DOI: 10.1002/chem.201001414

Assembly and Disassembly of a Metastable Bis-phosphine-Based Copper(I) Helicate

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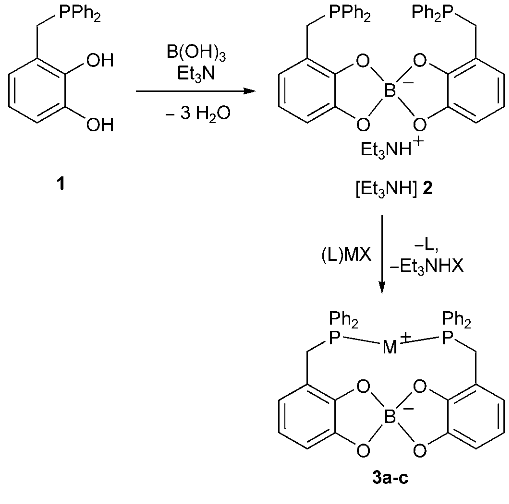
The synthesis of chelate complexes from bidentate ligands that are formed by self-assembly of simpler monodentate fragments has recently been developed as a new concept with considerable potential for application in catalysis studies.[1] Ligand assembly can be accomplished through direct pairing of fragments with complementary binding motifs,[2] or by fixing two ligand fragments to a suitable template.[3] The individual components normally join through noncovalent interactions such as hydrogen bonding,[2] formation of coordinative bonds,[3] or electrostatic attraction (e.g. anion sequestering),[4] which allow rapid assembly and disassembly of the aggregates and the correction of improper connections.

On the other hand, the same type of self-assembly processes was also successfully employed to generate supramolecular architectures such as molecular polygons and three-dimensional cages or polyhedra,[5] and even chiral helicates.[8] Controlled formation of these supramolecular architectures is normally accomplished either by mixing of preformed ligand strands with suitable metal ions or by hierarchical assembly of simple coordination compounds with additional binding sites or reactive units, which is triggered by, for example, displacement of a labile ligand, a redox reaction, or addition of suitable spacers.[8] In both methodologies, constituents and final product are in equilibrium, and the supramolecular architecture is considered to form the most stable aggregate under the chosen reaction conditions.[6–9]

We showed previously that catechol phosphine **1** assembles with various Lewis acids to give template-based bidentate phosphine ligands that readily formed metal complexes.[10] In particular, reaction with borates gave an anionic bidentate phosphine [HNEt$_3$]**2**, which was easily converted into a chelate complex **3a** upon treatment with silver triflate (Scheme 1).[11] In extending this chemistry to the other univalent coinage metal cations, we found now that the analogous Cu^I complex dimerizes unexpectedly upon crystallization to form a binuclear helicate that dissolves again as intact species in noncoordinating solvents but disassembles irreversibly to the monomeric complex when in contact with a donor solvent.



Scheme 1. **3a**: MX = AgOTf, L = ; **3b**: (L)MX = [(cyclooctene)AuCl]; **3c**: (L)MX = [Cu(MeCN)$_4$]OTf.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001414.

Reactions of [HNEt$_3$]**2** with cyclooctenegold(I) chloride in DMF and copper(I) triflate in acetonitrile proceeded in a similar manner as the reaction with silver triflate[11] to give a triethylammonium salt together with a complex that was readily isolated after precipitation with diethyl ether. The products were characterized by elemental analyses and spectroscopic data (see Experimental Section); the identification as the expected chelate complexes **3b** (M = Au) and **3c** (M = Cu) followed from analysis of the ^{1}H NMR spectra, which showed characteristic signal patterns (corresponding to the AB part of an ABX-type spin system) with similar chemical shifts for the diastereotopic methylene protons as had been observed for **3a**, and from the occurrence of peaks of pseudo molecular ions of the composition [M(**2**)H]$^+$ and [M(**2**)Na]$^+$ in (+)-ESI mass spectra, respectively. The structural assignment was confirmed by a single-crystal X-ray diffraction study for the gold complex **3b** (Figure 1). The crystals are isotypic to those of the silver complex **3a**[11] and contain likewise one solvent molecule (DMF) per formula unit, which exhibits no specific interactions with the chelate complex. The molecular structure of complex **3b** is as expected closely similar to that of **3a**. The phosphorus–metal distances (P–Au 2.340(1), 2.341(1) Å) are in the upper range of known bond lengths in bis-phosphinegold(I) complexes (2.31 ± 0.02 Å[12]) and thus shorter than in **3a** (Ag–P 2.447(2), 2.451(2) Å[11]). The P1-Au1-P2 angle of 164.94(4)° is approximately 10° larger than the corresponding angle in **3a** (154.4(1)°), and the distances between the metal atom and the closest borate oxygen atoms (3.18–3.22 Å) are at the same time notably longer (**3a**: 2.81–2.85 Å). As a consequence, the arrangement of ligands around the gold atom approaches more closely an undistorted linear coordination geometry, but it remains to be determined whether this effect reflects a stronger preference of the gold atom to adopt a linear two-coordination, or is simply a result of the geometrical constraints imposed by the ligand backbone.

