121. Synthesis and Reductive Complexation Properties of a Cone-Configurated Tetra[*p*-(*tert*-butyl)]calix[4]arene Incorporating Bipyridyl and Pyridine Subunits.
NMR Characterization and Crystal Structure of Its Chiral Copper(I) Complex

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The hetero-armed *p*-(*tert*-butyl)calix[4]arene **1** was synthesized by a stepwise procedure. This ligand presented a very strong complexing behavior towards Cu^I, giving the chiral complex **2** and parent species when reacted with Cu^{II} salts. High-resolution NMR techniques were employed for the characterization of **2**, demonstrating notably exchange processes between its two enantiomeric forms. The racemic nature of **2** was confirmed by X-ray crystal-structure analysis.

Introduction. – The pioneering synthetic work of *Gutsche* [1] has stimulated a variety of investigations on the structural modifications of calixarenes. In their cone conformation, calixarenes present a hydroxy-rich (hydrophilic) lower rim and a hydrocarbon-rich (lipophilic) upper rim, both of which are subject to transformations to derivatives. Specifically, elaboration of the lower rim with polar functional groups (*e.g.* acids, esters, and amides) thus produced podands tailor-made for the complexation of metal ions [2].

We recently noted that, in this field, the study of transition-metal cation complexation was poorly developed [3]. Nevertheless, the first few papers related to the incorporation of N-donor chelating pendant arms to calix[4]arene[1]) reported interesting complexation properties [4]. More recently, *Beer* [5], *Grigg* [6], and *Ziessel* [7] and coworkers prepared pre-organized calixarene-bipyridyl hybrids in the form of podands or barrelands where bipyridyl subunits were grafted in their 6- or 5-positions. Thus, some complexation studies with transition metals were described with regard to the preparation of chiral complexes (Cu^I, Ag^I) [5], pH-sensitive fluorescent probes (Ru^{II}) [6] and luminescent probes (lanthanides(III)) [7].

Our contribution in this field [3] began with the preparation of the full family of the *O*-[(2,2′-bipyridyl-6-yl)methyl]-substituted tetra-*p*-(*tert*-butyl)calix[4]arene tetrols in their cone configuration and to study their complexation behavior toward the Cu^I cation. All the ligands synthesized, except the fully *O*-substituted species, carry from one to three OH groups which can be functionalized selectively in a cascade mode with different heterocyclic or non-heterocyclic systems. Thus, the use of the same direct

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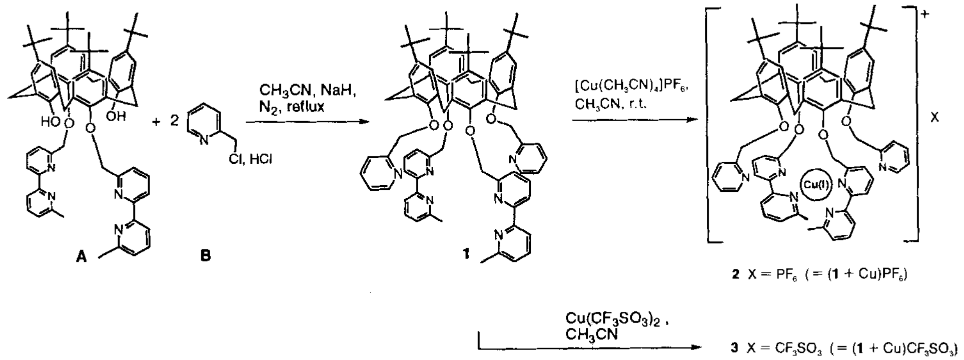
[1]) Calix[4]arene (= pentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene).

base-strength-driven regioselective *O*-alkylation process allows us to design ligands with coordination properties adapted to our desired metallic species.

The ability to prepare calixarenes bearing different numbers and kinds of complexing heterocyclic subunits should lead to the synthesis of ligands able to complex efficiently both redox states of a metal during an oxido-reduction process. To this end, we report the synthesis and characterization of the C_{2v} symmetrically hetero-functionalized *p*-(*tert*-butyl)calix[4]arene **1** bearing two opposite bipyridyl and two opposed pyridine moieties.

Ligand Synthesis. – The pre-functionalized calixarene **A** [3] was alkylated at the two residual OH positions using NaH as base in MeCN and 2-(chloromethyl)pyridine **B** [8] as alkylating agent (*Scheme*). The pure ligand **1** was obtained in 40% yield after purification by column chromatography (alumina) followed by radical centrifugally accelerated prep. TLC (silica gel (*Chromatotron*), MeOH gradient in CH_2Cl_2). Analyses of the ^{1}H- and ^{13}C-NMR spectra showed that **1** was in the cone conformation.

Scheme



The characteristic *AB* pattern for the bridging Ar–CH_2–Ar groups with chemical shifts in $CDCl_3$ (3.04, 4.06 ppm) and a J_{AB} value (12.7 Hz) analogous to the tetra-bipyridyl (see *Formula* 5 in [3]) was observed. Thus, replacing two symmetrical bipyridyl groups by their pyridine analogues does not produce a dramatic change in the general features of the cone conformation. Changing the solvent to CD_3CN modified the ^{1}H-NMR pattern of **1**: the 2 *s*'s of the *t*-Bu groups, the *AB* system, the 2 *s*'s of the OCH_2–(bpy or py) groups and the 2 *s*'s of the benzenic protons close up slightly; the latter undergo a downfield shift from 6.77 and 6.87 to 7.15 and 7.16 ppm, respectively, but the cone conformation is still indicated.

In accord with the empirical rules found by *de Mendoza et al.* [9], the cone conformation of **1** was deduced from the ^{13}C-NMR chemical shifts of Ar–CH_2–Ar and OCH_2–heterocycle, which appear at 31.02 and 77.81–78.2 ppm, respectively, in $CDCl_3$ The ^{13}C-NMR spectrum was slightly modified by changing the solvent from $CDCl_3$ to CD_3CN, but the chemical shifts of Ar–CH_2–Ar and OCH_2–heterocycle were always found in the cone-conformation area (30.275 and 77.77–77.93 ppm, resp.) indicating the absence of a strong solvent effect on the calixarene configuration.

Complexation Behaviour of 1 toward Cu^{I} and Cu^{II}. – We found in our previous report that the Cu^{I} cation was strongly stabilized by complexation with pendant bipyridyls (complexes with *Formulae* **6**, **7**, and **8** in [3]), giving orange-to-red solids or solutions very stable in air. We can imagine that in **1**, only the bipyridyl groups will participate in tetrahedral complexation of Cu^{I}, excluding the pyridine arms. These pyridine arms should become active in the octahedral coordination and stabilization of the higher oxidation state of the metal (*i.e.* Cu^{II}).

