Pulled Molecular Strings and Stacked Molecular Decks: Chelate-Ring Formation vs. Metal–Metal Bridging in Dicopper(I) Complexes of 2,2'-Bipyrimidine with Diphosphine Ligands of Variable Polymethylene Chain Length

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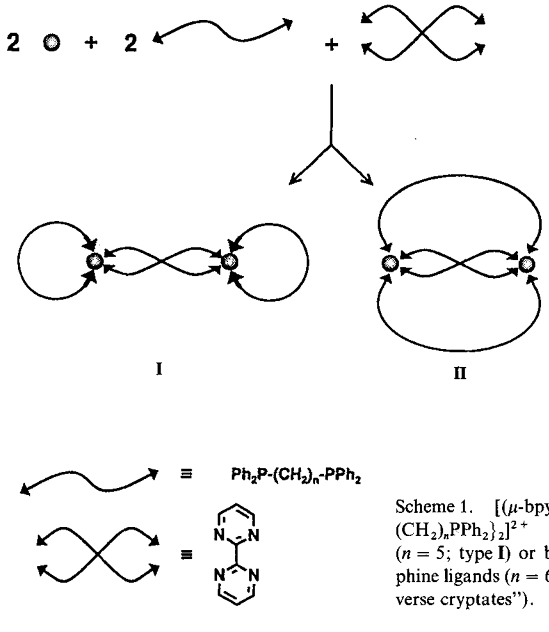
Abstract: The "self-assembly" reaction between bischelating 2,2'-bipyrimidine, metallic copper, Cu^{2+}, and two equivalents of bidentate $Ph_2P(CH_2)_nPPh_2$ produces crystallographically characterized dinuclear complexes with a $[Cu^I(\mu\text{-bpym})Cu^I]^{2+}$ core and chelating ($n = 5$; type **I**) or bridging diphosphine ligands ($n = 6, 8$; type **II**). Structures **II** may be designated as "inverse cryptate" arrangements. The structural data of the solids and the spectroscopic results for the dissolved species indicate a strained configuration in the case of complex $[(\mu\text{-bpym})Cu_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2]^{2+}$ (**6**) with $n = 6$. Once the polymethylene chain length is reduced one notch further to $n = 5$ (**5**), the diphosphines can no longer bridge but help to form eight-membered chelate rings (structure **I**). In this complex there is a distortion towards a trigonal-pyramidal coordination geometry at the copper(I) centers, which is supported by the formation of an "organic sandwich" arrangement between the central bpym acceptor and two phosphino phenyl rings.

Keywords
bridging ligands · chelate ligands · copper complexes · self-assembly · structure elucidation

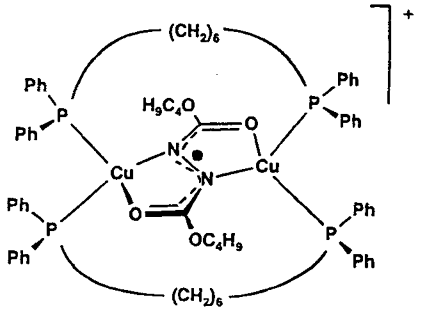
Introduction

Copper(I) centers are exceptionally well suited for structuring "metallasupramolecular" systems,[1] as is now well documented by the example of catenates[2] and molecular knots,[3] helical structures,[3a, 4] and molecular grids.[5] Among the reasons for this are the geometrical flexibility of ligand coordination at this $3d^{10}$ ion, including the ambiguity in the preferred coordination number between 4 and 3, and its ability to form rather stable bonds to "normal" ligands despite its low (i.e., monopositive) charge. Besides their structural significance in metallasupramolecular chemistry, copper(I) complexes have found interest as models for biological Cu^I sites,[6, 7] as tools in molecular biology,[8] as pharmacologically active compounds,[9] as catalysts for O_2 activation,[10] as light-emitting species,[11] and as photocatalysts.[12]



Scheme 1. $[(\mu\text{-bpym})Cu_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2]^{2+}$ with chelating ($n = 5$; type **I**) or bridging diphosphine ligands ($n = 6, 8$; type **II**, "inverse cryptates").