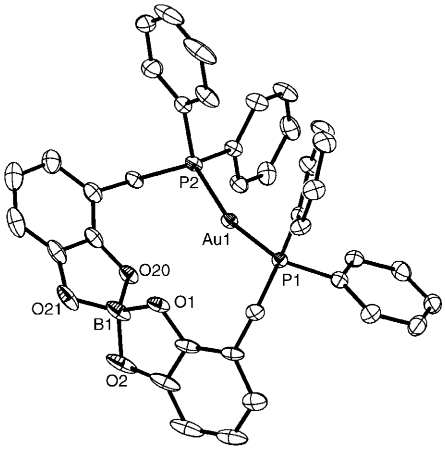


Figure 1. Molecular structure of **3b** (H atoms omitted for simplicity; 50 % probability thermal ellipsoids); selected bond lengths [Å] and angle [°]: Au1–P2 2.340(1), Au1–P1 2.341(1), B1–O21 1.478(5), B1–O2 1.486(4), B1–O1 1.492(4), B1–O20 1.493(4); P2-Au1-P1 164.94(4).

To confirm the structural assignment of the analogous copper complex, we grew single crystals by slow crystallization of the crude product from a DMF–Et$_2$O mixture. A single-crystal X-ray diffraction study disclosed, quite surprisingly, that the studied crystal contained not the expected mononuclear complex but rather a dimeric species **4** of composition [Cu$_2$(**2**)$_2$] (Figure 2). A solvate containing the same complex and two solvent molecules per formula unit was also obtained by recrystallization of the crude product from CHCl$_3$. Each metal atom in **4** is coordinated by one phosphorus and one oxygen atom of two ligands **2**, resulting in a distorted coordination geometry that is intermediate between tetrahedral and square planar. In turn, each anionic

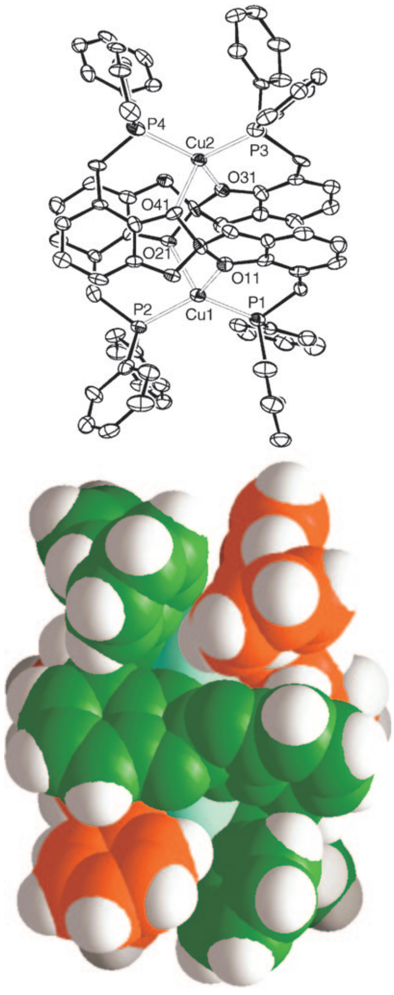


Figure 2. Molecular structure of **3b** (top: 50 % probability thermal ellipsoids, H atoms omitted for clarity; bottom: space-filling diagram showing atoms with their van-der-Waals radii); selected bond lengths [Å] and angles [°]:Cu1–O11 2.172(6), Cu1–O21 2.192(6), Cu1–P1 2.218(3), Cu1–P2 2.221(3), Cu2–O41 2.165(7), Cu2–O31 2.174(6), Cu2–P4 2.209(3), Cu2–P3 2.213(3), O11–Cu1 O21 95.6(2); O11-Cu1-P1 91.2(2), O21-Cu1-P1 125.5(2), O11-Cu1-P2 128.7(2), O21-Cu1-P2 88.7(2), P1- Cu1-P2 126.7(1), O41-Cu2-O31 96.2(2), O41-Cu2-P4 90.3(2), O31-Cu2-P4 123.7(2), O41-Cu2-P3 129.2(2), O31-Cu2-P3 89.6(2), P4-Cu2-P3 127.2(1).