Reacting a stoichiometric amount of **1** with tetrakis(acetonitrile)copper(I) hexafluorophosphate [10] in MeCN afforded an orange-red solution which was evaporated (*Scheme*). The resulting orange material was purified by chromatography (alumina, CH_2Cl/MeCN). The Cu^I complex **2** thus obtained was perfectly stable in air, and its solution in CD_3CN or $CDCl_3$ for NMR studies did not show appearance of paramagnetism over a one-month period.

Complex **2** was studied in CD_3CN and $CDCl_3$, the latter giving, contrary to our previous observations [3], much better peak resolution and spreading. Each type of proton was thus well defined in $CDCl_3$, and the apparent simplicity of the aromatic region suggested a high symmetry for the molecule.

Guided by the idea that **1** should also complex Cu^{II} with participation of the pyridine arms, giving thus an oxidant/reductant couple which should present redox catalytic properties, we tried to prepare the oxidized conjugate of **2**. Our first trial was carried out with a MeOH solution of $CuCl_2 \cdot 6\ H_2O$, neutralized with Et_3N to avoid the preliminary observed protonation of **1**, affording a brown mixture containing an orange-brown major compound which was recovered by chromatography (alumina or silica gel) and tested by NMR. We were surprised to find that this compound displayed a ^{1}H-NMR spectrum essentially identical to **2**, indicating a spontaneous reduction of Cu^{II} in Cu^I; this result was confirmed by its ES-MS analysis, giving the same mass profile and notably the cationic peak at 1258.5 ([**1** + Cu^I]$^+$). The treatment of this species with NH_4PF_6 afforded directly **2**, based on TLC (silica gel or alumina) and ^{1}H-NMR analysis.

Thinking that this reductive complexation could be effected with participation of the solvent (*i.e.*, MeOH being oxidized to formaldehyde), we changed both solvent and counter ion. Thus, reacting **1** with an excess (1.3 equiv.) of copper(II) bis(trifluoromethanesulfonate) in MeCN and in the presence of air afforded a brownish green solution in a very exothermic process. TLC control (alumina or silica gel) showed the presence of a major orange compound which was purified by chromatography, giving **3**. The ^{1}H-NMR analysis of the latter showed a spectrum similar to that of **2**, notably identical for the *AB* systems but slightly different in the aromatic region (protons H–C(3) (8.375 *vs.* 8.31 ppm) and H–C(3′) (8.085 *vs.* 8.02 ppm) of the bpy's showed a 0.6 ppm upfield shift probably due to a counter-anion effect ($CF_3SO_3^-$ *vs.* PF_6^-)).

The exothermicity displayed by this complexation process indicated that MeCN acts probably as a coordinating solvent, stabilizing thus the Cu^I species instead of Cu^{II} in the presence of **1**. We changed MeCN for a non-coordinating solvent such as 1,2-dichloroethane. The reaction of **1** with $Cu(CF_3SO_3)_2$ was not exothermic, and the resulting mixture showed on TLC plate the presence of a low amount of **3** and a major greenish spot which could be the copper(II) complex. ES-MS of the raw material indicated the presence of the cationic species [(**1** + Cu^{II})CF_3SO_3]$^+$ at 1408 mass units in addition to the cationic peak arising from **3** at 1258.5 ([**1** + Cu^I]$^+$). These encouraging results are under further investigation as is the electrochemical generation of the desired Cu^{II} complex from **2** or **3**.

NMR Study of 2 in $CDCl_3$. – Besides comparison of the ^{1}H-NMR spectra of **2** and **1**, attribution of the whole sprectrum of **2** required several 2D NMR techniques, NOESY (nuclear *Overhauser* effect spectroscopy), COSYLR (long-range correlation spectroscopy), gradient COSYDQF (double-quantum filtration correlation spectroscopy) [11], ROESY (rotating-frame *Overhauser* effect spectroscopy, with offset frequency compensation) [12], HSQC (heteronuclear single quantum coherence spectroscopy) [13], and finally HMBC (heteronuclear multibond coherence spectroscopy) [14]. In *Fig. 1*, complex **2** is represented as one of its enantiomeric forms (see below), displaying the main interesting parts for NMR analysis, *i.e.*, aromatic heterocycle and benzene protons, then bridging CH_2 spin systems.

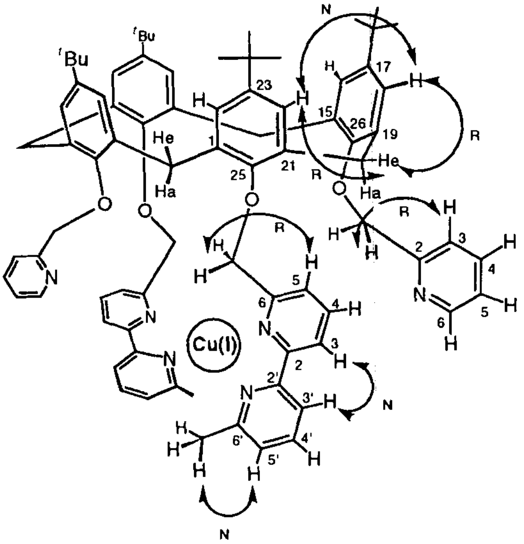


Fig. 1. *Schematic representation, atom numbering, and significant dipolar interactions between protons in complex* **2** (N = NOESY, R = ROESY)

The first observations which can be done comparing **2** to **1** are related to the chemical shifts of the different alkyl groups: the 2 *s*'s of the *p*-(*tert*-butyl) groups undergo a strong splitting (0.75–1.355 *vs.* 1.06–1.13 ppm); the *s* of the *Me*–bpy group undergoes an upfield shift from 2.62 to 1.75 ppm indicating a great influence of the metal on the bipyridyl group. The Ar–CH_2–Ar *AB* systems and the two OCH_2–heterocycle resonance signals of **2** are strongly modified compared to those of **1**. The OCH_2–bpy and OCH_2–py *s*'s and *AB* systems of Ar–CH_2–Ar detected in **1** transform into 8 *d*'s displayed between *ca.* 2.50 and 6.50 ppm, which can be organized as 4 *AB* systems, two of them representing the two OCH_2–bpy and OCH_2–py groups. This indicates the reduction of the local symmetry of the CH_2 groups around the metallic center and, by deduction, the formation of a chiral complex.

We tried to build back the molecule starting from a NOESY experiment, but COSYDQF allowed us in fact to understand its general feature. In this sense, direct correlations between components of *AB* systems, then between heterocyclic protons were found through a COSYDQF experiment. Thus appeared four couples of *d*'s located at 2.78–3.57, 2.87–4.175, 4.06–4.22, and 5.15–6.37 ppm and three groups of coupled protons, located at 6.675 (*d*), 6.926 (*dd*), 7.22 (*td*), and 8.23 (*d*) ppm (system *1*), at 7.29 (*d*), 7.82 (*t*), and 8.02 (*d*) ppm (system *2*), and at 7.40 (*d*), 8.11 (*t*), and 8.31 (*d*) ppm (system *3*). Two residual and independent spin systems, 2 close *s*'s at 6.265–6.285 ppm and a *s* at 7.10 ppm, were deduced from this experiment.

