

Chelating organophosphines: the use of comparative structural investigations to determine ligand properties¹

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Abstract

Chelating organophosphines are commonly used in stoichiometric or transition metal catalyzed reactions. Minor geometric or electronic changes in these ligands can cause substantial changes in the selectivity and reactivity of ligand modified catalysts.

In continuation of our systematic investigations of the steric requirements of typical ligands to transition metals, we wish to report the molecular structures of five chelating organophosphines. Four of these compounds are liquids at ambient temperature, and their crystal structures have been determined using single crystals obtained by use of in situ zone melting techniques on a diffractometer. The fifth phosphine presented in this work solidifies at elevated temperatures, and high resolution data in conjunction with the X–X method was used to locate the orientation and size of the lone pairs at the phosphorus atoms.

A novel technique to describe the accessibility of the phosphorus atom and its lone pair by molecular modeling techniques is also presented. © 1997 Elsevier Science S.A.

Keywords: Phosphorus; Chelating phosphines; X-ray structure; Electron deformation density; Multipole expansion; Cone angle

1. Description of the experimental procedures

The chelating phosphines investigated in this work are depicted in Scheme 1. They all contain an even number of bridging carbon atoms. With the exception of **5**, the compounds are liquids at ambient temperature. The melting behavior of all samples was examined using DSC techniques prior to crystal growth and X-ray experiments. All attempts to crystallize compounds containing odd numbers of chain carbon atoms have, so far, been unsuccessful, and these compounds solidify into glasses which could not be converted into single crystals [1]. Single crystals of **1–4** were obtained using crystal growing techniques described previously [2], using focused IR radiation or a CO₂ laser as the point source of heat. This technique has been adapted for use on a CAD4 diffractometer. To protect the air-sensitive samples from oxidation, they were sealed under argon in glass capillaries and transferred to the diffractometer

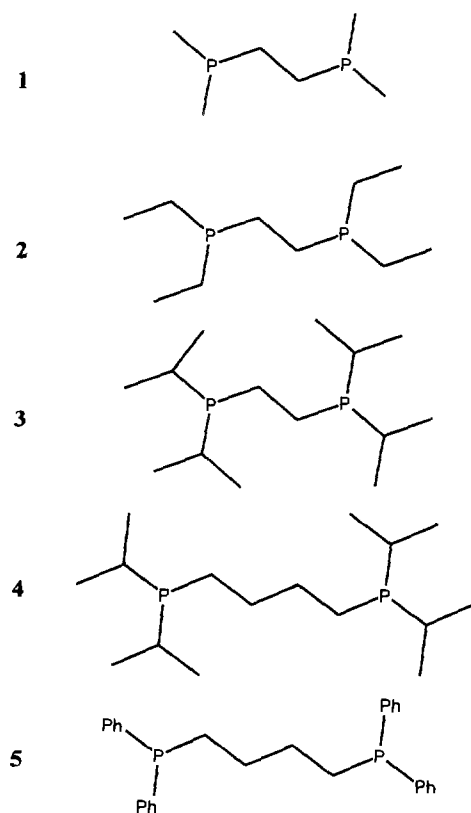
equipped with a low temperature device (gaseous nitrogen stream). As temperature changes in the coolant have to be kept as small as possible over considerable periods of time, a suitable cooling device had to be developed [3]. This device keeps the temperature at the capillary within 0.2 K of any desired value (100 to 295 K) for a long period of time (up to eight weeks) without serious icing. In addition, its programmable control was used to grow crystals just below their melting points.

2. Results and discussion

It is well documented that electronic effects as well as steric shielding effects play a dominant role in stabilizing phosphorus–transition metal complexes [4]. Chelating phosphines are usually complexed to one or more transition metals through both phosphorus atoms, however, single complexation is also known [5]. Since these ligands shield large portions of the ligand sphere of a transition metal, the steric effect is usually more pronounced than that of non-chelating phosphines. In addition, ring formation through complexation stabilizes

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¹ Dedicated to the memory of Professor Yuri Struchkov in recognition and admiration of his pioneering work on the structural chemistry and crystallography of organometallic compounds.



Scheme 1.

the organometallic species. This is particularly the case where five- and six-membered rings are formed. In enantioselective catalyses using chiral catalyst systems, the enantioselectivity of the reaction can decrease upon increasing the size of the ring chelate [6].

As a quantitative measure of the steric demands of phosphines, the cone angle concept was introduced by Tolman [4,7]: the values are derived from CPK molecular models or by using other simple mechanical tools. For rigid molecules such as PMe_3 and $\text{P}(\text{tBu})_3$, these crude values are in reasonable agreement with the values derived from our recent crystal structure investigation [8,9]. Contrary to the tabulated values for PEt_3 , $\text{P}(\text{nPr})_3$ and $\text{P}(\text{nBu})_3$, the experimental values of the cone angles for these ligands are significantly lower [8–10] (see Table 1). This difference is attributable to folding of the rotationally flexible alkyl substituents.

As all chelating phosphines included here have apparent structural similarity to the corresponding monophosphines, a comparative discussion is useful. We have shown recently that in all monophosphines investigated so far, the bonding angles at the phosphorus atoms reflect the steric strain and the steric demands of the substituents within these compounds more obviously than the changes in the C–P bond lengths involved.

