

# Bis(diphenylphosphino)methane and related ligands as hydrogen bond donors†

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A search of the Cambridge Structural Database reveals that the methylene group of coordinated bis(diphenylphosphino)methane and related ligands can act as a hydrogen bond donor, with H...O distances as short as 2.20 Å; analogous C-H...Cl<sup>-</sup> interactions are a feature of the packing of dppmSe complexes of silver(I) and gold(I).

Secondary bonding interactions have been the focus of increased interest for several years. The classical hydrogen bond is a well known structural phenomenon; the C-H...O hydrogen bond, at first a controversial postulate, is now accepted as an important factor in determining the nature and stability of solid-state structures.<sup>1</sup> It has been recognised that more acidic C-H groups are likely to provide stronger (shorter) hydrogen bonds, although the inverse correlation between length and strength may not be totally reliable.<sup>1</sup>

It is normal practice in X-ray structure determination to check newly determined structures for possible hydrogen bonds, and indeed this process can now be performed automatically for classical hydrogen bonds.<sup>2</sup> The search for C-H...X interactions is less well integrated into common program systems; correspondingly, it may be assumed that many such interactions fail to be reported. In this Institute, such searches have only recently become routine;<sup>3</sup> we use a default cutoff of 2.6 Å for the H...O distance, although appreciably longer interactions (up to 3 Å) have often been considered genuine hydrogen bonds.

In a recent study of six-membered heterocycles involving the P-CH<sub>2</sub>-P unit, we observed some strikingly short intermolecular C-H...O interactions (H...O 2.25, C...O 3.24 Å) involving the methylene group between the phosphorus atoms.<sup>4</sup> This prompted us to re-inspect some of our older structures involving organic phosphorus heterocycles, and we discovered two cases where we had overlooked short intermolecular contacts between the H atoms of a P-CH<sub>2</sub>-P unit and keto oxygens (H...O 2.38, 2.29 Å).<sup>5</sup>

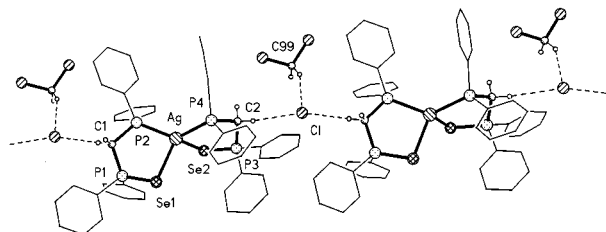
Another molecule involving the P-CH<sub>2</sub>-P group is the common ligand bis(diphenylphosphino)methane (dppm), Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>. The methylene hydrogens of dppm are known to be acidic, particularly in metal complexes; the deprotonated form of the ligand contains an additional donor, the methanide group.<sup>6</sup> It thus seemed likely that dppm complexes might display C-H...O hydrogen bonds.

A search of the Cambridge Structural Database<sup>7</sup> (Oct. 1997 version) was conducted for the fragment P-CH<sub>2</sub>-P with an intermolecular H...O contact of <2.5 Å to any O-C bond. The search was restricted to error-free, ordered structures. Apart from the two structures previously mentioned, a total of 23 structures (all of them complexes or clusters involving dppm or related ligands) with 28 C-H...O substructures were found. The geometry was in all cases acceptably linear (one C-H...O angle of 133°, all others > 143°). The shortest H...O contact was 2.20 Å.

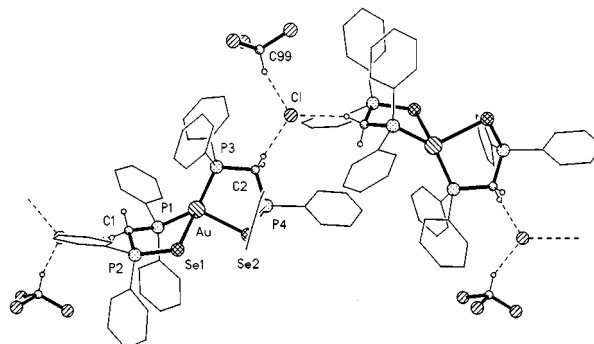
The hydrogen bonds can be classified as follows: M-CO<sub>terminal</sub>...H, 10 cases; M-CO<sub>bridging</sub>...H, 2; O<sub>solvent</sub>...H, 8; O<sub>anion</sub>...H, 3; ligand C=O...H, 5. In no case were the C-H...O hydrogen bonds mentioned in the original publication; in several cases it was explicitly stated that *no* unusual intermolecular contacts were observed. It should be noted that these relatively few examples represent the shortest such interactions;

there are presumably many more with somewhat longer H...O distances.