The aromatic region was expected to display two benzene and three heterocycle spin systems, one of the latter with four spins corresponding to the 2-substituted pyridine (system *1*), the two residual with three spins corresponding to the 2,6-disubstituted pyridine subunits of bipyridyl (systems *2* and *3*). The latter was built up from the *Me*–bpy group by NOESY or COSYLR experiments, giving the following sequence (proton, type of signal, chemical shift in ppm): Me (*s*, 1.75)→H–C(5′) (*d*, 7.29)→H–C(4′) (*t*, 7.82)→H–C(3′) (*d*, 8.02)→H–C(3) (*d*, 8.31)→H–C(4) (*t*, 8.11)→H–C(5) (*d*, 7.40). The NOE existing between H–C(3′) and H–C(3) is indicating that these two protons are located on the same side of the chelate and confirms the complexation of $\mathrm{Cu^I}$ by the two N-atoms.

Correlations between the $\mathrm{OC}H_2$ groups and the corresponding heterocycles were only found with ROESY experiments (*Fig. 2*). Thus, the downfield part of the short *AB* system (4.06–4.22 ppm) presented cross-peaks with the *d* at 6.675 ppm, allowing us to build, with the results of NOESY and COSYDQF experiments, the $\mathrm{OC}H_2$–pyridine sequence: $\mathrm{OCH_2}$ (*AB*, 4.06–4.22)→H–C(3) (*d*, 6.675)→H–C(4) (*t*, 7.22)→H–C(5) (*dd*, 6.926)→H–C(6) (*d*, 8.23). We found in the same time that the *pre*-assigned H–C(5) of bipyridyl presented cross-peaks with the upfield part of the large *AB* system (5.15–6.37 ppm), the latter corresponding thus to the $\mathrm{OC}H_2$–bipyridyl spin system.

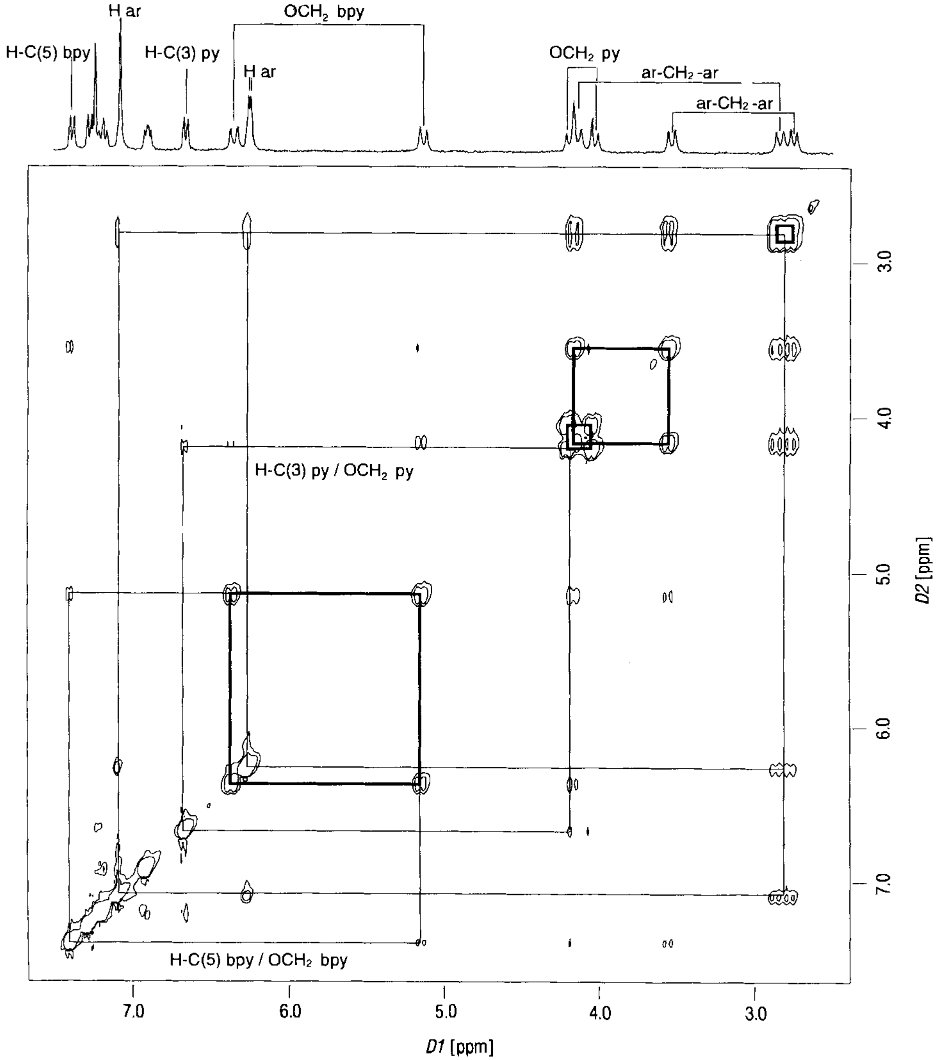


Fig. 2. *ROESY Correlations between aryl and bridging methylene protons in complex* **2**. All cross-peaks are negative except those connected with bold lines (exchange).

The expected two calixarenic benzene spin systems were found in fact represented, as deduced from COSY-DQF, as 3 *s*'s with relative integrations 2:1:1 at 7.10, 6.285, and 6.265 ppm, respectively. These two groups of signals, based on their relative intensities, presented NOE interactions and were assigned each one to one kind of benzene ring. Through-space ROESY interactions were also found between these three signals and both upfield parts of the two Ar–CH_2–Ar *AB* systems. These upfield components were thus attributed to the 'upper' protons (H_e (e = equatorial), in *Fig. 1*) of the methylene groups.

ROESY Experiments (*Fig. 2*; mixing time 200 ms) showed a strong exchange process occurring inside and between the four calixarenic CH_2 groups: in the corresponding two *AB* spin systems located at 2.78–3.57 and 2.87–4.175 ppm, the two high-field parts and the two low-field parts exchanged each other, as shown in *Fig. 2* (bold lines). This exchange process indicated that the calixarene ring undergoes a small torsion motion in the macrocyclic plane, nevertheless excluding a total interconversion of the cone. Simultaneously, an exchange occurs inside both the OCH_2–bipyridyl and OCH_2–pyridine *AB* systems, indicating in the case of the former the interconversion of the two bipyridyl chelating subunits around the Cu^I cation. This, added to the observed torsion motion in the macrocyclic plane, is consistent with the hypothesis of a racemic mixture. Both phenomena, which are certainly interdependent, are represented in *Fig. 3*.

