

the H_{1B} atoms and the Cu surface. The corresponding distance between the H_{1B} atoms of cyclopropane and the surface is 3.0 Å. It thus appears that the dispersion forces for cyclopropane are not quite strong enough to push the molecule as deeply into the surface, which results in a lesser degree of charge transfer into the molecule than occurs for cyclohexane.

Experimental Section

The UHV chamber used in these experiments was operated at a base pressure of $< 3.0 \times 10^{-10}$ Torr and has been described previously.^[19, 20] The RAIRS data were collected with a Digilab FTS 60A spectrometer with a liquid nitrogen cooled wide-band MCT detector in conjunction with external reflection optics, maximized for single grazing angle reflection. The crystal temperature was monitored by a chromel-alumel thermocouple lodged in a hole on the side of the crystal. The crystal could be cooled and heated within the temperature range of 100–950 K. The crystal was cleaned by sputtering with 1 keV Ar^+ ions for 30 min at 850 K and then annealed for 15 min at 850 K. The adsorbates were introduced into the chamber by using an effusive molecular beam doser located approximately 5 cm from the crystal. Cyclopropane (>99%) was obtained from Aldrich and used as received. Cyclohexane (>99%) was obtained from EM Science and degassed by freeze-pump-thaw cycles before introduction into the chamber. The pressure during dosing varied between 1×10^{-9} and 5×10^{-7} Torr. Exposures, reported in Langmuirs (1×10^{-6} Torr), are not corrected for the ion gauge sensitivity.

Ab initio calculations: The calculations for cyclopropane and cyclohexane adsorbed on Cu(111) closely follow an approach described previously.^[21] Briefly, high-quality ab initio Hartree–Fock calculations were carried out for a (7,3)-cluster exhibiting C_{3v} symmetry modeling a Cu(111) surface with a Cu lattice constant of 2.54 Å using a commercial software package (Gaussian 98^[22]). Correlation effects were included at the MP2 level. For the Cu atoms a 28-electron pseudopotential (see reference [21] and [23] for a detailed discussion) together with an extensive basis set for the remaining electrons was used together with a 6-311++ basis set for the C and the H atoms. This basis set has been demonstrated to be sufficiently large to account for the details of the alkane electronic structure seen in X-ray absorption spectroscopy^[24] and to the corresponding adsorption-induced changes in those data.^[21] Previous work has shown that this theoretical approach provides a very reasonable potential for the cyclopropane/Cu(111) interaction, giving good agreement with experimental quantities such as the binding energy and the curvature of the surface–molecule potential.^[21] All results reported here were obtained for the electronic ground state of the Cu(7,3)-cluster, which is a triplet state.

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Pentaphosphaferrocene as a Linking Unit for the Formation of One- and Two-Dimensional Polymers**

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Dedicated to Professor Joachim Strähle on occasion of his 65th birthday

Common approaches in the field of self-organization of discrete supramolecular^[1] aggregates, networks, and coordination polymers^[2] make use of N-donor containing ligands and N-heterocycles to connect different metal centers together. In contrast, however, our goal in this field has been the use of P_n -ligand complexes as linking moieties between metal cations to form well-oriented assemblies as well as one-dimensional (1D) and two-dimensional (2D) polymers.

The coordination chemistry of P_n -ligand complexes^[3] towards cationic metal centers (excluding cationic organometallic complex moieties^[4]) has so far been limited to the use of *cyclo*- P_3 -ligand complexes, such as [(triphos)M(η^3 - P_3)] (M = Co, Rh, or Ir; triphos = 1,1,1-tris(diphenylphosphanyl)methyl)ethane), which usually form metal-bridged dimers.^[5]

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In the reactions of the Co complex with CuBr, a multidecker Co complex containing a (CuBr)₆ middle deck was obtained,^[6] whereas for the Ir complex, the cationic product [((triphos)IrP₃)₃Cu₅Br₄]⁺ was formed.^[7] However, recently we were able to show that [(CpMo(CO)₂)₂(μ,η²-P₂)] (Cp = C₅H₅) can be used as a building block to connect Cu^I and Ag^I centers to form 1D polymers such as the complexes **1** and **2**.^[8] Further, we have tried to incorporate compound **3** (Cp* = C₅Me₅)^[9] into these investigations. In the past few years, the reaction behavior of **3** has been intensively examined by the group of O. J. Scherer.^[3f]

