

Reactions of 1,1'-Diphosphaferrocene with CuCl and CuBr Resulting in Cu₄P₄X₄Fe₂ (X = Cl, Br) Complexes with Adamantane-like Topologies

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Dedicated to Professor Gerd Becker on the Occasion of His 70th Birthday

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Abstract. Cu₄P₄X₄Fe₂ (X = Cl, Br) cages are formed upon reactions of octaethyl-1,1'-diphosphaferrocene (odpf) with the respective Cu^I halide in CH₂Cl₂/CH₃CN solvent mixtures. These cages have adamantoid Cu₄X₄P₂ cores with two planar anelated CuP₂Fe rings as the flaps. Both complexes **1** and **2** feature tri- and tetra-coordinate Cu^I ions and an additional acetonitrile solvent molecule in the crystal. In **1**, the solvent molecule is coordinated to one copper ion whereas it remains uncoor-

ordinated in **2**. The tricoordinate Cu^I ions show a slight pyramidalization at the metal atom and somewhat short contacts to the other tricoordinate Cu^I ion in **2** or the Cu₃-triangle in **1**. NMR spectroscopy revealed easy decoordination of the acetonitrile ligand from **1** and a dynamic "windshield-wiper"-type process that interconverts the differently coordinated phospholide rings of each odpf ligand and the tri- and tetra-coordinate Cu^I ions.

Introduction

Reactions of Cu^I halogenides with potentially chelating bidentate diphosphanes may result in a variety of products depending on the stoichiometry, the chelate bite angle and the steric bulk of the diphosphane ligands. More subtle influences come from the nature of the halide or the solvent. To illustrate the first point, complexes with CuX:P₂ (X = halide, P₂ = diphosphane ligand) stoichiometric ratios of 1:2 [1–5], 2:3 [1, 6], 1:1 [5, 7–19], 3:2, [14, 20] and 2:1 [21–23] were isolated from such reactions, many of them with P_mCu_nX_{n-l} (l = 0, 1, or 2) frameworks where the edges of linear or triangular Cu₂ or Cu₃ arrays are bridged by the diphosphane and the halide ligands. The observation of significant anticancer activities for complexes Cu(P₂)₂⁺ X⁻ and (η²-P₂)ClCu(μ,η¹:η¹-P₂)CuCl(η²-P₂)₂ [1, 2] and, more recently, of the interesting photophysical properties of complexes like {CuI}₂(μ-dppm)₂, Cu₃(μ₃-I)(μ-I)₂(μ-dppm)₂, Cu₄(μ₄-I)₂(μ-I)₂(μ-dppm)₂, or [ClCu(μ-Cl)(μ-dppm)₂Cu(dmcn)]⁺ and Cu₃(μ₃-X)₂(μ-dppm)₃⁺ [13–15] have given additional impetus to further forays into this area (dppm = 1,2-bis(diphenylphosphanyl)methane, dmcn = dimethylcyanamide).

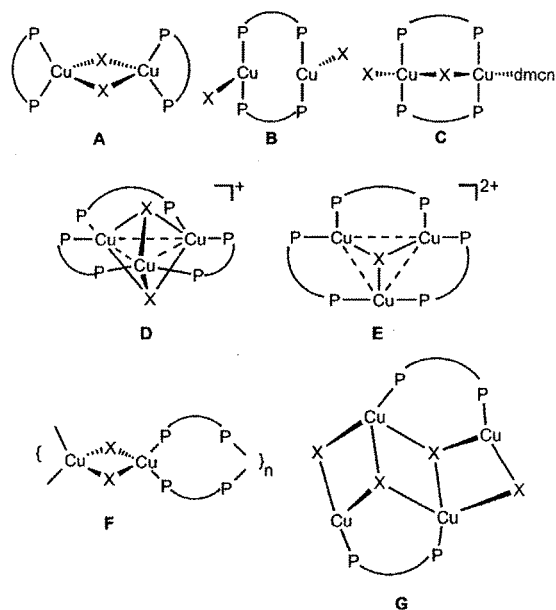
Complexes with a Cu:P₂ ratio of 1:1 display the largest structural versatility of all stoichiometries. Known structure types encompass discrete dinuclear complexes of types A–C [5, 10, 11, 14–16], triangular face- and edge-bridged complexes of types D and E [9, 12, 15] as well as chain-like one-dimensional polymers of type F where diamond-shaped Cu₂(μ-X)₂ units are each bridged by two diphosphane ligands (Scheme 1) [7, 8, 17–19, 21].