In bis(dimethylphosphino)ethane **1**, two methyl groups and the bridging ethylene group have to be considered as the sterically relevant substituents (Fig. 1). In the comparable monophosphines PMe_3 and PEt_3 , the C–P–C angles were found to be between $98.8(1)^\circ$ and $100.2(1)^\circ$ [9] for both molecules, as the replacement of one hydrogen atom of a methyl group by another methyl group does not introduce any additional steric strain. A similar observation has been made in **1**, wherein the C–P–C angles are between $98.9(1)^\circ$ and $99.4(1)^\circ$, agreeing well with those found in the corresponding monophosphines. The same holds for all pertinent atomic distances.

Table 1
Comparison of geometric data of monophosphines and chelating phosphines

	P–C(sp ³)	$\Sigma(\text{C–P–C})$	$\theta(\text{X-ray})$	$\theta(\text{CPK})^a$	Accessible surface (\AA^2)	RMS (\AA) ^b
PMe_3 ^c	1.833(4)	297.5(3)	113(2)	118(2)	6.2(1)	0.081
PEt_3 ^c	1.842(2)	298.4(3)	162(2)	132(2)	3.7(1)	0.110
$\text{P}(\text{nPr})_3$ ^d	1.848(2)	304.4(3)	144(2)	132(2)	4.6(1)	0.120
$\text{P}(\text{iPr})_3$ ^d	1.861(4)	309.6(6)	168(2)	160(2)	2.2(1)	0.144
$\text{PPh}(\text{iPr})_2$ ^c	1.857(2)	307.9(6)	159(2)	155(2) ^e	2.8(1)	0.143
$\text{P}(\text{nBu})_3$ ^f	1.844(2)	305.4(3)	159(2)	132(2)	4.5(1)	0.099
$\text{P}(\text{iBu})_3$ ^f	1.911(2)	322.3(3)	176(2)	182(2)	1.4(1)	0.119
$\text{Me}_2\text{P}-(\text{CH}_2)_2-\text{PMe}_2$	1.837(2)	297.3(3)	—	—	5.6(1)	0.085
$\text{PEt}_2-(\text{CH}_2)_2-\text{PEt}_2$	1.847(3)	298.5(3)	—	—	4.0(2)	0.097
$(\text{iPr})_2\text{P}-(\text{CH}_2)_2-\text{P}(\text{iPr})_2$	1.859(2)	304.2(3)	—	—	2.9(1)	0.089
$(\text{iPr})_2\text{P}-(\text{CH}_2)_4-\text{P}(\text{iPr})_2$	1.856(3)	304.8(3)	—	—	3.0(1)	0.331
$\text{Ph}_2\text{P}-(\text{CH}_2)_4-\text{PPh}_2$	—	303.7(3)	—	—	3.6(1)	0.583

^a Ref. [7].

^b Values result from RMS fits of the molecular structure found in the solid state and the minimized structure.

^c Ref. [9].

^d Ref. [10].

^e Ref. [11].

^f Ref. [8].

^g According to the approximate group additivity relationship for cone angles of unsymmetrical $\text{PX}_1\text{X}_2\text{X}_3$ ligands [7].

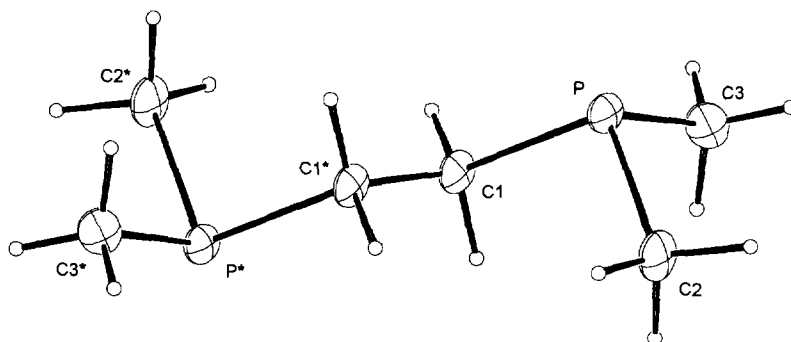


Fig. 1. An ORTEP II view of bis(dimethylphosphino)ethane (1) with displacement ellipsoids drawn at the 50% probability level. Selected distances [Å] and angles [°]: C1–C1* 1.529(2), P–C1 1.846(1), P–C2 1.830(2), P–C3 1.836(2); C1–P–C2 99.4(1), C1–P–C3 99.0(1), C2–P–C3 98.9(1).