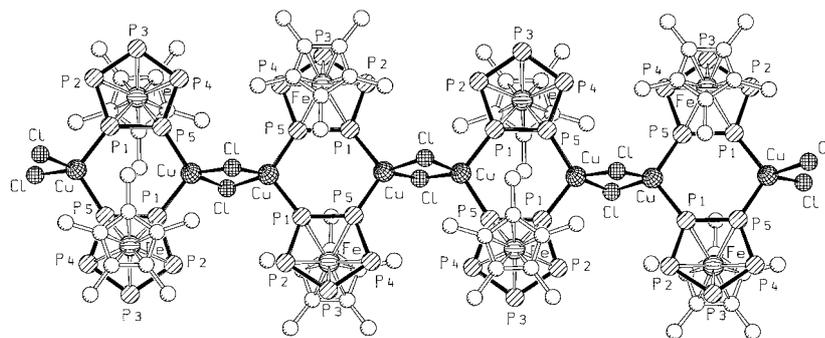
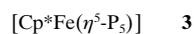
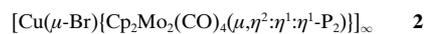
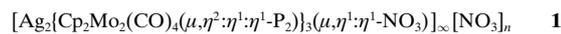
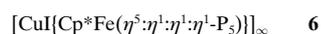
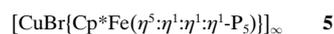
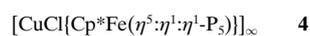


Figure 1. View of the 1D chain structure of complex **4** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P5 2.109(2), P1-P2 2.119(1), P2-P3 2.124(2), P3-P4 2.123(2), P4-P5 2.121(1), Cu-P1 2.286(1), Cu-P5 2.272(1), Cu-Cl 2.356(1), Cu-Cl' 2.342(1); P5-Cu-P1' 111.02(5), P5-P1-Cu 126.19(5), Cu'-Cl-Cu 83.94(4), Cl-Cu-Cl' 95.43(4).



Besides its capacity to form cationic triple-decker complexes^[10] or undergo P₅-transfer reactions,^[11] there are reactions known in which the *cyclo*-P₅ ring remains more or less intact, or is cleaved with formation of a P₅ chain, or P₄/P₁, P₃/P₂, or P₂ fragments.^[3f, 10–12] In the case where the *cyclo*-P₅ ring remains intact, η⁵:η¹, η⁵:η², and η⁵:η²:η²:η¹ coordination modes to organometallic fragments have been found,^[13] which are accompanied by a significant lengthening of the P–P bonds. Herein we report the first use of the *cyclo*-P₅ ligand complex **3** to form novel 1D and 2D polymers by the hitherto unknown 1,2-ligation and 1,3,4-ligation, respectively, to different Cu^I ions.

Complexes **4–6** were obtained by the reaction of **3** with CuX (X = Cl, Br, I) in solvent mixtures of CH₃CN and CH₂Cl₂



at ambient temperature. The yellow-brown crystals of the products are stable under nitrogen and in common solvents are insoluble without decomposition.^[14] All the products have been characterized by X-ray diffraction analysis.^[15]

In Figure 1 the linear 1D chain structure of **4** is depicted, it consists of planar six-membered Cu₂P₄ and four-membered Cu₂Cl₂ rings, alternately arranged in an orthogonal manner. The planar *cyclo*-P₅ rings are coplanar with the six-membered Cu₂P₄ units, and the coordination geometry around the Cu^I center is tetrahedral. Furthermore, the 1,2 coordination of the *cyclo*-P₅ ring to two different metal centers has not been observed before. The structure of **4** is reminiscent of the 1D polymeric structure of the Mo₂P₂-containing complex **2**, with the difference that, aside of the different P_n ligand used, the Cu₂Cl₂ moieties in **4** are bent along the Cl–Cl axis, and the Cu^I atoms are nonsymmetrically bound to the P (2.272(1) and 2.286(1) Å) and Cl atoms (2.356(1) and 2.342(1) Å). Interest-

