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Cyclohexylbis(hydroxymethyl)phosphane: A Hydrophilic Phosphane Capable of Forming Novel Hydrogen-Bonding Networks

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The cyclohexyl-substituted (hydroxymethyl)phosphane CyP-$(CH_2OH)_2$ (**1**) has been prepared by reaction of the corresponding primary phosphane $CyPH_2$ with aqueous formaldehyde. Compound **1** has been used as building block for the synthesis of new functionalized water-soluble phosphorus compounds. Thus, Mannich-type condensation of **1** with excess glycine affords the air-stable amino acid phosphane conjugate $CyP[CH_2N(H)CH_2COOH]_2$ (**2**). Simple oxidation of **1** with hydrogen peroxide and elemental sulfur leads to the crystalline chalcogenide derivatives $CyP(O)(CH_2OH)_2$ (**3**) and $CyP(S)(CH_2OH)_2$ (**4**). X-ray diffraction analyses of the latter revealed distinct intermolecular hydrogen bonding motifs and possess different types of hydrogen bond networks to each other due to the different proton acceptor ability of the chalcogen atom X of the P=X group (X = O, S): while the oxygen atom of the P=O moiety in **3** serves as proton acceptor, affording a P=O–HO bifurcated network, the sulfur atom of the P=S group denies hydrogen bonding interactions. In addition, the ligand ability of **1** has been studied towards Pt(+2) and Cu(+1) ions: Reaction of **1** with $Pt(COD)Cl_2$ (COD = cycloocta-1,5-diene) furnishes the air-stable complex *cis*-$[PtCl_2\{CyP(CH_2OH)_2\}_2]$ (**5**), while the crystalline dimeric Cu(+1) complex $[CuI\{CyP(CH_2OH)_2\}_2]_2$ (**6**) results from the reaction of CuI with two molar equivalents of **1**. The complex **6** shows a intermolecular hydrogen bonding pattern different from that of **1**, **3** and **4**, respectively. The new coordination compounds **5** and **6** represent metal-phosphane labelled alcohols which are promising building blocks for the synthesis of metal-based drugs.

Introduction

(Hydroxymethyl)phosphanes $[P(CH_2OH)_xR_{3-x}$; R = H, alkyl, aryl; x = 1, 2, 3] constitute an important class of functionalized hydrophilic phosphanes, which have gained considerable prominence in recent years. They are accessible by insertion of formaldehyde into the P–H bonds of secondary and primary phosphanes or PH_3 and combine the chemical properties of common organophosphane donor ligands with that of hydrophilic alcohols. In other words, such phosphanes are excellent precursors for the synthesis of a variety of water-soluble organic and organometallic phosphorus compounds. Since the P–CH_2OH moieties can easily be re-transformed into P–H bonds by liberation of formaldehyde molecules, (hydroxymethyl)phosphanes can be considered as masked primary or secondary organophosphanes (RPH_2, R_2PH; R = alkyl, aryl) which are less sensitive against air but more water-soluble in contrast to the latter. Therefore (hydroxymethyl)phosphanes can participate in a number of chemical reactions, which are typical of PH_3 or organophosphanes, including oxidation reactions,[1,2] nucleophilic substitution and addition reactions to activated multiple bonds[1,3] or formation of phosphonium salts via nucleophilic addition to alkylhalides.[2] Another well established type of reactions of (hydroxymethyl)phosphanes represents the Mannich-type condensation with amino-functionalized compounds like amines,[4] amino acids[5] or enzymes,[6] which leads to the formation of (aminomethyl)phosphanes containing a >P–CH_2–N< moiety. As Henderson and co-workers have demonstrated, the Mannich-type condensation is, for example, a feasible method for the immobilization of phosphanes to amino-functionalized polymer supports[7] and also render covalent linkage of enzymes to insoluble supports by using multifunctional (hydroxymethyl)phosphanes like $P(CH_2OH)_3$ as coupling reagent.[6] Such immobilized supports are of high interest for the development of a new class of catalysts,[6] which may find diverse application, for imagine. In this context, metal complexes of phosphane-derived biomolecules[8] as well as the coordination chemistry of water-soluble (hydroxymethyl)phosphane ligands have attracted considerable interest in the last decade for the design and development of new water-soluble catalysts[9] or metal-based drugs.[8] (Hydroxymethyl)phosphane ligands, especially the parent system $P(CH_2OH)_3$, have been employed to synthesize stable water-soluble complexes with catalytic active metals (e.g. Rh and Ir)[10] – for their use in biphasic catalysis[11] –

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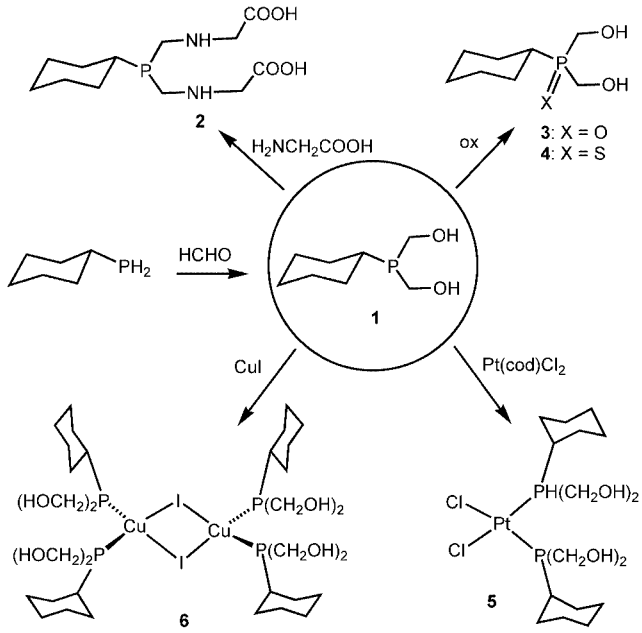
or with cytotoxic transition metals such as Pt and Au[12] for potential medical application. In addition, hydroxymethyl-functionalized phosphanes deserve not only attention as versatile phosphane ligands but also as versatile candidates for crystal engineering studies. Especially multifunctional bis(hydroxymethyl)phosphanes $RP(CH_2OH)_2$ and their chalcogenide derivatives $RP(X)(CH_2OH)_2$ (X = O, S) appear as potential building blocks for different hydrogen bonding pattern in solid state. However, there are only a few examples known, demonstrating that (hydroxymethyl) phosphanes and their chalcogenides[1] are able to form intermolecular hydrogen bonds. To our surprise, structural investigations are rather rare and only available for $(HOCH_2)_2P–CH_2CH_2–P(CH_2OH)_2$,[13] ferrocenyl (Fc)-substituted (hydroxymethyl)phosphanes,[2,14,15] and their derivatives $FcP(X)(CH_2OH)_2$ (X = O, S),[14,15] $FcCH_2P(S)(CH_2OH)_2$[2] and $FcCH(CH_3)P(S)(CH_2OH)_2$,[16] respectively. We report here the synthesis and characterization of a variety of new cyclohexyl-derived bis(hydroxymethyl) phosphane compounds. The versatile chemistry of the readily accessible phosphane $CyP(CH_2OH)_2$ (**1**) is demonstrated by several characteristic reactions, including Mannich-type condensation with glycine to form the amino acid phosphane conjugate **2** and simple oxidation reactions of the phosphorus atom with H_2O_2 and elemental sulfur, affording the new phosphane chalcogenides $CyP(X)(CH_2OH)_2$ (**3**) (X = O) and **4** (X = S), respectively. Additionally, initial studies on the coordination chemistry of ligand **1** were carried out towards Pt(+2) and Cu(+1) ions which lead to the new complexes **5** and **6** and represent metal-phosphane modified alcohols as potential precursors for metal-based drugs. In order to learn more about the molecular association of different bis(hydroxymethyl) phosphorus moieties with and without P=X functions (X = O, S) via hydrogen bonds, the structures of **1**, **3**, **4** and **6** were also established by X-ray diffraction analyses.