Crystal data for 1. $C_6H_{18}P_2$, molar mass 150.1 $g\ mol^{-1}$, colorless, cylindrical crystal shape (0.2 mm diameter, 1.0 mm height), $a = 5.081(1)$, $b = 5.824(2)$, $c = 8.681(1)\ \text{Å}$, $\alpha = 106.48(3)$, $\beta = 92.47(2)$, $\gamma = 111.37(2)^\circ$, $V = 226.3\ \text{Å}^3$, $T = 102\ K$, $T_{\text{melt}} = 273\ K$, $T_{\text{growth}} = 269\ K$, $d_{\text{calc}} = 1.10\ g\ cm^{-3}$, $\mu = 3.90\ cm^{-1}$, $Z = 1$, triclinic, space group $P\bar{1}$ [No. 2], Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71069\ \text{Å}$, measuring method ω - 2θ , 1052 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.65\ \text{Å}^{-1}$, 981 independent reflections, 953 observed reflections [$I \geq 2\sigma(I)$] for 69 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions found and refined isotropically, $R = 0.035$, $R_w = 0.047$ [$w = 1/\sigma^2(F_o)$], max. shift/error 0.02, final difference Fourier $\rho = 0.49\ e\ \text{Å}^{-3}$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Bis(diethylphosphino)ethane 2, with two ethyl groups and an ethano group as the sterically relevant substituents at the phosphorus atom, resembles the observed molecular structure of PEt_3 . All C–P and C–C

distances as well as the C–P–C and C–C–P angles and even the torsional angles of both compounds are nearly identical in the solid state (Fig. 2). Superposition of all non-hydrogen atoms of PEt_3 with the corresponding groups in both crystallographically independent half molecules of 2 result in RMS distances of only 0.04 and 0.10 Å. Small differences arise from rotational changes of the terminal CH_3 groups, and are probably induced by low energy crystal packing effects.

Crystal data for 2. $C_{10}H_{24}P_2$, molar mass 206.3 $g\ mol^{-1}$, colorless, cylindrical crystal shape (0.2 mm diameter, 0.6 mm height), $a = 9.002(8)$, $b = 9.093(6)$, $c = 10.086(7)\ \text{Å}$, $\alpha = 88.86(6)$, $\beta = 63.90(6)$, $\gamma = 64.15(6)^\circ$, $V = 652.0\ \text{Å}^3$, $T = 102\ K$, $T_{\text{melt}} = 235\ K$, $T_{\text{growth}} = 228\ K$, $d_{\text{calc}} = 1.05\ g\ cm^{-3}$, $\mu = 2.86\ cm^{-1}$, $Z = 2$, triclinic, space group $P\bar{1}$ [No. 2], Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71069\ \text{Å}$, measuring method ω - 2θ , 2987 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.65\ \text{Å}^{-1}$, 2774 independent reflections, 2505 observed reflections [$I \geq 2\sigma(I)$] for 205 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions found and refined isotropically, $R = 0.049$,

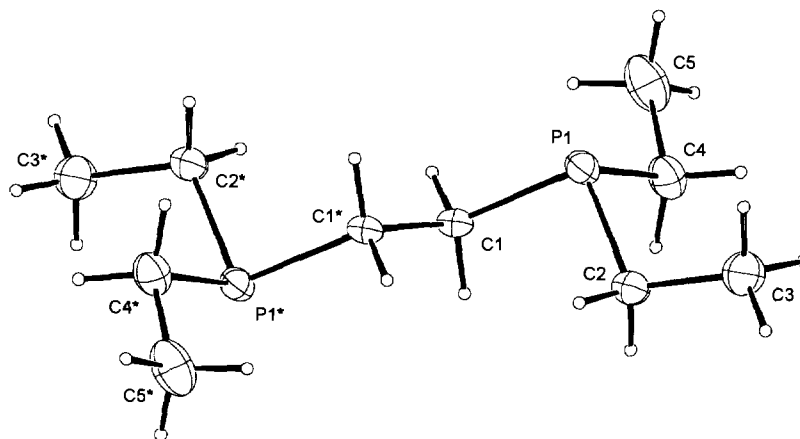


Fig. 2. Molecular structure of bis(diethylphosphino)ethane (2) (only one of the two independent half molecules is shown). Selected distances [Å] and angles [°]: C1–C1* 1.528(1), P1–C1 1.844(1), P1–C2 1.838(1), P1–C4 1.843(1); C1–P1–C2 99.4(1), C1–P1–C4 99.2(1), C2–P1–C4 100.1(1).

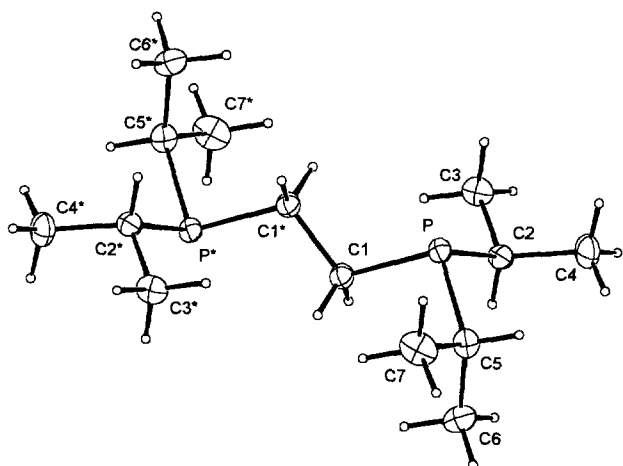


Fig. 3. Molecular structure of bis(diisopropylphosphino)ethane (**3**). Selected distances [Å] and angles [°]: C1–C1* 1.530(2), P–C1 1.860(2), P–C2 1.856(2), P–C3 1.860(2); C1–P–C2 100.8(1), C1–P–C5 101.2(1), C2–P–C5 102.2(1), P–C2–C3 110.1(1), P–C2–C4 110.5(1), P–C5–C7 108.9(1), P–C5–C6 116.7(1).