Within our program of studying molecule-bridged dinuclear complexes with unusual optical, magnetic, and electron transfer properties we have recently established a first "inverse cryptate" structure **1** involving a central bridging bischelating radical ligand, two bridgehead Cu^I centers, and two bridging diphosphine



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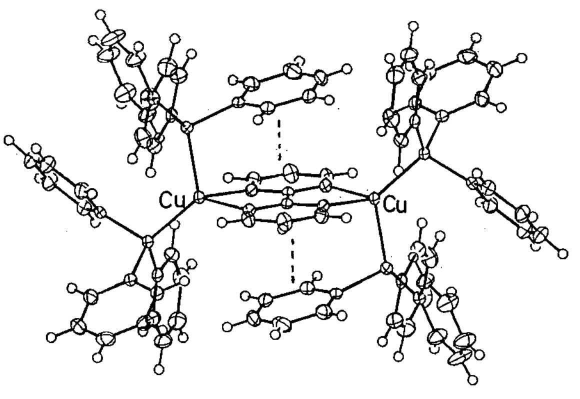
"straps", μ-Ph$_2$P-(CH$_2$)$_6$-PPh$_2$.[13] This structure was referred to as "inverse cryptate" because the metal ions rather than nitrogen donor atoms serve as bridgehead centers while an encapsulated donor-containing ligand occupies the central cavity instead of a metal cation. In a systematic study we have now tried to establish where the border lies between such "inverse cryptate" triply bridged dicopper(I) structures and the "normal" situation, which involves chelating behavior of the diphosphines.[14]

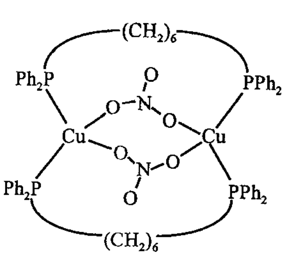
The bischelate ligand used was the "linearly" bridging π-acceptor 2,2′-bipyrimidine (bpym),[7, 15–17] and the variable in our study was the number n, the length of the polymethylene chain in the diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$. As a structural reference system, we could use a related complex [(μ-bpym)Cu$_2$(PPh$_3$)$_4$](BF$_4$)$_2$ (**2**) with monodentate triphenylphosphine ligands.[7, 11c] This complex is characterized in the solid by a not uncommon[2, 7] type of tetrahedral to trigonal pyramidal distortion at the copper(I) centers, which results from an apparent attractive π–π–π interaction ("organic sandwich" structure) between the central bpym acceptor system and two of the phosphino phenyl rings (Fig. 1).[11c]



2 (dication)

Fig. 1. Stacked decks in the dication of **2**.

Recently, some species related to **1** were reported which involve weakly binding μ-η^1:η^1-nitrate (**3**) or μ-η^1:η^1-perchlorate (**4**) as encapsulated bridging ligands.[18]



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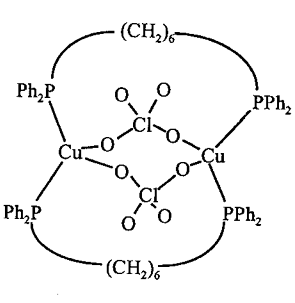

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Whereas dicopper(I) complexes with exclusively bridging ligands are considered rare,[19] there is an extensive body of recent structural data on bpym-bridged multinuclear copper(II) compounds, which were primarily studied for their magnetic exchange behavior.[16] In this work we report the complexes [(μ-bpym)Cu$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$](BF$_4$)$_2$ [n = 5 (**5**), 6 (**6**), 7 (**7**), and 8 (**8**)], which were obtained as exclusive products from the comproportionative four-component "self-assembly" process summarized in Equation (1).[7, 13, 20]

$$\text{bpym} + \text{Cu} + \text{Cu(BF}_4)_2 + 2\,\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2 \longrightarrow [(\mu\text{-bpym})\text{Cu}_2\{\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2\}_2](\text{BF}_4)_2 \qquad (1)$$

Compounds **5**, **6**, and **8** could be crystallized for X-ray structure analysis, revealing the transition between the chelate structure (**I**) with "organic sandwich" support and the "inverse cryptate" alternative (**II**) (Scheme 1).

Results and Discussion

Structure: Compounds **5**–**8** were obtained according to Equation (1) as orange-red materials which exhibit visible luminescence, particularly in the solid state.[11c, 21]

Crystallization of the complexes from methanol (**5**, **8**) or dichloromethane (**6**) gave crystals suitable for X-ray diffraction and structure analysis. The crystal data, conditions of measurement, and refinement parameters are summarized in Table 1.[22] Figures 2–4 show the molecular structures of the dications with some selected bond parameters. For an overall description and differentiation of the structures, some nonbonding distances and dihedral angles are valuable; these are listed for **2**, **5**, **6**, and **8** in Table 2.

All compounds [(μ-bpym)Cu$_2${μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$](BF$_4$)$_2$ have discrete ions in the crystal with no special intermolecular interactions. Compounds **5** and **6** crystallize with solvent molecules. For **5** there are two crystallographically independent but otherwise quite similar dications in the crystal. In each case, the dication possesses a center of symmetry.

