New Sterically Encumbered 2,9-Diarylphenanthrolines for the Selective Formation of Heteroleptic Bis(phenanthroline)copper(I) Complexes

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Dedicated to Prof. Dr. Dr. h. c. mult. Siegfried Hünig on the occasion of his 80th birthday

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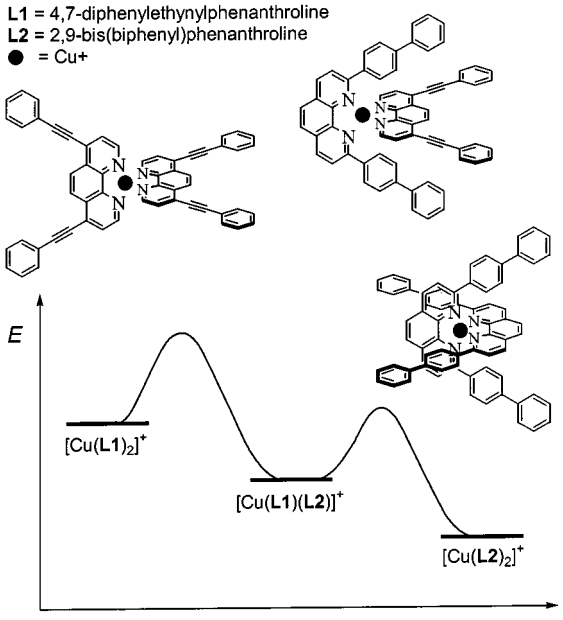
The synthesis and characterization of several 2,9-diarylphenanthrolines with anthracenyl substituents in the 2-position is described. These compounds were used to prepare a series of homoleptic and heteroleptic bis(phenanthroline)copper(I) complexes, whose cyclic voltammetry, UV/Vis and fluorescence data are investigated. From PM3 semiempirical calculations it becomes clear that two different strategies can be applied to prepare clean heteroleptic complexes.

Introduction

We have recently introduced a new concept to prepare heteroleptic bis(phenanthroline)copper(I)[1] and -silver(I)[2] complexes $[M(\mathbf{L1})(\mathbf{L2})]^+$ in a clean and well-defined manner using a ligand with bulky groups in the 2- and 9-positions. In metallosupramolecular chemistry, control of the clean formation of heteroleptic complexes is extremely valuable for highly selective self-assembly processes with two different ligands **L1** and **L2**, e.g. of linear and macrocyclic oligophenanthrolines,[3] as the number of potential aggregates is markedly reduced. Consequently, we have used this protocol for the synthesis of supramolecular boxes[3] of nanometer dimensions with appropriately spaced internal functional groups.

As bis(phenanthroline)copper(I) complexes are kinetically labile,[4] a thermodynamically controlled setup has to be found that favors the heteroleptic complex over the two alternative homoleptic complexes. In our concept,[1,2] 2,9-diaryl substitution at one phenanthroline (**L2**) plays a critical role. In combination with a second phenanthroline, which does not bear 2,9-aryl substituents (**L1**), the stability sequence of the resulting copper(I) complexes becomes predictable (Scheme 1); the corresponding homoleptic bis-2,9-diarylphenanthroline copper(I) complex $[Cu(\mathbf{L2})_2]^+$ is always the most stable because of the interplay of increased σ-basicity of **L2** and π-π interactions between the 2,9-aryl groups and the second phenanthroline core. The latter stabilization is present in $[Cu(\mathbf{L2})_2]^+$ four times, but only twice in $[Cu(\mathbf{L1})(\mathbf{L2})]^+$ and is absent in $[Cu(\mathbf{L1})_2]^+$.



Scheme 1

The straightforward concept to prepare $[Cu(\mathbf{L1})(\mathbf{L2})]^+$ is consequently based on the fact that we have to prevent the formation of the most stable complex $[Cu(\mathbf{L2})_2]^+$ through steric blocking, so that of the remaining complexes it is the heteroleptic $[Cu(\mathbf{L1})(\mathbf{L2})]^+$ that is the thermodynamically favored option. In earlier investigations[1,2] we successfully used **L2** = **1** and would like now to assess whether other aryl substituents, such as naphthyl and anthracenyl, at the phenanthroline would also be suited for the preparation of heteroleptic copper(I) complexes. In the present paper[5] we describe the preparation of ligands **2**–**5** (Scheme 2) and their potential in the selective heteroleptic copper(I) complex formation.

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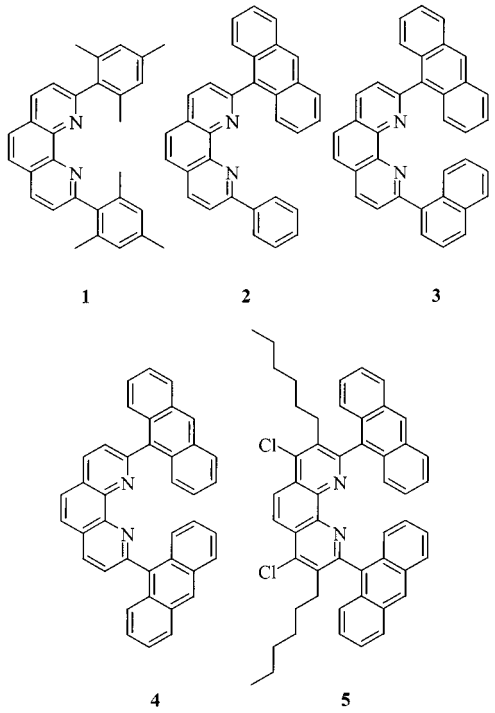


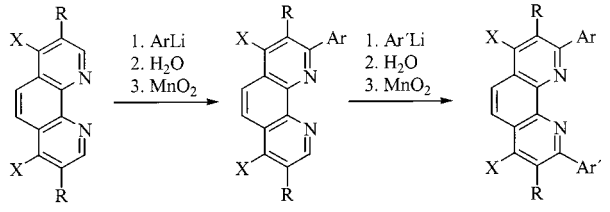
Scheme 2

Moreover, ligands **2**−**5** seemed to be promising candidates because a number of sensing supramolecules contain anthracene as a fluorescent subunit (or fluorophor) given its strong and well-characterized emission and its chemical stability.[6] For example, De Silva has developed many anthracene-based sensors for metal ions.[7] Additionally, compound **5** was prepared because the two hexyl groups at the 3- and 8-positions should increase the solubility of the system.[8]

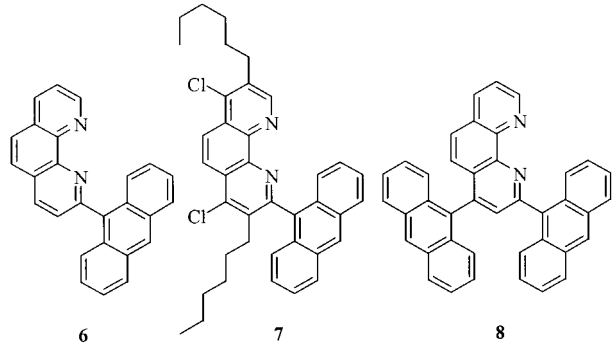
Results

Phenanthroline Ligands

Synthesis: For the preparation of the 2,9-substituted phenanthrolines, the two-step synthesis shown in Scheme 3 proved to be the method of choice and this is based on a strategy established earlier by Sauvage.[9] Simultaneous arylation of both the 2- and 9-positions of 1,10-phenanthroline either failed completely or proceeded with low yields. In order to overcome this problem, 1,10-phenanthroline was first reacted with a slight excess of the aryllithium reagent at room temperature, followed by hydrolysis and rearomatization of the intermediate with activated MnO_2. Subsequently, the procedure was repeated once again using the monoarylated phenanthrolines **6** and **7** (Scheme 4). The crude product could be purified either by recrystallization or by column chromatography on silica gel and subsequent recrystallization.