Results and Discussion

Synthesis and Characterization of 1–6

All reactions described in this work, that include the preparation of the starting compound $CyP(CH_2OH)_2$ (**1**) as well as the various syntheses performed with this precursor, are summarized in Scheme 1. A general procedure for the synthesis of hydroxymethyl-functionalized phosphanes involves hydrophosphanylation of the formyl group by addition of primary or secondary phosphanes to formaldehyde.[17] For the preparation of the title compound **1** we used $CyPH_2$[17] as starting material, which can easily be synthesized from commercially available and inexpensive chemicals. The formylation reaction of $CyPH_2$ with slight excess of aqueous formaldehyde solution (36.5%) at room temperature produced the bis(hydroxymethyl)phosphane (**1**) in almost quantitative yield (Scheme 1). The isolation of compound **1** can easily be achieved by removal of the solvent and excess formaldehyde in vacuo. The latter synthesis turned out to be much more efficient than the reported patent procedure,[18] by which **1** was obtained from the corresponding phosphonium salt by treatment with a base at 50 °C. However, no data concerning characterization of **1** were previously reported.



Scheme 1. Synthesis and reactions of $CyP(CH_2OH)_2$ **1**.

$CyP(CH_2OH)_2$ is an air-stable crystalline solid with an unpleasant odour, which is soluble in organic solvents as well as in water, due to its amphiphilic character. It was characterized by mass spectrometry, elemental analysis, NMR spectroscopy and X-ray diffraction analysis. The EI mass spectrum revealed the $[M]^+$ peak at m/z = 176 (19%) and respective fragment ions due to the elimination of formaldehyde and decomposition of the cyclohexyl group. The ^{31}P–NMR spectrum of **1** shows a broad singlet at δ = –11.4 ppm similar to the chemical shifts observed for related hydroxymethyl-functionalized phosphanes.[4] As expected, the ^1H-NMR spectrum of **1** reveals that the CH_2 protons of the PCH_2OH groups are chemically inequivalent (diastereotopic) and represent the AB part of an ABX spin system (A, B = ^1H; X = ^{31}P). The inequivalence of the methylene protons is caused by the pyramidally coordinated, prochiral phosphorus center. Simulation of the AB region of the ^1H NMR spectrum of **1** confirmed the observed eight-line pattern of higher order with partially overlapping signals for the CH_2 protons and their geminal coupling of J_{AB} = 13 Hz and two different $^2J_{P,H}$ coupling constants of 5.4 (P,A) and 3.9 Hz (P,B), respectively (Figure 1). Similar coupling patterns were also observed for other bis(hydroxymethyl) phosphanes like cam-$P(CH_2OH)_2$ (cam = 8-camphanyl)[19] and $FcP(CH_2OH)_2$,[14] which exhibit bulky groups directly bonded to the phosphorus atom.

As suggested previously[15] the close proximity of these bulky groups may cause restricted rotation around the P–CH_2 and/or CH_2–O bonds. The ability of **1** to associate via hydrogen bonds was confirmed by an X-ray diffraction analysis, showing that the molecules constitute a two-di-

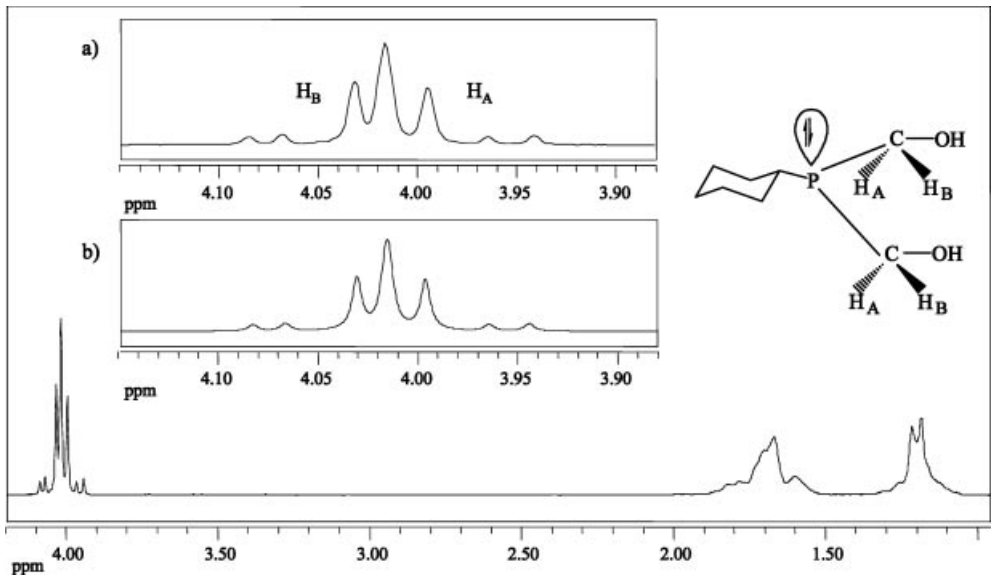


Figure 1. ^{1}H NMR-spectrum of **1**; a) measured; b) simulated.[20]

mensional hydrogen bond network with the OH groups serving as proton donors and acceptors (see next section). The apparently activated OH group of the hydroxymethyl-functionalized phosphane **1** can be used to synthesize various new phosphorus ligands in biomedical applications. Since phosphanyl-containing amino acids or peptides represent new carrier ligands for the development of novel metal-containing drugs, the synthesis of bio-compatible phosphorus compounds is of increasing interest. A possible synthetic route to such systems offers the Mannich-type condensation of the OH groups in (hydroxymethyl)phosphanes with the NH_2 groups in amino acids and peptides, respectively.[5] In fact, the Mannich-type condensation of CyP-$(CH_2OH)_2$ with 3.5-fold excess of glycine in oxygen-free water/ethanol at room temperature affords the phosphane-glycine conjugate CyP$[CH_2N(H)CH_2COOH]_2$ (**2**), in which each hydroxymethyl group was reacted with one glycine molecule (Scheme 1). Addition of excess molar amounts of glycine was necessary in order to prevent disubstitution reactions at the nitrogen centers. The glycine-derived phosphane **2** was obtained as an air-stable, colorless crystalline solid, which is moderately soluble in water, but insoluble in organic solvents. Due to the expected protonation of the amino functions and deprotonation of the COOH groups, **2** shows excellent solubility in aqueous Brønstedt acids and bases. The new conjugate **2** was characterized by NMR spectroscopy and ESI mass spectrometry. Solutions of *N*-protonated **2** in DCl/D_2O show one ^{31}P NMR resonance signal at δ = –24.4 ppm, similar to the values observed for related amino acid-functionalized phosphanes in acidic solutions.[5] The ^{1}H NMR spectrum exhibits two different sets of methylene protons: one for the methylene protons of the P–C*H*$_2$–N part and one for the NH_2^+–C*H*$_2$–COOH moiety. The first represents the AB part of an ABX spin system (A, B = ^{1}H; X = ^{31}P; J_{AB} = 14.1, $^2J_{P,A}$ = 1.0 and $^2J_{P,B}$ = 2.2 Hz), while the other is an AB spin system without ^{31}P coupling with a geminal A,B coupling of 17.2 Hz. In basic aqueous solutions ($NaOD/D_2O$), **2** is converted into the corresponding carboxylate with chemical equivalent methylene protons for the NH–CH_2–COO- moiety due to fast inversion of configuration at the nitrogen atom on the NMR time scale. However, this does not affect the AB pattern for the methylene protons of the P–CH_2–N moiety. The composition of **2** is proven by ESI mass spectrometry, recorded in negative mode, showing the $[M - H^+]$-ion peak at *m*/*z* = 289.3 as base-peak.