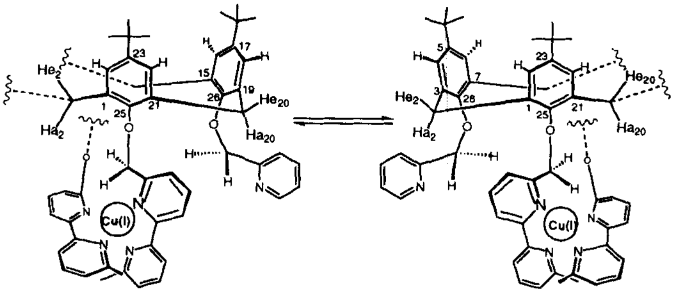


Fig. 3. *Schematic representation of the interconversion process in complex* **2**

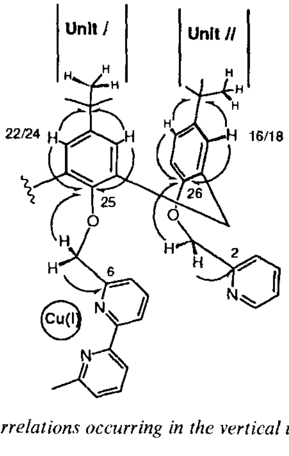


Fig. 4. *HMBC Correlations occurring in the vertical units of complex* **2**

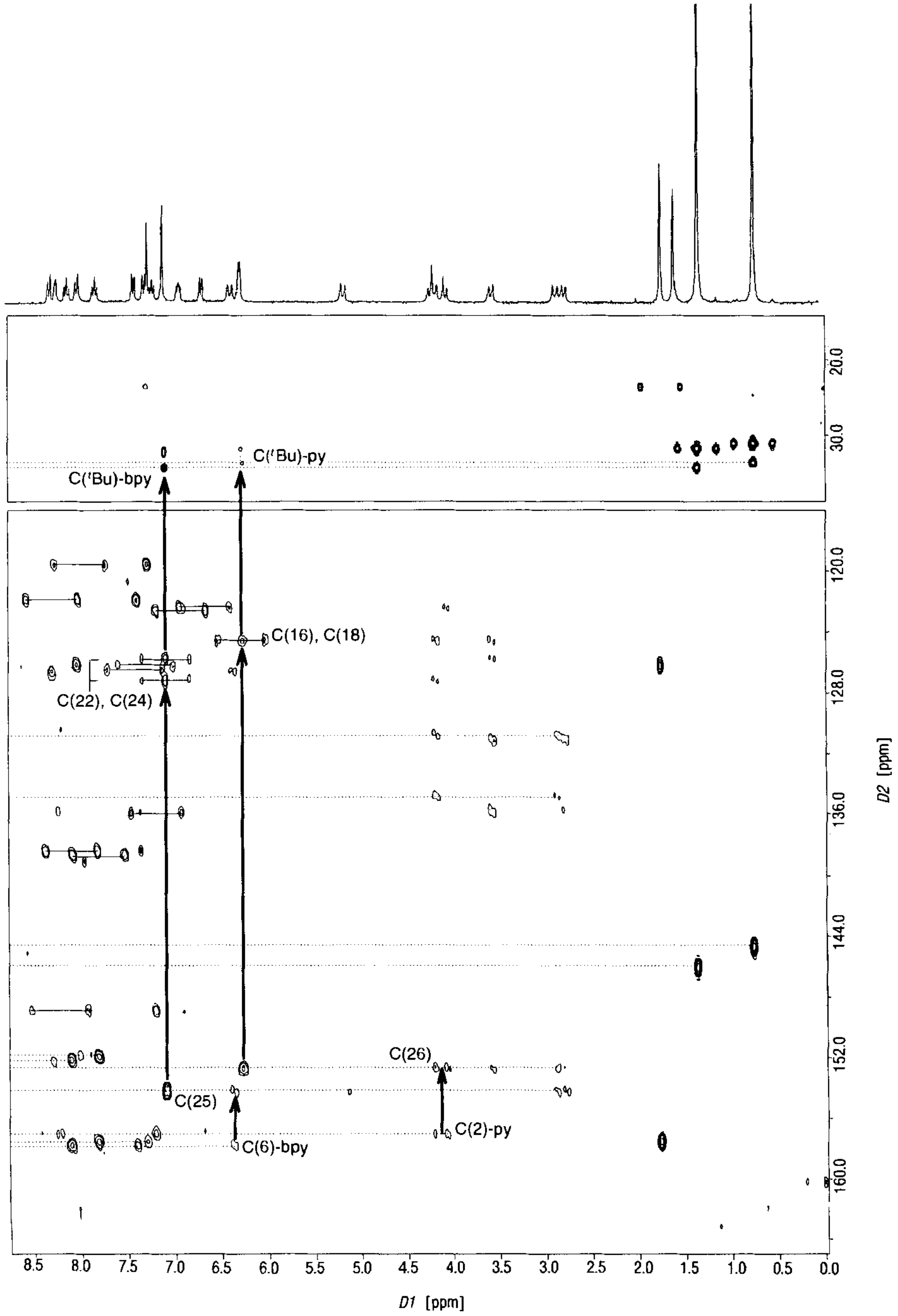


Fig. 5. *HMBC Experiment: vertical relationships* (bold arrows) *and quaternary C-atom assignments* (dotted lines) *in compound* **2**

Final assignments of H- and C-atoms were performed with HSQC and HMBC experiments which allowed us to define the vertical relationships along the cone axis. Thus, the molecular frame was cut into two symmetrical moieties containing each one two vertical units, unit *I* bearing the bipyridyl arm, and unit *II* the pyridine one (*Fig. 4*). All the unsubstituted C-atoms of the complex were assigned through HSQC experiments confirming notably COSYDQF correlation measurements within the four *AB* systems. The benzene C-atoms bearing the *s* proton at 7.10 ppm appeared as a *d* located at 127.03 and 125.61 ppm, while those bearing the two *s* protons at 6.265 and 6.285 ppm appeared as a single peak at 124.02 ppm. The C(2), C(2'), C(6), and C(6') of the bipyridyl moiety, C(2) of the pyridine moiety, as well as C(23), C(25), and Me_3C of unit *I*, and C(17), C(26), and Me_3C of unit *II* were assigned through a HMBC experiment. We also determined the vertical relationships in units *I* and *II* (*Fig. 5*), notably between the benzene protons at 7.10 ppm, the *t*-Bu signal at 1.355 ppm, and the OCH_2–bipyridyl, or between benzene protons at 6.265–6.285 ppm, the *t*-Bu signal at 0.75 ppm, and the OCH_2–pyridine.

Nevertheless, C(1), C(21), C(15), and C(19), then C(16), C(18), C(22), and C(24) as well as C(14) and C(20) were not assigned precisely due to the racemic nature of the molecule in solution.