Starting with compound **8**, a relaxed "inverse cryptate" situation was found, that is, bridging of both metal centers by bpym and the two diphosphine ligands (Fig. 2). The octamethylene chains are folded in order to fit into the available space. The complex dication of **6** exhibits a qualitatively similar structure (Fig. 3); however, there are significant structural differences with respect to the two other new structures reported here (Table 2). The distinct lengthening of the Cu–Cu and P1–P2a distances and the shortening of the P1–P2 distance indicate that the hexaphos ligand Ph$_2$P(CH$_2$)$_6$PPh$_2$ has become a rather short "strap" for this particular arrangement. The resulting strain clearly involves the Cu–P bonds, which now differ by 4.6 pm (1.4 pm in **8**); on the other hand, it is not reflected in the bond parameters of the hexamethylene chain, which are still normal. There was no strain observable in compound **1**, which also contains two hexaphos bridges but which involves a different bridging ligand that induces a smaller Cu–Cu distance of about 489 pm.[13] For Cu^{II}(μ-bpym)Cu^{II} systems, the Cu–Cu distances vary between 545 and 568 pm.[16] Considering the pulling together of the PPh$_2$ units by the shorter oligomethylene chain, it is clear that the P1-Cu-P2 angle of 133.0° for **6** is distinctly larger than the value of 122.2° for **8**. However, both compounds contain four-coordinate copper(I) centers with still similar bonds to both phosphorus donor atoms.

Tightening the strap one notch further in **5**, the oligomethylene link becomes too short to allow an "inverse cryptate" structure (**II**) with bridging diphosphine ligands; instead, the diphosphines now act as chelate ligands (alternative **I**). The resulting eight-membered chelate ring system is not unusual; a similar arrangement $\overline{\text{P-Mo-P-(CH}_2)_6}$ was reported recently.[14a] There is also a high degree of asymmetry at

Table 1. Crystal data collection and refinement parameters.

	5	**6**	**8**
emp. formula	$C_{66}H_{66}Cu_2N_4P_4\cdot 2BF_4\cdot 2CH_3OH$	$C_{68}H_{70}Cu_2N_4P_4\cdot 2BF_4\cdot 4CH_2Cl_2$	$C_{72}H_{78}Cu_2N_4P_4\cdot 2BF_4$
M [g mol^{-1}]	1403.89	1707.6	1424.0
crystal size [mm]	0.25 × 0.2 × 0.1	0.3 × 0.25 × 0.25	0.25 × 0.2 × 0.15
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ [ITC no. 14]	$P2_1/c$ [no. 14]	$P\bar{1}$ [no. 2]
a [pm]	2468.4(2)	1060.9(2)	948.0(2)
b [pm]	1079.9(1)	1817.2(4)	1344.9(2)
c [pm]	2516.8(2)	2112.4(4)	1393.8(3)
α [°]	90.0	90.0	74.00(1)
β [°]	100.16(1)	98.94(3)	71.17(1)
γ [°]	90.0	90.0	77.96(1)
V [pm^3]	$6603.7(11)\times 10^6$	$3932.4(11)\times 10^6$	$1602.8(8)\times 10^6$
Z	4	2	1
ρ (calcd) [g cm^{-3}]	1.412	1.442	1.475
no. reflections for unit cell determination	70 ($5\leq 2\theta\leq 24°$)	39 ($10\leq 2\theta\leq 24°$)	36 ($20\leq 2\theta\leq 30°$)
2θ range	$2\leq 2\theta\leq 48°$	$3\leq 2\theta\leq 48°$	$3\leq 2\theta\leq 58°$
scan type	ω	ω	ω (Wyckoff)
scan width [°]	1.3	1.2	1.2
scan speed [° min^{-1}]	3–60	variable, 8–60	2–29
index ranges	$0\leq h\leq 27$; $0\leq k\leq 12$; $-24\leq l\leq 24$	$0\leq h\leq 12$; $0\leq k\leq 20$; $-17\leq l\leq 19$	$0\leq h\leq 13$; $17\leq k\leq 18$; $-28\leq l\leq 28$
standard reflections	2 measured every 98 reflections		
reflections collected	10592	6553	8864
independent reflections	10325	6178	8864
observed reflections ($F<4\sigma(F)$)	5510	3958	7031
$F(000)$	2904	1748	738
$\mu(\mathrm{Mo_{K\alpha}})$ [mm^{-1}]	0.81	0.956	0.835
$R_1=\sum(\lvert F_0\rvert-\lvert F_c\rvert)/\sum\lvert F_0\rvert$	0.065	0.077	0.041
$R_2=[\sum\omega(\lvert F_0\rvert-\lvert F_c\rvert)^2/\sum\omega F_o^2]^{1/2}$	0.061 [$w=1/\sigma^2(F)+0.0006F^2$]	0.084 [$w=1/\sigma^2(F)+0.0036F^2$]	0.043 [$w=1/\sigma^2(F)+0.0006F^2$]
GoF $=[w(\lvert F_0\rvert-\lvert F_c\rvert)^2/n-p]^{1/2}$	1.32	1.31	1.38
max./min. electron-density residuals [$\times 10^{-6}$ e pm^{-3}]	1.10/−0.67	1.08/−1.23	0.58/−0.53