Oxidation of the phosphorus atom in **1** furnished the new crystalline chalcogenides CyP(X)$(CH_2OH)_2$ (**3**) (X = O) and (**4**) (X = S). The phosphane oxide **3** results by controlled oxidation of **1** with one equimolar amount of hydrogen peroxide in 81% yield (Scheme 1). The preparation of the phosphane sulfide homolog **4** was achieved in quantitative yield by stirring a solution of **1** in toluene with elemental sulfur at room temperature (Scheme 1). Both compounds are colorless crystalline solids, which are soluble in water and protic organic solvents like alcohols, but insoluble in apolar organic solvents in contrast to the parent phosphane **1**. The chalcogenides **3** and **4** were characterized by means of NMR spectroscopy and mass spectrometry. Their molecular structures were additionally confirmed by single-crystal X-ray diffraction analyses (see next section). As expected, the ^{31}P NMR chemical shifts of **3** (δ = 55.7 ppm) and **4** (δ = 54.5 ppm) are quite similar to values of related phosphane chalcogenides,[2,15] which usually appear at relatively low field. The ^{1}H NMR spectra of both compounds show unresolved overlapping multiplets for the methylene protons of the PCH_2OH groups, which indicate the expected chemical inequivalence (AB part of an ABX spin system; A, B = ^{1}H; X = ^{31}P) of the latter. The ^{13}C nucleus of the PCH_2OH groups exhibits a doublet in the $^{13}C\{^1H\}$ NMR spectra of **3** and **4**, respectively, with characteristically large ^1J(P,C) coupling constants (**3**: 75.6 Hz; **4**: 66.7 Hz) for phosphane chalcogenides.

In order to probe the coordination ability of **1**, the monodentate phosphane ligand was allowed to react with Pt(+2) and Cu(+1) compounds, since such metal complexes are of interest because of their important cytotoxic properties. In fact, the well established precursor $Pt(COD)Cl_2$ reacts with **1** in the molar ratio of 1:2 in dichloromethane at 25 °C, affording solely *cis*-$[PtCl_2\{CyP(CH_2OH)_2\}_2]$ (**5**) which can be isolated in 82% yield (Scheme 1). Complex **5** is an air-stable colorless crystalline solid, which is soluble in alcohols and moderate soluble in water. Its characterizations are based on multi-nuclear NMR spectroscopy, ESI-mass spectrometry and combustion analysis. Especially diagnostic is the $^{195}Pt\{^1H\}$ NMR spectrum of **5**, which shows one triplet at δ = –4523 ppm according to the coupling of the platinum nucleus with two chemically equivalent phosphorus atoms. The resulting $^1J_{Pt,P}$ coupling constant of 3490 Hz clearly indicates that the platinum atom has the *cis*-configuration.[21] This is evident by the fact that the corresponding *trans*-isomers of similar Pt complexes exhibit $^1J_{Pt,P}$ coupling constants which are around 1000 Hz lower than the values for *cis* complexes (e.g., *cis*-$[Pt\{P(CH_2OH)_3\}_2I_2]$: $^1J_{Pt,P}$ = 3227 Hz vs. *trans*-$[Pt\{P(CH_2OH)_3\}_2I_2]$: $^1J_{Pt,P}$ = 2162 Hz).[21] This trend can be simplified explained by the higher *trans*-influence of phosphorus compared to halide ligands, which weakens a Pt–P bond and hence lowers the Pt,P coupling constant. The ^{31}P NMR spectrum of complex **5** in CD_3OD shows one resonance signal at δ = 15.8 ppm for the two equivalent phosphorus nuclei. Additionally, ^{195}Pt-satellites can be observed, with the identical $^1J_{Pt,P}$ coupling constant as already observed in the corresponding ^{195}Pt NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum of complex **5** two unresolved multiplets were observed at δ = 36.0 ppm and δ = 54.8 ppm. Due to potential coupling with the adjacent phosphorus and platinum nuclei these signals are assigned to the carbon atoms, which are directly bonded to the phosphorus (C1–Cy and CH_2OH). As expected and similar to the "free" ligand **1** and its chalcogenides **3** and **4**, the methylene protons of the PCH_2OH groups of the complex **5** are chemically inequivalent. Thus, the ^1H NMR spectrum of **5** exhibits two broad multiplets at δ = 4.43 and 4.67 ppm for the inequivalent CH_2 protons, showing geminal coupling of 14 Hz and $^3J_{Pt,H}$ coupling constants of 18.6 Hz and 29.4 Hz, respectively, for the respective ^{195}Pt-satellites. The ESI mass spectra show the characteristic peak for the $[M - Cl]^+$ ion at m/z = 583.8 in positive mode and one for the $[M + Cl]^-$ ion peak at m/z = 653.8 in negative mode, which are typical for related platinum chloride complexes (e.g. *cis*-$[PtCl_2\{P(FcCH_2)(CH_2OH)_2\}_2]$).[15]

Similar reaction of $CyP(CH_2OH)_2$ ligand **1** with CuI in molar ratio of 1:2 in dichloromethane at room temperature (Scheme 1) furnished air-stable, colorless crystals of **6**, which are soluble in alcohols and moderate soluble in water. According to an X-ray structure analysis, compound **6** forms a dimer with two iodo-bridges between the Cu atoms and the dimers are associated via hydrogen bonds in a different motif than **1**, **3** and **4** (see next section). Complex **6** was also characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Its ^{31}P NMR spectrum in CD_3OD shows one resonance signal at δ = –7.9 ppm for the four chemically equivalent phosphorus atoms which is broadened ($h_{1/2}$ ca. 25 Hz) due to the presence of the $^{63/65}Cu$-quadrupole nuclei. Broadening of the resonance signals is also observed in the ^1H NMR spectrum of **6** which limits stereochemical information. While ESI-MS investigations of **6** were in contrast to **5** unsuccessful, FAB mass spectromeric measurements revealed at least the fragmention $[Cu\{CyP(CH_2OH)_2\}_2]^+$ at m/z = 415.2 as the largest fragment.

X-ray Crystal Structure Determinations

Crystal structure elucidations were performed for the compounds **1**, **3**, **4** and **6**. Because hydroxymethyl-functionalized phosphorus compounds represent oligoalcohol molecules, they have a large tendency to associate via hydrogen bonding which makes them to versatile building blocks for the construction of new architectures by molecular recognition for crystal engineering. In fact, the compounds show a different variety of hydrogen bonding networks. Single crystals of **1** suitable for an X-ray diffraction analysis were grown in EtOH/nBu$_2$O. (Table 1). However, the hydrogen-bonding network of **1** could not be analyzed by X-ray diffraction studies due to the moderate crystal quality. The compound crystallizes monoclinic with two independent molecules **1A** and **1B** in the unit cell (Figure 2). Their atomic distances and angles are practically identical and resemble the respective values observed for the related bis(hydroxymethyl) phosphanes $(Fc\text{-}P(CH_2OH)_2$,[15] $FcCH_2P(CH_2OH)_2$[2] or $(HOCH_2)_2P\text{–}CH_2CH_2\text{–}P(CH_2OH)_2$[13].

