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On the Chemistry of Pyrrole Pigments, XCI [1]: Copper Complexes of Pyridinologous Linear Tri- and Tetra-pyrroles as Cyclopropanation Catalysts

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Summary. In addition to two recently described pyridinologous linear tri- and tetrapyrroles a biisoquinologous system was prepared and its geometrical features derived by means of NMR measurements and force field calculations. The copper complexes of these three ligands were isolated and characterized, and then used as catalysts in the cyclopropanation of styrene. The results were found to be similar to those reported for a variety of catalysts in literature. Thus, it was demonstrated that these systems can be used in principle as catalysts.

Keywords. Pyridinologous linear tri- and tetrapyrroles; Copper chelates; ^{1}H-NMR spectra; Configuration; Conformation; Cyclopropanation catalyst.

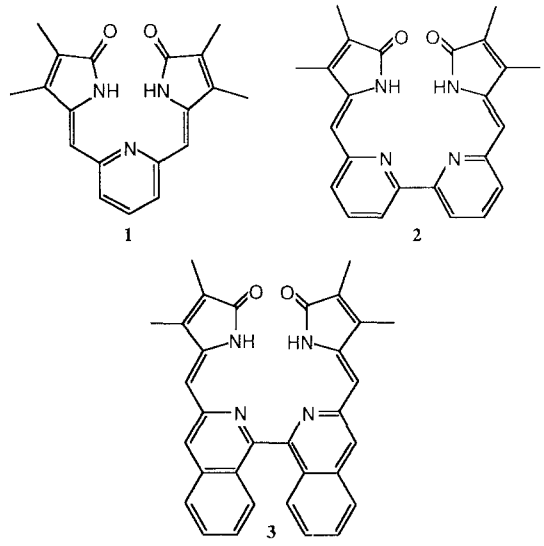
Zur Chemie von Pyrrolpigmenten, 91. Mitt. [1]: Kupferkomplexe pyridinologer linearer Tri- und Tetrapyrrole als Katalysatoren für die Cyclopropanierung

Zusammenfassung. Zusätzlich zu zwei jüngst beschriebenen linearen pyridinologen Tri- und Tetrapyrrolen wurde ein biisochinolylanaloges System dargestellt und seine Geometrie aus Kernresonanzmessungen und Kraftfeldrechnungen abgeleitet. Die Kupferkomplexe dieser drei Liganden wurden isoliert und charakterisiert und als Katalysatoren für die Cyclopropanierung von Styrol eingesetzt. Die Ergebnisse waren mit jenen aus der Literatur zahlreicher Komplexe vergleichbar. Damit konnte gezeigt werden, daß solche Systeme prinzipiell als Katalysatoren Verwendung finden können.

Introduction

Recently we studied the pyridinologous tri- and tetrapyrroles **1** and **2** among other analogous linear oligopyrroles [1]. They exhibited unique structural features as compared to common oligopyrroles [2]. As has been shown by means of zinc ions, these novel compounds also behave as ligands [1]. Accordingly, complexes with suited cations might be envisaged to be used as catalysts in organic synthesis.

As a model catalytic reaction we chose the cyclopropanation of alkenes for which a variety of catalysts have been described, and the details of such reactions have been well established [3]. We will now report our efforts to improve the space

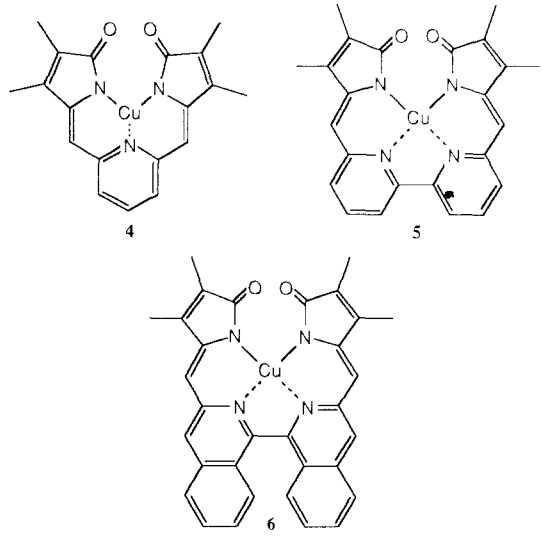


demanding structure of **2** by extending its aromatic system into the one of derivative **3**. The copper complexes of **1**–**3**, which are needed for cyclopropanation reactions will then be probed as catalysts.