Although this initial search was restricted to oxygen acceptors, it is clear that other electronegative elements should accept hydrogen bonds from dppm. In view of our interest in coinage metal complexes with selenium ligands,<sup>8</sup> we therefore determined structures of the type [(dppmSe)<sub>2</sub>M]<sup>+</sup>Cl<sup>-</sup> (**1a**, M = Ag, dichloromethane solvate; **1b**, M = Ag, ethanol solvate; **2a**, M = Au, chloroform solvate; **2b**, M = Au, ethanol solvate).<sup>‡§</sup> These are the first complexes involving P<sub>2</sub>Se<sub>2</sub> coordination at silver(I) and gold(I). The coordination at the metal atoms is distorted tetrahedral; angular distortions arise from the restricted bite of the ligands, but the gold complexes additionally display a major difference in Au-Se bond lengths (0.16 Å in **2b** and 0.30 Å in **2a**; values are given in Figs. 1 and 2). The structure of a two-coordinate gold(I) complex of the same ligand has been reported by Schmidbauer, *et al.*<sup>9</sup> and by chance belongs to the set of 23 compounds discussed above; it displays two C-H...O<sub>acetone</sub> hydrogen bonds.



**Fig. 1** The structure of **1a** in the crystal. Hydrogen atoms of the phenyl groups are omitted for clarity, radii are arbitrary. Dashed lines represent H bonds. Selected bond lengths (Å) and angles (°): Ag-Se1 2.7086(12), Ag-Se2 2.7749(13), Ag-P2 2.453(3), Ag-P4 2.439(2); bite angles P2-Ag-Se1 92.49(6), P4-Ag-Se2 91.40(6); H...Cl...H 164. The structures of **1b** (isostructural) and **2b** (equivalent packing) are similar to **1a**: **1b** Ag-Se1 2.7179(10), Ag-Se2 2.7643(10), Ag-P2 2.454(2), Ag-P4 2.440(2); P2-Ag-Se1 92.69(5), P4-Ag-Se2 91.64(5); H...Cl...H 159. **2b** Au-Se1 2.9459(12), Au-Se2 2.7891(12), Au-P2 2.306(3), Au-P4 2.319(2); P2-Au-Se1 89.64(7), P4-Au-Se2 91.61(7); H...Cl...H 160.



**Fig. 2** The structure of **2a** in the crystal. Hydrogen atoms of the phenyl groups are omitted for clarity, radii are arbitrary. Dashed lines represent H bonds. Selected bond lengths (Å) and angles (°): Au-Se1 3.0571(10), Au-Se2 2.7535(9), Au-P1 2.298(2), Au-P3 2.329(2); P1-Au-Se1 83.46(5), P3-Au-Se2 92.65(5), H...Cl...H 112.

**Table 1** Hydrogen bond geometry in compounds **1a,b**, **2a,b**

Compound, H bond	H...Cl-/Å	C...Cl-/Å	C-H...Cl-/°
<b>1a</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.87	3.839(9)	168
<b>1a</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.61	3.556(9)	160
<b>1a</b> , C-H <sub>solv</sub> ...Cl <sup>-</sup>	2.58	3.467(14)	149
<b>1b</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.82	3.779(6)	164
<b>1b</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.75	3.705(7)	163
<b>2a</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.64	3.576(7)	157
<b>2a</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.57	3.535(7)	166
<b>2a</b> , C-H <sub>solv</sub> ...Cl <sup>-</sup>	2.70	3.554(12)	144
<b>2b</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.68	3.616(9)	157
<b>2b</b> , C-H <sub>dppm</sub> ...Cl <sup>-</sup>	2.61	3.567(10)	163
<b>2b</b> , O-H <sub>solv</sub> ...Cl <sup>-</sup>		3.042(10)	

All four structures **1a,b**, **2a,b** display C-H...Cl hydrogen bonds (Table 1), which play a central role in determining the crystal packing. In each structure, the ions are connected into chains (Figs. 1 and 2) by hydrogen bonds C-H<sub>dppm</sub>...Cl<sup>-</sup>, whereby the chloride accepts two hydrogen bonds. Additionally, there is a C-H<sub>solv</sub>...Cl<sup>-</sup> contact from a solvent molecule in **1a** and **2a**, an O...Cl contact involving the ethanol of **2b**, and a similar contact in **1b**, in which however the ethanol is poorly resolved.