Table 1. Selected bond lengths [Å] and angles [°] for $CyP(CH_2OH)_2$ (**1**).

Molecule **1A**		Molecule **1B**	
lengths [Å]			
P(1)–C(7)	1.879(1)	P(2)–C(14)	1.896(9)
P(1)–C(15)	1.778(9)	P(2)–C(12)	1.790(9)
P(1)–C(13)	1.778(6)	P(2)–C(3)	1.770(5)
C(7)–O(4)	1.355(9)	C(14)–O(1)	1.362(1)
C(15)–O(3)	1.389(4)	C(12)–O(2)	1.333(2)
angles [°]			
C(7)–P(1)–C(15)	98.3(6)	C(14)–P(2)–C(12)	98.0(6)
C(7)–P(1)–C(13)	102.2(6)	C(14)–P(2)–C(3)	104.8(6)
C(15)–P(1)–C(13)	101.1(6)	C(12)–P(2)–C(3)	101.9(6)
P(1)–C(7)–O(4)	116.0(9)	P(2)–C(14)–O(1)	113.0(9)
P(1)–C(15)–O(3)	110.3(8)	P(2)–C(12)–O(2)	113.2(8)
O(1)···O(3)	2.620		
O(3)···O(4)	2.584		
O(4)···O(2)	2.651		

In contrast to the limited geometrical analysis of **1**, the crystal structure determinations of the phosphane derivatives $CyP(O)(CH_2OH)_2$ **3** and $CyP(S)(CH_2OH)_2$ **4** afforded better data sets (see Table 5) suitable for a topological analysis of the hydrogen-bonding networks. The latter revealed other types of hydrogen-bonding networks than that of the related ferrocenyl-substituted compounds $[FcP(X)(CH_2OH)_2$ (X = O, S),[15] $FcCH_2P(S)(CH_2OH)_2$,[2] and

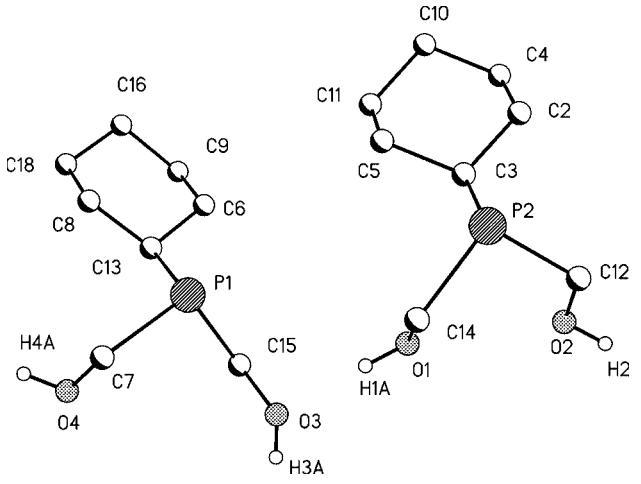


Figure 2. Molecular structure (without hydrogen atoms) of the two independent molecules of $CyP(CH_2OH)_2$ **1** in the unit cell.

$FcCH(CH_3)P(CH_2OH)_2$[16]] and presumably that of **1**. The molecular structures of compounds **3** and **4** are shown in the Figure 3 and Figure 6, respectively, while selected bond lengths and angles are given in the Table 2 and Table 3, respectively. The P–O bond length of 1.512 (4) Å in **3** is identical with that in $FcP(O)(CH_2OH)_2$ [1.510 (1) Å],[15] which represents the hitherto only known structure for this class of compounds. (Hydroxymethyl)phosphane oxides exhibit P=O groups which are favorable hydrogen-bond acceptors and therefore are predestined to form hydrogen bonds with proton donors like hydroxy groups. The hydrogen-bonding arrangement of compound **3** is shown in Figure 4, while Figure 5 depicts the crystal packing. In **3** each P=O group forms bifurcated hydrogen bonding interactions to the O–H groups of one neighboring molecule, with distances between hydrogen bonded oxygen atoms of 2.717 (6) Å for O(3)···O(1A) and 2.709 (6) Å for O(2)···O(1A), respectively. This leads to an arrangement of linked molecules via P=O···HO hydrogen bonds, where each molecule has solely two connected neighbors. As it is shown in the crystal packing of **3** (Figure 5), the one-dimensional chains are not linked to each other. The P=O···HO motif was also observed for the related compound $FcP(O)(CH_2OH)_2$.[15] but in contrast to **3**, $FcP(O)(CH_2OH)_2$ possesses a hydrogen-bonding network between three neighboring molecules, where each P=O unit forms hydrogen bonds to OH groups of different adjacent molecules.

As expected, the distances and angles around the P atom in the phosphane sulfide **4** (Table 3) are identical with that of the related compound $FcP(S)(CH_2OH)_2$.[7] The structure of **4** (Figures 6 and 7) shows a completely different hydrogen-bonding pattern compared to that of the oxide **3**. The hydrogen-bonding network and crystal packing of the sulfide **4** are presented in Figure 7 and Figure 8, respectively. Interestingly and in contrast to the oxygen atom in **3**, the sulfur atom in **4** is not involved in hydrogen-bonding. Hydrogen bonds are formed exclusively between the hydroxy groups, with each OH functionality acting as a donor in one and as an acceptor in another hydrogen bond. This

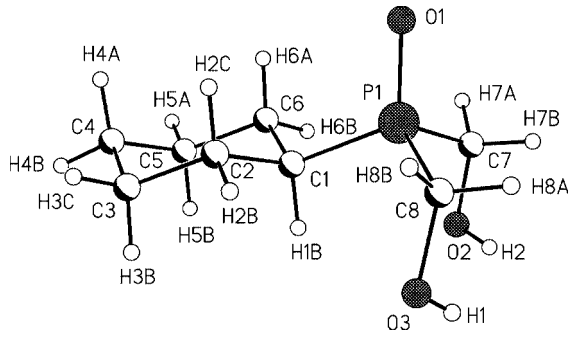


Figure 3. Molecular structure of $CyP(O)(CH_2OH)_2$ (**3**).

Table 2. Selected bond lengths [Å] and angles [°] for $CyP(O)(CH_2OH)_2$ (**3**).

P(1)–C(8)	1.808(6)	C(8)–P(1)–C(7)	107.9(3)
P(1)–C(7)	1.800(6)	C(8)–P(1)–C(1)	107.2(3)
P(1)–C(1)	1.795(6)	C(7)–P(1)–C(1)	107.7(3)
P(1)–O(1)	1.512(4)	C(8)–P(1)–O(1)	109.8(2)
C(8)–O(3)	1.422(6)	C(7)–P(1)–O(1)	109.4(2)
C(7)–O(2)	1.435(6)	C(1)–P(1)–O(1)	114.6(2)
O(3)–H(1)	0.71(5)	P(1)–C(8)–O(3)	114.0(4)
O(2)–H(2)	0.77(5)	P(1)–C(7)–O(2)	113.4(4)
H(1)···O(1A)	2.01(6)	C(8)–O(3)–H(1)	108(5)
H(2)···O(1A)	2.02(5)	C(7)–O(2)–H(2)	90(4)
O(3)···O(1A)	2.717(6)	O(3)–H(1)···O(1A)	171(6)
O(2)···O(1A)	2.709(6)	O(2)–H(2)···O(1A)	149(5)

Table 3. Selected bond lengths [Å] and angles [°] for $CyP(S)(CH_2OH)_2$ (**4**).