This structural diversity originates from the propensity of the halide to act as terminal, edge- or face-bridging ligand and of the diphosphane to coordinate in a monodentate, a bidentate chelating, or a bridging mode. Compared to the structural diversity exhibited by the 1:1 complexes, discrete copper(I) diphosphane adducts with a Cu:P₂ ratio of 2:1 are relatively scarce with Cu₄(μ₃-X)₂(μ-X)₂(μ-dppm)₂ (X = Cl, Br, I) as the most prominent examples (structure G in Scheme 1) [21–23]. The heavy atom framework is best described as featuring three annealed Cu₂X₂ rings in a "step" conformation where the two copper atoms at each side of the steps are interconnected by the phosphorus atoms of the same diphosphane ligand [21]. Amongst the diphosphanes used in copper halide chemistry is also octaethyl-1,1'-diphosphaferrocene (odpf). The latter has been reported to form [(odpf)₂Cu]⁺ PF₆⁻ when treated with [Cu(CH₃CN)₄]⁺ PF₆⁻ [24]. The ready availability of the related Au^I complex {ClAu}₂(μ-odpf) and of its octapropyl congener [25] suggested to us that a greater wealth of odpf Cu^I complexes awaits to be explored. We here report on the formation of Cu^I odpf complexes having unprecedented adamantane-like Cu₄X₄P₂Fe₂ heavy atom frameworks resulting from reactions of octaethyl-1,1'-diphosphaferrocene (odpf) with CuCl or CuBr in acetonitrile/dichloromethane mixtures. These complexes add new topologies to the few known structures of Cu^IX diphosphane complexes with 2:1 stoichiometries.

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Scheme 1. Framework structures of $\text{Cu}^{\text{I}}\text{X}$ diphosphine complexes of 1:1 (A–F) and 2:1 (G) stoichiometries.

Results and Discussion

The synthesis and structure of octaethyl-1,1'-diphosphaferrocene (odpf) have already been published [26]. The monoclinic unit cell was found to contain two different molecules with C_2 or C_{2h} conformations that differ with respect to the rotation of the individual phospholide rings and the orientations of the ethyl substituents. In the course of our investigations we obtained a triclinic modification of odpf with a unique C_i symmetric odpf molecule in the unit cell (see Figure 1 for an ORTEP). Crystal data and details pertaining to the structure solution are given in Table 1 whereas Table 2 lists the most pertinent bond lengths. As it was found in the previous structures, the phospholide rings are close to planar with the phosphorus atoms displaced by only 0.034 Å out of the best plane of the phospholide carbon atoms. All ethyl groups protrude away from the best phospholide planes as was found for the C_{2h} conformer of the monoclinic structure. The rings are almost perfectly staggered with uniform C–Ct–Ct'–P dihedrals of 34.6°, where Ct and Ct' denote the centroids of the phospholide rings. Average Fe–C distances of 2.076 Å, the Fe–P bond length of 2.2936(6) Å and the Fe–Ct distance of 1.655 Å are essentially identical to those of the previous structures and require no further comment. Individual molecules of odpf form rows along each of the unit cell axes in a stepped stair-like arrangement where the ethyl groups of adjacent molecules point towards the void between the individual decks of another odpf molecule or the central part of the phospholide ring of its immediate neighbors with no other intermolecular contacts than weak hydrophobic interactions between methyl protons belonging to different molecules. Figure S1 of the Supporting Information shows a view of the packing onto the bc plane

along the a axis with the shortest of these hydrophobic contacts of 2.396 Å (just 0.004 Å shorter than the sum of the Van der Waals radii) marked by a dotted line.

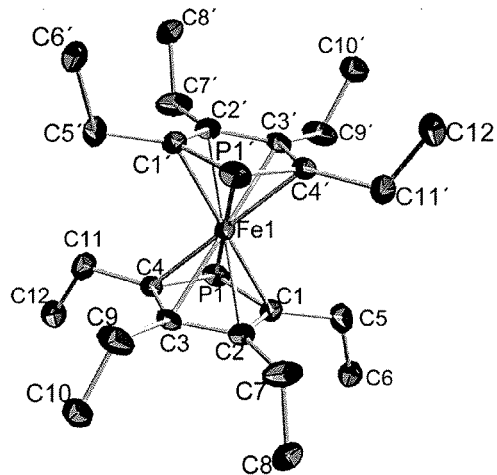


Figure 1. Structure of octaethyl-1,1'-diphosphaferrocene (odpf) as determined by X-ray crystallography; ellipsoids are drawn at a 50 % probability level.

Layering a CH_2Cl_2 solution of odpf with a solution of CuCl or CuBr in CH_3CN led, after complete diffusive mixing, to burgundy red solutions with the concomitant formation of red crystals in 65 to 74 % yields upon concentration. One specimen of each of these crystals was subjected to X-ray crystallography. The results of these studies showed the formation of cage compounds with a $\text{CuX}:\text{odpf}$ stoichiometry of 2:1, i.e. complexes of the general compositions $(\text{odpf})_2(\text{Cu}^{\text{I}}\text{X})_4$ in each case ($X = \text{Cl}$: 1, $X = \text{Br}$: 2). Details pertaining to the data collection, structure solution and refinement are provided in Table 1 whereas Table 3 summarizes the most pertinent interatomic distances and angles.