Results and Discussion

Synthesis

The synthesis of **3** was achieved by means of a base catalyzed condensation of two moles of 3,4-dimethyl-pyrrolin-2-one with 1,1′-biisoquinolyl-3,3′-dicarbaldehyde. The latter compound was obtained by oxidation of the corresponding dimethyl-biisoquinolyl derivative by means of molecular oxygen in moderate yield. The precursor, 3,3′-dimethyl-1,1′-biisoquinolyl, was generated by dimerizing 1-chloro-3-methylisoquinoline in analogy to the preparation of the corresponding bipyridine derivative [1]. The copper(II) complexes **4**–**6** were obtained by reacting the ligands



1–3 with copper(II) acetate. Their stoichiometry was proven by elemental analysis. Moreover, Job plots [4] of the three ligands with copper(II) ions displayed a clean 1:1 complexation.

Structural Aspects of **3**

As derived from the NOE's between the CH_3-4,4′ groups and the =CH– fragments, both "halves" of the free ligand **3** were found to be in the (*Z*) configuration. Additional NOE's between the =CH– fragments and the isoquinolyl-4,4′ protons indicated a more or less planar *synperiplanar* conformation at the exocyclic single bonds as it has been also derived for **2** [1] and its dipyrrinone analog [5]. An intramolecular hydrogen bond stabilizing this conformation was also inferred from the vibrational band at $3392\,cm^{-1}$. The pronounced three band absorption spectrum pointed to a molecule considerably twisted at the bond between the two isoquinoline moieties. This was in contrast to the conformational analysis of the ligand **2**, which has been shown to adopt a more or less planar *antiperiplanar* arrangement of the bipyridine fragment [1]. Moreover, the chemical shift of the protons in positions 8,8′ were found within the common region of heterocyclic protons and could therefore not be interpreted in terms of the conformational situation of the two aromatic rings. This observation was also in contrast to the results for **2** [1] where the protons in 3,3′ of the bipyridine moiety were strongly shifted due to the neighborhood of the nitrogen lone pairs in the *antiperiplanar* conformation.

Due to its well resolved and unequivocally assigned proton NMR signals, lanthanide induced shifts for all of the protons of **3** could be measured. Qualitatively, the rather large shift of the 8,8′ signals indicated a vicinity of these protons to the lanthanide coordination site at the lactam carbonyl groups. Thus, the presence of

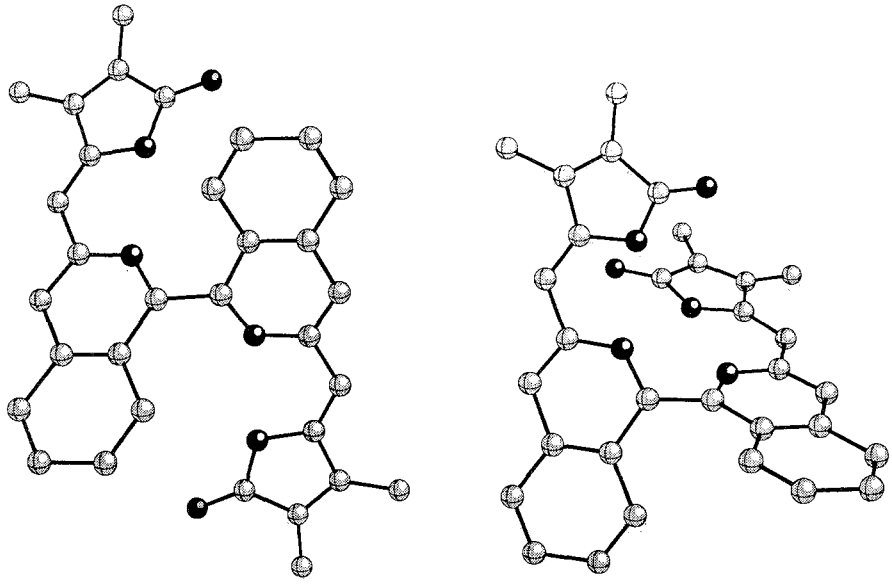


Fig. 1. Ball & Stick models [6] of the non hydrogen atoms of the *anticlinal* and *synclinal* conformers of **3** as derived from PCMODEL calculations