P(1)–C(7)	1.828(2)	C(7)–P(1)–C(8)	103.6(1)
P(1)–C(8)	1.833(2)	C(7)–P(1)–C(1)	106.02(9)
P(1)–C(1)	1.815(2)	C(8)–P(1)–C(1)	104.27(9)
P(1)–S(1)	1.954(8)	C(7)–P(1)–S(1)	111.33(7)
C(7)–O(2)	1.419(2)	C(8)–P(1)–S(1)	113.84(7)
C(8)–O(1)	1.415(3)	C(1)–P(1)–S(1)	116.56(7)
O(2)–H(2)	0.72(3)	P(1)–C(7)–O(2)	112.5(1)
O(1)–H(1)	0.77(2)	P(1)–C(8)–O(1)	110.9(1)
H(1)···O(2)	1.94(2)	C(7)–O(2)–H(2)	112(2)
H(2)···O(1)	1.98(3)	C(8)–O(1)–H(1)	109.(3)
O(1)···O(2)	2.686(2)	O(1)–H(1)···O(2)	164(3)
O(2)···O(1)	2.679(2)	O(2)–H(2)···O(1)	168(3)

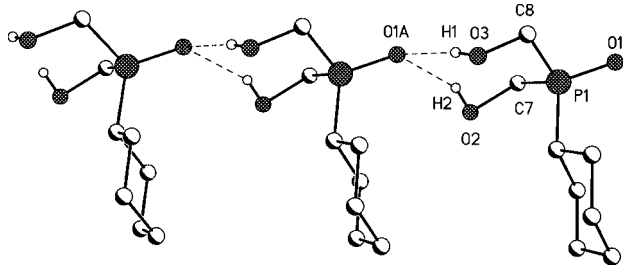


Figure 4. Intermolecular hydrogen bonds between **3** in the crystal.

leads to the formation of a two-dimensional hydrogen bonding network between three adjacent molecules, in which each molecule is crosslinked to four neighboring molecules.

Remarkably, the network of **4** with hydrogen bonded ten-membered rings is practically identical with that observed

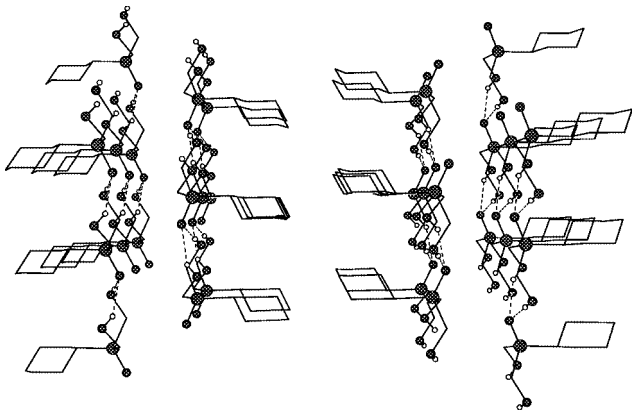


Figure 5. Crystal packing of $CyP(O)(CH_2OH)_2$ (**3**).

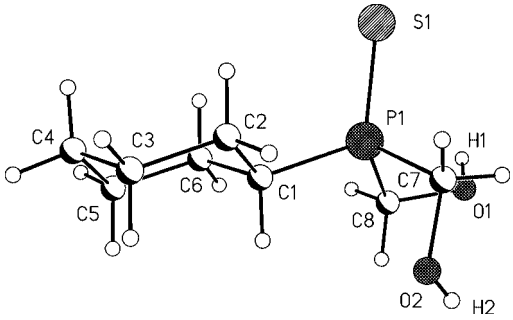


Figure 6. Molecular structure of $CyP(S)(CH_2OH)_2$ (**4**).

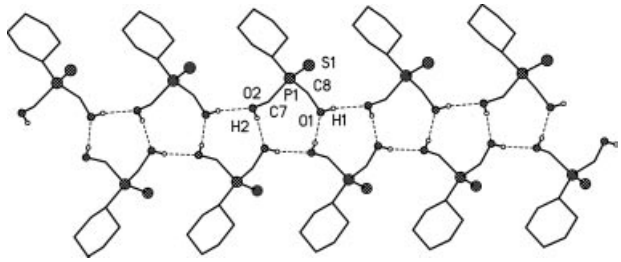


Figure 7. Two-dimensional network of **4** via hydrogen bonds.

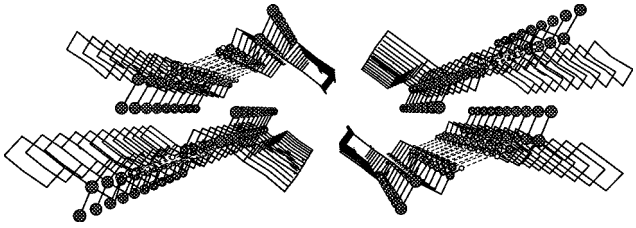


Figure 8. Crystal packing of $CyP(S)(CH_2OH)_2$ (**4**).

for the sulfur-free phosphane $FcP(CH_2OH)_2$[15] and reminiscent of that in the related sulfide $FcP(S)(CH_2OH)_2$.[15] In contrast to **4**, the hydrogen bonds in $FcP(S)(CH_2OH)_2$ are formed between three neighboring molecules with a network of alternating eight- and twelve-membered rings. However, in contrast to the sulfide **4** and $FcP(S)(CH_2OH)_2$, the structures of other related ferrocenyl-derived compounds $FcCH_2P(S)(CH_2OH)_2$[2] and $FcCH(CH_3)P(CH_2OH)_2$[16] show a hydrogen-bonding pattern with hydrogen bonds formed between the sulfur atom and hydroxy groups as well as between OH groups. The formation of O–H···S hydrogen bonds in $FcCH_2P(S)(CH_2OH)_2$ and $FcCH(CH_3)P(CH_2OH)_2$ on the one hand and the lack of O–H···S interactions in $FcP(S)(CH_2OH)_2$ and **4** on the other hand is rather peculiar. As already suggested previously,[15] the proximity of the bulky groups to the phosphorus centers in $FcP(S)(CH_2OH)_2$ and **4** may effectively shield the sulfur atoms and prevent hydrogen bonding interactions of the P=S group. Additionally, the sulfur atom of the P=S group is a much weaker hydrogen-bond acceptor compared to the P=O functionality.

As shown in the crystal packing diagrams of the compounds **3** (Figure 5) and **4** (Figure 8), the hydrophobic cyclohexyl groups have also an important influence on the aggregation behaviour of the molecules. Due to van der Waals interactions, the cyclohexyl groups are effectively stacked on each other, which leads to the formation of alternating hydrophobic and hydrophilic regions in the crystal packing.