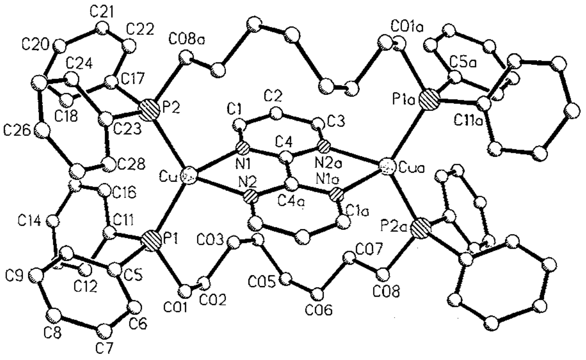


Fig. 2. Molecular structure of the dication in the crystal of **8**. Selected bond lengths [pm] and angles [°]: Cu–N1 207.6(2), Cu–N2 211.4(2), Cu–P1 227.2(1), Cu–P2 225.8(1), C4–C4a 143.6(4), N1-Cu-N2 76.7(1), P1-Cu-P2 122.2(1).

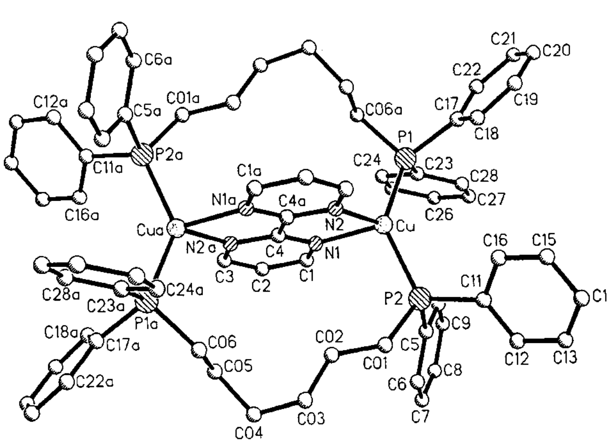


Fig. 3. Molecular structure of the dication in the crystal of $6\cdot 4CH_2Cl_2$. Selected bond lengths [pm] and angles [°]: Cu–N1 217.2(6), Cu–N2 214.1(6), Cu–P1 227.6(2), Cu–P2 223.0(2), C4–C4a 148.3(14), N1-Cu-N2 78.1(2), P1-Cu-P2 133.0(1).