The structure of $(\text{odpf})_2\text{Cu}_4\text{Br}_4 \cdot \text{CH}_3\text{CN}$ (2) is shown in Figure 2. Four CuBr units form a central wedge-shaped, puckered $\text{Cu}_4(\mu\text{-Br})_4$ ring which closely resembles the S_4N_4 or the $\alpha\text{-As}_4\text{S}_4$ cages. The four bromide anions lie in a common plane whereas the four copper atoms form a highly distorted tetrahedron with $\text{Cu}\cdots\text{Cu}$ distances and $\text{Cu}\cdots\text{Cu}\cdots\text{Cu}$ angles that range from 2.648 to 3.829 Å and from 50.5 to 78.0°, respectively. The copper atoms thus occupy the positions of arsenic in $\alpha\text{-As}_4\text{S}_4$ or of sulfur in the S_4N_4 cages. The transannular $\text{Cu}\cdots\text{Cu}$ pairs are each bridged by one phosphorus donor atom of the odpf ligand whereas the second phosphorus atom of the same odpf donor additionally coordinates one copper atom of each of these $\text{Cu}\cdots\text{Cu}$ pairs (Cu(1) and Cu(3)) in a terminal fashion. The odpf ligand thus acts in an unsymmetrical $\mu_2\kappa^2P, P'; \kappa^2P$ -bridging mode. This renders a central $\text{P}_2\text{Cu}_4\text{Br}_4$ framework of adamantane-like structure that comprises four annealed six-membered PCu_3Br_2 rings, each in a chair conformation. Each of the two outer flaps of the adamantoid core are laterally condensed to one CuP_2Fe four-membered ring made up of one tetracoordinate Cu^{I} ion, Cu(1) or Cu(3), and the two phosphorus and the iron atoms of one odpf ligand. The entire

Table 1. Information pertaining to crystal data, structure data collection and structure refinement of odpf and of compounds **1** and **2**.

	odpf	1	2
Empirical formula	C ₂₄ H ₄₀ FeP ₂	C ₅₀ H ₈₃ Cl ₄ Cu ₄ Fe ₂ NP ₄ ·CH ₂ Cl ₂	C ₄₈ H ₈₀ Br ₄ Cu ₄ Fe ₂ P ₄ ·CH ₃ CN
f. w. /amu	446.35	1414.69	1507.56
T /K	123	123	123
λ /Å	1.5148	1.54184	1.54184
Crystal system	triclinic	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
Unit cell dimensions			
a / Å	7.7155(4)	10.2662(12)	10.514(2)
b / Å	9.0053(5)	15.392(3)	10.879(2)
c / Å	9.0733(5)	20.508(5)	27.453(5)
a	90.532(5)	106.87(2)	95.50(2)
β	108.618(5)	97.104(14)	90.017(13)
γ	90.082(5)	100.246(12)	103.88(15)
V /Å ³	597.39(6)	2998.5(11)	3043.7(9)
Z	1	2	2
ρ _{calcd.} /Mg·m ⁻³	1.241	1.567	1.645
μ /mm ⁻¹	6.352	9.048	9.549
F(000)	240	1456	1516
Crystal color / size /mm	orange plate, 0.160 × 0.120 × 0.030	magenta plate, 0.380 × 0.090 × 0.040	purple rod, 0.130 × 0.040 × 0.010
θ range	5.14 ≤ θ ≤ 62.21	3.08 ≤ θ ≤ 62.10	3.24 ≤ θ ≤ 51.69
Index ranges	-8 ≤ h ≤ 8 -10 ≤ k ≤ 9 -10 ≤ l ≤ 10	-10 ≤ h ≤ 11 -17 ≤ k ≤ 17 -22 ≤ l ≤ 23	-10 ≤ h ≤ 10 -11 ≤ k ≤ 10 0 ≤ l ≤ 27
Refl. coll.	5876	22099	6600
Indep. Refl.	1741	9196	6000
Obsd. data [I > 2σ(I)]	1553	6856	4661
R _{int}	0.0263	0.0412	0.0000
Completeness to θ	0.915	0.972	0.983
Data/restraints/parameters	1741/0/128	9196/0/614	6600/0/598
Goodness-of-fit on F ²	1.046	1.065	0.988
Final R indices [I > 2σ(I)]	0.0326/0.0870	0.0555/0.1466	0.0419/0.1020
R indices (all data)	0.0363/0.0893	0.0761/0.1634	0.0648/0.1158
Largest diff. peak and hole / e·Å ⁻³	0.463/-0.230	1.224/-1.065	0.785/-0.618

Table 2. Selected bond lengths /Å for odpf.

Bond length /Å	Bond length /Å	Bond length /Å	Bond length /Å
Fe(1)–P(1)	2.2936(6)	Fe(1)–C(4)	2.064(2)
Fe(1)–C(1)	2.091(3)	Fe(1)–C(4)	2.088(2)
Fe(1)–C(2)	2.063(3)	Fe(1)–C ^a	1.655

a) centroid of the tetraethylphospholide ligand

(odpf)₂Cu₄Br₄ framework of **2** shows approximate (but not exact) inversion symmetry.