The structural elucidation of the copper complex **6** revealed another new type of hydrogen-bonding network. The molecular structure and the hydrogen-bonding pattern of complex **6** are represented in the Figure 9 and Figure 10, respectively, while selected distances and angles are given in Table 4. The centrosymmetric complex **6** is a dimer and possesses two iodo-bridges in a planar Cu_2I_2 ring. There are other CuI–phosphane complexes known, having a four-membered Cu_2I_2 core and terminal coordinated monodentate phoshane ligands (e.g. $[CuI(PPh_2Me)_2]_2{\cdot}SO_2$,[22] $[CuI(PH_2Ph)_2]_2$[23] and $[CuI(PMe_3)_2]_2$[24]). Complex **6** represents the first example of a Cu(+1) complex containing functionalized monodentate phosphane ligands coordinated to a CuI dimer. The distances and angles of compound **6** are unexceptional and similar to that of $[CuI(PMe_3)_2]_2$.[24]

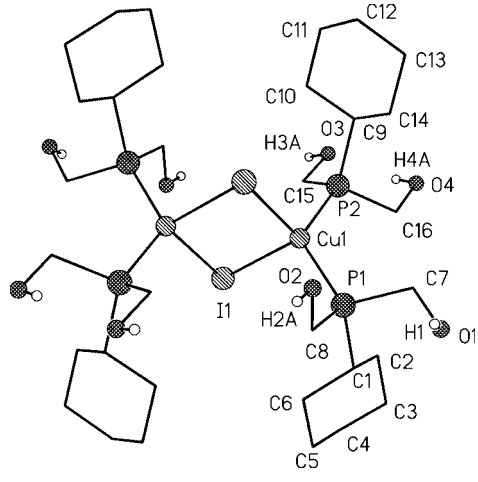


Figure 9. Molecular structure of $[CuI\{CyP(CH_2OH)_2\}_2]_2$ (**6**).

As expected, the crystal structure of **6** shows intermolecular hydrogen bonding interactions due to the presence of OH groups in the phosphane ligand. There exist two dif-

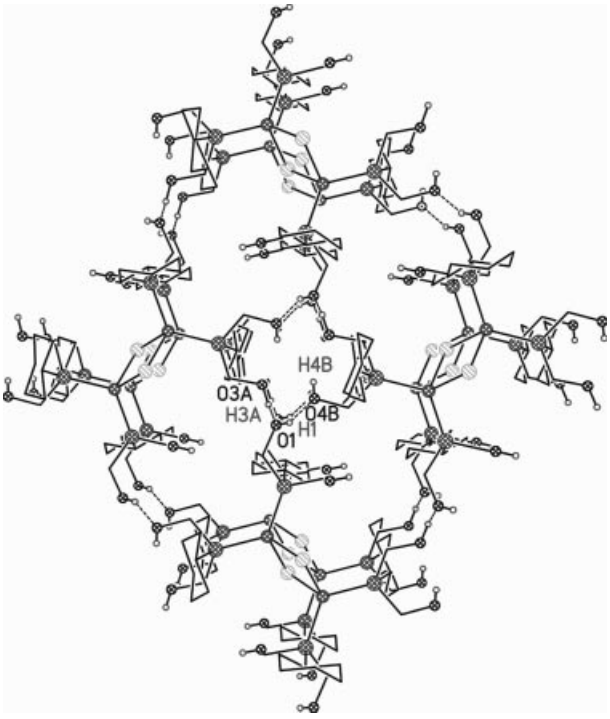


Figure 10. Hydrogen-bonding network in and crystal packing of $[CuI\{CyP(CH_2OH)_2\}_2]_2$ (**6**).

Table 4. Selected bond lengths [Å] and angles [°] of complex **6**.

Cu(1)–I(1)	2.716(4)	Cu(1)–I(1)–Cu′(1)	78.5(1)
Cu(1)–I′(1)	2.722(5)	I(1)–Cu(1)–I′(1)	101.4(1)
Cu(1)–P(1)	2.258(4)	P(1)–Cu(1)–P(2)	123.45(7)
Cu(1)–P(2)	2.257(4)	P(1)–Cu(1)–I(1)	109.0(1)
P(1)–C(7)	1.839(7)	P(1)–Cu(1)–I′(1)	105.70(7)
P(1)–C(8)	1.851(7)	P(2)–Cu(1)–I′(1)	111.7(1)
P(1)–C(1)	1.851(7)	P(2)–Cu(1)–I(1)	103.3(1)
P(2)–C(15)	1.843(7)	Cu(1)–P(1)–C(7)	114.2(2)
P(2)–C(16)	1.830(7)	Cu(1)–P(1)–C(8)	115.0(2)
P(2)–C(9)	1.838(7)	Cu(1)–P(2)–C(15)	113.2(2)
C(7)–O(1)	1.416(8)	Cu(1)–P(2)–C(16)	112.2(2)
C(8)–O(2)	1.412(8)	P(1)–C(7)–O(1)	114.4(5)
C(15)–O(3)	1.439(7)	P(1)–C(8)–O(2)	112.7(4)
C(16)–O(4)	1.449(8)	P(2)–C(15)–O(3)	113.1(4)
		P(2)–C(16)–O(4)	114.0(4)
O(1)···O(4B)	2.702(8)	O(1)–H(1)···O(4B)	155.9(4)
O(3A)···O(1)	2.684(8)	O(3A)–H(3A)···O(1)	164.2(4)

ferent types of intermolecular hydrogen bonds with the distances between the hydrogen bonded oxygen atoms O(1)···O(4B) of 2.702(8) Å and O(3A)···O(1) of 2.684(8) Å, respectively (Figure 10). The hydroxy group O(1)–H(1) of phosphane ligand 1 [with P(1)] acts as a donor in one hydrogen bond and as an acceptor in a second hydrogen bond with two adjacent molecules **6**. The hydroxy groups O(3)–H(3) and O(4)–H(4) of phosphane ligand 2 [with P(2)] are each involved in only one hydrogen bonding with two neighboring molecules. At least each dimer molecule is associated via six hydrogen bonds with four adjacent molecules, with the neighboring dimers are oriented about 90° to the observed molecule. This leads to the formation of two-dimensional networks, which are parallel stacked on each other.

Conclusion

The amphiphilic cyclohexyl (hydroxymethyl)phosphane **1** is a valuable building block for designing novel hydrogen bonding networks. Using the versatile reactivity of phosphane **1** a variety of functionalized phosphorus compounds can be synthesized. Thus, Mannich-type condensation of **1** with glycine produced the air-stable amino acid functionalized phosphane **2**, and the crystalline derivatives **3** and **4** were prepared by simple oxidation reactions. The X-ray crystal structure diffraction analyses revealed completely different hydrogen bonding pattern for the oxide **3** and the sulfide **4**. While **3** shows intermolecular bifurcated hydrogen bonding interactions between the strong P=O acceptor and the O–H donor groups, the sulfur atom of **4** was not involved in any hydrogen bond. The hydrogen bonding network in **4** was exclusively formed by O–H···O–H interactions and was similar to that observed for the related phosphane $FcP(CH_2OH)_2$.[14,15] In addition, the coordination chemistry of **1** was studied which led to the air-stable complexes *cis*-$[PtCl_2\{CyP(CH_2OH)_2\}_2]$ (**5**) and $[CuI\{CyP(CH_2OH)_2\}_2]_2$ (**6**), respectively. The crystal structure of the latter revealed another new type of hydrogen-bonding network where one OH group of phosphane ligand 2 [with P(2)] is not involved in any hydrogen bond.