Scheme 3. 2,9-Diaryl-1,10-phenanthrolines from 1,10-phenanthroline by nucleophilic aromatic substitution followed by rearomatization



Scheme 4

Yields for the first arylation ranged from 37%−67% (for **7** and **6**, respectively), while the yield of the second step was heavily dependent on the steric bulk of the new substituents [with phenyl: 64%; with naphthyl: 25%, and anthracenyl: 21% (**4**)]. In contrast, the yield for the second arylation **7** → **5** was 59%. The structures of all new phenanthrolines were proved using ^1H and ^{13}C NMR spectroscopy and elemental analysis.

The yields of the nucleophilic aromatic substitution reactions are sometimes lower due to by-product formation. In the reaction of **6** with anthracenyllithium we actually isolated the 2,4-substituted phenanthroline **8** as the main product (39%). It is clear that steric shielding hampers the formation of **4** (21%) and directs arylation to the 4-position, a reaction that is not possible with **5**. An analogous regioselectivity has been reported for nucleophilic substitutions at pyridine, although this is a rare case.[10] However, to the best of our knowledge[11] this is the first time that a nucleophilic arylation has led preferentially to a 2,4-diarylphenanthroline.

Structural Characterization of the Ligands

X-ray Structure of 5: Because of its good solubility and the presence of two large anthracenyl rings, we investigated **5** in greater detail. Ligand **5** could readily be crystallized from dichloromethane and hence was investigated by X-ray crystallography. Figure 1 depicts the structure of **5** in the solid state from a top and a side view.

From Figure 1 one can clearly see the steric demand of the two large anthracenyl groups. To avoid repulsions between the two anthracenyl rings or between the anthracenyl ring and the hexyl groups the two anthracenyl moieties assume an almost orthogonal arrangement with regard to the phenanthroline plane (dihedral angle = 96°). The structure of ligand **5** is well described by the PM3 calculation, as demonstrated by the selected data provided in Table 1.

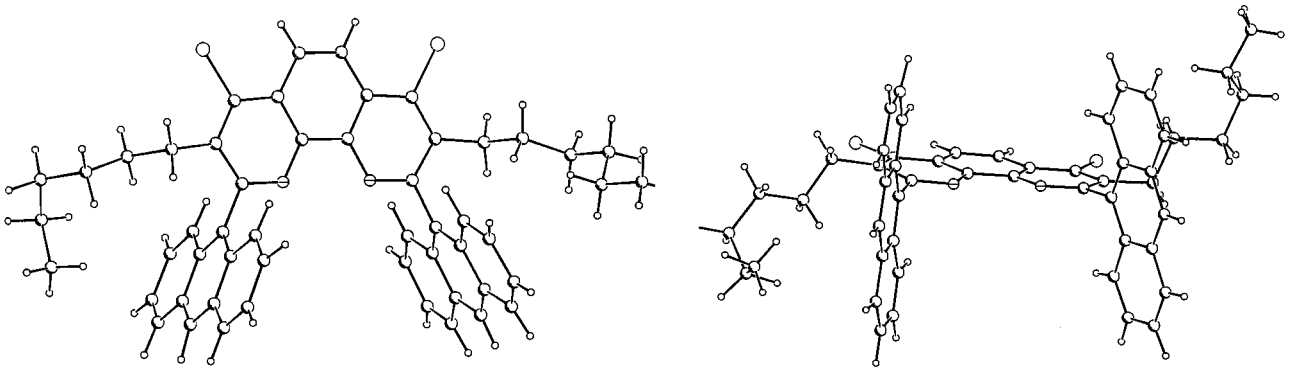


Figure 1. Schakal plot of 2,9-dianthracenyl-4,7-dichloro-3,8-dihexyl-1,10-phenanthroline (**5**)

Table 1. Selected data from X-ray structure analyses and PM3 calculations

Structure Dihedral angle of anthracene at 2-position [°]	**5** (X-ray)	**5** (PM3)	**4** (PM3)	**3** (PM3)	**2** (PM3)
N1−C1−C33−C38	95.83(20)	90.30	−90.49	−90.07	−91.06
N1−C1−C33−C46	−80.47(21)	−88.86	89.92	90.33	89.40
C2−C1−C33−C46	96.74(20)	91.38	−90.12	−89.72	−90.65
C2−C1−C33−C38	−86.96(22)	−89.46	89.47	89.88	88.90
Selected angles [°]					
N1−C1−C33	114.53(15)	116.69	118.49	119.47	118.47
C2−C1−C33	120.94(15)	121.55	119.77	119.78	119.78
C38−C33−C1	120.18(18)	119.87	119.77	119.76	119.73
C46−C33−C1	118.79(15)	119.67	119.74	119.75	119.79
Dihedral angle of second aryl ring [°]					
N2−C10−C19−C20	97.33(19)	90.70	−90.95	−115.50	177.06
N2−C10−C19−C32	−82.75(20)	−88.54	89.46	64.67	−2.91
C11−C10−C19−C32	95.24(20)	91.67	−90.58	−114.05	177.13
C11−C10−C19−C20	−84.69(20)	−89.09	89.01	65.78	−2.90
Selected angles [°]					
N2−C10−C19	115.45(13)	116.74	118.49	118.05	118.46
C11−C10−C19	120.49(14)	121.51	119.77	120.34	120.95
C20−C19−C10	119.40(12)	119.68	119.72	119.187	121.18
C32−C19−C10	119.71(16)	119.85	119.79	120.68	119.76
C−N bond length [Å]					
C1−N1	1.316(2)	1.340	1.340	1.340	1.341
C10−N2	1.318(2)	1.340	1.340	1.341	1.344
C5−N1	1.345(8)	1.374	1.376	1.376	1.376
C9−N2	1.354(20)	1.374	1.376	1.375	1.373

NMR Investigations: As one would anticipate, given the extended aromatic residues, the proton NMR spectra of **5** show a solvent dependence; i.e. the shifts vary with the solvent ($CDCl_3$ or [D_6]benzene). While the 5,6-H phenanthroline signal is not shifted, the signal of the 10-H at the anthracene substituents experiences a high-field shift from $\delta = 8.4$ ($CDCl_3$) to $\delta = 8.1$ ([D_6]benzene). After adding trifluoroacetic acid to the NMR solution in $CDCl_3$ the phenanthroline 5,6-H′s experience the expected down-field shift (by 0.2 ppm), but the doublet for 1-H and 8-H at the anthracene rings is shifted towards high field by about 0.3 ppm.