$R_w = 0.075$ [$w = 1/\sigma^2(F_o)$], max. shift/error 0.03, final difference Fourier $\rho = 0.50 \text{ e \AA}^{-3}$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Substitution of two hydrogen atoms of each methyl group in PMe_3 by additional methyl groups increases the steric strain remarkably. This can be deduced from the C–P–C angles in $\text{P}(\text{iPr})_3$, which change to $104.7(1)^\circ$ [10]. In bis(diisopropylphosphino)ethane **3**, with two isopropyl groups and one ethano group at the phosphorus atom, this strain is reduced considerably and the C–P–C angles range from $100.8(1)^\circ$ to $102.2(1)^\circ$ (Fig. 3). The P–C5–C6 angle increases to $116.7(1)^\circ$ as a consequence of intramolecular interactions. It is note-

worthy that both isopropyl groups in **3** are oriented exactly as in $\text{P}(\text{iPr})_3$, and are similar to the orientations in $\text{PPh}(\text{iPr})_2$ [11].

Crystal data for **3**. $\text{C}_{14}\text{H}_{32}\text{P}_2$, molar mass 262.4 g mol^{-1} , yellow-greenish, cylindrical crystal shape (0.2 mm diameter, 0.6 mm height), $a = 6.453(1)$, $b = 19.217(4)$, $c = 7.038(1) \text{ \AA}$, $\beta = 103.60(1)^\circ$, $V = 848.3 \text{ \AA}^3$, $T = 102 \text{ K}$, $T_{\text{melt}} = 252 \text{ K}$, $T_{\text{growth}} = 250 \text{ K}$, $d_{\text{calc}} = 1.03 \text{ g cm}^{-3}$, $\mu = 2.31 \text{ cm}^{-1}$, $Z = 2$, monoclinic, space group $P2_1/c$ [No. 14], Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71069 \text{ \AA}$, measuring method $\omega - 2\theta$, 2076 measured reflections ($\pm h, \pm k, \pm l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.65 \text{ \AA}^{-1}$, 1888 independent reflections, 1681 observed reflections [$I \geq 2\sigma(I)$] for 137 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions found and refined isotropically, $R = 0.036$, $R_w = 0.049$ [$w = 1/\sigma^2(F_o)$], max. shift/error 0.04, final difference Fourier $\rho = 0.48 \text{ e \AA}^{-3}$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The three chelating phosphines discussed so far are crystallographically characterized by a center of inversion located on the central C–C bond; only half of the molecules are crystallographically independent. As a consequence of this symmetry, the lone pairs at the phosphorus atoms point in opposite directions. This is not the case in bis(diisopropylphosphino)butane **4**. Despite this the two diisopropylphosphino groups in **4** have quite similar geometric arrangements, with the C–P–C angles ranging from $99.9(1)^\circ$ to $102.7(1)^\circ$ (Fig. 4). Moreover, all isopropyl groups in **4** have the same orientation as those in **3**, as well as in $\text{PPh}(\text{iPr})_2$ and $\text{P}(\text{iPr})_3$. Extrapolation from the molecular conformation of **4** indicates that the lone pairs at the phosphorus

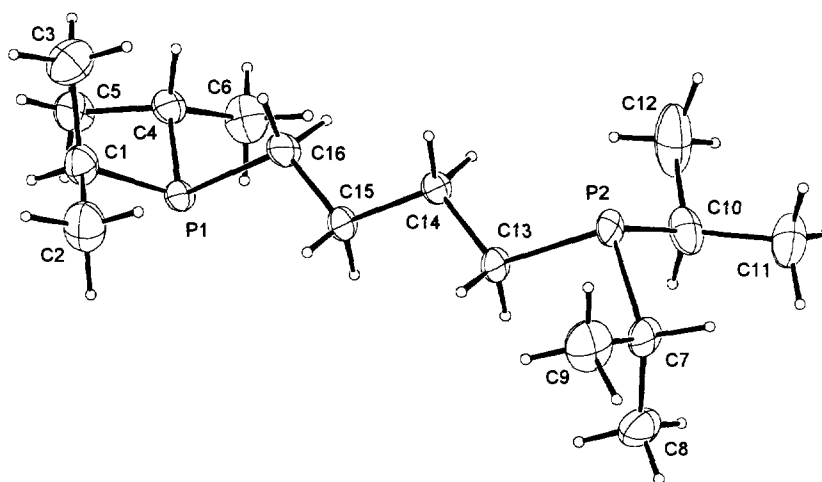


Fig. 4. Molecular structure of bis(diisopropylphosphino)butane (**4**). Selected distances [Å] and angles [°]: P1–C1 1.860(3), P1–C4 1.853(2), P1–C16 1.859(3), P2–C7 1.860(3), P2–C10 1.855(3), P2–C13 1.849(2); C16–P1–C4 $99.9(1)^\circ$, C16–P1–C1 $102.7(1)^\circ$, C4–P1–C1 $102.3(1)^\circ$, P1–C1–C3 $117.3(2)^\circ$, C13–P2–C10 $102.4(1)^\circ$, C13–P2–C7 $99.9(1)^\circ$, C10–P2–C7 $102.4(1)^\circ$, P2–C7–C8 $116.5(2)^\circ$.

atoms are nevertheless pointing away from each other. These results suggest that a more detailed investigation of the molecular structure of a chelating phosphine using more elaborate methods than normal structural analyses would be profitable.