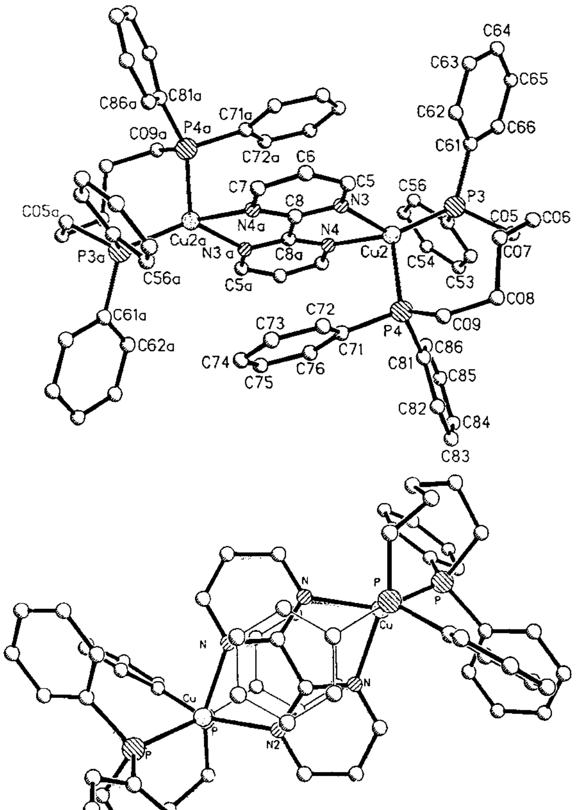


Fig. 4. Molecular structure of one crystallographically independent dication (no. 2) in the crystal of $5\cdot 2CH_3OH$ (side and top views). Selected bond lengths [pm] and angles [°], no. 1: Cu1–N1 211.2(7), Cu1–N2 209.1(7), Cu1–P1 222.5(2), Cu1–P2 229.0(2), C4–C4a 148.2(15), N1-Cu1-N2 79.1(3), P2-Cu1-P1 117.3(1); no 2: Cu2–N3 209.4(7), Cu2–N4 212.4(7), Cu2–P3 222.1(2), Cu2–P4 228.3(2), C8–C8a 148.7(16); N3-Cu2-N4 79.0(3), P3-Cu2-P4 116.0(1).

Table 2. Characteristic nonbonding distances d [pm] and angles θ [°] in (2,2′-bipyrimidine)dicopper(I) complexes.

	d_{CuCu}	d_{P1P2}	d_{P1P2a}	θ [a]	$\Delta\theta$
2	562.2	397.2	768.9	102.7, 134.7	32.0
5a	560.4	385.5	778.5	102.7, 140.2	37.5
5b	560.6	382.0	780.4	102.7, 142.1	39.4
6	576.4	413.2	752.6	111.4, 115.8	4.4
8	567.2	396.6	785.9	116.9, 122.9	6.0

[a] Angles between Cu–P bonds and corresponding N-Cu-N planes.

the copper centers in **5**. The distorted tetrahedral coordination geometry as observed for **6** and **8** is further distorted in the direction of a trigonal pyramidal (3 + 1) coordination, involving the further lengthening of one Cu–P bond and the shortening of the other at each side of the centrosymmetric dications in **5**. The most obvious feature of the distorted coordination geometry concerns the very different angles θ between the two Cu–P bonds and the corresponding N1-Cu-N2 plane; the differences $\Delta\theta$ are larger in **5** than in the triphenylphosphine derivative **2** and, of course, much more pronounced than in either **6** or **8** (Table 2). Such distortions reflect the rather facile change from four- to three-coordination at Cu^I centers;[23] they have been observed similarly in bis(1,10-phenanthroline)copper(I) complexes[2] and the various subspecies of Type 1 copper centers in blue copper proteins.[6]

The distortion at the individual metal sites in **5** is also reflected by the obvious nonplanarity of the $[Cu(\mu\text{-bpym})Cu]^{2+}$ core (Fig. 4); these distortions are, perhaps cooperatively, supported by a π-type stacking interaction in which two (P-)phenyl rings almost sandwich the central 2,2′-bipyrimidine heterocycle. Whereas the bischelate-forming bpym is a π acceptor,[7, 15] the phosphine-bound phenyl rings may rather be regarded as π-donating. The view from the top (Fig. 4) supports this notion of a π–π–π interaction; the closest inter*atomic* distance between the decks is d(C8a–C76) = 329.3 pm, and the dihedral angles between decks are 11.4 and 12.3° for the two crystallographically independent dications. Whereas the stacking interaction is thus slightly weaker in **5** relative to the analogue **2** with PPh_3 ligands,[7, 11c] the distortion towards a trigonal pyramidal coordination geometry at Cu^I is more pronouced in **5** (Table 2). Similar but more extended stacking to form a "pleated" structure has recently been reported for a metal-free arrangement;[24] the structural role of the metal here is that of a hinge.

The assignment of oxidation states $Cu^I(bpym^0)Cu^I$ for the central dicationic core is supported by the inter-ring distances of 143.6–148.7 pm for the 2,2′-bipyrimidine ligand in compounds **2**,[7] **5**, **6**, and **8**; the slight shortening in comparison to the value of 150 pm for free bpym[25] signifies some amount of π back-donation from the electron-rich metal centers to the π-acceptor ligand.[26] The two pyrimidine halves are coplanar; a very small dihedral angle of 1.1° was found for **2**[7] whereas $Cu^{II}(bpym)Cu^{II}$ compounds exhibit higher values.[16]

Correlation with spectroscopy and electrochemistry: In addition to their luminescence in the solid state and in solution,[11c, 21] the remarkable feature of dinuclear complexes like **2** is the chemically and electrochemically reversible one-electron reduction to paramagnetic monocations with the spin predominantly centered in the π^* MO of the central bischelating heterocycle.[7, 15, 27] Nevertheless, the presence of ^{63}Cu, ^{65}Cu, and ^{31}P coupling constants $a > 0.5$ mT[7, 27] indicates a certain amount of spin transfer from $bpym^{\bullet -}$ to the Cu–P bonds, which should be influenced by the structure.