Luminescence Properties: The emission spectra of the ligands **2**−**7** in dichloromethane were recorded (Figure 2) at room temperature upon excitation at 346 nm. The emission maxima appear between 439−472 nm.

Preparation of the Copper Complexes

Homoleptic Copper Complexes: To assess the feasibility of the various ligands **2**−**7** with regard to our concept (see Introduction) we checked whether they would easily form homoleptic complexes in the presence of copper(I). For ligands **2**, **3**, **6** and **7** the reaction with 0.5 equiv. of [Cu(MeCN)$_4$]BF_4 or [Cu(MeCN)$_4$]PF_6 in dichloromethane

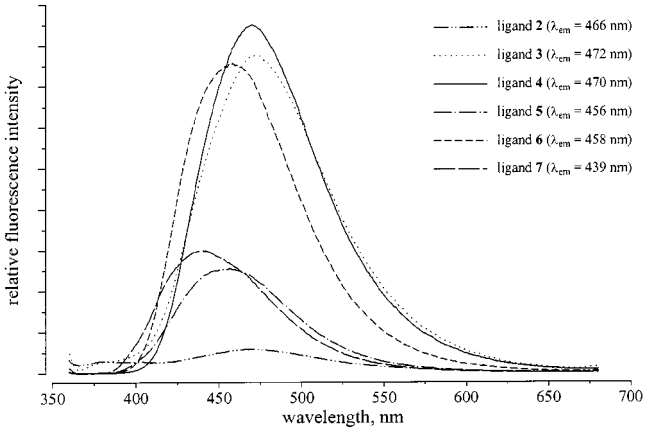
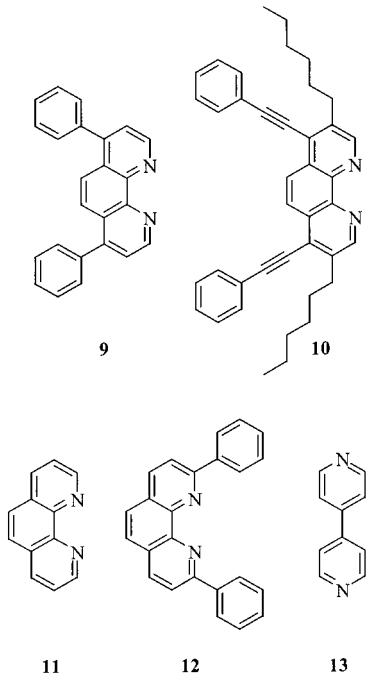


Figure 2. Luminescence spectra of various phenanthrolines at room temperature in CH_2Cl_2 solution (excitation at 346 nm where the absorbance of all the compounds is 1.11)

readily afforded the intensely red-colored homoleptic complexes $[Cu(\mathbf{2})_2]^+$, $[Cu(\mathbf{3})_2]^+$, $[Cu(\mathbf{6})_2]^+$, and $[Cu(\mathbf{7})_2]^+$ in good yields (50−85%) at room temperature.

By using the conditions described above, phenanthrolines **4** and **5** − with bulky anthracenyl groups at the 2- and 9-positions − only afforded yellow complexes, which were assigned as the monophenanthroline complexes $[Cu(\mathbf{4})(MeCN)_2]BF_4$ or $[Cu(\mathbf{5})(MeCN)_2]BF_4$. Additionally, the ^1H NMR spectra of the reaction mixtures showed signals for uncoordinated phenanthroline **4** or **5**. Even when the complexation was performed at 80 °C (in C_6D_6) for three hours the color of the solution did not turn red, indicating that a bis(phenanthroline)copper(I) complex had not been formed. The ESI mass spectrum shows a large ion peak at m/z = 874, which is indicative of the complex $[Cu(\mathbf{5})(MeCN)]^+$, and m/z = 833 for the ion $[Cu(\mathbf{5})]^+$. $[Cu(\mathbf{4})(MeCN)_2]BF_4$ was purified by recrystallization and characterized by elemental analysis.

Heteroleptic Copper Complexes: To test the suitability of the anthracenyl-substituted phenanthrolines **4** and **5** for the clean preparation of heteroleptic complexes, we treated them with 1 equiv. of 4,7-substituted ligands **9** or **10** (Scheme 5) in the presence of 1 equiv. of $[Cu(MeCN)_4]^+$ at room temperature. Evaporation of the solvent led to the precipitation of a red solid, yielding the heteroleptic complexes $[Cu(\mathbf{4})(\mathbf{9})]^+$, $[Cu(\mathbf{5})(\mathbf{9})]^+$, and $[Cu(\mathbf{5})(\mathbf{10})]^+$ in good yields.



Scheme 5

Characterization of the Copper Complexes

The identities of the copper(I) complexes could be established through elemental analysis, ESI mass spectrometry, IR and NMR spectroscopy.

^1H NMR Spectroscopy: The spectra exhibit well-resolved signals for the homoleptic as well as the heteroleptic complexes in CD_2Cl_2 or $CDCl_3$, which is true even for the sterically loaded complex $[Cu(\mathbf{3})_2]PF_6$. A 2D ROESY ^1H NMR experiment clearly confirms its highly shielded structure. Rotation about the anthracene-phenanthroline axes is no longer possible, as shown by the fact that the inner and the outer ring of the anthracenes can be differentiated. From the literature it is known that aryl substituents with a lower steric demand lead to broadening of the Ar−H signals,[12] and in the absence of *ortho* substituents the aryl rings are free to rotate relative to the phenanthroline on the NMR time scale.[13]

The formation of the heteroleptic complexes is indicated by characteristic ^1H NMR shifts. Coordination of the 2,9-

Table 2. Characteristic ^1H NMR chemical shifts of the 2,9-substituted-1,10-phenanthrolines in heteroleptic complexes

	Phenanthroline core			Arene groups
	δ(4,7-H)	δ(5,6-H)	δ(3,8-H)	δ(aryl-H)
4[a]	8.50	8.07	7.87	8.45, 7.96, 7.83, 7.28−7.41
$[Cu(\mathbf{4})(\mathbf{9})]^+$ [b]	8.97	8.46	8.27	7.41, 7.31, 7.23, 6.92−7.13
5[a]		8.62		8.40, 7.90, 7.17−7.40
$[Cu(\mathbf{5})(\mathbf{9})]^+$ [a]		8.78		7.43, 7.08−7.17, 6.91−6.95
$[Cu(\mathbf{5})(\mathbf{10})]^+$ [a]		8.79		7.10−7.24, 6.98−7.03

[a] In $CDCl_3$. − [b] In CD_2Cl_2.

substituted ligands to the positively charged metal center results in typical downfield shifts for all protons at the phenanthroline core (Table 2). In contrast, the 2,9-H′s at the 4,7-substituted phenanthroline experience a strong high-field shift (Table 3). This is due to the shielding effect of the anthracenyl (and other aryl) groups placed below and above the aromatic plane of the second phenanthroline, i.e. the one with 4,7-substituents, in the tetrahedral copper complex.