The Cu^I ions thus come as pairs of tetra- and tricoordinate atoms with distorted tetrahedral or trigonal planar coordination. As expected, the Cu–P and Cu–Br bond lengths of the tricoordinate copper ions are appreciably shorter than those of the tetrahedrally coordinated ones with average values of 2.200 (Cu–P) and 2.386 (Cu–Br) Å for Cu(2) and Cu(4) as compared to 2.326 and 2.440 Å for Cu(1) and Cu(3). The annealed four-membered Cu(1),P(1),P(2),Fe(1) and Cu(3),P(3),P(4),Fe(2) rings are nearly planar with folding angles of just 1.5 or 1.9°. Restrictions imposed by the rather rigid odpf framework render the P(1)–Cu(1)–P(2) and P(3)–Cu(3)–P(4) angles somewhat acute at 102.85(8) and 103.03(8). Steric strain within the odpf–Cu^I chelate is also evidenced by a displacement of the phosphorus atoms out of the best planes of their respective phospholide rings by an average of 0.13 Å with a slight elongation of the Fe–P bond lengths (range 2.304(2) to 2.349(2) Å) with respect to free odpf [*d*(Fe–P) = 2.2936(6) Å], and by a tilting of the two phospholide rings of the odpf entities by 6.9 or 7.5°. All these results differ from free odpf where the individual phospholide rings are strictly planar and parallel [26]. The two odpf subunits of **2** are orthogonal to each others with interplanar angles of 89.1° to 89.8° between the best planes of phospholide rings that belong to different odpf moieties.

Of note is the displacement of both tricoordinate Cu^I atoms, Cu2 and Cu4, by 0.158 Å (Cu(2)) or 0.157 Å (Cu(4)) out of the best planes of their coordinated ligands towards the other tricoordinate Cu^I atom. This renders the Cu(2)···Cu(4) distance of 2.648(2) Å somewhat shorter than the nominal sum of their Van der Waals radii of ca. 2.80 Å. There is an ongoing discussion about the relevance and nature of Cu^I···Cu^I “cuprophilic” interactions [27, 28] and many examples where such interactions were invoked to explain short Cu^I···Cu^I contacts were reported [29–33]. There are, however, also other examples of even shorter structure-imposed Cu^I···Cu^I contacts in the probable absence of such interactions [15]. We just note here, that the inward bending of the Cu(2) and Cu(4) ions in **2** results in a somewhat acute Cu(2)–Br(4)–Cu(4) angle of 66.61(5)°

Table 3. Selected bond lengths /Å and angles /° for the (odpf)₂Cu₄Br₄ and the (odpf)₂Cu₄Cl₄ cages present in compounds **2** and **1**.

1		2	
Cu(1)–Cl(1)	2.346(2)	Cu(1)–Br(1)	2.4398(14)
Cu(1)–Cl(2)	2.310(2)	Cu(1)–Br(3)	2.4781(14)
Cu(1)–P(1)	2.330(2)	Cu(1)–P(1)	2.325(2)
Cu(1)–P(2)	2.317(2)	Cu(1)–P(2)	2.324(2)
Cu(2)–Cl(3)	2.249(2)	Cu(2)–Br(2)	2.3677(14)
Cu(2)–Cl(4)	2.275(2)	Cu(2)–Br(4)	2.4126(14)
Cu(2)–P(2)	2.203(2)	Cu(2)–P(2)	2.199(2)
Cu(3)–Cl(1)	2.316(2)	Cu(3)–Br(1)	2.4294(14)
Cu(3)–Cl(4)	2.313(2)	Cu(3)–Br(2)	2.5225(15)
Cu(3)–P(4)	2.259(2)	Cu(3)–P(3)	2.335(2)
Cu(3)–N(1)	2.076(6)	Cu(3)–P(4)	2.321(2)
Cu(4)–Cl(2)	2.308(2)	Cu(4)–Br(3)	2.3533(14)
Cu(4)–Cl(3)	2.373(2)	Cu(4)–Br(4)	2.4099(14)
Cu(4)–P(3)	2.323(2)	Cu(4)–P(4)	2.202(2)
Fe(1)–P(1)	2.342(2)	Fe(1)–P(1)	2.349(2)
Fe(1)–P(2)	2.323(2)	Fe(1)–P(2)	2.309(2)
Fe(2)–P(3)	2.347(2)	Fe(2)–P(3)	2.343(2)
Fe(2)–P(4)	2.329(2)	Fe(2)–P(4)	2.315(2)
Cu(4)–P(4)	2.310(2)	Fe(1)–PC _{4,a} ^{a)}	1.690
Fe(1)–PC _{4,a} ^{a)}	1.682	Fe(1)–PC _{4,b} ^{b)}	1.681
Fe(1)–PC _{4,b} ^{b)}	1.688	Fe(2)–PC _{4,c} ^{c)}	1.690
Fe(2)–PC _{4,c} ^{c)}	1.682	Fe(2)–PC _{4,d} ^{d)}	1.680
Fe(2)–PC _{4,d} ^{d)}	1.690	P(1)–Cu(1)–P(2)	102.85(8)
P(1)–Cu(1)–P(2)	102.65(6)	Br(1)–Cu(1)–Br(3)	111.13(5)
Cl(1)–Cu(1)–Cl(2)	105.12(6)	Br(1)–Cu(1)–P(1)	109.50(7)
Cl(1)–Cu(1)–P(1)	105.27(7)	Br(1)–Cu(1)–P(2)	113.81(7)
Cl(1)–Cu(1)–P(2)	111.08(6)	Br(3)–Cu(1)–P(1)	101.58(7)
Cl(2)–Cu(1)–P(1)	112.61(6)	Br(3)–Cu(1)–P(2)	116.65(6)
Cl(2)–Cu(1)–P(2)	102.65(6)	Br(2)–Cu(2)–Br(4)	111.75(5)
Cl(3)–Cu(2)–Cl(4)	115.07(7)	Br(2)–Cu(2)–P(2)	130.49(7)
Cl(3)–Cu(2)–P(2)	127.10(7)	Br(4)–Cu(2)–P(2)	116.36(7)
Cl(4)–Cu(2)–P(2)	114.70(7)	Br(1)–Cu(3)–Br(2)	108.72(5)
Cl(1)–Cu(3)–Cl(4)	111.01(7)	P(3)–Cu(3)–P(4)	103.03(8)
Cl(1)–Cu(3)–P(4)	116.78(6)	Br(1)–Cu(3)–P(3)	110.38(7)
Cl(4)–Cu(3)–P(4)	116.84(7)	Br(1)–Cu(3)–P(4)	115.37(5)
Cl(1)–Cu(3)–N(1)	102.2(2)	Br(2)–Cu(3)–P(3)	106.29(7)
Cl(4)–Cu(3)–N(1)	107.8(2)	Br(2)–Cu(3)–P(4)	112.57(7)
P(4)–Cu(3)–N(1)	100.0(2)	Br(3)–Cu(4)–Br(4)	113.36(5)
Cl(2)–Cu(4)–Cl(3)	111.11(6)	Br(3)–Cu(4)–P(4)	127.90(8)
P(3)–Cu(4)–P(4)	103.29(6)	Br(4)–Cu(4)–P(4)	117.36(7)
Cl(2)–Cu(4)–P(3)	105.60(6)		
Cl(2)–Cu(4)–P(4)	119.21(7)		
Cl(3)–Cu(4)–P(3)	107.02(7)		
Cl(3)–Cu(4)–P(4)	109.58(6)		