X-Ray Crystal Structure of Complex 2. – A crystal of **2**·(toluene)$_3$, obtained by slow evaporation of $CHCl_3$ from a toluene/$CHCl_3$ solution of complex **2**, was inserted in a glass capillary. The intensity data were obtained with an *Enraf-Nonius-CAD-4* diffractometer using graphite-monochromatized CuK_α radiations (λ 1.54178 Å). The preliminary calculations (*Lorentz* and polarization, decay and adsorption) were made by SDP programs [15]; the structure was solved by direct methods using the program MULTAN [16] and refined by least-squares methods with SHELX93 [17]. H-Atoms were localized at their theoretical positions. Experimental data are presented in *Table 1*.

Table 1. *X-Ray Diffraction Measurements of Compound* **2**

Empirical formula	$C_{80}H_{86}CuF_6N_6O_4P \cdot 3\ C_7H_8$	Absorption correction factors	
Formula weight	1678.54	minimum	0.5677
Cell dimensions		maximum	0.9971
a [Å]	25.54 (1)	Decay correction	
b [Å]	16.594 (4)	loss of intensity linear correction	−10.3%
c [Å]	24.37 (1)	No. of unique reflections	18294
β [°]	114.87 (5)	No. of observed reflections ($I > 2\sigma(I)$)	7327
Space group	$P2_1/c$	R (observed reflections)	0.132
Z	4	Goodness of fit	1.177
λ_{Cu} [Å]	1.54178	D_c [g/cm^3]	1.058
Maximum $\sin\theta/\lambda$ [Å^{-1}]	0.6203		

One of the *t*-Bu groups of the macrocycle exhibited a disorder with occupancies of 57 and 43%. Around the P-atom of the PF_6^- anion, the six F-atoms had two disordered positions in a ratio of 65 and 35%, resp. The benzene rings in the three toluene molecules had to be constrained to regular hexagones and refined as rigid bodies with a unique isotropic thermal parameter for each molecule; the three molecules exhibited a disorder, each of them with two positions with occupancies of 55 and 45% for two of them and 62 and 38% for the other one. Only the C-atom of one Me group of the toluene molecules was localized; the other Me groups were probably disordered around the benzene rings. At the end of the refinement, the constraints had to be maintained, the values of the thermal parameters remained high, and most Me groups remained unlocalized. All attempts to solve better these three toluene molecules were unsuccessful. The final R was 0.132 for 7327 reflections and the goodness-of-fit was 1.177.

X-Ray diffraction analysis of complex **2** was performed to determine the geometry about the Cu^I cation and to confirm its helical nature as well as its racemic composition, as inferred from the NMR data. The structure obtained is depicted in *Fig. 6*. The arrangement of the molecule in the unit cell (*Fig. 7*) shows how the existence of a symmetry plane in the crystallographic space group ($P2_1/c$) is correlated with the existence of two enantiomeric molecules in the crystal in a ratio 50:50. The atom numbering

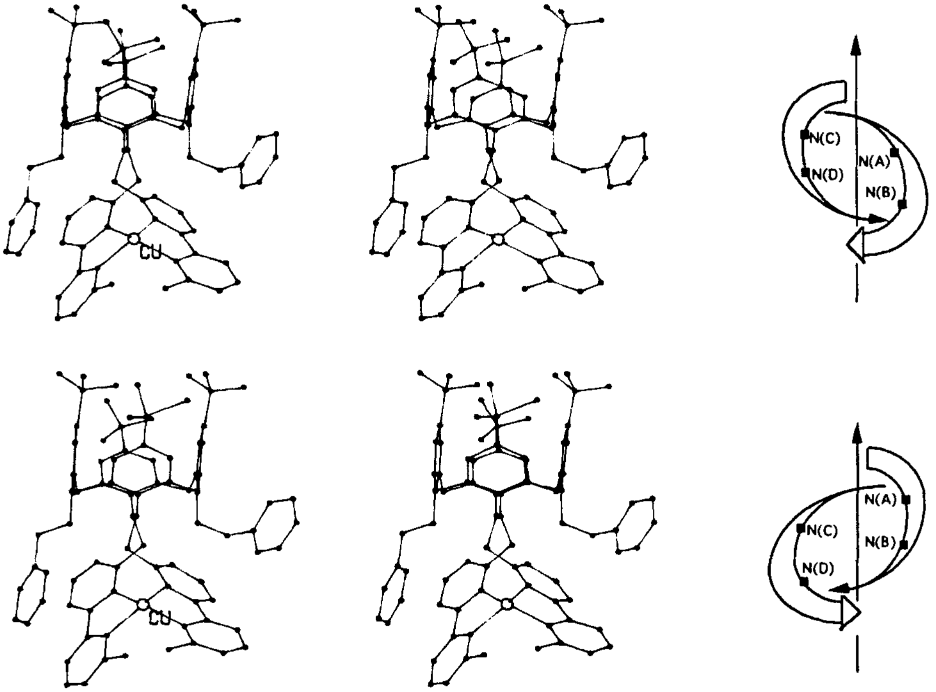


Fig. 6. *Stereoviews of the two enantiomers of complex* **2**

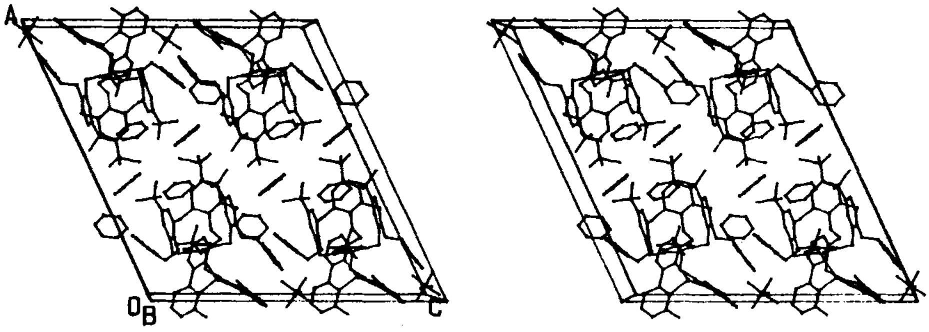


Fig. 7. *Stereoview of the unit cell in a crystal of complex* **2**

of the calixarene, bipyridyl, and pyridine substructures was retained (see *Fig. 8*) to be closer to the numbering used for the NMR attributions. Selected distances and bond angles around Cu^{I} are listed in *Table 2*, dihedral angles between bipyridyl and pyridine planes in *Table 3*. The calixarene macrocycle adopts a boat-shaped (C_{2v}) cone conformation with rings bearing the pyridine pendant arms E and F (see *Fig. 8*) almost parallel (2(9)°) and those bearing the bipyridyl subunits almost perpendicular (88.2(8)°). The length of the cavity can be approximated at the upper rim by the C(50)–C(170) and