Table 3. Characteristic ^{1}H NMR chemical shifts of the 4,7-substituted-1,10-phenanthrolines in heteroleptic complexes

	δ(2,9-H)	δ(5,6-H)	δ(3,8-H)
9[a]	9.22	7.84	7.57
[Cu(**4**)(**9**)]$^+$ [b]	7.14	7.45	6.59
[Cu(**5**)(**9**)]$^+$ [a]	7.03	7.44	6.60
10[a]	9.05	8.43	
[Cu(**5**)(**10**)]$^+$ [a]	7.41	8.08	

[a] In $CDCl_3$. − [b] In CD_2Cl_2.

Electrochemical Data: The oxidation behavior of the homoleptic and heteroleptic copper(I) complexes was studied by cyclic voltammetry. All compounds undergo a reversible one-electron oxidation process, which can be attributed to the $Cu^I \rightarrow Cu^{II}$ couple.[14] The redox potentials (Table 4) range from 0.0−0.3 V for the homoleptic complexes [Cu(**6**)$_2$](BF$_4$), [Cu(**7**)$_2$](PF$_6$), and the heteroleptic complexes [Cu(**4**)(**9**)](PF$_6$), [Cu(**5**)(**9**)](PF$_6$) and [Cu(**5**)(**10**)](PF$_6$). For the complexes whose copper center is shielded efficiently the redox potential is somewhat higher.

Table 4. Electrochemical data of various copper(I) complexes

Compound	$E_{1/2}$ [a]	ΔE_p
[Cu(**6**)$_2$](BF$_4$)	−0.05	107
[Cu(**7**)$_2$](PF$_6$)	0.22	130
[Cu(**2**)$_2$](PF$_6$)	0.50	74
[Cu(**3**)$_2$](PF$_6$)	0.56	68
[Cu(**4**)(CH$_3$CN)$_2$](BF$_4$)	0.53	193
[Cu(**4**)(**9**)](PF$_6$)	0.16	103
[Cu(**5**)(**9**)](PF$_6$)	0.23	156
[Cu(**5**)(**10**)](PF$_6$)	0.28	134

[a] Half-wave potentials $E_{1/2}$ (V vs. ferrocene/ferrocenium) of copper(I) complexes determined by cyclic voltammetry in dichloromethane at $\nu = 100$ mVs^{-1} (electrolyte: 0.1 M Bu_4NPF_6).

Photophysical Data: Absorption data for the homoleptic and heteroleptic complexes in dichlormethane are shown in Table 5. All complexes absorb in a broad region of the UV and visible spectrum. They show very intense ligand-centered (LC) bands in the UV region and much weaker metal-ligand charge-transfer (MLCT) bands in the visible region. The MLCT bands are very broad because the copper(II) complex involved in the electronic transition has an equilibrium geometry very different from that of the ground state copper(I) system.[13]

Table 5. Room temperature absorption data of various copper(I) complexes in dichloromethane at room temperature

Complex	λ_{max} [nm] (ε) [M^{-1}cm^{-1}]
[Cu(**6**)$_2$](BF$_4$)	457 470 (4090)
[Cu(**7**)$_2$](PF$_6$)	470 (6130)
[Cu(**2**)$_2$](PF$_6$)	457 (2640)
[Cu(**3**)$_2$](PF$_6$)	456 (3830)
[Cu(**4**)(**9**)](BF$_4$)	474 (6900)
[Cu(**5**)(**9**)](PF$_6$)	499 (9400)
[Cu(**5**)(**10**)](PF$_6$)	496 (13400)

The homoleptic complexes with the more sterically demanding ligands **2** and **3** exhibit lower absorption wavelengths than the complexes with the 2-substituted phenanthrolines **6** and **7**. This fact is equally clear in the solid state, as the former complexes appear orange whereas the latter complexes are deep red. Moreover, a low-energy shoulder is observed for [Cu(**2**)$_2$]$^+$ and [Cu(**3**)$_2$]$^+$, which can be attributed to distortion of the complexes from D_{2d} symmetry.[15] Such distortion is not possible for complexes [Cu(**2**)$_2$]$^+$ and [Cu(**3**)$_2$]$^+$ because of the steric bulk of the four 2,9-substituents (see also calculated structures).

The room-temperature emission spectrum of [Cu(**3**)$_2$]$^+$ was investigated in dichloromethane. The complex shows an almost complete quenching of fluorescence (at 472 nm).

Quantum Chemical Calculations: To gain a better understanding of the thermodynamics we decided to study the complex equilibria using PM3[16] semi-empirical calculations with parameters for copper (Table 6). Systematic deviations caused by the parametrization should be small due to error cancelation in the calculation of equilibria (or isodesmic reactions).

As the PM3 calculations gave a good prediction about the structure of ligand **5** we also evaluated some of the structural characteristics of the complexes. Of particular interest are the structures of compounds [Cu(**2**)$_2$]$^+$, [Cu(**3**)$_2$]$^+$, [Cu(**4**)$_2$]$^+$, and [Cu(**4**)(**9**)]$^+$ (see Discussion).

*Reaction of **5** with 4,4′-Bipyridine (**13**):* As the large anthracenyl moieties preclude formation of the homoleptic complex [Cu(**5**)$_2$]$^+$, we expected that **5** would also form well-defined Cu^I complexes with ligands binding less strongly than phenanthrolines. The shielded environment about copper in [Cu(**5**)]$^+$ should also bring about some kinetic stabilization. When we treated **5** with 4,4′-bipyridine (**13**) in the presence of copper(I) (molar ratio 2:1:2), only one species was found in solution according to the ^{1}H NMR spectrum, which was indicative of the bisheteroleptic complex [Cu$_2$(**5**)$_2$(**13**)](PF$_6$)$_2$. The protons of the bipyridine moiety exhibit a strong high-field shift ($\Delta\delta = 2.1$ ppm for 2-,2′-H and 1.5 ppm for 3-,3′-H protons), a situation clearly indicative of a heteroleptic complex in which **13** is symmetrically buried in the cavity of two ligands **5**. Unfortunately, crystals of this compound could not be obtained for X-ray analysis, presumably due to the fact that the copper(I) centers weakly bind acetonitrile and dichloromethane, as evidenced by elemental analysis and ES mass spectrometry. For

Table 6. PM3 calculated (see ref.[16]) heats of formation of the ligands and the corresponding homoleptic and heteroleptic complexes