Crystal data for **4**. $C_{16}H_{36}P_2$, molar mass 290.4 g mol^{-1} , colorless, cylindrical crystal shape (0.2 mm diameter, 0.8 mm height), $a = 10.125(3)$, $b = 14.351(3)$, $c = 13.909(3) \text{ \AA}$, $\beta = 110.59(2)^\circ$, $V = 1891.9 \text{ \AA}^3$, $T = 102 \text{ K}$, $T_{\text{melt}} = 262 \text{ K}$, $T_{\text{growth}} = 257 \text{ K}$, $d_{\text{calc}} = 1.02 \text{ g cm}^{-3}$, $\mu = 2.12 \text{ cm}^{-1}$, $Z = 4$, monoclinic, space group $P2_1/a$ [No. 14], Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71069 \text{ \AA}$, measuring method $\omega-2\theta$, 4663 measured reflections ($\pm h, +k, +l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.65 \text{ \AA}^{-1}$, 4306 independent reflections, 3289 observed reflections [$I \geq 2\sigma(I)$] for 307 refined parameters, structure solved by direct methods, non-hydrogen atoms refined anisotropically, H atom positions found and refined isotropically, $R = 0.047$, $R_w = 0.051$ [$w = 1/\sigma^2(F_o)$], max. shift/error 0.03, final difference Fourier $\rho = 0.54 \text{ e \AA}^{-3}$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. EDD investigation of bis(diphenylphosphino)butane by X–X methods

Owing to ill-defined crystal shapes for compounds obtained by crystal growing experiments, more detailed experimental studies of electron deformation densities have failed so far in our hands. We therefore decided to select the chelating phosphine $\text{Ph}_2\text{PC}_4\text{H}_8\text{PPh}_2$, which is a solid at ambient temperature, for electron deformation density (EDD) investigations to study its molecular and

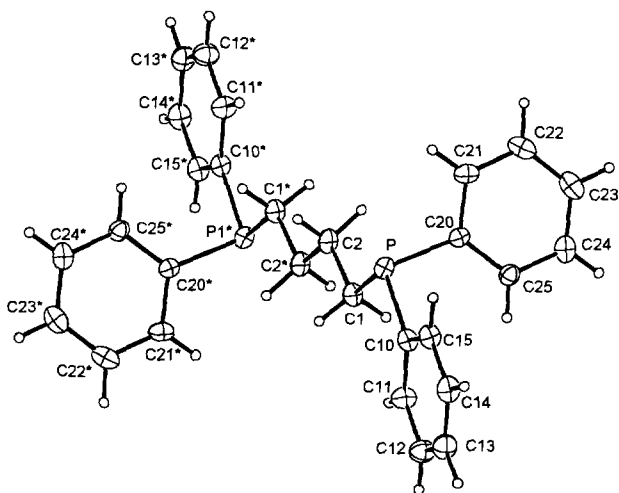


Fig. 5. Molecular structure of bis(diphenylphosphino)butane (**5**). For bond distances and angles see Fig. 8.

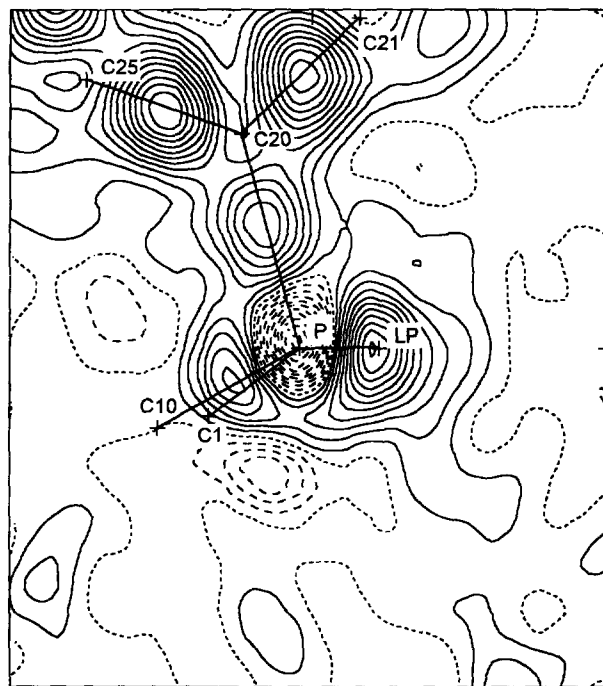


Fig. 6. EDD distribution in the plane C20–P–LP of bis(diphenylphosphino)butane; contours at 0.1 e \AA^{-3} , zero and negative contour lines are dashed.

electronic structure by X–X methods, even though its solid state structure has been reported previously [12]. The experimental conditions for data collection and structure refinement match our earlier published procedures [13]: the coordinates and anisotropic displacement parameters of the heavier elements were taken from a conventional refinement on F using the high order data (cut at 0.65 \AA^{-1}) only, while all hydrogen parameters are those from full data refinement. The full data set was also used for the multipole expansion refinement.