a)–d) centroids of the tetraethylphospholide ligands containing phosphorus atoms P(1) to P(4), respectively.

whereas the other Cu–Br–Cu angles are in the range 78.99(5) to 103.68(5)°. The sum of all bonding angles of 358.6° for the tricoordinate copper ions in **2** indicates, however, an only slight pyramidalization.

Individual (odpf)₂Cu₄Br₄ cages of **2** pack in rows along the *b* axis and are weakly interconnected via odpf CH⋯Br contacts of 3.027 Å, which is only 0.023 Å shorter than the sum of the VdW radii. A view along the *a* axis where these contacts are indicated by dotted lines is shown in Figure S2 of the Supporting Information. Although there is one CH₃CN solvent molecule present per cage and despite the presence of two tricoordinate Cu^I ions and the rather high affinity of the Cu^I ion towards the CH₃CN ligand, the solvent molecules just fill the voids

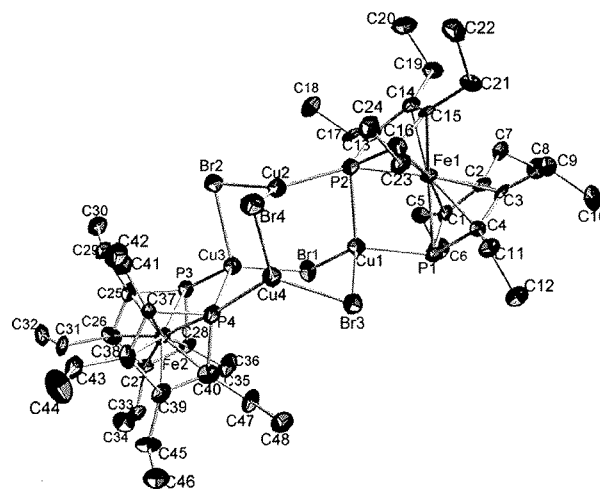


Figure 2. Structure of the (odpf)₂Cu₄Br₄ cage as it is present in **2**; ellipsoids are drawn at a 50 % probability level.

between the cages without having any obvious contact to the cages. This may be due to a dynamic process that exchanges the identities of the tri- and tetracoordinate Cu^I ions in solution (vide infra).

The (odpf)₂Cu₄Cl₄·CH₃CN·CH₂Cl₂ cage of **1** exhibits essentially the same adamantanoid core structure with diamond-shaped, annealed, four-membered CuP₂Fe rings and the same μ,κP,P',κP-coordination mode of the odpf ligands as they are present in **2**. The only difference is the coordination of the CH₃CN solvent molecule to Cu(3). This leaves Cu(2) as the only tricoordinate Cu^I ion of this structure (Figure 3). Despite the displacement of Cu(2) by 0.23 Å out of the plane spanned by its immediately attached donor atoms P(2), Cl(3) and Cl(4) toward the triangle formed by the remaining copper atoms, neither the Cu(2)–Cl(3)–Cu(4), nor the Cu(2)–Cl(4)–Cu(3) or the Cu(2)–P(2)–Cu(1) bond angles are unusually acute compared to the remaining ones at the tetracoordinate copper ions.