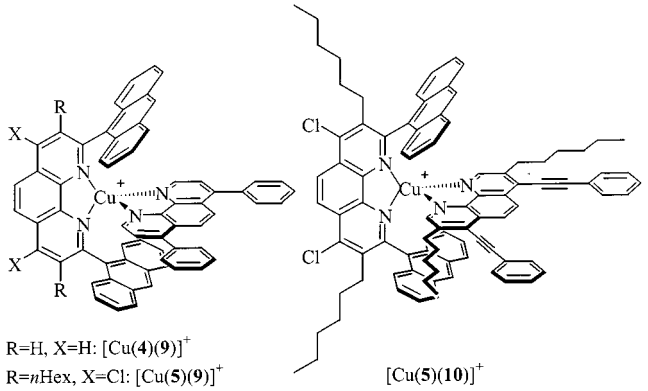
Ligand	ΔH_f [kcal mol^{-1}]	Homoleptic complex	ΔH_f [kcal mol^{-1}]	Heteroleptic complex	ΔH_f [kcal mol^{-1}]
1	73.3	$[Cu(\mathbf{1})_2]^+$	161.2	$[Cu(\mathbf{4})(\mathbf{9})]^+$	327.3
2	164.2	$[Cu(\mathbf{2})_2]^+$	329.8	$[Cu(\mathbf{4})(\mathbf{11})]^+$	275.8
3	183.9	$[Cu(\mathbf{3})_2]^+$	373.0	$[Cu(\mathbf{1})(\mathbf{9})]^+$	193.4
4	207.0	$[Cu(\mathbf{4})_2]^+$	431.8	$[Cu(\mathbf{9})(\mathbf{11})]^+$	195.1
6	139.3	$[Cu(\mathbf{6})_2]^+$	277.2	$[Cu(\mathbf{3})(\mathbf{9})]^+$	304.7
9	124.3	$[Cu(\mathbf{9})_2]^+$	246.4	$[Cu(\mathbf{9})(\mathbf{12})]^+$	245.1
11	71.6	$[Cu(\mathbf{11})_2]^+$	144.0	$[Cu(\mathbf{11})(\mathbf{12})]^+$	193.8
12	122.3	$[Cu(\mathbf{12})_2]^+$	242.4	$[Cu(\mathbf{2})(\mathbf{9})]^+$	286.2

example, mass analysis showed a peak for $[Cu_2(\mathbf{5})_2(\mathbf{13})(CH_3CN)]^{2+}$ at $m/z = 932.0$. In a collisionally activated dissociation (CAD)[17] experiment, complex $[Cu_2(\mathbf{5})_2(\mathbf{13})(CH_3CN)]^{2+}$ readily fragments to form the ion $[Cu(\mathbf{5})]^+$ at $m/z = 833.2$.

Discussion

Formation of the Complexes

The present investigation has disclosed phenanthrolines **4** and **5** as suitable new ligands for controlling the clean preparation of heteroleptic bis(phenanthroline)copper(I) complexes. It is important to state that the heteroleptic complexes $[Cu(\mathbf{4})(\mathbf{9})]^+$, $[Cu(\mathbf{5})(\mathbf{9})]^+$, and $[Cu(\mathbf{5})(\mathbf{10})]^+$ (Scheme 6) were formed without the need for external control from reaction conditions, such as sequence of addition, reaction temperature etc.



R=H, X=H: $[Cu(\mathbf{4})(\mathbf{9})]^+$
R=*n*Hex, X=Cl: $[Cu(\mathbf{5})(\mathbf{9})]^+$

$[Cu(\mathbf{5})(\mathbf{10})]^+$

Scheme 6

It is well-known that copper(I) phenanthroline complexes with sterically unimpeded ligands are kinetically labile at room temperature (rates $> 6.2 \times 10^4$),[4] and so we have to assume that in the reactions

$$[Cu(CH_3CN)_4]^+ + \mathbf{4} + \mathbf{9} \rightarrow [Cu(\mathbf{4})(\mathbf{9})]^+$$
(no formation of $[Cu(\mathbf{4})_2]^+$ and of $[Cu(\mathbf{9})_2]^+$)

$$[Cu(CH_3CN)_4]^+ + \mathbf{5} + \mathbf{9} \rightarrow [Cu(\mathbf{5})(\mathbf{9})]^+$$
(no formation of $[Cu(\mathbf{5})_2]^+$ and of $[Cu(\mathbf{9})_2]^+$)

the formation of the homoleptic complexes is suppressed by thermodynamic and/or kinetic factors. Indeed, all heteroleptic complexes in Scheme 6 are characterized by a phenanthroline having two large anthracenyl rings in the 2- and 9-positions. In independent experiments we could verify that even under harsh conditions the formation of $[Cu(\mathbf{4})_2]^+$ and $[Cu(\mathbf{5})_2]^+$ does not occur. In contrast, homoleptic complexes were afforded readily with ligands whose 2- and 9-positions were less shielded, e.g. **2**, **3**, **6**, and **7**. However, the question remains as to whether the formation of $[Cu(\mathbf{4})_2]^+$ and $[Cu(\mathbf{5})_2]^+$ is impeded thermodynamically or kinetically.

To answer this question we employed PM3 calculations, although this method does entail a major restriction as, strictly speaking, such calculations are only relevant for the gas phase. Neglecting this constraint, it becomes clear from the calculations that all complexes, even the sterically loaded ones, are thermodynamic minimum structures (for heats of formation, see Table 6). To probe the PM3 calculations we investigated the equilibrium $[Cu(\mathbf{L1})_2]^+ + [Cu(\mathbf{L2})_2]^+ \rightarrow 2\,[Cu(\mathbf{L1})(\mathbf{L2})]^+$ (see Scheme 1). Accordingly, $[Cu(\mathbf{L2})_2]^+$ is favored over $[Cu(\mathbf{L1})(\mathbf{L2})]^+$ by 1.4 kcal mol^{-1}, while experimentally it is favored by roughly 1 kcal mol^{-1}.[18]

Next, we tried to understand the stability of the complexes by evaluating different factors, such as σ-basicity, π-π stacking and steric strain. The critical assessment of the two subsequent equilibria,

$$[Cu(\mathbf{11})_2]^+ + 2 \times \mathbf{12} \rightleftarrows [Cu(\mathbf{12})_2]^+ + 2 \times \mathbf{11} \qquad \Delta H_{rxn} = -3.0 \text{ kcal mol}^{-1},$$

$$[Cu(\mathbf{9})_2]^+ + 2 \times \mathbf{12} \rightleftarrows [Cu(\mathbf{12})_2]^+ + 2 \times \mathbf{9} \qquad \Delta H_{rxn} = 0 \text{ kcal mol}^{-1}$$

indicates that, according to PM3, ligand **12** (with its 2,9-diaryl substituents) forms a more stable homoleptic complex than the parent compound **11**, but this must be due to an increase of the σ-basicity brought about by the 2,9-phenyl groups, and not by π-π stacking. π-π Stacking between the 2,9-aryls and the second phenanthroline is not recognized by PM3 as a stabilizing motif due to the fact that $[Cu(\mathbf{9})_2]^+$ and $[Cu(\mathbf{12})_2]^+$ exhibit the same stability. This is definitely a shortcoming of PM3, since we[18] and others[19] have seen clear structural indications for π-π stacking in phenanthroline copper(I) complexes. Despite this deficiency, PM3 should be useful to evaluate the steric strain encountered in the complex formation with large ligands. To establish a reference point we have defined arbitrarily that the σ-basicity of ligand **12** matches the σ-basicity of 2,9-diaryl-substituted ligands **2**–**4**. As a consequence,

the equilibrium between homoleptic complexes of **12** and **2**−**4** should reflect the steric crowding in the complex.