an *anticlinal* conformer was made plausible. Quantitative calculations using the LIS program [7] yielded an *anticlinal* conformer characterized by a dihedral angle at the 1,1′-bond of 110° and a small twisting at the two other exocyclic bonds of about 15°. The R-factor of this conformer was found to be 3.7%. A rather shallow minimum in the conformational R-factor hypersurface indicated the possibility of a conformational mixture. However, treatment of the system as a mixture of the *synclinal* and *anticlinal* conformers did not improve the R-factor. This result was due, of course, to the introduction of an additional variable.

By means of PCMODEL calculations two rather shallow minima in the energy hypersurface for the rotation at the biisoquinoline 1,1′ bond of **3** were found. They corresponded to the *synclinal* and *anticlinal* conformers characterized by twist angles of 52 and 129 degrees. Within the two "halves" the dihedral angles at the exocyclic single bonds displayed only small deviations ($< 5°$) from planarity. The *synclinal* conformer was deduced to be of the same stability as the *anticlinal* conformer. The transition barrier between these two rather flat conformational minima was estimated to amount to only 1 kJ/mol. The barriers to be surmounted for enantiomerization of the two respective conformers was derived to be > 100 kJ/mol and 58 kJ/mol, thus making the experimental resolution of the racemate rather improbable. Ball & Stick models of the two conformer skeletons were provided in Fig. 1. Taking together the results of calculations and experiments, a mixture of two conformers corresponding to *synclinal* and *anticlinal* arrangements seemed to be present in solutions of **3**.

The likely presence of more than one conformer together with rather low interconversion and enantiomerization barriers was also corroborated by the low fluorescence quantum yield ($\Phi_f = 0.002$, chloroform as the solvent). Compared to the fluorescence quantum yields of **1** and **2** ($\Phi_f(\mathbf{1}) = 0.05$, $\Phi_f(\mathbf{2}) = 0.1$ [1], ethanol as the solvent; $\Phi_f(\mathbf{2}) = 0.13$, chloroform as the solvent) which have been shown to adopt rather rigid single conformer states, this value indicated a pronounced conformational mobility of the system. The fluorescence spectrum of **3** was characterized by a Stokes shift of 32 nm. This value was small compared to the 163 nm which have been measured for **2** [1]. Thus, it was at the border line for the assignment of a Zwitterionic excited state species derived from a proton transfer from the pyrrolinone nitrogen to the isoquinoline nitrogen. Unfortunately, the absorption spectra of free **3** and its protonation product could not be recorded in a protic aqueous solvent due to solubility problems. Therefore, they could not be used for a spectrophotometric determination of ground and excited state acidities to settle the question of proton transfer in the excited state.

Structural Aspects of the Copper Complexes **4–6**

Due to the paramagnetism of the copper complexes **3–6** their structural aspects could not be advanced by means of NMR spectroscopy. Instead, PCMODEL calculations were used to approximate their geometry. These calculations resulted in pronounced energetic minima corresponding to distorted coordination spheres of the central ions.

The ligand in **4** adopted a *synclinal–synclinal* conformation considerably twisted (47°) at the two single bonds, whereas the exocyclic double bonds were only slightly

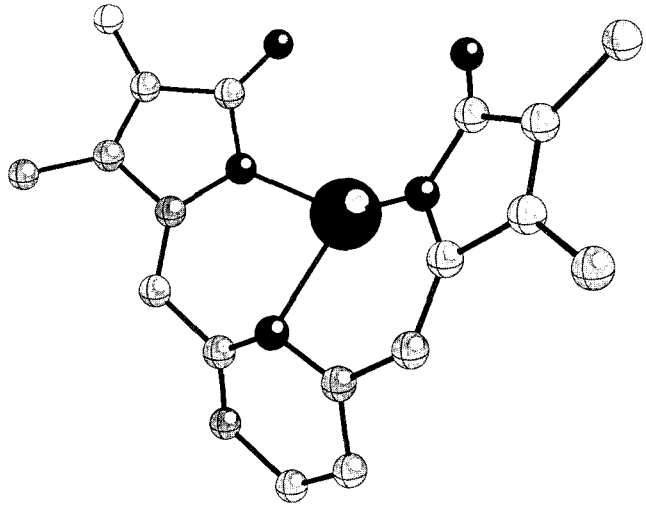


Fig. 2. Ball & Stick model [6] of the non hydrogen atoms of **4** as derived from PCMODEL calculations