Copper coordination of the odpf phosphorus atoms has the same structural consequences as in the bromide analog **2**, i.e. a slight displacement of the phosphorus atoms out of the planes of the four phospholide carbon atoms and a tilting of the best phospholide planes of the same odpf molecule by 6.7° or 7.2°, respectively. Again, the two odpf subunits are almost orthogonal to each others with interplanar angles of 82.8° to 85.1° between the phospholide ligands of different odpf entities.

(Odpf)₂Cu₄Cl₄·CH₃CN·CH₂Cl₂ cages pack as dimers along the *c* axis of the unit cell which are held together by a total of six hydrogen bonds involving weak CH⋯Cl interactions between one methyl proton of a pendant C₂H₅ group of the tetraethylphospholide ligand and a CH₂Cl₂ chlorine atom (H(43B)⋯Cl(5) = 2.901 Å), stronger H⋯Cl contacts between one of the CH₂Cl₂ protons to Cl(1) of the cage (H(51A)⋯Cl(1) = 2.620 Å) and additional contacts between one of the methyl protons of the CH₃CN ligand to Cl(4) of the cage (H50B⋯Cl(4) = 2.836 Å). One such hydrogen bonded

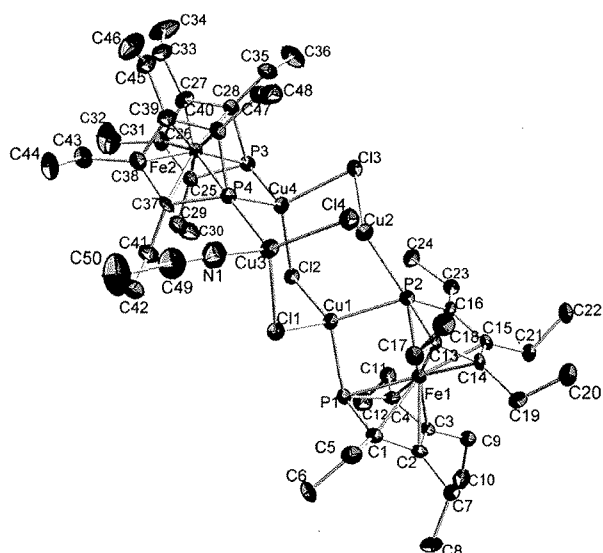


Figure 3. Structure of the $(\text{odpf})_2\text{Cu}_4\text{Cl}_4\cdot\text{CH}_3\text{CN}$ cage present in compound **1**. Ellipsoids are drawn at a 50 % probability level.

dimer with the $\text{H}\cdots\text{Cl}$ contacts indicated by dotted lines is shown in Figure 4.

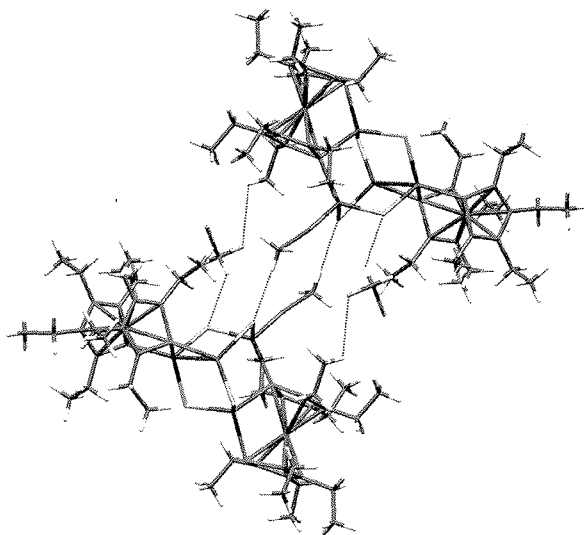
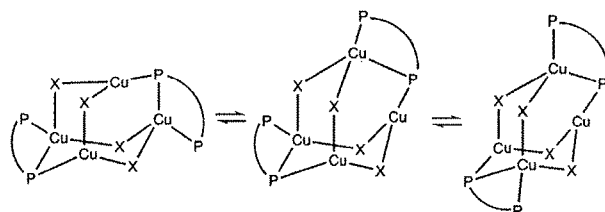


Figure 4. View of a hydrogen bonded dimer of $(\text{odpf})_2\text{Cu}_4\text{Cl}_4\cdot\text{CH}_3\text{CN}\cdot\text{CH}_2\text{Cl}_2$; hydrogen bonds are indicated by thin dotted lines.

In ^1H NMR spectroscopy cages **1** and **2** display just two sharp triplet resonance signals for the methyl protons, one for the ethyl groups in the neighboring and one for those at the remote positions of the phospholide phosphorus atoms each (see Figure S3 of the Supporting Information). Owing to their diastereotopic nature, four resonance signals are observed for the ethylene protons. Despite the presence of the acetonitrile solvent molecule in the crystals no resonance signals assigna-

ble to the CH_3CN protons were observed for dissolved crystalline samples in CD_2Cl_2 solutions. This may be the result of a dynamic process involving a coordination–decoordination equilibrium or the loss of CH_3CN from the solids upon the evacuation process during sample preparation. Samples prepared for combustion analysis also suffer easy loss of the CH_3CN solvent molecule. ^{31}P NMR spectra show just one sharp singlet resonance near -145 ppm (Figures S4 and S5 of the Supporting Information). This resonance signal is considerably downfield from that of uncoordinated odpf ($\delta = -66$ in CDCl_3) but also at higher field as in the $[(\text{odpf})_2\text{Cu}]^+$ cation ($\delta = -163.7$) [24].