$$[Cu(\mathbf{12})_2]^+ + 2 \times \mathbf{2} \rightleftarrows [Cu(\mathbf{2})_2]^+ + 2 \times \mathbf{12}$$
$$H_{strain} = \Delta H_{rxn} = +3.6 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{12})_2]^+ + 2 \times \mathbf{3} \rightleftarrows [Cu(\mathbf{3})_2]^+ + 2 \times \mathbf{12}$$
$$H_{strain} = \Delta H_{rxn} = +7.4 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{12})_2]^+ + 2 \times \mathbf{4} \rightleftarrows [Cu(\mathbf{4})_2]^+ + 2 \times \mathbf{12}$$
$$H_{strain} = \Delta H_{rxn} = +20.0 \text{ kcal mol}^{-1}$$

The strain enthalpy (H_{strain}) in the homoleptic complexes indeed increases with the size of the 2,9-diaryl substituents. In particular, a substantial strain increase is observed when we compare ligand **4** (the same should apply for ligand **5**) with **2** or **3**.

A look at the thermodynamics of the equilibria involving heteroleptic complexes $[Cu(\mathbf{L})(\mathbf{11})]^+$ is also very informative. With ligands **L** = **9** and **12** there is no clear predisposition for the heteroleptic complex. However, the bulky ligands (**L** = **2**−**4**) exhibit an increasing preference for the heteroleptic complex with increasing demand in the series: **4** > **3** > **2** (measured in $[Cu(\mathbf{L})(\mathbf{9})]^+$).

$$[Cu(\mathbf{9})_2]^+ + [Cu(\mathbf{11})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{9})(\mathbf{11})]^+$$
$$\Delta H_{rxn} = -0.2 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{11})_2]^+ + [Cu(\mathbf{12})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{11})(\mathbf{12})]^+$$
$$\Delta H_{rxn} = +1.2 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{2})_2]^+ + [Cu(\mathbf{9})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{2})(\mathbf{9})]^+$$
$$\Delta H_{rxn} = -3.8 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{3})_2]^+ + [Cu(\mathbf{9})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{3})(\mathbf{9})]^+$$
$$\Delta H_{rxn} = -10.0 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{4})_2]^+ + [Cu(\mathbf{9})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{4})(\mathbf{9})]^+$$
$$\Delta H_{rxn} = -23.6 \text{ kcal mol}^{-1}$$
$$[Cu(\mathbf{4})_2]^+ + [Cu(\mathbf{11})_2]^+ \rightleftarrows 2\,[Cu(\mathbf{4})(\mathbf{11})]^+$$
$$\Delta H_{rxn} = -24.2 \text{ kcal mol}^{-1}$$

The obvious conclusion from these calculations is that the clean formation of heteroleptic complexes can be brought about by purely thermochemical factors that are controlled by the 2,9-substituents. The thermodynamic preference for heteroleptic complexes with ligands **2**−**4** is apparently due to strain in the homoleptic complexes $[Cu(\mathbf{2}-\mathbf{4})_2]^+$, which is liberated when the heteroleptic complex is formed.

Inspired by our calculations we now wanted to test experimentally whether formation of the heteroleptic complex $[Cu(\mathbf{3})(\mathbf{9})]^+$ is possible despite the fact that a stable complex $[Cu(\mathbf{3})_2]^+$ is known. Indeed, the reaction of ligands **3** and **9** in presence of 1 equiv. of $[Cu(MeCN)_4]BF_4$ at room temperature yielded the heteroleptic complex $[Cu(\mathbf{3})(\mathbf{9})]^+$ in quantitative yield, as evidenced by ^{1}H NMR and ESI mass spectrometry. This is clear evidence for a new way to control heteroleptic bis(phenanthroline)copper(I) complexes just on the basis of their thermodynamic preference. Steric blocking of the formation of the most stable homoleptic complex is no longer needed.

While thermodynamic control of heteroleptic complex formation is certainly the exclusive element to guide the formation of $[Cu(\mathbf{3})(\mathbf{9})]^+$, this is most likely not the case with $[Cu(\mathbf{4})(\mathbf{9})]^+$. While we have not been able to calculate the transition state (TS) for the reaction $[Cu(CH_3CN)_4]^+ + 2 \times \mathbf{4} \rightarrow [Cu(\mathbf{4})_2]^+$, the analysis of structural models clearly indicates that there will be enormous strain in the TS. As such, we suggest that the formation of $[Cu(\mathbf{4})_2]^+$ is precluded by its high TS energy.

Ligands **4** and **5** do not undergo homoleptic complex formation and so they are ideal candidates to react with weaker ligands, such as 4,4′-bipyridine (**13**). This ligand is of particular interest as palladium-4,4′-bipyridine complexes play an important role in molecular triangles and squares.[20] Compound **13** is also often used in the field of *crystal engineering* to prepare coordination polymers.[21,22] In our case, however, only formation of $[Cu_2(\mathbf{5})_2(\mathbf{13})](PF_6)_2$ was observed. The complex carries two additional ligands at copper(I), such as acetonitrile. Because a solid state structure is not available, we present here the PM3 calculated structure that rationalizes the strong NMR shift effects observed in the proton spectrum (Figure 3).

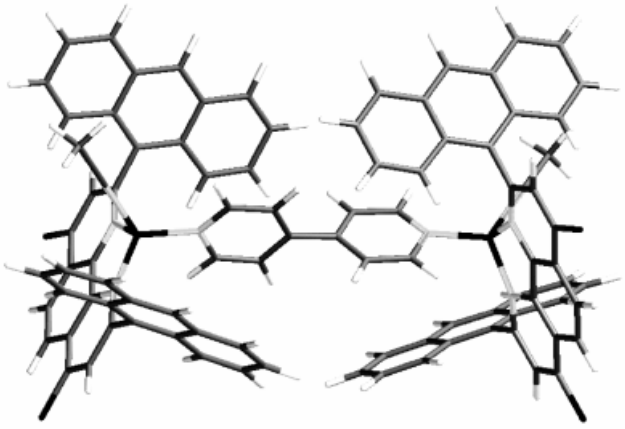


Figure 3. PM3 calculated structure of complex $[Cu_2(\mathbf{5})_2(\mathbf{13})](PF_6)_2$ including two bound acetonitrile ligands

