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# $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$; A molecule with a symmetrical formula but an unsymmetrical structure

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## Abstract

The diphosphazane ligand $(CH_2O)_2PN(Et)P(OCH_2)_2$ reacts readily with $[Co_2(CO)_8]$ to form the red-black complex $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$. A single crystal X-ray diffraction study of this complex shows the two cobalt atoms linked by a metal–metal bond of length 2.635(2) Å, and by two bridging diphosphazane ligands. Both cobalt atoms are five-coordinate with an identical set of ligands, comprising the other cobalt atom, two carbonyl groups and two phosphorus donor atoms. However, one cobalt atom has near trigonal-bipyramidal coordination while the other has highly distorted square-pyramidal coordination, the apical positions in both cases being occupied by phosphorus atoms. Significantly, the different coordination at each cobalt atom is achieved by the twisting of each diphosphazane ligand about the Co–Co bond; the Co–P–P–Co torsion angles are 29 and 40 °. Indeed, in solution, rapid twisting of the diphosphazane ligands renders the phosphorus atoms equivalent on the NMR time scale, as evidenced by a single peak in the $^{31}P\{^1H\}$ NMR spectrum of the molecule. The solution and solid state structures of the title compound are compared with those previously reported for the closely-related complex $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$.

## Introduction

Diphosphazane ligands of the type $R_2PN(R')PR_2$ (R = alkyl, aryl, alkoxy, aryloxy group, etc., R′ = alkyl group) in which the two donor phosphorus atoms are linked through a single atom are excellent bridging ligands. Thus, we are making use of ligands of this type to stabilise a variety of di-, tri- and poly-nuclear organometallic compounds to fragmentation [1], in much the same way as the ubiquitous dppm ligand is being used [2]. Of relevance here are the diphosphazane ligand derivatives of $[Co_2(CO)_8]$ that have been synthesised [3–5], those of stoichiometry

$[Co_2(CO)_4\{R_2PN(R')PR_2\}_2]$ being of particular interest [4,5]. The crystal and molecular structures of one such compound viz. $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, has been determined [4] and found to be most unusual, in that the two cobalt atoms have different coordination geometries despite having identical sets of ligands. It was therefore of interest to us to ascertain whether this structure is an inherent property of the complex or whether, as has been suggested [4], the unusual structure in the solid state is a consequence of crystal packing effects. For this reason a new diphosphazane ligand of relatively small size viz. $(CH_2O)_2PN(Et)P(OCH_2)_2$ has been synthesised and reacted with $[Co_2(CO)_8]$ to give the closely related compound $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$, whose structure was then determined. The results of this investigation are reported here.

## Results and discussion

Initial attempts to synthesise the $(CH_2O)_2PN(Et)P(OCH_2)_2$ ligand employed a conventional route involving reaction of $Cl_2PN(Et)PCl_2$ with ethylene glycol in the presence of excess triethylamine [4,6]. Unfortunately, this procedure resulted in the formation of an oil from which the pure ligand could not be isolated. The successful route used is based on the following reaction, and involves prior formation of 2-chloro-1,3,2-dioxaphospholane [7]:

$$2(CH_2O)_2PCl + 3EtNH_2 \rightarrow (CH_2O)_2PN(Et)P(OCH_2)_2 + 2[EtNH_3]Cl$$

The ligand was isolated as a colourless crystalline and extremely hygroscopic solid, which was characterised by its $^1H$ NMR and mass spectra. The preparation of $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ by reaction of the ligand with $[Co_2(CO)_8]$ has been described [5].

### *Molecular structure of* $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ *(I)*

Crystals of $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ (I) comprise discrete molecules separated by normal intermolecular contact distances, shortest values of various types being C...C 3.54, C...O 3.24 and O...O 3.19 Å. Figure 1 gives a perspective view of the molecule and shows the atom labelling scheme. Table 1 summarises the interatomic distances and those angles not centred on the cobalt atom; the latter are given in Table 3.