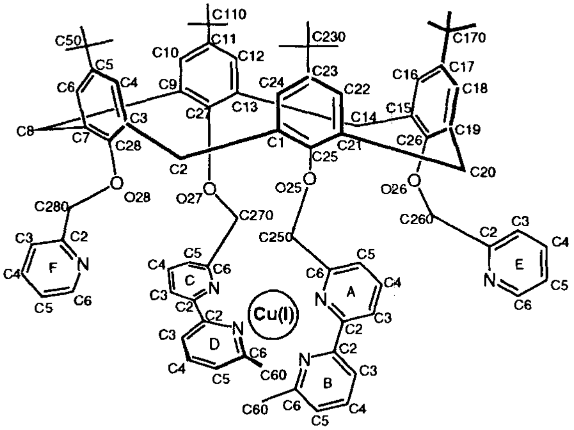


Fig. 8. *X-Ray diffraction analysis of* **2**: *Atom numbering* (arbitrary)

Table 2. *Selected Distances* [Å] *and Bond Angles* [°] *around* Cu^I *in Complex* **2**. For numbering, see *Fig. 8*.

Cu–N(A)	2.017 (8)	Cu–N(E)	4.774 (7)	N(A)–Cu–N(B)	82.5 (3)
Cu–N(B)	2.053 (6)	Cu–N(F)	5.485 (9)	N(A)–Cu–N(C)	140.0 (3)
Cu–N(C)	2.004 (6)	Cu–O(25)	4.198 (6)	N(A)–Cu–N(D)	119.9 (3)
Cu–N(D)	2.044 (9)	Cu–O(26)	4.683 (5)	N(B)–Cu–N(C)	122.6 (2)
		Cu–O(27)	4.156 (6)	N(B)–Cu–N(D)	112.6 (3)
		Cu–O(28)	4.224 (7)	N(C)–Cu–N(D)	81.4 (3)

Table 3. *Dihedral Angles* [°] *in and between Bipyridyl and/or Pyridine Pendant Arms in* **2**

AB/E	AB/F	CD/E	CD/F	AB/CD	A/B	C/D	E/F
74.5 (5)	80.6 (3)	19.7 (5)	8 (1)	87.5 (2)	18.6 (9)	12 (1)	12.7 (8)

C(110)–C(230) distances (5.51(2) and 11.49(2) Å, resp.); at the lower rim, by the O(28)–O(26) and O(25)–O(27) distances (5.505(7) and 3.436(7) Å, resp.). The four C-atoms are displayed at the summits of an almost regular rhombus of mean side of 6.530 Å, with a compression at the C(170) summit. The same observation can be done for the four O-atoms for which the mean side is 3.257 Å. The C-atoms of the four CH_2 bridges are coplanar ($X^2 = 28$). The dihedral angles between their mean plane and the benzene rings have the following values: 134.1(3), 135.4(1), 85.6(2), and 83.9(2)° for rings bearing the heterocyclic systems AB, CD, E, and F, respectively.

The Cu^I atom is coordinated to the two bipyridyl groups with a distorted tetrahedral geometry. The average value of the four corresponding Cu–N distances is 2.03 Å, close to the values found in the literature for simple $[Cu(diimine)_2]^+$ complexes [18]. The shortest distances found for Cu–N(A) and Cu–N(C) (2.017(8) and 2.004(6) Å, resp.) combined with the N(A)–Cu–N(C) bond angle (140.0(3)°) confirm the distortion from the ideal tetrahedron and are consistent with the fact that the pyridine rings A and C which are attached to the calixarenic platform through the OCH_2 bridges are spatially constrained.

This effect can be also observed by the angles N(B)–Cu–N(C) (122.6(2)°), N(A)–Cu–N(D) (119.9(3)°), and, less significantly, N(B)–Cu–N(D) angle (112.6(3)°).

The pyridine rings B and D which possess more degrees of freedom around the Cu^I center can equilibrate the N(A)–Cu–N(C) distortion. Considering the position of the Cu-atom with respect to the normal bonding planes of the four coordinating rings, the distortion is greater for A and D (0.647(1) and 0.602(1) Å, resp.) than for B and C (0.190(1) and 0.120(1) Å, resp.). The high values detected for A and D indicate that the free electron pair of the N-atom tends to overlap perpendicularly the corresponding Cu d orbital.

The six pyridine rings are planar ($0 < X^2 > 24$). The bipyridyl moieties are distorted from planarity as reflected by the dihedral angles between A and B (18.6(9)°) and C and D (12(1)°) and the corresponding average planes are almost perpendicular (87.5(2)°) around the Cu^I center.

The pyridine rings E and F are found almost parallel to each other (12.7(8)°), parallel to the bipyridyl CD (E: 19.7(5)°; F: 8(1)°), and perpendicular to the bipyridyl group AB (E: 74.5(3)°; F: 80.6(3)°). This, added to the observed distances Cu–N(E) (4.774(7) Å) and Cu–N(F) (5.485(9) Å), tends to indicate that N(E) and N(F) do not interact with the Cu-atom.

Comparison of the strongly distorted nature of complex **2** in the solid state with its high symmetry in solution leads us to the conclusion that the crystal packing is dominating in the orientation of the pyridine rings E and F as well as in the differentiation of the coordination characteristics of the pyridine moieties A, B, C, and D around the Cu^I center.

All other distances between the PF_6 group, toluenes, and calixarene correspond to *van der Waals* interaction.

Conclusion. – Podants based on calixarene carrying N-donor groups demonstrated excellent complexing behavior toward Cu^I species [3] [5]. To complete and develop our previous work in this domain, we prepared, with the aim of complexing both reduced and oxidized forms of the couple Cu^I/Cu^{II}, the 'long plus short arms'-functionalized calixarene **1** containing bipyridyl and pyridine subunits. This compound gave very surprisingly the chiral Cu^I complex starting either from Cu^I or Cu^{II} salts, indicating for **1** a strong tetrahedral complexation behavior.

The Cu^I complex **2** was studied in solution with high-resolution NMR techniques allowing the assignment of most protons and C-atoms and giving the preliminary conclusion of the presence of a racemic mixture. The chirality is metal-centered, and exchange processes occur between both enantiomeric forms of **2** in solution.

Structural investigation by X-ray diffraction analysis confirmed our results. Electrochemical and chemical oxidation of **2**, its catalytic properties, and its complexing behavior toward organic substrates are currently under investigation, as well as the studies of analogues of **1** based on compounds **1** with the *Formulae* **1**–**4** of our previous report [3].