Structure and Properties of the Complexes

Structure: To date there are no crystal structures available for the complexes and for this reason we have used the PM3 calculated structures (Figure 4) to obtain an idea about the arrangement of the phenanthroline and aryl residues. We noted above that the PM3 structure of **5** is in good agreement with the X-ray structure. One has to bear in mind, however, that the PM3 calculations failed to reproduce the weak π-π interaction between the 2,9-aryl groups and the phenanthroline. As this may lead to some distortion in the complex we only want to discuss a few key elements. For example, the angle between the two phenanthrolines is 90° (for $[Cu(\mathbf{4})(\mathbf{9})]^+$) and 87° (for $[Cu(\mathbf{2})]^+$ and $[Cu(\mathbf{3})]^+$), but 80° for $[Cu(\mathbf{4})]^+$. Accordingly, with increased bulk there are deviations from ideal tetrahedral coordination. In complex $[Cu(\mathbf{4})(\mathbf{9})]^+$ the arrangement of the ligands is hardly impeded by strain, but heavy distortions at the metal center and the phenanthroline and the 2,9-aryl substituents do show up in the strained homoleptic complexes. For example, the anthracenyl rings (10° to 14°) and the phenanthroline units (6° to 13°) are severely distorted from

planarity on going from $[Cu(\mathbf{2})]^+$ to $[Cu(\mathbf{4})]^+$, but are planar in the unstrained complex $[Cu(\mathbf{4})(\mathbf{9})]^+$.

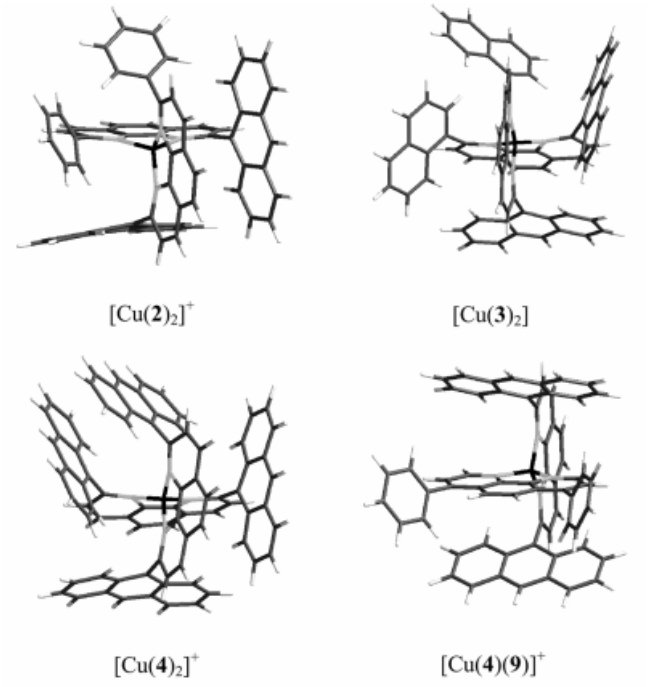


Figure 4. PM3 calculated structures of a few copper complexes

Electrochemical Measurements: The values for the oxidation potential are in the expected range for phenanthroline-type complexes.[23,24] It has been reported that these values depend on the nature of the substituents at the phenanthroline and that the redox potential becomes more positive when the metal ion is subjected to steric constraints that prevent rearrangement in the coordination sphere upon oxidation.[25] Comparison of the homoleptic and heteroleptic complexes shows that the oxidation potentials for the homoleptic complexes are higher than those for the heteroleptic ones because of the rigidity at the metal center. Moreover, the small ΔE_p values for $[Cu(\mathbf{2})_2](PF_6)$ and $[Cu(\mathbf{3})_2](PF_6)$ indicate that their reorganization is rather small on going from Cu^I to Cu^{II}, a situation in contrast to that observed with the other complexes. The results are in agreement with those found in earlier investigations.[12]

On going from $[Cu(\mathbf{4})(\mathbf{9})](PF_6)$ to $[Cu(\mathbf{5})(\mathbf{9})](PF_6)$, phenanthroline **4** is replaced by **5**, a ligand with additional alkyl groups in the 3,8-positions, and thus a small decrease of the oxidation potential is expected as alkyl groups are better σ-donors.[25] However, the reverse is found. Presumably, the back strain effect of the alkyl groups leads to a tighter arrangement at the metal center in $[Cu(\mathbf{5})(\mathbf{9})](PF_6)$.

Luminescence of Ligands and Complexes: Upon excitation at 346 nm all phenanthrolines **2**−**7** exhibit a fluorescence at 439−472 nm that is broadened due to interactions with the solvent. In agreement with textbook knowledge[26] we assign this emission to the $S_1 \rightarrow S_0 + h\nu$ radiative transition of the excited anthracenyl group attached to the 2- (and 9-) position of the phenanthroline core. Apparently, the sp^2-nitrogen donor atoms of the phenanthroline cannot quench the fluorescence, while efficient quenching is usually observed with appended tertiary amines.[27] In the series **2**−**4** (Figure 2), the emission maximum stays roughly the same, but the fluorescence intensity decreases in the order **4** > **3** >> **2**. Such behavior is to be expected from the well-known free rotor effect,[26] as in this series the twisting motion about the phenanthroline and 2,9-diaryl axis is clearly facilitated. When we compare **4** with **5** and **6** with **7** a strong decrease in the fluorescence intensity is registered, which could be due to the presence of 4- and 7-chloro substituents.[28]

Fluorescence at 472 nm is not observed upon complexation of **3** with copper(I). As the absorption maximum of $[Cu(\mathbf{3})_2]^+$ is located at 456 nm, the photoexcited anthracene is quenched by the MLCT process.[29] As a consequence, recognition of the uncomplexed ligand **3** by copper(I) is indicated through fluorescence quenching and, in principle, ligand **3** could be used as a quenchofluorimetric detector[30] towards Cu^I ions.

Conclusion

A series of homoleptic and heteroleptic bis(phenanthroline)copper(I) complexes is presented that is based on ligands carrying sterically bulky groups at the 2- and 9-positions. For the clean preparation of heteroleptic complexes two concepts are elaborated. The first one is based on the fact that steric blocking kinetically prevents the formation of the homoleptic complex having 2,9-diaryl substituents at the phenanthroline. The second one relies on the thermodynamic destabilization of the homoleptic complex having 2,9-diaryl substituents.

Experimental Section

General Remarks: $[Cu(MeCN)_4]BF_4$ [31] and $[Cu(MeCN)_4]PF_6$ [32] were prepared according to literature procedures. All other chemicals were commercially available and used without further purification. The solvents were distilled before use and dried with appropriate desiccants (CH_2Cl_2 from P_2O_5, MeCN from P_2O_5 and NaH, DMSO from calcium sulfate under reduced pressure). − ^1H NMR spectra were recorded on either Bruker AC 200 (200 MHz) or Bruker AC 250 (250 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference). − IR spectra were recorded on a Perkin−Elmer 1605 FT-IR spectrophotometer. − Microanalyses were carried out with a Carlo Erba 1106 Elemental Analyzer. − Electrospray mass spectra (ES-MS) were recorded with a ThermoQuest LCQ Deca Finnigan. − Electrochemical measurements were performed with a Potentiostat Modell 362, Princeton Applied Research.