The X-ray diffraction analysis confirms a dinuclear structure for I in which the two cobalt atoms are linked by a metal–metal bond and by two bridging diphosphazane ligands (see Fig. 1). The Co(1)–Co(2) distance of 2.635(2) Å corresponds to a single Co–Co bond and may be compared to the value observed in $[Co_2(CO)_8]$, 2.525 Å [8]. Interestingly, it is significantly shorter than the value of 2.698(1) Å found in the closely-related complex $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (II) [4]. The $(CH_2O)_2PN(Et)P(OCH_2)_2$ ligand is a slightly weaker donor than the $(MeO)_2PN(Et)P(OMe)_2$ ligand, as indicated by a comparison of the positions of the $\nu(CO)$ stretching frequencies in the infrared spectra of I [5] and II [4], and this could account for the shorter Co–Co distance in I. At the same time the "tied-back" $(CH_2O)_2PN(Et)P(OCH_2)_2$ ligand is smaller in size than the tetramethoxydiphosphazane ligand, and this could have the effect of shortening the Co–Co bond length through a reduction in steric repulsions within the complex. Thus, it is not clear whether electronic or steric effects (or both) are responsible for the

Table 1

Selected interatomic distances (Å) and angles (°) for $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.635(2) | Co(1)–P(1) | 2.153(4) |
| Co(1)–P(4) | 2.123(4) | Co(2)–P(2) | 2.162(4) |
| Co(2)–P(3) | 2.115(4) | P(1)–N(1) | 1.69(1) |
| P(1)–O(5) | 1.61(1) | P(1)–O(6) | 1.64(1) |
| P(2)–N(1) | 1.68(1) | P(2)–O(7) | 1.60(1) |
| P(2)–O(8) | 1.60(1) | P(3)–N(2) | 1.67(1) |
| P(3)–O(9) | 1.61(1) | P(3)–O(10) | 1.61(1) |
| P(4)–N(2) | 1.70(1) | P(4)–O(11) | 1.64(1) |
| P(4)–O(12) | 1.62(1) | O(5)–C(5) | 1.44(2) |
| O(6)–C(6) | 1.46(2) | O(7)–C(7) | 1.45(2) |
| O(8)–C(8) | 1.52(2) | O(9)–C(9) | 1.43(2) |
| O(10)–C(10) | 1.48(2) | O(11)–C(11) | 1.44(2) |
| O(12)–C(12) | 1.46(2) | N(1)–C(13) | 1.48(2) |
| N(2)–C(15) | 1.50(2) | | |
| Co(1)–P(1)–O(5) | 116.1(4) | Co(1)–P(1)–O(6) | 123.9(4) |
| Co(1)–P(1)–N(1) | 114.4(4) | O(5)–P(1)–O(6) | 94.5(5) |
| O(5)–P(1)–N(1) | 102.5(5) | O(6)–P(1)–N(1) | 101.8(5) |
| Co(2)–P(2)–O(7) | 118.2(4) | Co(2)–P(2)–O(8) | 114.2(4) |
| Co(2)–P(2)–N(1) | 114.6(4) | O(7)–P(2)–O(8) | 96.9(5) |
| O(7)–P(2)–N(1) | 107.7(6) | O(8)–P(2)–N(1) | 102.9(5) |
| Co(2)–P(3)–O(9) | 112.7(4) | Co(2)–P(3)–O(10) | 117.8(4) |
| Co(2)–P(3)–N(2) | 118.9(4) | O(9)–P(3)–O(10) | 95.3(4) |
| O(9)–P(3)–N(2) | 103.1(5) | O(10)–P(3)–N(2) | 105.7(5) |
| Co(1)–P(4)–O(11) | 118.5(3) | Co(1)–P(4)–O(12) | 121.9(4) |
| Co(1)–P(4)–N(2) | 113.0(4) | O(11)–P(4)–O(12) | 94.4(5) |
| O(11)–P(4)–N(2) | 102.4(5) | O(12)–P(4)–N(2) | 103.4(5) |
| P(1)–O(5)–C(5) | 114 (1) | P(1)–O(6)–C(6) | 111 (1) |
| P(2)–O(7)–C(7) | 116 (1) | P(2)–O(8)–C(8) | 112 (1) |
| P(3)–O(9)–C(9) | 114 (1) | P(3)–O(10)–C(10) | 110 (1) |
| P(4)–O(11)–C(11) | 114 (1) | P(4)–O(12)–C(12) | 116 (1) |
| P(1)–N(1)–P(2) | 110.9(6) | P(1)–N(1)–C(13) | 124.9(9) |
| P(2)–N(1)–C(13) | 125.1(9) | P(3)–N(2)–P(4) | 113.9(6) |
| P(3)–N(2)–C(15) | 122.8(8) | P(4)–N(2)–C(15) | 123.2(8) |

variations in Co–Co distances in these and other [3,9] dicobalt complexes of bridging diphosphazane ligands.