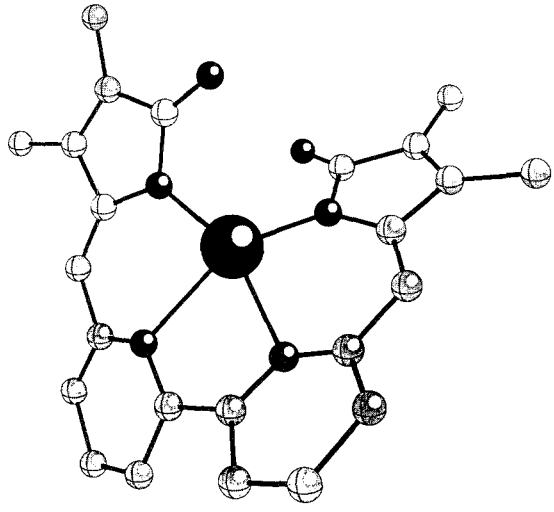


Fig. 3. Ball & Stick model [6] of the non hydrogen atoms of **5** as derived from PCMODEL calculations

deformed by only 3°. The central atom resided in a distorted tetrahedral to pyramidal coordination sphere. From an elemental analysis it followed that one molecule of chloroform was present as a solvate for every two molecules of **4** in the crystalline state. However, there was no indication of the presence of an additional ligand (methanol, acetate) in this complex. The interconversion barrier between the enantiomeric conformers of **4** was estimated to amount only 10 kJ/mol. A Ball & Stick model of its skeleton was provided in Fig. 2.

The complexes **5** and **6** were found to exhibit very similar structural features. The ligand in these two complexes adopted a *synclinal* conformation at the bond joining the two heterocyclic rings. This bond became twisted by 38 degrees. Within the two "halves" th single bonds are in *synperiplanar* conformations with an angle of twist of approximately 12 degrees. Accordingly, the central cation resides in a deformed planar coordination sphere. Enantiomerization of the complexes **5** and **6** was estimated to be hindered by about 40 and 95 kJ/mol. To illustrate the structural

features of the two complexes, a Ball & Stick model of the skeleton of **5** was provided in Fig. 3.

Although systems which owe their chirality to a C_2 symmetrical geometry of the molecule should be ideally suited for chromatographic resolution on triacetyl- or tribenzoyl-cellulose [8], all efforts to achieve this goal failed. This could be due to two reasons. Either the enantiomerization barrier of the complex was too low, or the exchange of the cation in solution was too fast to allow for the isolation of the enantiomers. The first possibility was favored by the force field calculations discussed above.

Cyclopropanation Reactions

The catalytic cyclopropanation of styrene using the racemic complexes **4–6** as catalysts and ethyldiazoacetate as the carbene source proceeded in good yields. The *trans* diastereomer of the resulting cyclopropane carboxylic ester was preferred over its *cis* diastereomer. The observed diastereospecifities of about 73:27 obviously were not influenced by the bulkiness of the ligand system indicating similar coordination geometries at the catalytic centers. These values were also similar to those which have been observed for other ligands [3, 9]. The turnover rate of about 150 was also in agreement with these previous experiments. Thus, it was demonstrated by the example of the cyclopropanation reaction that transition metal complexes of pyridinologous linear tri- and tetrapyrroles are in principle potential candidates of catalysts in organic synthesis.