As no phase transition occurs during cooling, the solid state structure of **5** at 100 K is similar to an earlier study at ambient temperature [12], with the exception that the central C–C bond located about a center of inversion now has the expected length ($1.530(1) \text{ \AA}$) and not, as earlier, $1.619(9) \text{ \AA}$. The central carbon skeleton is almost linear: the torsional angle about the P–C–C–C framework amounts to 2.37° . Both phenyl rings at the phosphorus atom are planar within $\pm 0.002 \text{ \AA}$. As in numerous phosphorus–phenyl compounds, the average bond angle at the aromatic *ipso*-carbon atoms is reduced from the ideal value of 120° to 118.4° , while the remaining internal phenyl angles average $120.3(5)^\circ$. The angles *trans* to the *ipso*-position are $119.7(1)^\circ$ [14]. Fig. 5 shows the molecular structure of bis(diphenylphosphino)butane (**5**). Relevant geometric data of **5** are summarized in Table 1 and Fig. 8. As given by the crystallographic symmetry, both phosphorus atoms are in *trans*-position to each other, with the lone pairs

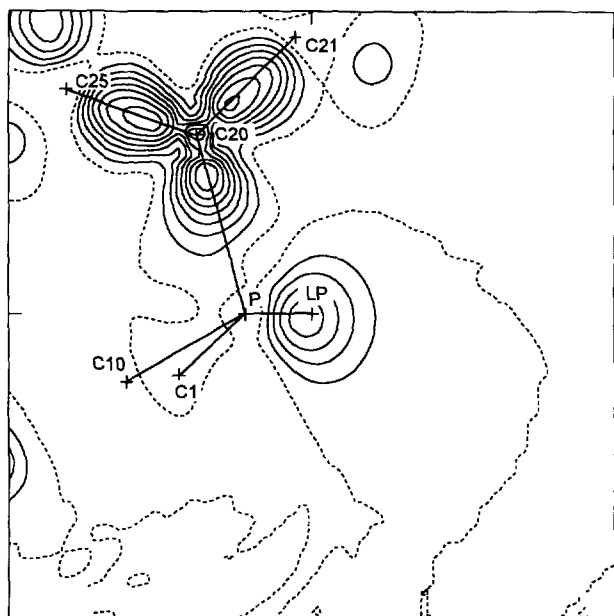


Fig. 7. Static EDD distribution in the plane C20–P–LP of bis(diphenylphosphino)butane; contours at $0.1\text{e}\text{\AA}^{-3}$, zero and negative contour lines are dashed.

pointing in opposite directions. Prior to complexation, the molecular skeleton has to be reoriented.

Crystal data for **5**. $\text{C}_{28}\text{H}_{28}\text{P}_2$, molar mass

426.5 g mol^{-1} , colorless, $0.17 \times 0.43 \times 0.56\text{ mm}^3$, $a = 6.122(1)$, $b = 8.061(2)$, $c = 23.414(2)\text{ \AA}$, $\beta = 93.01(1)^\circ$, $V = 1153.8\text{ \AA}^3$, $T = 102\text{ K}$, $d_{\text{calc}} = 1.23\text{ g cm}^{-3}$, $\mu = 1.95\text{ cm}^{-1}$ (analytical absorption correction, transmission_{max} = 1.089, transmission_{min} = 1.033), $Z = 2$, monoclinic, space group $P2_1/n$ (No. 14), Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71069\text{ \AA}$, measuring method ω – 2θ , 21698 measured reflections ($\pm h$, $\pm k$, $\pm l$ at different ψ angles), averaged to 5286 ($R_{\text{av}} = 0.034$), of which 4397 were observed [$I \geq 2\sigma(I)$], $[(\sin \theta)/\lambda]_{\text{max}} = 0.84$, $R = 0.049$, $R_w = 0.053$ [$w = 1/\sigma^2(F_o)$] for 192 parameters, structure solved by direct methods, H atom positions found and refined isotropically, multipole expansion: $R = 0.030$, $R_w = 0.032$ [$w = 1/\sigma^2(F_o)$] for 163 parameters, $[(\sin \theta)/\lambda]_{\text{max}} = 0.84$, coordinates and anisotropic displacement parameters fixed at their positions obtained from the high order refinement for C and P multipole coefficients up to the octopole level. Atomic coordinates, bond lengths and angles and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

Most interestingly, one of the phenyl rings attached to the phosphorus atom is coplanar with the central carbon skeleton. The torsional angle C1–P–C10–C11 is 3.34° , while C1–P–C20–C21 is 75.7° . The P–C_{sp³} bond