The atoms of the $Co_2(CO)_4$ moiety are nearly coplanar (see Table 2) and, moreover, the best least-squares plane through the atoms of the $Co_2(CO)_4$ group is

Table 2

Least-squares best plane through the $Co_2(CO)_4$ group and deviations (Å) of the atoms from the plane

Equation[a]: $0.5146x + 6.6809y + 10.9801z = 4.4514$ Å

| | | | |
|---|---|---|---|
| Co(1) | −0.207 | Co(2) | −0.013 |
| C(1) | 0.035 | C(3) | 0.006 |
| C(2) | −0.193 | C(4) | 0.126 |
| O(1) | 0.304 | O(3) | −0.023 |
| O(2) | −0.241 | O(4) | 0.205 |

[a] The variables $x$, $y$ and $z$ are fractional coordinates.

an approximate mirror plane for the molecule. As has been noted previously [4] a planar $M_2(CO)_4$ group seems to be an inherent structural feature of compounds in which two metal atoms are bridged by two ligands e.g. the $Co_2(CO)_4$ group in II [4] as well as the $Fe_2(CO)_4$ group in $[Fe_2(CO)_4\{(Me)_3CC{\equiv}CC(Me)_3\}_2]$ [10] are nearly planar. It is also significant that the carbonyl ligands of the $Co_2(CO)_4$ group in I are not all terminal; one, C(2)–O(2), is borderline semi-bridging (see Fig. 1). That this is the case, is indicated by calculation of the ratio of the Co(2)–C(2) distance of 2.66 Å to the Co(1)–C(2) distance of 1.68(1) Å i.e. 1.58. This value is just below the value of 1.60 that has, for practical purposes, been taken as the boundary value to distinguish between terminal and semi-bridging carbonyls [11]. A borderline semi-bridging carbonyl was also observed in II [4] and thus it also appears to be an inherent structural feature of molecules of this type. Brown and coworkers have suggested [4] that intramolecular non-bonded repulsions are responsible for the presence of a semi-bridging carbonyl in II. This is probably also the case in I, despite the smaller size of the $(CH_2O)_2PN(Et)P(OCH_2)_2$ ligand.

Table 3

Bond angles (°) at the cobalt atoms in $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$

| | | | |
|---|---|---|---|
| Angles referred to a square-pyramid of minimum repulsion [a] | | | |
| Apical–basal angles (ideal angle 104°) | | | |
| P(4)–Co(1)–P(1) | 103.9(1) | C(4)–Co(2)–Co(1) | 119.7(5) |
| P(4)–Co(1)–C(1) | 103.9(5) | C(4)–Co(2)–C(3) | 121.8(6) |
| P(4)–Co(1)–C(2) | 118.8(5) | C(4)–Co(2)–P(2) | 93.0(5) |
| P(4)–Co(1)–Co(2) | 93.0(1) | C(4)–Co(2)–P(3) | 93.5(5) |
| Lateral basal–basal angles (ideal angle 87°) | | | |
| Co(2)–Co(1)–P(1) | 85.6(1) | Co(1)–Co(2)–P(2) | 85.5(1) |
| Co(2)–Co(1)–C(2) | 72.2(4) | Co(1)–Co(2)–P(3) | 85.5(1) |
| P(1)–Co(1)–C(1) | 94.5(5) | P(2)–Co(2)–C(3) | 90.2(5) |
| C(1)–Co(1)–C(2) | 95.4(6) | P(3)–Co(2)–C(3) | 92.0(5) |
| Diagonal basal–basal angles (ideal angle 152°) | | | |
| Co(2)–Co(1)–C(1) | 162.5(5) | Co(1)–Co(2)–C(3) | 118.5(5) |
| P(1)–Co(1)–C(2) | 132.2(5) | P(2)–Co(2)–P(3) | 170.7(1) |
| Angles referred to a trigonal-bipyramid | | | |
| Axial–axial angles (ideal angle 180°) | | | |
| Co(2)–Co(1)–C(1) | 162.5(5) | P(2)–Co(2)–P(3) | 170.7(1) |
| Axial–equatorial angles (ideal angle 90°) | | | |
| Co(2)–Co(1)–P(1) | 85.6(1) | P(2)–Co(2)–Co(1) | 85.5(1) |
| Co(2)–Co(1)–P(4) | 93.0(1) | P(2)–Co(2)–C(3) | 90.2(5) |
| Co(2)–Co(1)–C(2) | 72.2(5) | P(2)–Co(2)–C(4) | 93.0(5) |
| C(1)–Co(1)–P(1) | 94.5(5) | P(3)–Co(2)–Co(1) | 85.5(1) |
| C(1)–Co(1)–P(4) | 103.9(5) | P(3)–Co(2)–C(3) | 92.0(5) |
| C(1)–Co(1)–C(2) | 95.4(6) | P(3)–Co(2)–C(4) | 93.5(5) |
| Equatorial–equatorial angles (ideal angle 120°) | | | |
| P(1)–Co(1)–P(4) | 103.9(5) | Co(1)–Co(2)–C(3) | 118.5(5) |
| P(1)–Co(1)–C(2) | 132.5(5) | Co(1)–Co(2)–C(4) | 119.7(5) |
| P(4)–Co(1)–C(2) | 118.7(5) | C(3)–Co(2)–C(4) | 121.8(6) |