Experimental Section

General Remarks: All manipulations were performed under dry and oxygen-free argon. Solvents were dried according to standard methods and saturated with argon or degassed, respectively. The NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer at room-temperature. Chemical shifts δ are given in ppm and were referenced against Me_4Si (^1H, ^{13}C; using residual protonated solvent peak or the carbon resonance, respectively), 85% H_3PO_4 (^{31}P) and H_2PtCl_6 in D_2O (^{195}Pt). ESI-mass spectrometric analysis were performed in the positive and the negative mode using a Bruker Esquire 3000 instrument. The EI- and FAB-mass spectra were recorded at a VG instruments Autospec/EBEE spectrometer. Elemental analyses were carried out on a VarioEL (CHN) elemental analyzer. $CyPH_2$[25] and $PtCl_2(COD)$[26] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and without further purification.

Preparation of $CyP(CH_2OH)_2$ (1): Aqueous formaldehyde (36.5%, 4.23 mL, 56.0 mmol) was placed in oxygen-free ethanol (10 mL) and purged with argon at room temperature for 30 min. Then a solution of $CyPH_2$ (2.60 g, 22.4 mmol) in 10 mL of oxygen-free ethanol was added dropwise and the mixture was stirred overnight at 25 °C. After removal of the solvent in vacuo the residual colorless solid is recrystallized from ethanol/di-*n*-butyl ether at –15 °C. Yield: 3.86 g, (98%). $C_8H_{17}O_2P$ (176.2): calcd. C 54.6, H 9.7; found C 54.4, H 10.1. ^1H NMR (250.13 MHz, D_2O): δ = 1.00–1.40 (m, 5 H, Cy), 1.44–1.98 (m, 6 H, Cy), 3.98 (dd, $^2J_{P,H}$ = 5.4, $^2J_{H,H}$ = 13.0 Hz, 2 H, PCH_2), 4.05 (dd, $^2J_{P,H}$ = 3.9, $^2J_{H,H}$ = 13.0 Hz, 2 H, PCH_2) ppm. ^{13}C NMR (62.90 MHz, D_2O): δ = 26.2 (s, C4-Cy),

26.4 (d, $^3J_{P,C}$ = 10.6 Hz, C3-, C5-Cy), 29.2 (d, $^2J_{P,C}$ = 12.0 Hz, C2-, C6-Cy), 29.4 (d, $^1J_{P,C}$ = 13.8 Hz, C1-Cy), 57.3 (d, $^1J_{P,C}$ = 10.4 Hz, PCH_2) ppm. ^{31}P NMR (101.25 MHz, D_2O): δ = –11.4 (br. s) ppm. EI-MS: *m/z* (%) = 176 [M^+ (19)], 146 [$M^+ - CH_2O$ (18)], 115 [$CyPH^+$ (17)], 83 [Cy^+ (70)], 55 [$C_4H_7^+$ (100)] 41 [$C_3H_5^+$ (74)].

Preparation of $CyP[CH_2N(H)CH_2COOH]_2$ (2): A solution of glycine (0.83 g, 11.38 mmol) in degassed water (3.5 mL) was added via a syringe to phosphane **1** (0.57 g, 3.24 mmol) in 1.5 mL oxygen-free ethanol and stirred overnight at 25 °C. The formed solid was filtered off and the filtrate evaporated giving the product as a colorless crystalline solid. Yield: 808 mg (86%). ^1H NMR (250.13 MHz, DCl/D_2O): δ = –0.92 to –0.80 (m, 5 H, Cy), –0.31 to –0.05 (m, 6 H, Cy), 1.61 (br. d, $^2J_{H,H}$ = 14.1 Hz, 2 H, PCH_2), 1.76 (dd, $^2J_{P,H}$ = 2.2, $^2J_{H,H}$ = 14.1 Hz, 2 H, PCH_2), 2.16 (d, $^2J_{H,H}$ = 17.2 Hz, 2 H, CH_2COOH), 2.20 (d, $^2J_{H,H}$ = 17.2 Hz, 2 H, CH_2COOH) ppm. ^{13}C NMR (62.90 MHz, DCl/D_2O): δ = 24.9 (s, C-4-Cy), 25.9 (d, $^3J_{P,C}$ = 11.3 Hz C-3-, C-5-Cy), 27.8 (d, $^2J_{P,C}$ = 10.8 Hz, C-2-,C-6-Cy), 32.8 (d, $^1J_{P,C}$ = 4.6 Hz, C-1-Cy), 43.6 (d, $^1J_{P,C}$ = 18.8 Hz, PCH_2), 48.4 (d, $^3J_{P,C}$ = 7.6 Hz, CH_2COOH), 168.0 (s, COOH) ppm. ^{31}P NMR (101.25 MHz, DCl/D_2O): δ = –24.4 (br. s) ppm. ESI-MS (negative mode): 289.3 [$M - H^+$].

Preparation of $CyP(O)(CH_2OH)_2$ (3): Aqueous hydrogen peroxide (0.3%, 6 mL) was added to a solution of compound **1** (100 mg, 0.568 mmol) in 20 mL methanol and stirred in air for 10 min. The solvent was removed at a rotor vapour, co-evaporated twice with water (2 × 10 mL) and washed with dry ether (10 mL). After drying in vacuo the product **3** was obtained as colorless crystalline solid. Yield: 87 mg (81%). $C_8H_{17}O_3P$ (192.2): calcd. C 50.0, H 8.9; found C 50.4, H 9.3. ^1H NMR (250.13 MHz, D_2O): δ = 1.10–1.41 (m, 4 H, Cy), 1.58 –1.85 (m, 6 H, Cy) 1.98 (m, 1 H, H1–Cy) 4.02 (m, 4 H, PCH_2) ppm. ^{13}C NMR (62.90 MHz, D_2O): δ = 24.4 (d, $^4J_{P,C}$ = 1 Hz, C-4-Cy), 25.7 (d, $^3J_{P,C}$ = 3.4 Hz, C3-, C-5-Cy), 25.9 (d, $^2J_{P,C}$ = 12.7 Hz, C-2,C-6-Cy), 32.2 (d, $^1J_{P,C}$ = 61.8 Hz, C-1 Cy), 54.8 (d, $^1J_{P,C}$ = 75.6 Hz, PCH_2) ppm. ^{31}P NMR (101.25 MHz, D_2O): δ = 55.7 (br. s) ppm. ESI-MS (negative mode): 191.3 [$M - H^+$].

Preparation of $CyP(S)(CH_2OH)_2$ (4): Elemental sulfur (86 mg, 2.670 mmol) was added to a solution of phosphane **1** (470 mg, 2.670 mmol) in 10 mL toluene at room temperature. While stirring for 30 min the sulfur disappeared and a colorless solid was formed. After evaporation of the solvent the residue was re-dissolved in ethanol (8 mL) and filtered. The solvent was again partly removed in vacuo and diethyl ether was added causing the product to precipitate. The solid was filtered off and dried in vacuo yielding **4** as a colorless crystalline solid. Yield: 555 mg (100%). $C_8H_{17}O_2SP$ (208.2): calcd. C 46.15, H 8.23; found C 45.9, H 8.15. ^1H NMR (250.13 MHz, D_2O): δ = 1.10–1.81 (m, 11 H, Cy), 4.18 (m, 4 H, PCH_2) ppm. ^{13}C NMR (62.90 MHz, D_2O): δ = 25.1 (s, C-4 Cy), 25.5 (d, $^3J_{P,C}$ = 3.8 Hz, C3-, C5-Cy), 26.5 (d, $^2J_{P,C}$ = 16.7 Hz, C-2,C-6 Cy), 32.8 (d, $^1J_{P,C}$ = 52.3 Hz, C-1Cy), 58.1 (d, $^1J_{P,C}$ = 66.7 Hz, PCH_2) ppm. ^{31}P NMR (101.25 MHz, D_2O): δ = 54.5 (s) ppm. EI-MS: *m/z* (%) = 208 [M^+ (69)], 178 [M^+-CH_2O (9)], 127 [$M^+ - Cy + H$ (47)], 126 [$M^+ - Cy + 2H$ (38)], 108 [$M^+ - Cy - OH$ (100)], 83 [Cy^+ (39)], 78 [$HP(S)CH_2^+$ (84)], 55 [$C_4H_7^+$ (82)], 41 [$C_3H_5^+$ (70)].

