.043
C(233)	0.4274(6)	0.1272(6)	0.3491(5)	0.043
O(233)	0.4245(5)	0.0891(4)	0.3067(3)	0.015

least-squares refinement cycles. Refinement-minimizing  $\sum w(|F_o| - |F_c|)^2$  was performed using a version of SHELX-76 amended for the refinement of large structures [18]. A difference Fourier synthesis for **2**, following the location of all the anticipated non-hydrogen atoms, showed high peaks consistent with the presence of a  $\text{CH}_2\text{Cl}_2$  solvate molecule and inclusion of the C and Cl atoms significantly improved the overall model for the structure. H atoms were included in the refinements as fixed contributions to  $F_c$ . For **1** the two unique molecules in the asymmetric unit were refined



TABLE 6. Final positional and equivalent thermal parameters for  $\text{PhCCo}_3(\text{CO})_9(\text{dppm})_2$  (2)

Atom	x	y	z	$U_{\text{eq}}/U_{11}$
Co(1)	0.1885(2)	0.2081(1)	0.3202(1)	0.019
Co(2)	0.2754(2)	0.1243(1)	0.3404(1)	0.021
Co(3)	0.3128(2)	0.1837(1)	0.2420(1)	0.021
C(1)	0.178(1)	0.1546(5)	0.2434(8)	0.015(4)
C(2)	0.098(1)	0.1279(5)	0.1778(8)	0.020(4)
C(3)	-0.010(1)	0.1371(6)	0.1629(9)	0.025(4)
C(4)	-0.086(1)	0.1113(6)	0.102(1)	0.037(5)
C(5)	-0.056(2)	0.0758(7)	0.056(1)	0.051(6)
C(6)	0.052(1)	0.0672(7)	0.069(1)	0.047(5)
C(7)	0.128(1)	0.0930(6)	0.1285(9)	0.031(4)
P(1)	0.0720(3)	0.1977(1)	0.3891(2)	0.020
C(41)	0.078(1)	0.2475(6)	0.4657(8)	0.021(4)
C(42)	0.116(1)	0.2944(5)	0.4569(9)	0.020(4)
C(43)	0.120(1)	0.3323(6)	0.5137(9)	0.026(4)
C(44)	0.086(1)	0.3242(6)	0.5807(9)	0.028(4)
C(45)	0.047(1)	0.2769(6)	0.5913(9)	0.031(5)
C(46)	0.039(1)	0.2389(6)	0.5333(8)	0.022(4)
C(51)	-0.074(1)	0.1890(5)	0.3497(8)	0.020(4)
C(52)	-0.142(1)	0.2284(5)	0.3541(8)	0.017(4)
C(53)	-0.254(1)	0.2210(5)	0.3259(8)	0.020(4)
C(54)	-0.295(1)	0.1751(6)	0.2931(9)	0.033(5)
C(55)	-0.226(1)	0.1361(6)	0.2882(9)	0.026(4)
C(56)	-0.116(1)	0.1431(6)	0.3162(8)	0.024(4)
C(10)	0.115(1)	0.1421(5)	0.4565(8)	0.014
P(2)	0.1766(3)	0.0925(2)	0.4103(2)	0.024
C(61)	0.255(1)	0.0540(6)	0.4967(9)	0.025(4)
C(62)	0.313(1)	0.0752(7)	0.570(1)	0.038(5)
C(63)	0.380(1)	0.0459(6)	0.629(1)	0.037(5)
C(64)	0.391(1)	-0.0058(6)	0.615(1)	0.042(5)
C(65)	0.337(1)	-0.0286(7)	0.543(1)	0.042(5)
C(66)	0.269(1)	0.0027(6)	0.4838(9)	0.028(4)
C(71)	0.068(1)	0.0480(5)	0.3638(9)	0.023(4)
C(72)	-0.004(1)	0.0319(6)	0.406(1)	0.034(5)
C(73)	-0.087(1)	0.0014(6)	0.372(1)	0.036(5)
C(74)	-0.102(1)	-0.0159(6)	0.293(1)	0.038(5)
C(75)	-0.031(1)	-0.0015(6)	0.250(1)	0.029(4)
C(76)	0.052(1)	0.0298(5)	0.2846(9)	0.021(4)
P(3)	0.1181(3)	0.2701(2)	0.2358(2)	0.021
C(81)	0.184(1)	0.3324(5)	0.2454(8)	0.014(4)
C(82)	0.146(1)	0.3691(6)	0.1847(9)	0.029(4)
C(83)	0.195(1)	0.4162(6)	0.1941(9)	0.030(4)
C(84)	0.275(1)	0.4283(6)	0.261(1)	0.036(5)
C(85)	0.313(1)	0.3932(6)	0.322(1)	0.033(5)
C(86)	0.266(1)	0.3439(6)	0.314(1)	0.035(5)
C(91)	-0.019(1)	0.2905(6)	0.2215(9)	0.022(4)
C(92)	-0.103(1)	0.2676(6)	0.1668(9)	0.030(4)
C(93)	-0.207(1)	0.2818(6)	0.155(1)	0.041(5)
C(94)	-0.229(1)	0.3217(6)	0.201(1)	0.042(5)
C(95)	-0.145(1)	0.3477(6)	0.2561(9)	0.035(5)
C(96)	-0.041(1)	0.3318(6)	0.2662(9)	0.031(5)
C(20)	0.110(1)	0.2520(5)	0.1306(8)	0.017
P(4)	0.2411(3)	0.2286(2)	0.1307(2)	0.023
C(101)	0.209(1)	0.1934(5)	0.0329(9)	0.022(4)
C(102)	0.109(1)	0.1868(6)	-0.0197(9)	0.036(5)
C(103)	0.095(1)	0.1577(5)	-0.0894(9)	0.028(4)
C(104)	0.176(1)	0.1358(6)	-0.109(1)	0.040(5)
C(105)	0.277(1)	0.1418(7)	-0.056(1)	0.046(5)
C(106)	0.295(1)	0.1706(6)	0.014(1)	0.036(5)
C(111)	0.305(1)	0.2860(5)	0.1079(9)	0.019(4)
C(112)	0.270(1)	0.3090(5)	0.0326(9)	0.023(4)