Experimental Part

Melting points were taken by means of a Kofler hot stage microscope (Reichert, Vienna). ^{1}H NMR, IR-, UV-VIS-, and M-spectra were recorded using the Bruker-WM-360-, Biorad-FT-IR-45-, Hitachi-U-3210-, and Hewlett-Packard 5989A-instruments. Proton signal and stereochemical assignments were achieved using decoupling the NOE measurements on degassed solutions; *TMS* was used as the internal reference. For the LIS – experiments Eu(*fod*)$_3$ ("Merck") was used as the shift reagent. The shifts were found to be linear in the region of 0.33 mole percent of added shift reagent. Spectrophotometric titrations were recorded using a methanol water mixture (9/1) with H_2SO_4 as the acid [10]. Chloroform of fluorescence quality (Merck) was used for the fluorescence measurements on degassed solutions; Rose Bengal was used as quantum yield standard. Copper(II) acetate was obtained from Merck, styrene (purum) from Fluka, and ethyl diazoacetate from Aldrich. 2-Amino-propionic acid ethyl ester was prepared by means of the Fischer-Speier method [11]. 3,4-Dimethyl-3-pyrrolin-2-one was prepared according to [12]. Force field calculations were executed using the PCMODEL program of Serena Software, Bloomington; Figs. 1–3 were drawn on Apple Macintosh computers using the Ball & Stick program [6] of Cherwell Scientific, Oxford. Elemental analysis (C, H, N) of **3–6** gave satisfactory results.

Ethyl 2-Phthalimido-propionate ($C_{13}H_{13}NO_4$)

Prepared from ethyl-2-amino-propionate and phthalic acid anhydride by heating without solvent. After crystallization from cyclohexane the product was obtained in 98% yield; m.p. 61–63 °C (61–63 °C [13]). IR (KBr) $\nu = 2993, 1736, 1719, 1389\,cm^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 1.24 (t, $J = 7.3$ Hz, CH_3), 1.70 (d, $J = 7.1$ Hz, CH_3), 4.20 (q, $J = 7.1$ Hz, CH_2), 4.95 (q, $J = 7.3$ Hz, CH), 7.60–7.78 (m, H_{ar}-4,5), 7.83–7.92 (m, H_{ar}-3,6) ppm.

4-Hydroxy-3-methyl-2H-isoquinolin-1-one ($C_{10}H_{13}NO_2$)

Prepared by the phthalimidoacetic ester rearrangement of the phthaliminopropionic ester described above with sodium ethoxide [13]. After crystallization from methanol/water the product was obtained in 64% yield; m.p. 138–140 °C. IR (KBr) $\nu = 3456, 3142, 2860, 1659, 1644\,cm^{-1}$. ^{1}H-NMR (200 MHz, CD_3OD, δ): 2.29 (s, CH_3), 7.47 (t, $J = 7.2$ Hz, H_{ar}-7), 7.73 (t, $J = 7.2$ Hz, H_{ar}-6), 7.93 (m, H_{ar}-8), 8.24 (m, H_{ar}-5) ppm.

3-Methyl-2H-isoquinolin-1-one ($C_{10}H_9NO$)

To the solution of 20 g (0.11 mol) of the isoquinolinone described above in 110 ml hydroiodic acid, 8 g of red phosphor was added, and the mixture was stirred at 130 °C for 3 days. The reaction mixture was poured into 400 ml water, and 100 ml chloroform was added. The precipitate was filtered off and the organic layer was separated. The aqueous layer was extracted with chloroform (2 × 50 ml). The combined organic layers were washed with aqueous $NaHSO_3$ solution and with water, dried with anhydrous Na_2SO_4, and evaporated in *vacuo*. The residue was crystallized from benzene to yield 7.13 g (41%); m.p. 210–211 °C (210–211 °C [13]). IR (KBr) $\nu = 3165, 3036, 2863, 1667\,cm^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 2.42 (s, CH_3), 6.32 (s, CH-4), 7.42 (m, H_{ar}-6,7), 7.61 (m, H_{ar}-8), 8.38 (m, $J = 8.0$ Hz, H_{ar}-5), 11.34 (s, NH) ppm.

1-Chloro-3-methyl-isoquinoline ($C_{10}H_8ClO$)

Prepared from the isoquinolone described above with phosphoroxychlorid as given in [14]. By means of steam distillation the product was obtained in 84% yield; m.p. 34–35 °C (35–36 °C [14]). IR (KBr) $\nu = 3053, 2985, 2957, 1623, 757\,cm^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 2.65 (s, CH_3), 7.41 (s, CH-4), 7.63 (m, H_{ar}-6,7,8), 8.26 (m, H_{ar}-5) ppm.