[a] See text.

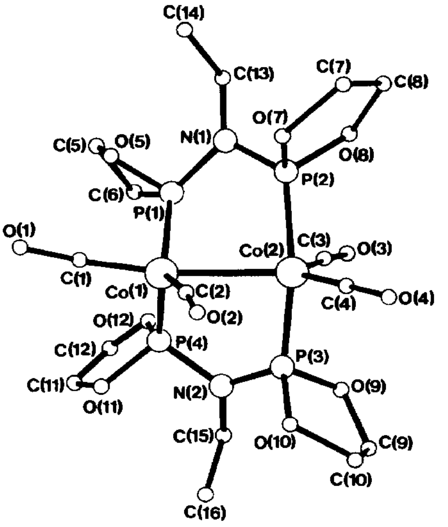

Fig. 1. The molecular stereochemistry of $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ showing the atom labelling.

Each cobalt atom is bonded to an identical set of five ligands comprising the other cobalt atom, two carbonyl groups and two phosphorus donor atoms. The geometries at each cobalt atom are not the same; Co(2) is best described as having near trigonal-bipyramidal coordination with P(2) and P(3) in the axial positions, while Co(1) has irregular square-pyramidal coordination with P(4) in the apical position. This can be seen from Fig. 1 and also from the bond angle data listed in Table 3, in which the ten angles around each cobalt atom are grouped in such a way as to reveal their similarity to the angles expected for an idealised trigonal-bipyramid and for an idealised square-pyramid. The referent square-pyramid in Table 3 is not one with the metal atom in the basal plane but the somewhat more realistic one corresponding to minimum Coulombic repulsion in an equal-bond distances, equal-charges model for which the apical–basal angles have been calculated to be 104° [13]. In fact the coordination around Co(1) is so irregular that an alternative description of its geometry as irregular trigonal-bipyramidal with C(1) and Co(2) in the apical positions is also possible (see Fig. 1 and Table 3). However, even if the geometry around Co(1) is described as being trigonal-bipyramidal, the positions of the ligands in the coordination spheres of the two cobalt atoms would not be the same. In view of the fact that Co(1) and Co(2) have identical sets of ligands this is a most unusual situation. Different coordination geometries for the two cobalt atoms in the closely related complex, II, also have been observed [4]; one cobalt is trigonal-bipyramidal and the other square-pyramidal, but the situation is not exactly analogous to that in I, since the positions occupied by the ligands in the cobalt coordination spheres in II are different to those occupied in I. In II, the trigonal-bipyramidal cobalt atom has the other cobalt atom and a carbonyl group in the axial positions, while the square-pyramidal cobalt atom has a carbonyl group in the apical position [4]. Differences between the precise arrangement of ligands in the coordination spheres of the cobalt atoms in I and II can be probably ascribed to the different steric requirements of the $(CH_2O)_2PN(Et)P(OCH_2)_2$ and $(CH_3O)_2PN(Et)P(OCH_3)_2$ ligands. More significant, however, is the fact that in both I and II the two cobalt atoms display different stereochemistries; thus this would appear to be an inherent structural feature of molecules of this type.