Preparation of *cis*-$[PtCl_2\{CyP(CH_2OH)_2\}_2]$ (5): Phosphane **1** (218 mg, 1.236 mmol) and $Pt(COD)Cl_2$ (231 mg, 0.618 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred for 2 h at room temperature. After standing for another 4 h at 25 °C the formed solid was filtered off and dried in vacuo giving the product as a colorless crystalline solid, which may be recrystallized from hot methanol. Yield: 313 mg (82%). $C_{16}H_{34}Cl_2O_4P_2Pt$ (618.4): calcd. C 31.1, H 5.5; found C 31.2, H 5.8. ^1H NMR (250.13 MHz, [D_4]MeOH): δ = 1.21 –1.79 (m, 12 H, Cy-H3,–H4,–H5), 1.83 (br. m, 4 H, Cy-H2,-H6), 2.21 (br. m, 4 H, Cy-H2,-H6), 2.58 (br. m, 2 H, Cy-H1), 4.43 (m, $^2J_{H,H}$ = 14.0, $^2J_{P,H}$ = 0.8, $^3J_{Pt,H}$ = 18.6 Hz, 4 H, PCH_2), 4.67 (m, $^2J_{H,H}$ = 14.0, $^2J_{P,H}$ = 2.0, $^3J_{Pt,H}$ = 29.4 Hz, 4 H, PCH_2) ppm. ^{13}C NMR (62.90 MHz, [D_4]MeOH): δ = 26.2 (br. s, C-4 Cy), 27.2/27.4 (d, $^3J_{P,C}$ = 6.0 Hz, C-3, C-5 Cy), 29.8 (br. s, C2-,C6-Cy), 36.0 (m, C-1 Cy), 54.8 (m, PCH_2) ppm. ^{31}P NMR (101.25 MHz, [D_4]-MeOH): δ = 15.8 [s; Pt-satellites (d), $^1J_{Pt,P}$ = 3490 Hz] ppm.

Table 5. Crystallographic data for compounds **1**, **3**, **4** and **6**.

	1	**3**	**4**	**6**
Empirical formula	$C_8H_{17}O_2P$	$C_8H_{17}O_3P$	$C_8H_{17}O_2PS$	$C_8H_{17}Cu_2I_2O_8P_4$
Formula mass	179.19	192.19	208.25	1085.62
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P2_1/n$
Cell constants				
a [Å]	34.28(2)	6.613(3)	15.882(5)	9.48(2)
b [Å]	5.161(4)	31.132(16)	6.4485(16)	17.39(3)
c [Å]	22.210(5)	5.4195(19)	11.102(3)	13.99(2)
β [°]	110.21(2)	114.014(14)	108.740(5)	107.81(8)
Volume [Å^3]	3687(5)	1019.2(8)	1076.7(5)	2196(7)
Z	16	4	4	2
Density (calculated) [Mg·m^{-3}]	1.269	1.252	1.285	1.642
Absorption coefficient [mm^{-1}]	0.251	0.239	0.412	2.562
Crystal size [mm]	0.3 x0.2 × 0.2	0.3 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Theta range for data collection	1.93 to 22.50	2.62 to 25.01	2.71 to 30.01	2.31 to 25.07
Reflections collected	2644	3799	5351	7412
Independent reflections	1974 (R_{int} = 0.1165)	1486 (R_{int} = 0.0879)	2730 (R_{int} = 0.0309)	3572 (R_{int} = 0.0337)
Goodness-of-fit on F^2	1.069	1.033	1.028	1.028
R indices [$I > 2\sigma(I)$]	R_1 = 0.1167, wR_2 = 0.2390	R_1 = 0.0790, wR_2 = 0.1874	R_1 = 0.0452, wR_2 = 0.1061	R_1 = 0.0468, wR_2 = 0.1194
R indices (all data)	R_1 = 0.2223, wR_2 = 0.2664	R_1 = 0.1250, wR_2 = 0.2142	R_1 = 0.0672, wR_2 = 0.1140	R_1 = 0.0616, wR_2 = 0.1302
Largest diff. peak/hole [e·Å^{-3}]	0.474/–0.448	0.443/–0.518	0.438/–0.305	2.456/–0.850

^{195}PtNMR (53.52 MHz, [D$_4$]MeOH): δ = –4523 (t, $^1J_{Pt,P}$ = 3502 Hz) ppm. ESI-MS (positive mode): 583.8 [M – Cl]. ESI-MS (negative mode): 653.8 [M + Cl].

Preparation of [CuI{CyP(CH$_2$OH)$_2$}$_2$]$_2$ (6): A solution of phosphane **1** (107 mg, 0.61 mmol) in 3 mL of CH_2Cl_2 was added dropwise to a suspension of CuI (58 mg, 0. 305 mmol) in 3 mL of CH_2Cl_2 at room temperature. After stirring for 4 h at 25 °C the solvent was removed under reduced pressure and the solid re-dissolved in 2 mL hot degassed methanol. Colorless crystals of product **6** were formed during 1 day standing at 25°, which were filtered off and dried in vacuo. Yield: 152 mg (92%). $C_{32}H_{68}Cu_2I_2O_8P_4$ (1085.7): calcd. C 35.4, H 6.3; found C 34.9, H 6.0. ^{1}H NMR (250.13 MHz, [D$_4$]MeOH): δ = 1.10–1.88 (m, 40 H, Cy), 2.01–2.20 (m, 4 H, 1-H Cy), 4.11 (br. s, 16 H, PCH$_2$) ppm. ^{31}P NMR (101.25 MHz, [D$_4$]MeOH): δ = –7.97 (br. s, $w_{1/2}$ = 35 Hz) ppm. FAB-MS: *m*/*z* (%) = 415.2 [Cu{CyP(CH$_2$OH)$_2$}$_2^+$ (30)], 239.3 [CuCyP(CH$_2$OH)$_2^+$ (24)], 176.2 [CyP(CH$_2$OH)$_2^+$ (34)].

X-ray Crystallographic Study: Crystals of **1**, **3**, **4** and **6** were mounted on top of a thin glass fiber. Data were collected with a a Bruker-AXS SMART1000 diffractometer with graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å). The crystal data are summarized in Table 5. Structures were solved by direct methods (SHELX-97) and refined (SHELXL-97) by full-matrix least-squares methods. Except for **1**, the positions of the O–H hydrogen atoms were localized in the difference Fourier map and refined. All other hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined. CCDC-260936 to -260938 (for **3**, **4**, **6**) and -283461 (for **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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