3,3'-Dimethyl-1,1'-biisoquinolinyl ($C_{20}H_{16}$)

Prepared in analogy to the corresponding bipyridine derivative [1] from 1-chloro-3-methylisoquinoline. After column chromatography on silica gel using chloroform/ether (4:1) as eluent the product was obtained in 73% yield; m.p. 202–203 °C. IR (KBr) $\nu = 3090, 2983, 1622, 1587\,cm^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 2.78 (s, $2CH_3$), 7.35 (m, H_{ar}-7,7'), 7.58 (m, H_{ar}-4,4',6,6',8,8'), 7.87–82 (d, $J = 8.1$ Hz, H_{ar}-5,5') ppm. ^{13}C-NMR (90 MHz, $CDCl_3$, δ): 23.6, 118.3, 125.3, 125.5, 125.7, 126.4, 129.5, 136.7, 150.1, 157.1 ppm. UV-VIS ($CHCl_3$): $\lambda_{max} = 275(7\,730), 332(10\,590)$ nm(ε).

1,1'-Biisoquinolinyl-3,3'-dicarbaldehyde ($C_{20}H_{12}O_2$)

A solution of 2.5 g (8.8 mmol) of the dimethyl-biisoquinolyl described above in 50 ml bromobenzene/dioxane (4:1) was refluxed for 6 days. The excess of the solvent was removed by distillation. The solid residue was dissolved in 25 ml chloroform. The chloroform solution was washed with aqueous $NaHCO_3$ solution and water, dried with anhydrous Na_2SO_4 and evaporated in *vacuo*. The residue was crystallized to yield 690 mg (25%); m.p. 295–296 °C. IR (KBr) $\nu = 2803, 2677, 1706\,cm^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 7.77 (m, H_{ar}-6,6',7,7',8,8'), 8.19 (d, $J = 8.1$ Hz, H_{ar}-5,5'), 8.61 (s, H_{ar}-4,4'), 10.32 (s, 2CHO) ppm. ^{13}C-NMR (90 MHz, $CDCl_3$, δ): 121.0, 126.5, 128.6, 129.1, 129.9, 130.8, 135.7, 145.2, 157.4, 192.5 ppm. UV-VIS ($CHCl_3$): $\lambda_{max} = 304(11\,570), 317(11\,570), 330(10\,500)$ nm(ε).

3,3'-Bis-(3,4-dimethyl-2-pyrrolin-5-methylidene)-methyl-1,1'-biisoquinolinyl (**3**; $C_{32}H_{26}N_4O_2$)

Prepared from the dialdehyde described above and 3,4-dimethyl-3-pyrrolin-2-one in analogy to **1** and **2** [1]. The product was obtained in 75% yield; m.p. not until 300 °C. IR (KBr) $\nu = 3392$, 1715,

1144 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$, δ): 1.87 (s, $2CH_3$-3,3'), 2.15 (s, $2CH_3$-4,4'), 6.23 (s, 2 =CH–), 7.41 (dd, $J_{7-8} = 7.4$ Hz, $J_{7-6} = 8.1$ Hz, H-7,7'), 7.64 (d, $J = 7.4$ Hz, H-8,8'), 7.69 (dd, $J_{6-5} = 8.2$ Hz, $J_{6-7} = 8.1$ Hz, H-6,6'), 7.82 (s, H-4,4'), 7.91 (d, $J = 8.2$ Hz, H-5,5'), 9.74 (s, 2NH) NOE: $CH_{3-4} \leftrightarrow$ =CH–, =CH–$\leftrightarrow$H-4. LIS (200 MHz, $CDCl_3$, c[Eu(*fod*)$_3$/c[**3**] = 0.323): 44(CH_3-4,4'), 55(H-6,6'), 60(H-5,5'), 76(H-4,4'), 78(=CH–), 86(H-7,7'), 103(CH_3-3,3'), 146(H-8,8'), 473 (NH) Hz. ^{13}C-NMR (90 MHz, $CDCl_3$, δ): 8.6, 9.7, 104.5, 121.8, 126.1, 126.9, 127.3, 127.9, 129.0, 131.0, 140.5, 141.5, 148.3, 157.3, 172.1, 194.7 ppm. IR (KBr): $\nu = 3392$, 1715, 1144 cm^{-1}. UV-VIS ($CHCl_3$): $\lambda_{max} = 343(64071)$, 356(66700), 394(30633) nm(ε). MS(70 eV, < 200 °C): due to insufficient volatility the MS could not be obtained. UV-VIS spectra of free **3** and its protonation product could not be recorded due to their insufficient solubilities in the aqueous protic solvent system. Therefore pK_a and pK_a^* values could not be determined. Fluorescence (chloroform): $\lambda_{excit} = 356$ nm, $\lambda_{fluo} = 426$ nm, $\Phi_f = 0.002$. Fluorescence of **2** in chloroform as the solvent: $\lambda_{excit} = 380$ nm, $\lambda_{fluo} = 549$ nm, $\Phi_f = 0.13$.