Two parameters may be used to define the conformations of the five-membered rings in I; $\phi$, which is the Co–P–P–Co torsion angle and $\delta$ which is the angle between the least-squares plane through the atoms of the $Co_2P_2$ unit, and the plane through the atoms of the $P_2N$ unit. Since $\phi$ and $\delta$ are both non-zero for both Co–P–N–P–Co rings in I (see Table 4), they both have $C_1$ symmetry. The torsion angle $\phi$ is large for both ligands and, moreover, different for the two ligands (29 and 40°) which illustrates the flexibility of a diphosphazane ligand and, in particular, its ability to accommodate different geometries at the two metal atom centres. Thus the ligands have adopted conformations consistent with an approximately linear P(2)–Co(2)–P(3) linkage of 170.7(1)° (the three-fold axis of the trigonal-bipyramidal cobalt atom) and consistent with a P(1)–Co(1)–P(4) angle of 103.9(1)° which agrees well with the ideal apical-basal angle of 104° for a square-pyramid.

To illustrate the ability of diphosphazane ligands to twist ($\phi \neq 0$) and buckle ($\delta \neq 0$) values of the relevant parameters are listed in Table 4 for a selection of dinuclear complexes in which the two metal atoms are bridged by two diphosphazane ligands. A conclusion which may be drawn from Table 4 is that when, in addition to the diphosphazane ligands, another group or atom bridges the two metal atoms, the diphosphazane ligands tend not to twist i.e. in these cases $\phi$ is zero or very small. Presumably the additional bridging group sterically hinders any twisting of the diphosphazane ligand. To further illustrate the flexibility of the diphosphazane ligand we have plotted in Fig. 2 the effect of increasing the M–P–P–N (M = metal) torsion angle ($\phi$) on the M–P–N valence angle. This curve was obtained by use of an equation derived by Schubert et al. [14], and is calculated by making the following assumptions; the P–N–P angle is 120°, the P–N, M–P and M–M distances are 1.65, 2.22 and 2.73 Å respectively, these being typical values for these parameters. Figure 2 shows that even quite large changes in $\phi$ result in very small changes in the angle at the phosphorus atom e.g. using our model, increasing

Table 4

$\phi$ and $\delta$ values [a] for M–P–N–P–M rings (M = metal) in bridging diphosphazane ligands

| Complex | $\phi$(°) | $\delta$(°) | Ref. |
|---|---|---|---|
| $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$ | 29 | 16 | This work |
| | 40 | 13 | |
| $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}_2]$ | 35 | 21 | 4 |
| | 41 | 16 | |
| $[Rh_2(CO)_3\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ | 21 | 14 | 15 |
| | 26 | 13 | |
| $[Rh_2Cl_2(CO)\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ | 25 | 13 | 16 |
| | 43 | 20 | |
| $[Fe_2(CO)_5I\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ | 28 | 13 | 17 |
| | 30 | 12 | |
| $[Fe_2(\mu\text{-}Br)(CO)_4\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]^+$ | 4 | 13 | 17 |
| $[Rh_2Cl_2(\mu\text{-}CO)(CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ | 2 | 7 | 18 |
| | 1 | 1 | 18 |

[a] $\phi$ is the M–P–P–M torsion angle. $\delta$ is the angle between the least-squares plane through the atoms of the $Co_2P_2$ unit and the plane defined by the atoms of the $P_2N$ unit.

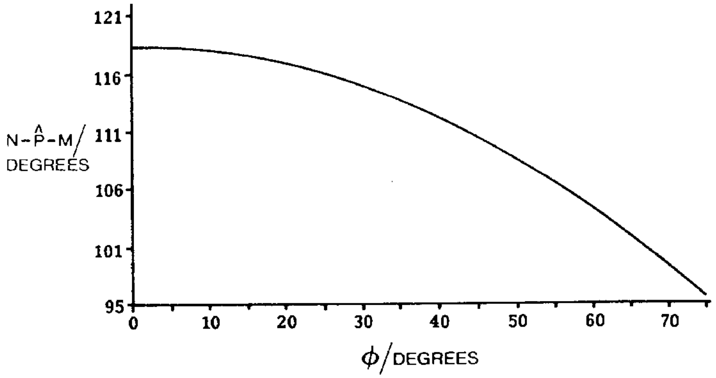

Fig. 2. Plot showing the dependence of the M–P–N angle on the M–P–P–M torsion angle (φ) for bridging diphosphazane ligands. (See text)