A second database search,<sup>7</sup> this time for C-H...Cl contacts, also proved fruitful; a total of 28 hydrogen bonds in 21 structures were found with H...Cl < 2.8 Å and C-H...Cl > 130°. These contacts can be classified as: 14 C-H<sub>dppm</sub>...Cl<sub>coord</sub>; 12 C-H<sub>dppm</sub>...Cl<sup>-</sup>, 2 C-H<sub>dppm</sub>...Cl<sub>(other anions)</sub>. Only one of these contacts was mentioned explicitly as an interaction with dppm in the original publications;<sup>10</sup> it should however be stressed that it was until recently not usual to look for hydrogen bonds involving C-H units. As an example of an unrecognised hydrogen bond, we can again cite our own work; the structure of [(dppm)<sub>2</sub>Au<sub>3</sub>Cl<sub>2</sub>]<sup>+</sup>[(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>AuCl]<sup>-</sup><sup>11</sup> involves a contact C-H<sub>dppm</sub>...Cl<sub>anion</sub> with H...Cl 2.70 Å, C-H...Cl 139°.

It may be concluded that coordinated dppm is capable of acting as a C-H...X hydrogen bond donor; in such cases it presumably exerts a significant influence on structure and stability, although to the best of our knowledge this possibility has not previously been discussed in detail. An obvious corollary is that structures of complexes of dppm and related ligands should be routinely screened for such hydrogen bonds.

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## Notes and references

† Dedicated to Professor Armand Blaschette on the occasion of his 65th birthday.

‡ Bis[(diphenylphosphino)(diphenylphosphineselenido)methane]silver(I) chloride **1** was obtained from dppmSe and AgCl in 2:1 molar ratio in acetone; after filtration, the product was precipitated in 67% yield with light petroleum. Crystals were grown by diffusion of light petroleum into a solution of **1** in dichloromethane (**1a**) or by diffusion of diethyl ether into a solution of **1** in ethanol (**1b**).

Bis[(diphenylphosphino)(diphenylphosphineselenido)methane]gold(I) chloride **2** was obtained from the reaction of dppmSe with a suspension of (tht)AuCl (tht = tetrahydrothiophene) in 2:1 molar ratio in toluene, followed by precipitation with diethyl ether (yield 66%). Crystals were grown by diffusion of diethyl ether into a solution of **2** in chloroform (**2a**) or ethanol (**2b**).

Satisfactory elemental analyses and consistent NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>77</sup>Se) were obtained.

§ *X-Ray structure determinations*: data were measured at -100 °C on a Siemens P4 diffractometer using Mo-Kα radiation. Absorption corrections using psi-scans (**2b**: SHELXA<sup>2</sup>). Structures were refined on F<sup>2</sup> using all reflections (program SHELXL-93<sup>2</sup>). Hydrogen atoms were included using a riding model; C-H bond lengths (and H...X contacts) are thus systematically shortened with respect to the true values.

*Crystal data*: **1a**, 1·3CH<sub>2</sub>Cl<sub>2</sub>: C<sub>53</sub>H<sub>50</sub>AgCl<sub>7</sub>P<sub>4</sub>Se<sub>2</sub>, *M* = 1324.75, monoclinic, *C2/c*, *a* = 38.984(7), *b* = 14.010(2), *c* = 21.952(4) Å, β = 101.534(12)°, *V* = 11747(4) Å<sup>3</sup>, *Z* = 8, μ = 2.0 mm<sup>-1</sup>, 10 989 reflections, 10 260 unique, *wR2* 0.201, *R1* 0.066.

**1b**, 1·3.5EtOH: C<sub>57</sub>H<sub>65</sub>AgClO<sub>3.5</sub>P<sub>4</sub>Se<sub>2</sub>, *M* = 1231.21, monoclinic, *C2/c*, *a* = 39.315(7), *b* = 22.285(3), *c* = 22.214(3) Å, β = 100.538(10)°, *V* = 12 043(3) Å<sup>3</sup>, *Z* = 8, μ = 1.7 mm<sup>-1</sup>, 21 045 reflections, 10 577 unique, *wR2* 0.101, *R1* 0.051.

**2a**, 2·2CHCl<sub>3</sub>: C<sub>52</sub>H<sub>46</sub>AuCl<sub>7</sub>P<sub>4</sub>Se<sub>2</sub>, *M* = 1397.80, monoclinic, *P2<sub>1</sub>/c*, *a* = 12.917(2), *b* = 22.285(3), *c* = 19.050(3) Å, β = 99.850(10)°, *V* = 5403.0(13) Å<sup>3</sup>, *Z* = 4, μ = 4.6 mm<sup>-1</sup>, 14 225 reflections, 9509 unique, *wR2* 0.108, *R1* 0.046.

**2b**, 2·EtOH: C<sub>52</sub>H<sub>50</sub>AuClO<sub>4</sub>Se<sub>2</sub>, *M* = 1205.14, orthorhombic, *Pna2<sub>1</sub>*, *a* = 22.425(3), *b* = 13.713(2), *c* = 16.035(2) Å, *V* = 4930.9(11) Å<sup>3</sup>, *Z* = 4, μ = 4.7 mm<sup>-1</sup>, 11 215 unique reflections, *wR2* 0.104, *R1* 0.048. CCDC 182/987.

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