ligand coordinates as a μ_2-bridging unit to both metals. Since the sense of the twist in the spirocyclic backbone is the same for both template-centered bis-phosphine moieties in an individual complex, the whole assembly represents a chiral two-stranded helicate, both enantiomers of which crystallize as a racemate.

To resolve the origin of the apparent discrepancies in the results of the spectroscopic and X-ray diffraction studies, we performed a more thorough analytical survey of the specimen obtained by either rapid precipitation from the reaction mixture or slow crystallization, respectively. ^{31}P CP-MAS NMR spectra revealed that the bulk materials exhibit clearly different spectroscopic signatures. The spectrum of the crude product consists of a single spinning sideband manifold with an isotropic chemical shift of $\delta = -9.9$ ppm and a multiplet structure arising from spin-coupling with the adjacent $^{63/65}$Cu nuclei. In contrast, the crystalline material displays two spinning sideband manifolds of equal intensity with a similar multiplet structure but distinctly different isotropic chemical shifts of $\delta = -18.8$ and -22.3 ppm (Figure 3); the signal duplication indicates that the local environment of two of the four crystallographically independent phosphorus atoms differs perceptibly from that of the other two. The ^{31}P NMR spectrum of a solution prepared by dissolving crystalline **4** in the noncoordinating solvent $CDCl_3$ displayed a single resonance with a chemical shift ($\delta^{31}P = -17.7$) that is close to the average isotropic shift in the solid state but differs clearly from the value of $\delta = -9.3$ ppm observed for the crude product before crystallization, thus indicating that the difference between both materials persists in solution. This finding was corroborated by a comparison of the ^{1}H NMR spectra, in which in particular the signals of the diastereotopic methylene protons exhibited large deviations ($\delta = 3.63$ and 3.42 ppm in the spectrum of the crude complex vs. $\delta = 2.89$ and 1.62 ppm for a solution of crystalline **4**).

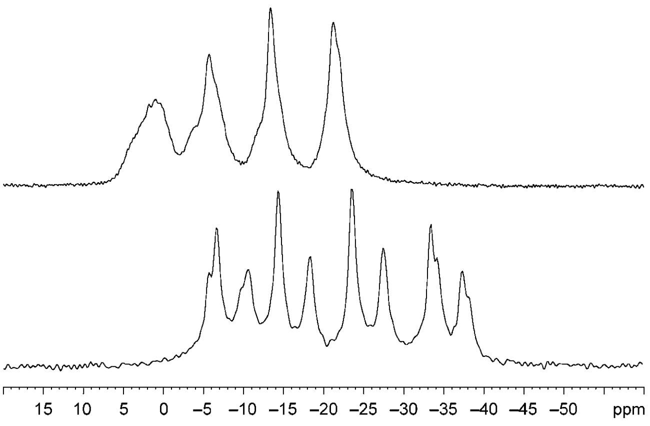
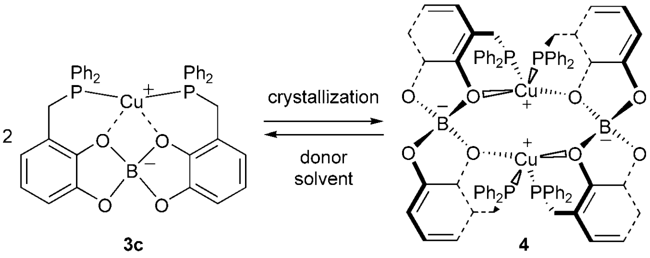


Figure 3. Isotropic lines of the 161.9 MHz ^{31}P CP-MAS spectra of **3c** (top, $\nu_{rot} = 15$ kHz) and **4** (bottom, $\nu_{rot} = 14$ kHz). The displayed patterns can be interpreted as one (**3c**, $\delta_{iso} = -9.9$) or two (**4**, $\delta_{iso} = -18.8$, -22.3) multiplets with quartet splitting due to scalar and residual dipolar coupling between ^{31}P and $^{63/65}$Cu ($I = 3/2$) nuclei.