ingly, the P–P bond between the coordinating atoms P1 and P5 is slightly shorter (2.109(2) Å) than the remaining P–P bonds of the *cyclo*-P₅ ring (2.119(1)–2.124(1) Å), whereas the latter are nearly consistent with those of the uncoordinated molecule **3** (2.117(4) Å), as determined by electron diffraction.^[16] However, compared to the P–P bonds in the related complex [Cp*Fe(μ,η⁵-P₅)] (**7**; Cp* = η⁵-C₅Me₄Et; 2.088(3)–2.108(3) Å), determined by single-crystal X-ray structure analysis, the P–P bonds of **4** are slightly lengthened.^[17] Nevertheless, this coordination behavior of the *cyclo*-P₅ moiety in **4** is in contrast to the previously observed lengthening of the P–P bonds on the coordination of organometallic fragments to the *cyclo*-P₅ ring.^[13] For example, the additional side-on coordination of an organometallic fragment at the *cyclo*-P₅ ring in [Cp*Fe(μ,η⁵:η²-P₅)Cp*Ir(CO)] leads to a lengthening of the corresponding P–P bond to 2.359(2) Å.^[13b] Furthermore, η¹ coordination of the [(Cp*Ir(CO))₂] unit in [Cp*Fe(μ,η⁵:η¹-P₅)(Cp*Ir(CO))₂]^[13a] leads to P–P bond lengths about the coordinating P atom of 2.166(3) and 2.170(3) Å as well as a significant bending of the *cyclo*-P₅ ring, which results in a P₄P₁ arrangement. In contrast, therefore, the *cyclo*-P₅ units in the polymers **4–6** are still essentially planar.^[18]

In the crystal lattice of both **5** and **6** the distorted tetrahedrally coordinated Cu^I atoms are surrounded by one halogen atom and three P atoms each coming from three different [Cp*Fe(η⁵-P₅)] fragments (Figure 2). Thus, a new η⁵:η¹:η¹:η¹ coordination mode is obtained which result in a novel 1,3,4 substitution pattern at the *cyclo*-P₅ ring. In contrast to the structure of **4**, and as a result of the additional third coordination of the Cu^IX moiety at the *cyclo*-P₅ rings in **5** and **6**, novel 2D coordination polymers are formed where the layers are separated by the Cp*Fe moieties (Figure 3). The structure of **6** (space group *P* $\bar{4}$ 2₁*c*) is similar to that of **5** (space group *P* $\bar{4}$ 2₁*m*) except that the latter possesses no symmetry plane within the crystallographic *c* axis, which leads to a mirror plane within the Cp*FeP₅ moieties of **6**. Within the layers of **5** and **6** (Figure 4) there is an alternating array of six-membered Cu₂P₄ rings and novel Cu₄P₁₂ rings. The Cu₂P₄ rings are in a boatlike conformation, unlike the previously reported planar Cu₂P₄ rings in the 1D polymer of **2**. The P–P distances within the nearly planar^[18] *cyclo*-P₅ moieties of **5** (2.099(2)–2.108(2) Å) and **6** (2.114(3)–2.120(3) Å), are comparable to

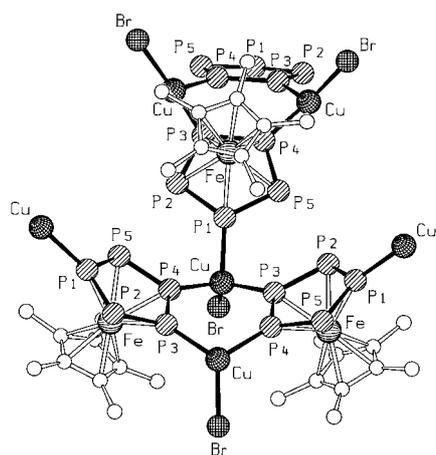


Figure 2. View of the coordination geometry around a Cu atom within the polymeric structure of complex **5** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P5 2.106(2), P1-P2 2.108(2), P2-P3 2.104(2), P3-P4 2.101(2), P4-P5 2.099(2), Cu-P1 2.320(1), Cu-P3 2.278(1), Cu-P4 2.281(1), Cu-Br 2.343(1); P1-Cu-P3 103.01(5), P1-Cu-P4 103.98(5), P3-Cu-P4 104.48(5), P1-Cu-Br 101.24(4), P3-Cu-Br 122.27(5), P4-Cu-Br 119.03(4).