Taken together, the NMR spectroscopic results suggest that (i) the cages of complexes **1** and **2** share the same structure in fluid solution with dissociation of the acetonitrile ligand from **1** upon dissolution, (ii) the nature of the halide exerts only a negligible influence on the ^{31}P NMR shift of the odpf ligands, and, most importantly, (iii) that a dynamic process is operative, which interconverts the tri- and tetracoordinate Cu^{I} ions and the terminally coordinated and the bridging phospholide rings of each individual odpf ligand. This process may be described as a “windshield-wiper” sliding movement of the odpf ligands along the $\text{Cu}(1)\cdots\text{Cu}(2)$ and the $\text{Cu}(3)\cdots\text{Cu}(4)$ vectors (see Scheme 2). This process simultaneously explains the presence of just one set of resonance signals for ethyl groups in the 2,5 and in the 3,4-positions of the phospholide rings. Attempts to investigate this dynamic process by variable temperature NMR spectroscopy showed no evidence of decoalescence upon cooling besides a slight broadening of the respective NMR signals (see Figure S6 of the Supporting Information). We thus conclude that this dynamic process is highly efficient and is still operative even at temperatures as low as 203 K.



Scheme 2. Proposed “windshield-wiper” type movement of the odpf ligands along the bridged $\text{Cu}\cdots\text{Cu}$ vectors as an explanation of the dynamic interconversion of tri- and tetracoordinate Cu^{I} ions and the bridging as well as the terminally coordinated odpf phospholide rings (schematized).

The close match of UV/Vis spectra of **1** and **2** and between spectra recorded for fluid solutions and for powdered crystalline samples provide further evidence for the identity of the $(\text{odpf})_2(\text{CuX})_4$ ($X = \text{Cl}, \text{Br}$) cages and for the preservation of the cage structures in fluid solution (see Figure 5 and Figures S7 and S8 of the Supporting Information). Electronic spectra feature more intense bands at 348 and 406 nm for **2** (345 and 405 nm for **1**) and weaker absorptions at 495 and 581 nm for **2** (495 and 578 nm for **1**) in both the solid state and in solution. With reference to the extensive literature on particularly the

cubane shaped $\text{Cu}_4(\mu_3\text{-X})_4\text{L}_4$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{L} = \text{pyridine derivative}$) [34, 35] and other Cu^{I} halide clusters [36] and the optical spectra of 1,1'-diphosphaferrocenes [37] the major bands likely originate from the halide \rightarrow phospholide charge-transfer and odpf-based d-d/ $\text{Fe}\rightarrow$ phospholide charge-transfer whereas the lower intensity bands may arise from "cluster-centered" halide \rightarrow Cu^{I} and Cu^{I} d \rightarrow s transitions.

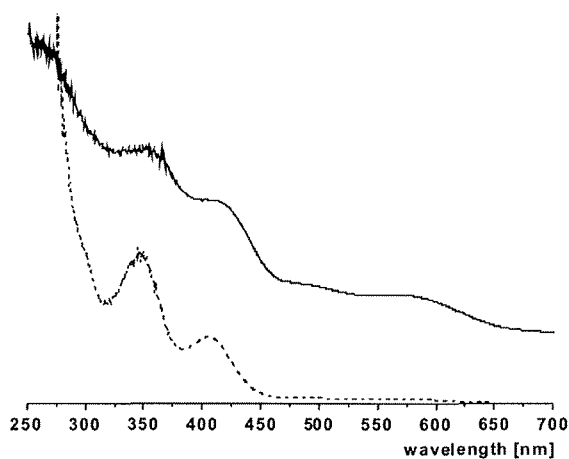


Figure 5. Comparison of the UV/Vis spectrum of compound **2** in CH_2Cl_2 solution (dotted line) and as a powdered solid (solid line).

Conclusions

Adamantoid $\text{Cu}_4\text{X}_4\text{P}_2$ cages comprising tetra- and tricoordinate Cu^{I} ions and unsymmetrically bridging odpf ligands acting in the $\mu, \kappa P, P', \kappa P$ -binding mode are formed upon the reaction of octaethyl-1,1'-diphosphaferrocene (odpf) with CuCl ($\text{X} = \text{Cl}$, **1**) or CuBr ($\text{X} = \text{Br}$, **2**) in dichloromethane/acetonitrile solvent mixtures. These cages add a new structure type to the relatively scarce examples of $\text{Cu}^{\text{I}}\text{X}$ -diphosphane adducts having a 2:1 stoichiometry. Despite the high affinity of the Cu^{I} ion towards CH_3CN and the large excess of this solvent present during the formation of cages **1** and **2**, one or two Cu^{I} ions remain tricoordinate. This even goes to the extreme of a co-crystallized CH_3CN molecule without any obvious contacts to the "bare", unsolvated $\text{Cu}_4\text{Br}_4\text{P}_2$ cage of **2**. This may be related to a "windshield-wiper"-like movement of the odpf ligands along the $\text{Cu}\cdots\text{Cu}$ vector they span. This dynamic process simultaneously interconverts the three- and the tetracoordinate Cu^{I} ions and the terminally coordinated and the bridging phospholide rings of each odpf ligand of the static structures. Such dynamic interconversion is indicated by the observation of just one singlet resonance in ^{31}P NMR spectroscopy and just one set of resonance signals each for the ethyl groups in the 2,5 or in the 3,4-positions of the phospholide heterocycles.