φ from 0 to 45° results in a decrease in the M–P–N angle of only about 8°. This suggests that angle strain caused by twisting of the diphosphazane ligand is minimal. In fact the P–N–P angle in the coordinated bridging diphosphazane ligand is often less than 120° (e.g. 110.9(6) and 113.9(6)° in I) which has the effect of opening-up the M–P–N angle thus allowing even greater twisting before angle strain at the phosphorus atoms becomes too severe.

As has been reported previously, the complexes I [5] and II [4] both exhibit a single broad resonance in their room temperature $^{31}P\{^1H\}$ NMR spectra. This indicates that their structures in solution are not the same as in the solid state; indeed the $^{31}P\{^1H\}$ NMR data suggests a symmetrical average structure for I and II in solution. Our interpretation is that the thermodynamically favoured structure is the unsymmetrical one found in the crystal but that, in solution, the molecule rapidly interconverts from one enantiomer to another through a symmetrical transition state. The fact that the interconversion is rapid on the NMR time scale indicates a very low potential energy barrier to the interconversion of the two enantiomers. This is consistent with the high degree of flexibility of the diphosphazane ligand to twisting (vide supra) since, in the transition state, the M–P–P–M torsion angle (φ) is presumably zero. Thus, it can be concluded that the very unusual unsymmetrical structures found for complexes I and II in the solid state, are intrinsic to the molecules and that the solid state structure of II is not, as has been suggested [4], a consequence of crystal packing effects.

## Experimental

### *Synthesis of* $(CH_2O)_2PN(Et)P(OCH_2)_2$

A dry chloroform solution (50 ml) of 2-chloro-1,3,2-dioxaphosphalane (50 g; 0.39 mol) was added dropwise to a stirred solution of ethylamine (26.68 g; 0.59 mol) in 300 ml of dry chloroform kept at −20°C. The reaction was complete after 1 h as evidenced by the absence of further precipitation of ethylaminohydrochloride. The salt was filtered off at room temperature and the filtrate reduced to about half its original volume. When the solution was kept overnight at about 0°C, $(CH_2O)_2PN(Et)P(OCH_2)_2$ separated as a colourless crystalline solid. Crude yield 36.9 g; 83%. Recrystallisation was from dry chloroform/petroleum ether. The ligand is extremely hygroscopic, and contact with water was avoided at all times. Mass spectrum: *m/e* 225; other peaks: *m/e*, 182 [$-N(C_2H_5)$]; *m/e*, 137 [$-(CH_2O)_4$]; *m/e*, 136 [$-(C_2H_5)P(OCH_2)_2$]; *m/e*, 91 [$-N(C_2H_5)P(OCH_2)_2$]; *m/e*, 74 [$-(CH_2O)_2P(OCH)_2$]. $^1$H NMR spectrum ($\delta$ scale, relative to $SiMe_4$, measured in $CDCl_3$); 4.32 (multiplet, $OCH_2CH_2O$, 4-H); 3.16 (sextet, $NCH_2$, 2-H); 1.22 (triplet, $CH_3$, 3-H).

### *X-ray crystallography of* $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$

*Crystal data:* $C_{16}H_{26}Co_2N_2O_{12}P_4$; orthorhombic, $a$ 17.327(8), $b$ 8.814(4), $c$ 16.851(7); $V$ 2573.5 Å$^3$; $D_c$ 1.75 g cm$^{-3}$, $D_m$ 1.73(1) g cm$^{-3}$; $Z = 4$; space group

Table 5

Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2$ $\times 10^4$ for Co and P, $\times 10^3$ for C, N and O) for $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}_2]$