Experimental Part

General. See [3]. Moreover: All NMR experiments, except COSYLR and HMBC, were performed in the phase-sensitive mode. COSYDQF, HSQC, and HMBC used gradients for coherence selection. Acquisition parameters for ROESY: $SW = 2994$ Hz, $SI = 2, k$, relaxation delay $D1 = 1.5$ s, mixing time $\tau_m = 200$ ms with a $(\gamma/2\pi)B_1 = 2$ kHz, and $NE = 512$ increments for the second dimension; data processing with the FELIX 1.0 package in the phase-sensitive mode with a square sine bell window function in the two dimensions and a final matrix size of $1k \times 1k$ of reals. Gradient HMBC: $SW = 2994$ Hz, $SI = 1\ k$, $D1 = 1.5$ s for the 1 H dimension, and $SW = 12077$ Hz, NE = 512 for the indirect C dimension; 6 G cm^{-1} Z gradient; data processing with the FELIX 1.0 package in the absolute mode, with a 90°-shifted square sine bell in the two dimensions and a final matrix size of $1k \times 1k$ of reals.

*6,6″-{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis{[(pyridin-2-yl)methoxy]calix[4]arene-25,27-diyl}bis(oxymethylene)}bis[6′-methyl-2,2′-bipyridyl]* (**1**). Calixarene **A** [3] (0.62 g, 0.61 mmol) and NaH (0.18 h, 7.5 mmol) were mixed in refluxing MeCN (30 ml) under N_2 during 45 min. The resulting mixture was then cooled to r.t. and solid **B** [8] (0.3 g, 1.8 mmol) added in one portion. After 50 min, the temp. was brought to 60° for 0.5 h. MeCN was evaporated, the residue dissolved in CH_2Cl_2 (20 ml), and the solid filtered off. The org. phase was concentrated and then chromatographed (alumina, CH_2Cl_2, then silica gel (*Chromatotron*) CH_2Cl_2/MeOH 100:0→97:3): pure **1** (0.29 g, 39%). Impure fractions were collected for further purification. White powder. M.p. 115–116°. UV (MeCN): 288.8 (34400). IR: 2800–3000 (C–H, Ar, py); 1570.4 (C–N, py). ^{1}H-NMR ($CDCl_3$): 1.06 (*s*, 2 *t*-Bu); 1.13 (*s*, 2 *t*-Bu); 2.62 (*s*, 2 *Me*–bpy); 3.04, 4.06 ('*q*', *AB*, $J_{AB} = 12.7$, 4 Ar–CH_2–Ar); 4.96 (*s*, 2 OCH_2–py); 5.15 (*s*, 2 OCH_2–bpy); 6.77 (*s*, 4 H, Ar); 6.87 (*s*, 4 H, Ar); 6.94–7.00 (*m*, 2 H, py); 7.12 (*d*, $J = 7.5$, 2 H, bpy); 7.20 (*td*, $J = 8$, 2, 2 H, py); 7.42 (*d*, $J = 7.5$, 2 H, bpy); 7.60–7.72 (*m*, 2 H of bpy, 2 H of py); 7.96 (*d*, $J = 7.7$, 2 H, bpy); 8.19 (*d*, $J = 7.7$, 2 H, bpy); 8.44 (br. *d*, $J = 4$, 2 H, py). ^{1}H-NMR (CD_3CN): 1.17 (*s*, 2 *t*-Bu); 1.18 (*s*, 2 *t*-Bu); 2.55 (*s*, 2 *Me*–bpy); 2.96, 4.21 ('*q*'. *AB*, $J_{AB} = 12$, 4 Ar–CH_2–Ar); 4.85, 4.88 (2*s*, 2 OCH_2–py, 2 OCH_2–bpy); 7.09 (*dd*, $J = 7.7$, 0.8, 2 H–C(5)(bpy)); 7.15 (*s*, 4 H, Ar); 7.16 (*s*, 4 H, Ar); 7.18 (*dt*, $J = 7.6$, 1, 2 H–C(5′)(bpy)); 7.21 (*td*, $J = 7.8$, 2, 2 H–C(4)(py)); 7.63 (*t*, $J = 7.7$, 2 H–C(4′)(bpy)); 7.69 (*m*, 2 H–C(6)(py)); 7.71 (*t*, $J = 7.7$, 2 H–C(4)(bpy)); 7.73 (*td*, $J = 7.8$, 2, 2 H–C(5)(py)); 7.89 (*dt*, $J = 7.7$, 1, 2 H–C(3′)(bpy)); 8.24 (*dd*, $J = 7.9$, 0.8, 2 H–C(3)(bpy)); 8.49 (*m*, 2 H–C(3)(py)). ^{13}C-NMR ($CDCl_3$): 24.67 (*Me*–bpy); 31.02 (Ar–CH$_2$–Ar); 31.42 (Me_3C); 31.52 (Me_3C); 33.85 (Me_3C); 33.92 (Me_3C); 77.81, 78.20 (OCH$_2$–bpy, OCH$_2$–py); 118.24, 119.57, 123.03, 123.18, 136.94, 137.12 (CH (bpy)); 122.23, 136.30, 148.53 (CH (py)); 125.27, 125.35 (CH (Ar)); 133.41, 134.00, 144.81, 144.86 (C_o, C_p (Ar)); 152.77, 152.85 (C(2), C(2′)(bpy)); 157.62, 157.66 (C(6), C(6′)(bpy)); 155.25, 155.75 (C_{ipso} (Ar)); 158.20 (C(2)(py)). ^{13}C-NMR (CD_3CN): 23.67 (*Me*–bpy); 30.28 (Ar–CH$_2$–Ar); 30.70 (Me_3C); 33.83 (Me_3C); 77.77, 77.932 (OCH$_2$–bpy, OCH$_2$–py); 117.76, 119.37, 122.50, 123.67, 123.80, 125.23, 125.39, 136.38, 137.05, 137.27, 148.52 (CH (Ar, bpy, py); 134.81, 145.96, 146.12, 152.68, 155.18, 156.78, 157.80, 157.89 (C_o, C_p, C_{ipso} (Ar); C(2), C(2′), C(6), C(6′)(bpy); C(2)(py)). ES-MS: 1196.4 ($[M + H]^+$), 1218.4 ($[M + Na]^+$), 1104.7 ($[M - (CH_2{-}py) + H]^+$). Anal. calc. for $C_{80}H_{86}N_6O_4$ (1195.61): C 80.37, H 7.25, N 7.03; found: C 80.41, H 7.24, N 6.98.