Since we encountered during the spectroscopic monitoring of crystallization attempts in several cases solutions whose NMR spectra displayed both described sets of signals at the same time, the solvent-dependent signal shifts must be interpreted as indicating the presence of two complexes with distinguishable molecular structures. Considering the results of the ESI-MS studies and the similarity of the ^{1}H NMR data of the crude product with those of the silver and gold complexes **3a,b**, it is reasonable to assume that reaction of the anionic ligand **2** with a copper salt produces first a mononuclear complex **3c** with a similar molecular structure as **3a,b**. Isolation of crystalline **4** from such solutions is then rationalized by assuming that **3c** is possibly in equilibrium with a marginal concentration of its dimer (Scheme 2), which is apparently less soluble and exhibits a greater tendency for crystallization.



Scheme 2. Mutual conversion between **3c** and **4**.

Further light on the postulated interconversion between both complexes was shed when we found that after addition of [D$_7$]DMF to a solution of **4** in $CDCl_3$ the original NMR signals were immediately replaced by those assigned to **3c**, and that this change was accompanied by a significant increase in the diffusion coefficient (DOSY measurements gave $D = 2.1(3) \times 10^{-10}\,m^2s^{-1}$ for **4** in pure $CDCl_3$ at 303 K vs. $4.5(1) \times 10^{-10}\,m^2s^{-1}$ after addition of 20 vol% [D$_7$]DMF). These results give not only direct proof for the transformation of **4** into **3c** but indicate also that the conversion is associated with a marked reduction in molecular size, in accord with a monomeric nature of **3c** as compared to dimeric **4**. Furthermore, observation of *spontaneous* conversion of **4** into **3c** upon addition of DMF to a $CDCl_3$ solution, in connection with the finding that solutions of **3c** in $CDCl_3$ or CD_2Cl_2 fail to undergo a reverse reaction, allows us to conclude that conversion of **4** into **3c** is a thermodynamically favorable process and **3c** must thus be considered as the more stable isomer in solution, and that DMF catalyzes apparently the conversion between both complexes. While these findings seem at first glance similar to previous observations of monomer–dimer equilibria involving helicates,[6] they differ in the respect that the monomer is not stabilized by extra solvent coordination,[6a] and that the existence of the intact helicate in solution is attributed essentially to the fact that disassembly of the dimers is apparently kinetically hindered in the absence of a coordinating solvent. As a consequence, cleavage of the dimer is practically irreversible, and the solutions of **4** in noncoordinated solvents may be considered as metastable.

The considerations on the mutual conversion between **3c** and **4** were further supported by the results of DFT calculations, which were performed by using the B3LYP functional with sdd and 6-31 g(d) basis sets for Cu and the lighter atoms, respectively.[13] Molecular structures were first calculated by energy optimization in the gas phase, and relative energies were then recomputed with the inclusion of a PCM model to simulate the effect of solvation. Finally, Gibbs free energies ΔG^{298} were estimated by adding to the solution energies the thermal correction to the Gibbs free energies obtained from frequency calculations on the isolated complexes. The computed molecular structures resemble closely the experimentally observed structures of copper complex **4** and the silver and gold complexes **3a**,**b**, respectively, apart from subtle conformational changes; the largest deviations affect the metal coordination geometry in the monomeric complex where formal replacement of the heavier coinage metal atoms by copper coincides with a sharpening of the P-Cu-P angle to 135.1° and a concomitant shortening of the Cu−O contacts (2.342, 2.585 Å). The computed total energy of complex **4** was predicted to be identical (in $CHCl_3$) or only 1.1 kcal mol^{-1} lower (in DMSO) than that of two molecules of **3c**, thus giving no clear preference for either species. This picture changes, however, when the Gibbs free energies are compared, as cleavage of dimeric **4** into two independent units of **3c** is now predicted to be clearly exergonic in both DMSO ($\Delta G^{298}{}_{,calcd} = -17.7$ kcal mol^{-1}) and $CHCl_3$ ($\Delta G^{298}{}_{,calcd} = -17.7$ kcal mol^{-1}). Although the absolute magnitude of ΔG^{298} may still be debatable, these results suggest clearly that **3c** represents the thermodynamically favored species in solution; on the other hand, the slightly higher intrinsic (i. e. energetic) stability of **4** is in accord with the observed preference for this species in the crystalline state where entropy is less important.