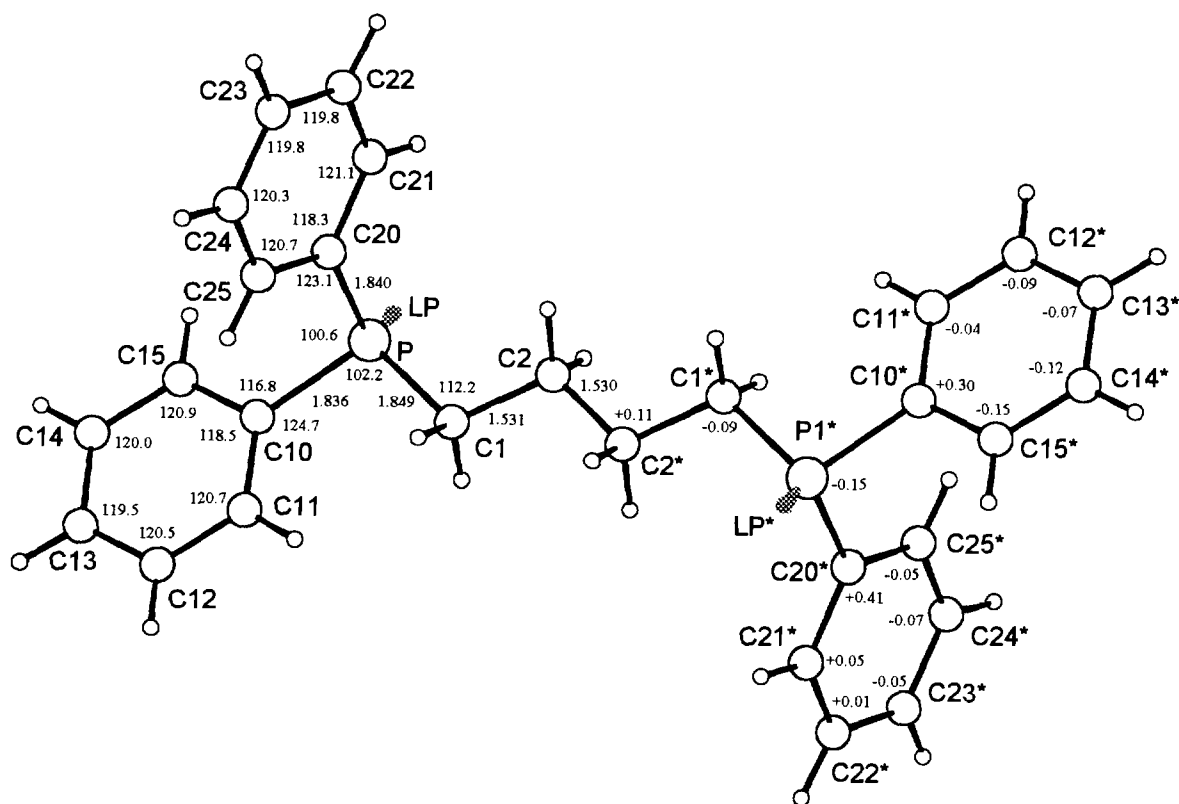


Fig. 8. Bis(diphenylphosphino)butane; some geometric data are depicted on the left-hand side while atomic charges as obtained from the monopole population of the multipolar refinement are shown on the right-hand side. Angles involving the lone pair position: C1–P–Lp 105° , C10–P–Lp 130° , C20–P–Lp 114° .

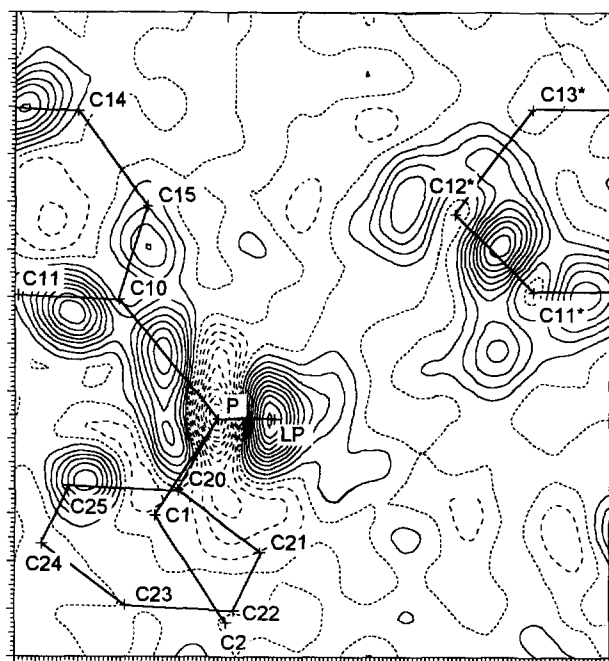


Fig. 9. EDD distribution in the plane C10–P–LP of bis(diphenylphosphino)butane with the lone pair pointing to a phenylic carbon atom, or rather hydrogen atom, of a neighboring molecular unit; contours at $0.1 \text{ e} \text{ \AA}^{-3}$, zero and negative contour lines are dashed.

length is $1.848(1) \text{ \AA}$ and, as one would expect, somewhat longer than the $\text{P}-\text{C}_{\text{aromatic}}$ bond lengths of $1.835(1)$ and $1.839(1) \text{ \AA}$ respectively. These values are in good

agreement with previously determined $\text{P}-\text{C}_{\text{aromatic}}$ distances in similar compounds [11,15], however, they differ substantially from those obtained by statistical search in the CSD bank [16], where 4537 examples give an average $\text{P}-\text{C}_{\text{aromatic}}$ distance of 1.819 \AA . This difference can be attributed to complexation of almost all of the compounds included in this search.