Copper(I) Complexes of Ligand **1**. *Complex* **2** *from* **1** *and Copper(I) Salt*: A soln. of $[Cu^I(MeCN)_4]PF_6$ (0.025 g, 0.67 mmol) in MeCN (1 ml) was added under stirring to a mixture of **1** (0.08 g, 0.067 mmol) and MeCN (3 ml). Upon addition, **1** dissolved and the resulting orange soln. was filtered and then evaporated to give raw **2**. After purification by column chromatography (Al_2O_3, CH_2Cl_2/MeCN (99:1 then 97:3), the product was dissolved in CH_2Cl_2 (5 ml) and precipitated with excess Et_2O: pure **2** (0.085 g, 90%). Orange powder. M.p. 238–239°. UV (MeCN): 263 (32290), 300.8 (31140), 445 (4212 MLCT). IR: 851 (PF_6^-). ^{1}H-NMR ($CDCl_3$): 0.75 (*s*, 2 *t*-Bu of unit *II*); 1.355 (*s*, 2 *t*-Bu of unit *I*); 1.75 (*s*, 2 *Me*–bpy); 2.78, 3.57 ('*q*', *AB*, $J_{AB} = 12.7$, 2 Ar–CH_2–Ar); 2.87, 4.175 ('*q*', *AB*, $J_{AB} = 13.3$, 2 Ar–CH_2–Ar); 4.06, 4.22 ('*q*', *AB*, $J_{AB} = 12.5$, 2 OCH_2–py); 5.15, 6.37 '*q*', *AB*, $J_{AB} = 12.7$, 2 OCH_2–bpy); 6.265 (*s*, 2 H, Ar of unit *II*), 6.285 (*s*, 2 H, Ar of unit *II*); 6.675 (*d*, $J = 7.7$, 2 H–C(3)(py)); 6.926 (2*d*, $J = 7.0$, 2 H–C(5)(py)); 7.10 (*s*, 4 H, Ar of unit *I*); 7.22 (*td*, $J = 7.6$, 1.7, 2 H–C(4)(py)); 7.29 (*d*, $J = 7.6$, 2 H–C(5′)(bpy)); 7.40 (*d*, $J = 7.6$, 2 H–C(5)(bpy)); 7.82 (*t*, $J = 7.8$, 2 H–C(4′)(bpy)); 8.02 (*d*, $J = 7.9$, 2 H–C(3′)(bpy)); 8.11 (*t*, $J = 7.8$, 2 H–C(4)(bpy)); 8.23 (*d*, $J = 7.0$, 2 H–C(6)(py)); 8.31 (*d*, $J = 7.8$, 2 H–C(3)(bpy)). ^{13}C-NMR ($CDCl_3$): 23.57 (*Me*–bpy); 31.01 (Me_3C of unit *II*); 31.68 (Me_3C of unit A); 31.78 (Ar–CH$_2$–Ar); 32.40 (Ar–CH$_2$–Ar); 33.34 (Me_3C of unit *II*); 34.06 (Me_3C of unit *I*); 78.12, 78.45 (OCH$_2$–py); 79.48 (OCH$_2$–bpy); 119.46 (C(3)(bpy)); 121.76 (C(3′)(bpy)); 122.25 (C(3)(py)); 122.43 (C(5)(py)); 142.42 (C(16), C(18), unit *II*, calix); 125.61 (C(22) or C(24) (unit *I*, calix)); 126.07 (C(5′)(bpy)); 126.43 (C(5)(bpy)); 127.03 (C(22) or C(24) (unit *I*, calix)); 130.75, 131.06, 134.88, 135.84 (C(1), C(21) (unit *I*, calix) and C(15), C(19) (unit *II*, undetermined, calix); 135.78 (C(4)(py)); 138.29 (C(4)(bpy)); 138.51 (C(4′)(bpy)); 144.69 (C(17) (unit *II*, calix)); 146.25 (C(23) (unit *I*, calix)); 148.73 (C(6)(py)); 151.87 (C(2′)(bpy)); 152.17 (C(2)(bpy)); 152.76 (C(26) (unit *II*, calix)); 154.26 (C(25) (unit *I*, calix)); 157.04 (C(2)(py)); 157.55 (C(6')(bpy)); 157.80 (C(6)(bpy)). ES-MS: 1258.4 ([**1** + Cu^I]$^+$), 1196.1 ([**1** + H]$^+$), 1166.5 ([**1** + Cu^I – (CH_2-py)]$^+$), 1104.8 ([**1** + H – (CH_2-py)]$^+$). Anal. calc. for $C_{80}H_{86}CuF_6N_6O_4P \cdot H_2O$ (1420.13): C 67.57, H 6.24, N 5.91; found: C 67.67, H 6.13, N 5.95.

Complex **3** *from* **1** *and Copper(II) Salt:* A soln. of $Cu^{II}(CF_3SO_3)_2$ (0.04 g, 0.11 mmol) in MeCN (0.5 ml) was added all at once to a soln. of **1** (0.1 g, 0.083 mmol) in MeCN (3 ml). The exothermic reaction afforded a brownish-green soln. which was stirred for 1 h and then evaporated to give an orange solid. Column chromatography (alumina, CH_2Cl_2) was performed to retain unreacted Cu^{II} salt and was followed by flash chromatography (silica gel, CH_2Cl_2/MeCN 92:8): pure **3** (0.07 g, 70%). Orange powder. M.p. 248–249°. IR: 1271, 1193 ($CF_3SO_3^-$). ^{1}H-NMR ($CDCl_3$): 0.753 (*s*, 2 *t*-Bu of unit *II*); 1.353 (*s*, 2 *t*-Bu of unit *I*); 1.76 (*s*, 2 *Me*–bpy); 2.77, 3.56 ('*q*', *AB*, J_{AB} = 12.5, 2 Ar–CH_2–Ar); 2.86, 4.16 ('*q*', *AB*, J_{AB} = 13, 2 Ar–CH_2–Ar); 4.05, 4.21 ('*q*', *AB*, J_{AB} = 12.5, 2 OCH_2–py); 5.15, 6.37 ('*q*', *AB*, J_{AB} = 12.6, 2 OCH_2–bpy); 6.266 (*s*, 2 H, Ar of unit *II*); 6.284 (*s*, 2 H, Ar of unit *II*); 6.67 (*d*, *J* = 7.7, 2 H–C(3)(py)); 6.92 (2*d*, *J* = 7.0, 2 H–C(5)(py)); 7.10 (*s*, 4 H, Ar of unit *I*), 7.21 (*td*, *J* = 7.6, 1.8, 2 H–C(4)(py)); 7.29 (*d*, *J* = 7.6, 2 H–C(5')(bpy)); 7.40 (*d*, *J* = 7.6, 2 H–C(5)(bpy)); 7.84 (*t*, *J* = 7.8, 2 H–C(4')(bpy)); 8.08 (*d*, *J* = 8, 2 H–C(3')(bpy)); 8.13 (*t*, *J* = 7.8, 2 H–C(4)(bpy)); 8.235 (*d*, *J* = 7.0, 2 H–C(6)(py)); 8.375 (*d*, *J* = 7.8, 2 H–C(3)(bpy)). ES-MS: 1258.4 ([**1** + Cu^I]$^+$), 1166.5 ([**1** + Cu^I – (CH_2–py)]$^+$), 983.2 ([**1** – (CH_2–bpy) – (CH_2–bpy)]$^+$).

Treatment of **3** with an excess of $(NH_4)PF_6$ in MeCN, followed by chromatography (alumina, CH_2Cl_2) afforded pure **2** (0.069 g, 98%).

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