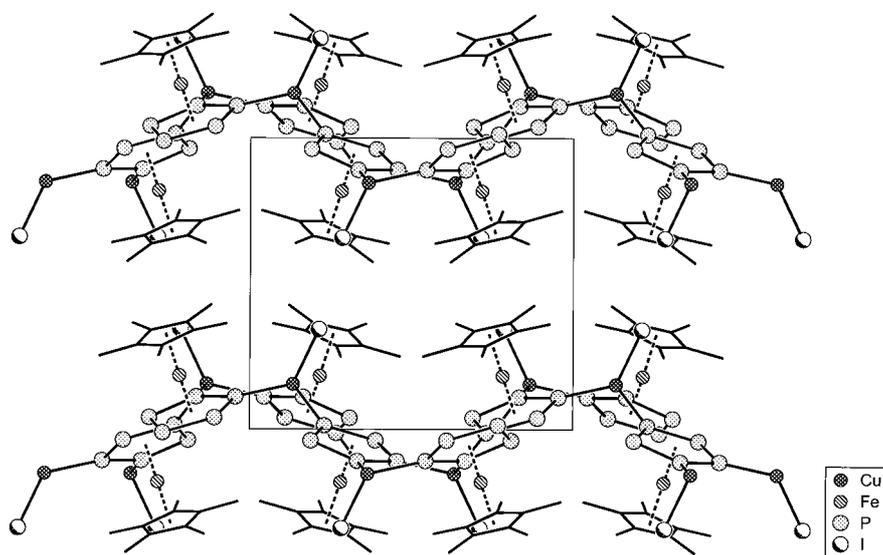


Figure 3. View of the zigzag 2D layer structure of complex **6** along the *b* axis (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.114(3), P1-P1' 2.116(4), P2-P3 2.120(3), P3-P2' 2.120(3), Cu-P1 2.296(2), Cu-P1' 2.296(2), Cu-P3 2.332(3), Cu-I 2.549(2); P1-Cu-P1' 106.59(12), P1-Cu-P3 105.15(9), P1'-Cu-P3' 105.14(9), P1-Cu-I 119.28(7).

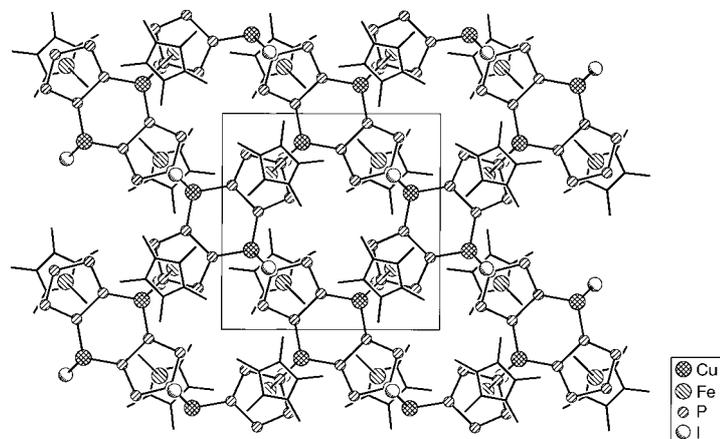


Figure 4. View of layer of the 2D structure of complex **6** orthogonal to the *a,b* plane (H atoms are omitted for clarity).

the distances within **4** and are slightly shorter than those of the uncoordinated **3** (2.117(4) Å)^[16] but slightly elongated in comparison to the related complex **7** (2.088(3)–2.108(3) Å).^[17] Thus, as already discussed for **4**, the coordination of Cu^I halides in **5** and **6** does not influence the corresponding P–P bond lengths.

The tendency for the reaction of **3** with CuCl on the one hand and CuBr/CuI on the other to yield products with disparate structures is surprising and difficult to explain. Whereas within the CuCl product **4** the linear chains are separated from each other by π stacking between Cp* and *cyclo-P*₅ moieties of different chains, **5** and **6** form 2D networks through additional metal coordination to the *cyclo-P*₅ rings rather than π stacking.

In summary, the results have shown that in addition to [[CpMo(CO)₂]₂(μ , η^2 -P₂)], the complex [Cp*Fe(η^5 -P₅)] (**3**) can also be successfully used as a linking unit for coordination polymers, which opens perspectives to generate novel well-defined assemblies and networks. In contrast to previously reported reactivity studies of **3** with organometallic complexes, where the P–P bond lengths of the products have been significantly lengthened and the *cyclo-P*₅ ring is partially distorted, the P–P bonds of the planar *cyclo-P*₅ ring in the new coordination polymers **4**–**6** do not differ significantly to those of **3**.