As exemplified in Fig. 6, the lone pair could be identified and located in the EDD refinement. It is also evident in the static model maps from the multipole expansion (Fig. 7), in which two of the quadrupolar terms indicate its location. Although the numerical values have to be interpreted with great caution, it can be seen in Fig. 8, which includes the position of the lone pair (LP), that the tetrahedral geometry at the P atom is confirmed by the lone pair position. It appears to be approximately coplanar with one of the phenyl rings (torsional angle $\text{LP}-\text{P}-\text{C}(20)-\text{C}(21)$ 15°). Most interestingly, the lone pair points towards a phenylic carbon atom, or rather a hydrogen atom of a neighboring molecular unit. These intermolecular interactions are depicted in the electron deformation density maps (Fig. 9), as well as in the packing diagram given in Fig. 10. These interactions are not located within the aromatic plane of the phenyl ring, as can be seen from the EDD map defined by the best plane through the phenyl ring in question. A detailed analysis of the static electron densities by methods developed by Bader [17] reveals no unexpected features. The $\text{C}_{\text{aromatic}}-\text{C}_{\text{aromatic}}$ bonds are

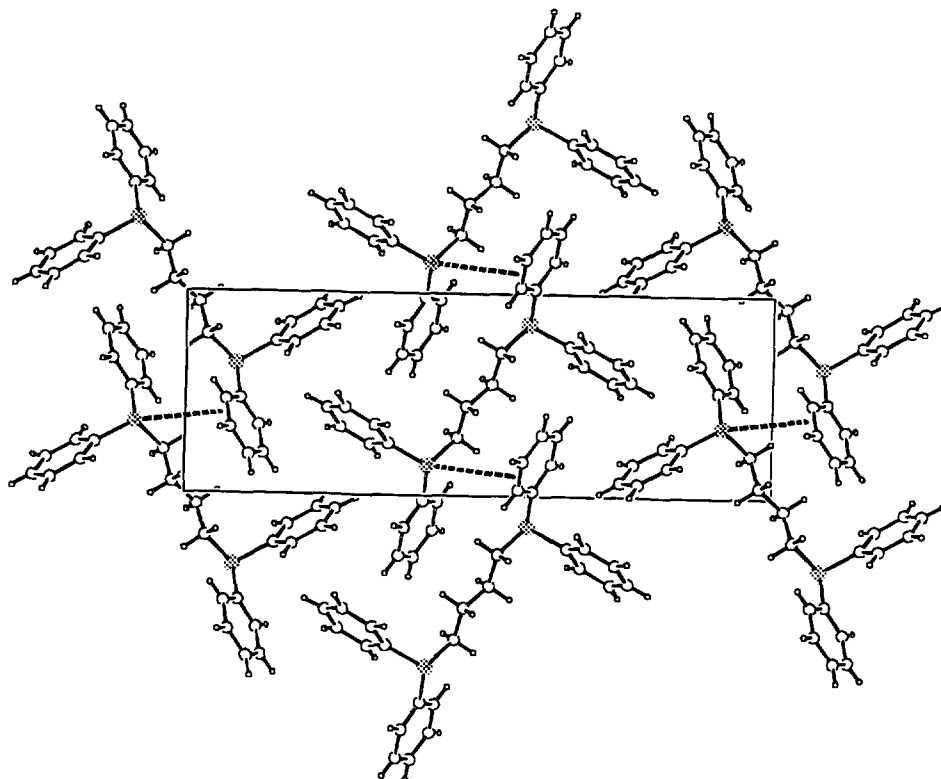


Fig. 10. A projection of the bis(diphenylphosphino)butane unit cell along the a -axis; dashed lines mark the intermolecular interactions.

of an elliptic shape, whereas the $C_{sp^3}-C_{sp^3}$ bond as well as the $P-C_{sp^3}$ bond are essentially circular.

The right-hand side of Fig. 8 shows atomic charges as obtained from the monopole population of the multipolar refinement. While the *ipso*-carbon atoms of the phenyl rings are positively charged, the phosphorus atoms bear a negative charge of $0.15 e^-$.

All relevant structural data of this comparative investigation are listed in Table 1 (further details are given in the deposited supplementary data). This includes the sum of the $C-P-C$ angles used to characterize the geometry at the phosphorus atoms, as well as the experimental cone angle and the cone angles as obtained from CPK models. A CAMD method to describe the accessible surface of transition metals in catalytic systems has been developed and described recently [18]. We have adopted this procedure to obtain accessible surfaces of phosphines and chelating phosphines described in this study. These values are included in Table 1, and they should give a more realistic numerical value than methods mentioned above to describe the steric strain and thus the complexing abilities of organophosphines.

In the course of this work the applicability of atomic force field parameters for phosphorus using the Tripos force field were reinvestigated [11,19,20]. Our own phosphorus parameters [11], which were optimized for phosphines bearing aromatic ligands, were checked. Matching of the modelled molecules and the molecular geometries, as found in the crystal structures, indicate a reasonably good quality for our phosphorus parameters (Table 1), although some calculated $C-P-C$ angles are too large ($3-6^\circ$). **4** and **5** show the largest deviations (RMS values) due to significant deviations in the torsional angles, and this might be due to packing effects which have not been taken into account by conventional molecular modeling techniques.

All crystal structures were solved using SHELX-86 [21]. SHELXL-93 [22] was used for localizing all atoms, whereas the final refinements were carried out using GFMLX (highly modified version of ORFLS [23]) and the enantiomorph-polarity estimation of Flack [24] based on *F*. To refine the multipolar parameters, the program MOLLY [25] was applied. Topological investigations of the electron density were carried out using XD [26].

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