Experimental Section

The synthesis of odpf was conducted under an atmosphere of purified nitrogen under Schlenk techniques according to the published proce-

dures [26]. Cage compounds **1** and **2** were prepared in a nitrogen-filled glove-box. Solvents were dried with application of the appropriate drying procedures and freshly distilled prior to use or saturated with nitrogen and stored in pre-dried storage vessels over molecular sieves. UV/Vis spectra were recorded with an Omega 20 Bruins Instruments spectrometer. ^1H and ^{31}P NMR spectra were recorded on CD_2Cl_2 or CDCl_3 solutions of the respective complex with a Bruker Avance 250, a Bruker Avance 400 or a Bruker Avance 600 MHz spectrometer with either the resonance signal of the residual protonated solvent or external H_3PO_4 as the reference. C,H,N analyses were conducted at in-house facilities.

(Odpf) $_2$ (CuCl) $_4$ ·CH $_3$ CN·CH $_2$ Cl $_2$ (1**):** Inside a nitrogen-filled glove-box a solution of octaethyl-1,1'-diphosphaferrocene (odpf) (62 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) was layered with a solution of CuCl (28 mg, 0.28 mmol) in CH_3CN (3 mL). Complete mixing of the two phases occurred over 2 weeks to give an intense red solution. The solvent volume was reduced to 3 mL and afterwards stored at 15 °C, which caused the formation of deep red needle-like crystals within 4 days. These crystals were isolated by filtration and briefly dried in vacuo. Yield: 68 mg (0.104 mmol), 74 %. $\text{C}_{50}\text{H}_{84}\text{Cl}_8\text{Cu}_4\text{Fe}_2\text{P}_4$: C, 41.17; H, 5.80; found: C, 41.20; H, 5.54. ^1H NMR (CD_2Cl_2 , 293 K): $\delta = 1.15$ (t, $^3J_{\text{H,H}} = 7.3$ Hz, 24 H, CH_3), 1.20 (t, $^3J_{\text{H,H}} = 7.5$ Hz, 24 H, CH_3), 1.50–1.65 (m, 8 H, CH_2), 1.80–1.95 (m, 8 H, CH_2), 2.10–2.25 (m, 8 H, CH_2), 2.50–2.65 (m, 8 H, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz): $\delta = -145.17$.

(Odpf) $_2$ (CuBr) $_4$ ·CH $_3$ CN (2**):** Inside a nitrogen-filled glove-box a solution of octaethyl-1,1'-diphosphaferrocene (odpf) (97 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) was layered with a solution of CuBr (63 mg, 0.44 mmol) in CH_3CN (4 mL). After complete mixing of the two phases over 2 weeks the solvent volume was reduced to 3 mL and afterwards stored at 15 °C. After 6 days red-brown needle-shaped crystals had formed which were isolated from the solution and briefly dried in vacuo. Yield: 104 mg (0.143 mmol, 65 %). $\text{C}_{48}\text{H}_{80}\text{Br}_4\text{Cu}_4\text{Fe}_2\text{P}_4$: C, 39.31; H, 5.50; found: C, 39.03; H, 5.58. ^1H NMR (CD_2Cl_2 , 293 K): $\delta = 1.14$ (t, $^3J_{\text{H,H}} = 7.3$ Hz, 24 H, CH_3), 1.21 (t, $^3J_{\text{H,H}} = 7.5$ Hz, 24 H, CH_3), 1.49–1.66 (m, 8 H, CH_2), 1.84–1.98 (m, 8 H, CH_2), 2.15–2.27 (m, 8 H, CH_2), 2.50–2.60 (m, 8 H, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz): $\delta = -145.04$.

All X-ray data were collected at 123 K using an Oxford Gemini Ultra area detector equipped with an Oxford Diffraction Cryojet Cooler with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184$ nm). The structures were solved by direct methods (SIR-97) [38] and refined by full-matrix anisotropic least-squares (SHELXL97) [39]. The hydrogen atoms were calculated geometrically and a riding model was used during refinement process. Crystallographic data for odpf (CCDC-758941), **1** (CCDC-758940) and **2** (CCDC-758942) have been deposited at the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033, or E-Mail: deposit@ccdc.cam.ac.uk.

Supporting Information

Packing diagrams of the new triclinic form of odpf and of individual cages of **1** (Figures S1 and S2); ^1H and ^{31}P NMR spectra of **1** and **2** (Figures S3–S6); comparison of the UV/Vis spectra in fluid solution and for powdered crystals of **1** (Figure S7 and S8).

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