A further notable result of the computational studies is the failure of all attempts to locate a structure of a monomeric complex [Cu(**2**)(dmf)] with an additional solvent molecule; this finding supports the hypothesis that the relative stability of **3c** in solution is not due to formation of a stable solvate, and that the solvent acts merely as a catalyst in the cleavage of the dimer.

In summary, we have shown that monomeric complex **3c** produced by the reaction of the anionic bis-phosphine **2** with Cu^+ dimerizes under formation of a helicate **4** during crystallization. The helicate dissolves without decomposition in noncoordinating solvents, but disassembles immediately upon addition of a donor solvent such as DMF. The observed behavior implies that solutions of **4** are thus metastable, and the persistence of the helicate as dominant species in solution is attributed to the fact that its disassembly is impeded by a sufficiently high kinetic barrier.

Experimental Section

Complex 3b: Solid [(cyclooctene)AuCl] (33 mg, 0.096 mmol) was added to a solution of $[NEt_3H]$**2** (70 mg, 0.096 mmol) in dry DMF (5 mL), and the resulting mixture was stirred for 1 h at room temperature. The solution was kept overnight at 4 °C to give colorless crystals of **3b**, suitable for X-ray analysis, which were decanted off and dried in vacuum. The remaining solution was diluted with excess Et_2O to yield a colorless precipitate, which was dried in vacuum (71 mg, yield 84 %, m.p. 246 °C). Elemental analysis (%) calcd for $C_{38}H_{30}AuBO_4P_2\cdot 1/2DMF$: C 55.89 H 3.98 N 0.86; found: C 54.53 H 3.72 N 0.86; (+)-ESI-MS: *m/z*: 821.14 $[MH]^+$, 843.13 $[MNa]^+$; (−)-ESI-MS: *m/z*: 855.11 $[MCl]^-$; ^1H NMR ($CDCl_3$): δ = 7.66–7.26 (m, 20 H, Ph), 6.74 (d, $^3J_{HH} = 7.8$ Hz, 2 H, C_6H_3), 6.37 (t, $^3J_{HH} = 7.8$ Hz, 2 H, C_6H_3), 5.96 (d, $^3J_{HH} = 7.8$ Hz, 2 H, C_6H_3), 4.11 (d of pseudo-t, $^2J_{PH} = 3.6$ Hz, $^2J_{HH} = 13.6$ Hz, 2 H, CH_2), 3.68 ppm (d of pseudo-t, $^2J_{PH} = 4.3$ Hz, $^2J_{HH} = 13.6$ Hz, 2 H, CH_2); $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.5$ ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 36.6$ ppm.

Complex 3c: Solid $[Cu(CH_3CN)_4]SO_3CF_3$ (260 mg, 0.69 mmol) was added to a solution of $[NEt_3H]$**2** (500 mg, 0.69 mmol) in dry MeCN (20 mL). The mixture was stirred for 30 min at room temperature, and the resulting solution then diluted with excess Et_2O to yield a colorless precipitate (370 mg, 78 %), which was dried in vacuum. (+)-ESI-MS: *m/z*: 687.10 $[MH]^+$, 709.09 $[MNa]^+$; ^1H NMR ($[D_7]DMF/CD_2Cl_2$): δ = 7.77–7.66 (m, 4 H, Ph), 7.66–7.46 (m, 12 H, Ph), 7.46–7.34 (m, 4 H, Ph), 6.69 (d, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 6.54 (t, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 5.43 (d, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 3.63 (d of pseudo-t, $^2J_{PH} = 2.4$ Hz, $^2J_{HH} = 13.2$ Hz, 2 H, CH_2), 3.42 ppm (d of pseudo-t, $^2J_{PH} = 5.2$ Hz, $^2J_{HH} = 13.2$ Hz, 2 H, CH_2); $^{11}B\{^1H\}$ NMR ($[D_7]DMF/CD_2Cl_2$): $\delta = 14.7$ ppm; $^{31}P\{^1H\}$ NMR ($[D_7]DMF/CD_2Cl_2$): $\delta = -9.3$ ppm.