While the static structures of the complex dications in the crystalline state were discussed and rationalized above, the dissolved complexes may reveal linkage equilibria and other dynamic behavior. We therefore analyzed the complexes **5**, **6**, and **8** by ^1H and ^{31}P NMR in [D$_2$]dichloromethane solution between 190 and 300 K. The observed line-broadening effects at higher temperatures (see Fig. 5, Table 3, and Experimental Procedure) indicate dynamic processes occurring on the NMR timescale; they also reveal the existence of *two* ^{31}P resonances for **6** (Table 3) and the formation of triorganophosphine oxide signals at $\delta = +20 - +60$ (^{31}P NMR) after longer contact of the dissolved species with air (Cu^I catalysis).

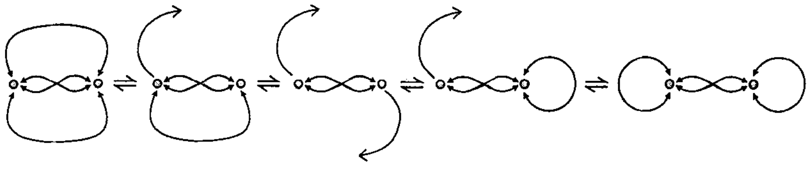
Table3. Spectroscopic and electrochemical data for complexes.

	5	**6**	**7**	**8**
^{31}P NMR in CD_2Cl_2				
δ	−5.70 [a]	−2.33 [a] −14.04	−2.52 [a]	−1.98 [b]
UV/Vis in $CHCl_3$				
λ_{max2} [nm] [c]	363	348	365	357
λ_{max1} [nm] [d]	462sh	435sh	436sh	426sh
Cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6				
E_{red} [V] [e,f]	−1.28	−1.17	−1.20	−1.13
EPR [g]				
g	2.0017	2.0026	– [j]	2.0020
a (^1H) [mT] [h]	0.467	0.50	–	0.50
a (^{14}N) [mT]	0.213	0.213	–	0.213
a (^{63}Cu) [mT] [i]	0.71	0.79	–	0.67
a (^{31}P) [mT]	0.92	1.00	–	0.90

[a] Broad at 300 K, narrowing at lower temperatures. [b] Very broad at 300 K, narrowing at lower temperatures. [c] Molar extinction coefficient $\varepsilon = 5000 \pm 500\,M^{-1}cm^{-1}$. [d] Molar extinction coefficient $\varepsilon = 3000 \pm 500\,M^{-1}cm^{-1}$. [e] Potentials in V vs. $Cp_2Fe^{+/0}$, $100\,mVs^{-1}$ scan rate, peak potential differences 60–100 mV. [f] Irreversible oxidation processes at about +1.0 V vs. $Cp_2Fe^{+/0}$. [g] EPR of one-electron reduced forms (cationic complexes) in CH_2Cl_2/0.1 M Bu_4NPF_6. [h] a(H-5,5′) of bpym. [i] $a(^{65}Cu) = 1.07 \times a(^{63}Cu)$. [j] Not determined.

Both effects suggest equilibria based on the lability of the Cu–P bond; Scheme 2 illustrates how the subsequent cleavage and reformation of two Cu–P bonds could i) contribute to the conversion between structures **I** and **II**, and ii) produce intermediate arrangements with three-coordinate copper(I), coordinated and uncoordinated triorganophosphine groups.

Dinuclear compounds[28] and solid state materials[29] with both four- and three-coordinate Cu^I centers are well known and so are oligocopper(I) systems with exclusive tricoordination.[19, 23] The structural results described for complex **5** suggest that the inversion-symmetric arrangement should prevent the formation of significant amounts of completely free diphos-



I **II**

c.n. 4,4 3,4 3,3 3,4′ 4′,4′

Scheme 2. Interconversion of structures **I** and **II**, showing intermediates with three-coordinate copper(I).

phine ligands; further decrease of the coordination number from three to two is also unlikely. Nevertheless, the appearance of two signals for dissolved **6** that are assigned to coordinated ($\delta = -2.33$, broad) and free diphenylalkylphosphine groups (-14.04) in the ^{31}P NMR spectrum indicates partial Cu–P bond cleavage (Scheme 2), probably to relieve the strain observed in solid **6** (Fig. 3, Table 2) and in agreement with the biologically relevant[6] ambivalence with regard to the preferred coordination number 3 or 4 of copper(I).[7, 19] A third alternative to recombination to either structure **I** or **II** would be the formation of coordination polymers. This possibility has not been observed for the compounds discussed here; the entropically favored formation of ring structures in either **I** or **II** seems to dominate over intermolecular linking by the diphosphine ligands. We consider the bonds between the copper(I) centers and rigid, basic, bischelating 2,2′-bipyrimidine more inert than the Cu–P bonds; a different situation exists when weakly coordinating anions such as nitrate (**3**) or perchlorate (**4**) serve as encapsulated $\mu,\eta^1:\eta^1$-bridges between copper(I) centers.[18]