Experimental Section

4–**6**: A solution of CuX (0.15 mmol; X = Cl (15 mg), Br (21 mg), I (28 mg)) in CH₃CN (3 mL) and CH₂Cl₂ (2 mL) was added to a solution of **3** (52 mg, 0.15 mmol) in CH₂Cl₂ (5 mL) at room temperature. This mixture was allowed to stand for two days, and yellow-brown crystals of **4** (33 mg, 0.067 mmol, 49%), **5** (65 mg, 0.13 mmol, 89%), and **6** (78 mg, 0.14 mmol, 93%), respectively, were formed. The products were collected by filtration and washed with 2 mL each of CH₂Cl₂ and CH₃CN, and then dried under vacuum; **4**: 0.5 CH₂Cl₂; elemental analysis (%) calcd for C_{10.5}H₁₆Cl₂CuFeP₅ (487.37): C 25.88, H 3.28; found: C 26.03, H 3.22; **5**: elemental analysis (%) calcd for C₁₀H₁₅BrCuFeP₅ (489.39): C 24.54, H 3.09; found C 24.64, H, 3.15; **6**: elemental analysis (%) calcd for C₁₀H₁₅ICuFeP₅ (536.40): C 22.39, H 2.82; found C 22.30, H 2.96.

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- [15] Crystal structure analyses of **4**–**6** were performed on STOE IPDS diffractometers with MoK_α radiation (λ = 0.71073 Å) for **5** and AgK_α radiation (λ = 0.56087 Å) for **4** and **6**. The structures were solved by direct methods with the program SHELXS-97^[19a] and full-matrix least-squares refinement on F² in SHELXL-97^[19b] was performed with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **4**: 0.5 CH₂Cl₂; C_{10.5}H₁₆Cl₂CuFeP₅, M_r = 487.37, crystal dimensions 0.20 × 0.14 × 0.04 mm³, monoclinic, space group C2/c (No. 15), a = 20.184(4), b = 16.885(3), c = 13.860(3) Å, β = 129.33(3)°, T = 203(2) K, Z = 8, V = 3653.7(13) Å³, ρ_{calcd} = 1.772 Mg m⁻³, μ = 1.382 mm⁻¹, 3831 independent reflexes (R_{int} = 0.0365, 2θ_{max} = 42°), 3128 observed with F_o = 4σ (F_o), 190 parameters, R₁ = 0.0370, wR₂ = 0.0974. **5**: C₁₀H₁₅BrCuFeP₅, M_r = 489.37, crystal dimensions 0.20 × 0.20 × 0.01 mm³, tetragonal, space group P4₂c (No. 114), a = b = 12.147(2), c = 21.859(4) Å, T = 200(1) K, Z = 8, V = 3225.2(9) Å³, ρ_{calcd} = 2.016 Mg m⁻³, μ = 5.170 mm⁻¹, 3152 independent reflexes (R_{int} = 0.0777, 2θ_{max} = 52°), 2681 observed with F_o = 4σ (F_o), 168 parameters, R₁ = 0.0345, wR₂ = 0.0809. **6**: C₁₀H₁₅CuFeIP₅, M_r = 536.36, crystal dimensions 0.10 × 0.10 × 0.10 mm³, tetragonal, space group P4₂m (No. 113); a = b = 12.372(2), c = 11.241(2) Å, T = 203(1) K, Z = 4, V = 1720.6(5) Å³, ρ_{calcd} = 2.071 Mg m⁻³, μ = 2.258 mm⁻¹, 8297 independent reflexes (R_{int} = 0.1663, 2θ_{max} = 40°), 1475 observed with F_o = 4σ (F_o); 94 parameters, R₁ = 0.0496, wR₂ =

0.1312. CCDC 175139–175141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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- [17] O. J. Scherer, T. Brück, G. Wolmershäuser, *Chem. Ber.* **1988**, *121*, 935–938.
- [18] Mean deviation from planarity: 0.0098(6) Å (**4**), 0.0293(9) Å (**5**), 0.0350 (20) Å (**6**).
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Structure and Synthesis of the Natural Heptachloro-1'-methyl-1,2'-bipyrrole (**Q1**)

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A number of anthropogenic organohalogen compounds such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and chlorinated pesticides (DDT, toxaphene, lindane, and others) are recognized as persistent, bioaccumulative, and toxic chemicals.^[1] The majority of these substance classes are ubiquitously distributed in the environment, and long-term exposure is one of the major threats to humans and wildlife from these substances.^[2] The scientific interest in anthropogenic halogenated compounds is reflected in the fate of these contaminants and related compounds in the environment, which was reported on in more than 1000 publications in the past 40 years.

More than 3600 naturally occurring organohalogens have been identified to date.^[3] The total amount of these compounds is not known, but is probably higher than currently known.^[4] It was thought that these natural products are neither persistent nor lipophilic, and thus do not accumulate in the lipids of higher organisms. This hypothesis is currently under reconsideration, as recent work has resulted in the detection of a series of unknown halogenated compounds that

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