Cu(II) Complexes – General Procedure

Copper(II) complexes were prepared by adding a saturated solution of copper(II) acetate in methanol/water (1:1) to the solution of the ligand in chloroform. A twofold molar excess of copper(II) acetate was employed throughout. The mixture was refluxed for 2–4 h. To remove the excess of the metal ion, the mixture was washed with water, then dried with anhydrous Na_2SO_4, and evaporated in *vacuo*. The residue was crystallized from chloroform/*n*-hexane to yield the product. The Cu(II) complexes **4–6** did not melt until 300 °C. Job plots [4] for the concentrations of **1–3** *versus* the concentration of Cu(II) ions proved the formation of 1:1 complexes.

3,4-Dimethyl-5-{2-[6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl]methylidene}-3-pyrrolin-2-one-copper(II) (**4**; $C_{19}H_{17}N_3O_2Cu$)

Yield 87%; m.p. not until 300 °C. IR (KBr) $\nu = 1668$, 1595, 1152, 1125, 1107 cm^{-1}. UV-VIS ($CHCl_3$): $\lambda_{max} = 320(16\,400)$, 469(7 030), 502(6 640) nm(ε). Despite extensive drying in *vacuo*, elemental analysis indicated the presence of one mole crystal chloroform per two moles of the complex.

6,6'-Bis-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-methyl-2,2'-bipyridyl-copper(II) (**5**; $C_{24}H_{20}N_4O_2Cu$)

Yield 87%; m.p. not until 300 °C. IR(KBr) $\nu = 1668$, 1595, 1152, 1125, 1107 cm^{-1}. UV-VIS ($CHCl_3$): $\lambda_{max} = 322(18\,730)$, 409(23 780) 494(4 010) nm(ε).

3,3'-Bis-(3,4-dimethyl-2-pyrrolin-5-methylidene)-methyl-[1,1']-biisoquinolinyl-copper(II) (**6**; $C_{32}H_{24}N_4O_2Cu$)

Yield 83%; m.p. not until 300 °C. IR (KBr) $\nu = 1688$, 1594, 1141, 1109 cm^{-1}. UV-VIS ($CHCl_3$): $\lambda_{max} = 337(37\,700)$, 395(28 620) nm(e). Cyclic chromatographic resolution of **6** on triacetyl- and tribenzoyl-cellulose with ethanol as the eluent failed.

General Procedure for the Cyclopropanation of Styrene with Ethyl Diazoacetate Catalyzed by **4–6**

To a mixture of 0.011 mmol of the respective catalyst (**4–6**), 5 ml of 1,2-dichloroethane and 0.2 ml (1.66 mmol) styrene under argon, 10 drops of a solution of ethyl diazoacetate (0.23 ml, 2.16 mmol) in 1,2-dichloroethane (1 ml) were added with stirring and heating in an oil bath to 85 °C during 30 min to activate the system. The mixture was then cooled to 60 °C, and the rest of the solution of ethyl diazoacetate was continuously added within 2 h by means of a syringe pump. After addition, stirring at 60 °C was continued for about 2 h. The mixture was concentrated *in vacuo* to give a reddish oil

which was chromatographed (TLC, 20 × 20 × 2) with hexane/ethyl acetate (9:1) to yield the *cis*- and *trans*-ethyl-2-phenyl-cyclopropane-carboxylates. The relative amounts of the respective cyclopropanation products were analyzed by ^{1}H-NMR spectroscopy: **4**: yield 79%; 27% *cis*: 73% *trans*; **5**: yield 89%; 27% *cis*: 73% *trans*; **6**: yield 78%; 28% *cis*: 72% *trans*.

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