In addition to "on–off" equilibria[18] as shown in Scheme 2 and as assumed for the strained "borderline" structure **6**, the generally observed line-broadening processes can involve vibrational equilibration of Cu–P1 and Cu–P2a bonds, and especially the torsional motions within the partially flexible oligomethylene chains of the diphosphine ligands. A well-documented example is complex **8**, which exhibits one δ(H-4,6,4′,6′) signal in the ^1H NMR spectrum at 280 K in CD_2Cl_2 but two split signals at 190 K (Fig. 5).

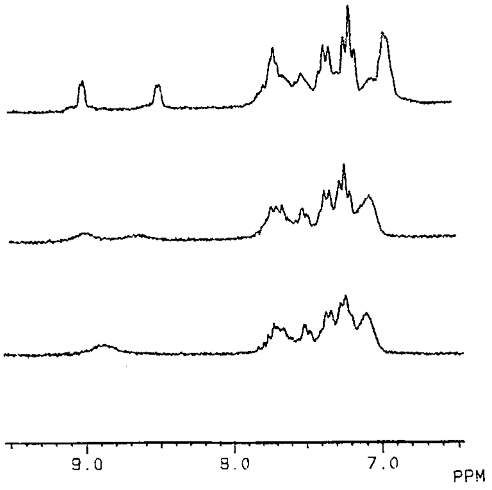


Fig. 5. ^1H NMR spectra of **8** in CD_2Cl_2 at 190, 260, and 280 K (from top to bottom).

The EPR results of one-electron reduced, that is, monocationic species (Table 3) clearly demonstrate the interaction of four equivalent ^{31}P nuclei with the unpaired electron, which is primarily localized in the 2,2′-bipyrimidine ligand π system. There is also a hyperfine interaction with two equivalent copper centers, with ^{63}Cu and ^{65}Cu present in natural abundance of 69.2% and 30.8%, respectively. This situation produces three isotope combinations, $^{63}Cu/^{63}Cu$ (47.9%), $^{63}Cu/^{65}Cu$ (42.6%), and $^{65}Cu/^{65}Cu$ (9.5%), and thus three EPR sub-spectra; both isotopes have a nuclear spin of $I = {}^3/_2$, but the nuclear g factor and thus the hyperfine splitting is larger by about 7% for ^{65}Cu.[7, 30]

What are the electrochemical and EPR spectroscopic features (Table 3) that correlate with the structural results? Compound **5** is distinguished by a rather negative reduction potential, whereas the radical cation form of **6** stands out by large $^{63,65}Cu$ and ^{31}P hyperfine coupling in the EPR spectrum. The low E_{red} value of **5** agrees with a qualitatively different structure **I**, in which additional π donation from P-phenyl rings (Fig. 4) can diminish the reducibility of the bpym π system. Concerning the EPR results, we have shown above that **6** exhibits a distortion which creates large P-Cu-P angles of 133.0° and thus increased overlap between the Cu–P σ bonds and the bpym π system. This structurally caused interaction is responsible for the increased EPR hyperfine splitting of the ^{31}P and $^{63,65}Cu$ nuclei (Table 3).

Conclusion

We have presented a striking example of how the structural flexibility of Cu^I allows for the construction of topologically unusual arrangements within the concept of molecular architecture. The resulting structural variations affect physical properties, and the most interesting effects were observed for those strained species situated at the border between two different linkage modes, **I** (**5**) and **II** (**6**). Within the set of three systematically analyzed analogues presented, the effects of alkyl chain length restriction and stacking between metal-hinged aromatic "deck" ligands has been observed, demonstrating the excellent suitability of copper(I) for supporting noncovalent interactions.

Experimental Procedure

Materials: Compounds **5** and **6** [7] and the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 7$ and 8) [31] were obtained following literature procedures.

Compounds $[(\mu\text{-bpym})Cu_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2](BF_4)_2$, $n = 7$ (7) and $n = 8$ (8): A suspension containing bpym (158 mg, 1 mmol), copper powder (95 mg, 1.5 mmol), $Cu(BF_4)_2$ (237 mg, 1 mmol), and $Ph_2P(CH_2)_nPPh_2$ (2 mmol) was heated under reflux for 1 h in dichloromethane/methanol (50 mL, 5/1 v/v). The unreacted copper powder was filtered out of the hot orange-red solution, which was then reduced to 25 mL, treated with *n*-hexane (25 mL) and left to crystallize at −15 °C. The precipitated microcrystals were washed with diethyl ether and dried under vacuum. Although the solid compounds are air-stable, the dissolved species produce ^{31}P NMR signals of phosphine oxides after prolonged contact with air.