TABLE 6 (continued)

Atom	x	y	z	$U_{\text{eq}}/U_{11}$
C(113)	0.311(1)	0.3543(6)	0.0162(9)	0.030(4)
C(114)	0.390(1)	0.3780(6)	0.0753(9)	0.031(5)
C(115)	0.428(1)	0.3556(6)	0.155(1)	0.035(5)
C(116)	0.384(1)	0.3092(6)	0.1687(9)	0.026(4)
C(13)	0.284(1)	0.2335(6)	0.405(1)	0.025(4)
O(13)	0.3505(8)	0.2483(4)	0.4630(6)	0.028
C(21)	0.313(1)	0.0672(6)	0.303(1)	0.028(5)
O(21)	0.3412(9)	0.0317(4)	0.2788(7)	0.045
C(23)	0.392(2)	0.1360(6)	0.425(1)	0.035(5)
O(23)	0.4706(9)	0.1430(4)	0.4747(7)	0.046
C(31)	0.382(1)	0.1383(6)	0.2031(9)	0.027(4)
O(31)	0.4366(9)	0.1097(4)	0.1818(7)	0.050
C(33)	0.425(1)	0.2159(6)	0.306(1)	0.026(4)
O(33)	0.5014(9)	0.2332(4)	0.3500(7)	0.041
Cl(1)	0.678(1)	0.0061(6)	0.954(2)	0.417
C(120)	0.502(2)	0.0420(5)	0.8831(7)	0.295
Cl(2)	0.377(4)	0.985(1)	0.848(2)	0.155

independently in alternating least-squares cycles with all the non-hydrogen atoms assigned anisotropic temperature factors. The data set obtained for 2 limited anisotropic refinement to the Co, P and carbonyl O atoms together with the C and Cl atoms of the  $\text{CH}_2\text{Cl}_2$  solvate.

Final positional and thermal parameters are given for 1 in Table 5 and for 2 in Table 6. A full listing of the bond lengths and angles, thermal parameters of the non-hydrogen atoms, positional and thermal parameters for the calculated H atoms, observed and calculated structure factors and mean plane data for both molecules are available from the authors (JS).

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