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Co(1) | 1922(1) | 2097(2) | 2500 | 286(3) [a] |
| Co(2) | 410(1) | 2333(2) | 2604(1) | 292(3) [a] |
| P(1) | 1915(2) | 2240(4) | 3775(2) | 329(7) [a] |
| P(2) | 635(2) | 4052(4) | 3490(2) | 326(7) [a] |
| P(3) | 380(2) | 553(4) | 1763(2) | 301(7) [a] |
| P(4) | 1876(2) | −269(4) | 2269(2) | 282(7) [a] |
| O(1) | 3509(7) | 2987(14) | 2350(8) | 86(4) |
| O(2) | 1510(7) | 4131(14) | 1249(7) | 66(3) |
| O(3) | −454(7) | 508(13) | 3745(7) | 70(3) |
| O(4) | −405(6) | 4403(12) | 1581(7) | 63(3) |
| O(5) | 2730(6) | 2627(11) | 4190(6) | 52(3) |
| O(6) | 1727(5) | 805(10) | 4360(6) | 43(2) |
| O(7) | 792(5) | 5748(10) | 3196(6) | 51(3) |
| O(8) | −80(6) | 4430(11) | 4047(6) | 51(3) |
| O(9) | −419(5) | −375(10) | 1781(6) | 41(2) |
| O(10) | 325(5) | 1006(10) | 838(6) | 41(2) |
| O(11) | 2538(5) | −1015(9) | 1696(6) | 39(2) |
| O(12) | 1982(5) | −1519(10) | 2968(5) | 45(2) |
| N(1) | 1329(6) | 3597(13) | 4146(6) | 37(3) |
| N(2) | 1046(6) | −812(11) | 1815(6) | 32(2) |
| C(1) | 2866(8) | 2525(15) | 2415(9) | 49(4) |
| C(2) | 1626(7) | 3309(15) | 1790(8) | 37(3) |
| C(3) | −73(8) | 1236(16) | 3311(9) | 44(4) |
| C(4) | −74(8) | 3577(16) | 1996(8) | 40(3) |
| C(5) | 2941(11) | 1606(21) | 4816(11) | 74(5) |
| C(6) | 2437(10) | 162(18) | 4675(10) | 58(4) |
| C(7) | 256(10) | 6884(19) | 3490(10) | 65(5) |
| C(8) | −287(10) | 6105(21) | 4043(11) | 70(5) |
| C(9) | −755(9) | −608(17) | 1015(9) | 52(4) |
| C(10) | −456(10) | 688(18) | 530(10) | 59(4) |
| C(11) | 2954(11) | −2249(20) | 2058(10) | 68(5) |
| C(12) | 2560(9) | −2684(16) | 2820(9) | 53(4) |
| C(13) | 1423(9) | 4294(19) | 494(9) | 53(4) |
| C(14) | 1937(11) | 5747(22) | 4894(12) | 78(5) |
| C(15) | 928(7) | −2361(15) | 1468(8) | 40(3) |
| C(16) | 1112(9) | −2432(19) | 578(10) | 58(4) |

[a] Equivalent isotropic temperature factors defined by $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star (a_i a_j)$.

$Pca2_1$; $\mu$(Mo-$K_\alpha$) 16.4 $cm^{-1}$; $F(000)$ 1384. Black crystal of dimensions 0.77 × 0.54 × 0.31 mm used for data collection.

Intensity data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). A least-squares fit of high-angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $3 \leq 2\theta \leq 46°$ using the $\omega$–$2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed no decrease in intensity during data collection. Lorentz and polarisation, but no absorption corrections were made. Of the 1868 unique reflections measured, 1648 were classed as observed ($I > 3\sigma(I)$) and these were used for the solution and refinement of the structure.

The two cobalt atoms were located from a three-dimensional Patterson function calculated using the program SHELX [15]. A Fourier synthesis phased on the two cobalt atoms revealed possible positions for the phosphorus atoms, but was complicated by the presence of a false mirror plane generated due to the near equality of the cobalt atom $z$ coordinates. This false symmetry was broken by adding phosphorus atoms one at a time to the phasing model. Subsequent difference electron density maps revealed the positions of all the remaining non-H atoms. H atoms were not located. With anisotropic temperature factors for the Co and P atoms, and individual isotropic temperature factors for the C, N and O atoms, a unit weights full-matrix least-squares refinement (174 variables) converged at a final convention $R$ factor of 0.050. A final difference map was featureless with a maximum peak height of 0.8 eÅ$^{-3}$. Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors are given in Table 5.

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