Compound **7**: 564 mg, 40% (crystallized material). ^1H NMR (250 MHz, CD_3OD): $\delta = 0.6–2.4$ (brm, 28 H, CH_2), 7.28–7.78 (m, 42 H, H-5,5′ and phenyl H), 9.04 (brs, 4 H, H-4,4′,6,6′); $C_{70}H_{74}B_2Cu_2F_8N_4P_4$ (1410.0): calcd C 59.63 H 5.29 N 3.97, found C 59.40 H 5.46 N 3.88%.

Compound **8**: 708 mg, 50% (crystallized material). ^1H NMR (250 MHz, CD_3OD): $\delta = 0.9–2.5$ (brm, 32 H, CH_2), 7.14–7.71 (m, 42 H, H-5,5′ and phenyl H), 8.98 (brs, 4 H, H-4,4′,6,6′); ^1H NMR (250 MHz, CD_2Cl_2, 280 K): $\delta = 0.8–2.4$ (brm, 32 H, CH_2), 7.0–7.8 (m, 42 H, H-5,5′ and phenyl H), 8.90 (brs, 4 H, H-4,4′6,6′); ^1H NMR (250 MHz, CD_2Cl_2, 190 K): $\delta = 0.7–2.4$ (brm, 32 H, CH_2), 6.8–7.9 (brm, 42 H, H-5,5′ and phenyl H), 8.50 (brs, 2 H, H-4,4′), 9.02 (brs, 2 H, H-6,6′); $C_{72}H_{78}B_2Cu_2F_8N_4P_4$ (1424.0): calcd C 60.73 H 5.52 N 3.93, found C 61.40, H 5.51, N 4.36%.

Instrumentation: EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER 035 M gaussmeter and a HP 5350 B microwave counter. ^1H NMR spectra were recorded on a Bruker AC 250 spectrometer, UV/Vis absorption spectra were recorded on Shimadzu UV 160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in dichloromethane/0.1 M Bu_4NPF_6 with a three-electrode configuration (glassy carbon electrode, Pt counter electrode Ag/AgCl reference) and a PAR M 273 potentiostat and function generator. The ferrocenium/ferrocene couple served as internal reference.

X-ray crystal structure determination: Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-hexane into dilute solutions (CH_3OH for **5** and **8**, CH_2Cl_2 for **6**); they were selected in nujol and sealed in glass capillaries. Compounds **5** and **6** each crystallize with eight molecules of solvent per unit cell. During X-ray data collection of compound **6**, a decrease of intensity of selected reflections was observed as a consequence of crystal decomposition (slow loss of solvent). Although the measurements, especially for weak reflections, were done with relatively high scan speed, two crystals of **6** were necessary to cover the 2θ range. Electron density distribution in ΔF maps for **6** as well as high thermal displacement parameters and the extremely anisotropic behavior of the chlorine atoms suggest a disorder in orientation of the CH_2Cl_2 molecules; the best results were obtained by a more arbitrary splitting of the Cl positions. There are also indications of disorder in the BF_4^- anions in compound **5**; however, attempts to split the F positions were unsuccessful.

Data collection: four circle Siemens P4 diffractometer (**5**, **6**); four circle Syntex P2_1 (**8**); $Mo_{K\alpha}$ (graphite-monochromated) radiation; $T = -100\,^{\circ}C$. Structure solution: Patterson method (**5**), direct methods (**6**, **8**). Corrections: Lorentz and polarization effects. Refinement: blocked full-matrix least squares; 811 (**5**), 433 (**6**), 563 (**8**) parameters refined; quantity minimized $\sum w(F_0 - F_c)^2$; anisotropic thermal displacement parameters for non-hydrogen atoms except those of CH_2Cl_2 molecules (isotropic); for **5** and **6**, hydrogen atoms calculated in ideal geometrical positions with C–H bond length of 96 pm, fixed U_{iso} at 800 pm^2 ("riding model"); for (**8**), after geom. positioning refined with isotropic thermal displacement parameters; scattering factors: *Int. Tables for X-Ray Crystallography, Vol. IV*, Kynoch, Birmingham (UK), **1974**; Shelxtl PC program system, Siemens Analytical X-Ray Instruments, Release 4.1, May **1990**.

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