Complex 4: Crude complex **3** was dissolved in little DMF. Et_2O was added until the solution turned cloudy, indicating the onset of precipitation. Addition of more drops of DMF produced a clear solution that was stored at room temperature. Colorless crystals (m.p. 336 °C) formed, which were collected by filtration. Elemental analysis (%) calcd for $C_{38}H_{30}CuBO_4P_2$: C 66.44, H 4.40; found: C 65.90, H 4.56; ^1H NMR ($CDCl_3$): δ = 7.45–6.94 (m, 20 H, Ph), 6.36 (t, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 6.20 (d, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 5.81 (d, $^3J_{HH} = 7.6$ Hz, 2 H, C_6H_3), 2.89 (d of pseudo-t, $^2J_{PH} = 4.2$ Hz, $^2J_{HH} = 16.0$ Hz, 2 H, CH_2), 1.62 ppm (d, $^2J_{HH} = 16.0$ Hz, 2 H, CH_2); $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.5$ ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -17.7$ ppm.

Crystal structure determinations: Crystallographic data were collected on a Bruker Nonius Kappa CCD diffractometer by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 123(2) K (**3b**, **4**·2 $CHCl_3$) or on a Bruker Smart APEX II diffractometer equipped with an Incoatec microfocus X-ray source[14] ($Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å) at 100(2) K (**4**). Direct methods (SHELXS-97[15]) were used for structure solution and refinement (SHELXL-97,[16] full-matrix, least-squares on F^2). Hydrogen atoms were refined by using a riding model. **3b**: Colorless crystals, $C_{41}H_{37}AuBNO_5P_2$, $M_r = 893.43$ g mol^{-1}, crystal size 0.36 × 0.12 × 0.08 mm, monoclinic, space group *Cc* (no. 9), $a = 18.993(1)$, $b = 15.182(1)$, $c = 14.915(1)$, $\beta = 122.75(1)°$, $V = 3617.1(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.641$ Mg m^{-3}, $F(000) = 1776$, $\mu = 4.203$ mm^{-1}, semiempirical absorption correction from equivalents, min/max. transmission 0.4839/0.7298, 35 368 reflections ($2\ \theta_{max} = 55°$), 8234 unique [$R_{int} = 0.031$], 463 parameters, R_1 ($I > 2\sigma(I)$) = 0.018, wR_2 (all data) = 0.034, largest difference peak and hole 0.404 and −0.439 eA^{-3}. **4**: Colorless crystals, $C_{76}H_{60}B_2Cu_2O_8P_4$, $M_r = 1373.82$ g mol^{-1}, crystal size 0.018 × 0.008 × 0.005 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.6532(11)$, $b = 12.8362(11)$, $c = 22.515(3)$ Å, $\alpha = 93.904(6)$, $\beta = 96.695(7)$, $\gamma = 119.170(4)°$, $V = 3138.3\ (5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.454$ Mg m^{-3}, $F(000) = 1416$, $\mu = 2.284$ mm^{-1}, semiempirical absorption correction from equivalents, min/max. transmission 0.9600/0.9887, 21 316 reflections ($2\theta_{max} = 115°$), 8316 unique [$R_{int} = 0.079$], 829 parameters, R_1 ($I > 2\sigma(I)$) = 0.107, wR_2 (all data) = 0.218, largest diff. peak and hole 4.459 and −0.428 eA^{-3}. **4**·2 $CHCl_3$: Colorless crystals, $C_{76}H_{60}B_2Cu_2O_8P_4\cdot 2\,CHCl_3$, $M_r = 1612.56$ g mol^{-1}, crystal size 0.45 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.$ 12.752(2) Å, $b = 12.870(2)$ Å, $c = 22.781(4)$ Å, $\alpha = 83.00(2)°$, $\beta = 82.23(2)°$, $\gamma = 73.27(2)°$, $V = 3534.1(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.515$ Mg m^{-3}, $F(000) = 1648$, $\mu = 0.978$ mm^{-1}, semiempirical absorption correction from equivalents, min/max. transmission 0.6277/0.9280, merohedral twin with 2 domains (BASF 0.217(2)), 31575 reflections ($2\theta_{max} = 50°$), 12354 unique [$R_{int} = 0.093$], 902 parameters, 6 restraints, R_1 ($I > 2\sigma(I)$) = 0.107, wR_2 (all data) = 0.299, largest diff. peak and hole 1.231 and −1.304 eA^{-3}. CCDC-777627 (**3b**), CCDC-777652 (**4**), and CCDC-777628 (**4**2CHCl$_3$) 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.

Acknowledgements

The Deutsche Forschungsgemeinschaft (Grant Gu415/12-1) is acknowledged for financial support. M.N. thanks The Academy of Finland (proj. no. 128800) for financial support.

Keywords: copper · helical structures · phosphane ligands · self-assembly · X-ray diffraction

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Received: May 21, 2010