The solvent used for photophysical studies was CH_2Cl_2 (Merck, Uvasol). UV/Vis spectra were recorded on a J&M TIDAS II absorption spectrometer, while the emission spectra were obtained with a Spex Fluorolog 2 spectrofluorometer. To make comparisons possible in the emission measurements, the absorbance A for all ligands was the same (A = 1.11) at the excitation wavelength λ_{exc} = 346 nm.

The calculations were performed using *Spartan Pro* with the parameter set PM3(tm) for transition metals.[33] The geometries were

optimized using the Merck molecular force field (MMFF) and refined using the semiempirical method PM3(tm).

4,7-Dichloro-3,8-dihexyl-1,10-phenanthroline and 4,7-diethynylphenyl-3,8-dihexyl-1,10-phenanthroline were synthesized as reported previously.[8]

2-(9-Anthracenyl)-1,10-phenanthroline (6): A 1.5 M solution of *n*-butyllithium in pentane (6.60 mL, 9.90 mmol) was slowly added to a solution of 9-bromoanthracene (2.40 g, 9.32 mmol) in 100 mL of diethyl ether at 0 °C. The solution was allowed to stir for 60 min at 0 °C. A suspension of 1,10-phenanthroline (1.00 g, 5.48 mmol) in 40 mL of toluene was added. The solution first became yellow and then turned dark violet. The mixture was stirred for 48 h at room temperature. After the addition of water (60 mL) the layers were separated and the aqueous layer was extracted three times with dichloromethane (3 × 10 mL). The combined organic extracts were stirred with 20 g of activated MnO_2 for 2 h. The mixture was dried with $MgSO_4$ and filtered. After evaporation of the filtrate the resulting solid was separated by column chromatography (SiO_2, trichloromethane, R_f = 0.62). The second fraction contained the pale yellow product (1.30 g, 67% yield). − M.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.29−7.34 (m, 2 H, 2′-H, 7′-H), 7.40−7.48 (m, 2 H, 3′-H, 6′-H), 7.58 (d, *J* = 8.9 Hz, 2 H, 1′-H, 8′-H), 7.60 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1 H, 8-H), 7.83 (d, *J* = 8.2 Hz, 1 H, 3-H), 7.88 (d, *J* = 8.9 Hz, 1 H, 6-H), 7.95 (d, *J* = 8.9 Hz, 1 H, 5-H), 8.07 (d, *J* = 8.4 Hz, 2 H, 4′-H, 5′-H), 8.28 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1 H, 7-H), 8.44 (d, *J* = 8.2 Hz, 1 H, 4-H), 8.57 (s, 1 H, 10′-H), 9.15 (dd, *J* = 4.4 Hz, *J* = 1.7 Hz, 1 H, 9-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 122.9 (C-8), 125.0 (C-3), 125.3, 125.6, 126.4, 126.5, 126.8, 127.4, 128.3, 129.0, 130.5, 131.3, 135.8, 135.9, 136.0, 137.8, 146.4 (C-10a), 146.5 (C-1a), 150.5 (C-9), 158.9 (C-2). − IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1}, 1617, 1586, 1504, 1482, 1387, 1192, 844, 731, 668. − $C_{26}H_{16}N_2$: calcd. C 87.62, H 4.52, N 7.86; found C 87.39, H 4.76, N 7.59.

2-(9-Anthracenyl)-4,7-dichloro-3,8-di-*n*-hexyl-1,10-phenanthroline (7): To a solution of 9-bromoanthracene (4.98 g, 19.0 mmol) in dry diethyl ether (150 mL) was added dropwise 1.5 M *n*-butyllithium (13 mL) and the mixture was stirred for 9 h at 0 °C. After the addition of 4,7-dichloro-3,8-hexyl-1,10-phenanthroline (2.43 g, 6.42 mmol) the mixture was stirred for 3 d at room temperature. After hydrolysis with water (50 mL) and separation of the phases, the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were stirred with activated MnO_2 (30.0 g, 343 mmol) for 1 h. The mixture was dried over magnesium sulfate and then filtered. After removing the solvent in vacuo, the residue was purified by column chromatography (SiO_2, trichloromethane, R_f = 0.76) and recrystallized from cyclohexane/*n*-hexane (1:1) to yield a yellow solid (1.40 g, 37%). − M.p. 161 °C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.58 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.79−0.90 (m, 2 H, CH_2), 0.87 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.22−1.44 (m, 10 H, CH_2), 1.61−1.70 (m, 4 H, CH_2), 2.54 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.98 (t, *J* = 7.8 Hz, 2 H, CH_2), 7.23−7.47 (m, 6 H, anthracenyl), 8.06 (d, *J* = 8.9 Hz, 2 H), 8.48 (d, *J* = 9.5 Hz, 1 H, 6-H), 8.55 (d, *J* = 9.5 Hz, 1 H, 5-H), 8.57 (s, 1 H, 10′-H), 8.92 (s, 1 H, 9-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.7, 14.0, 21.9, 22.5, 28.4, 28.9, 29.0, 29.6, 30.5, 31.4, 31.5, 31.6, 107.8, 123.5, 123.6, 125.0, 125.8, 125.9, 126.2, 126.5, 127.5, 128.4, 130.5, 131.4, 134.3, 135.4, 137.0, 137.2, 141.0, 142.5, 152.1 (C-9), 159.7 (C-2). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (m, Ar−H), 2953, 2926, 2855 (s, C−H), 1605 (m), 1570 (s), 1534 (s, arom. C=C), 1464 (s, C−H), 1391 (s), 1347 (m), 1316 (m), 1233 (m), 1040 (m, Ar−Cl). − $C_{38}H_{38}Cl_2N_2$: calcd. C 77.00, H 6.47, N 4.73; found C 76.71, H 6.51, N 4.62.

Synthesis of 2,9-Substituted Phenanthrolines: A typical procedure is shown here for compound **2**.

2-(9-Anthracenyl)-9-phenyl-1,10-phenanthroline (2): Under an inert atmosphere a 1.5 M solution of *tert*-butyllithium in pentane (1.40 mL, 2.10 mmol) was added to bromobenzene (298 mg, 1.86 mmol) in 5 mL of anhydrous diethyl ether at 0 °C. After 1 h stirring at 0 °C the solution was added dropwise to a suspension of **6** (178 mg, 500 μmol) in 10 mL of anhydrous toluene. The resulting deep-red solution was stirred overnight at room temperature. Water (10 mL) was then added. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined extracts were stirred with activated MnO_2 (2.00 g, 23.0 mmol) for 2 h, by which time the intense yellow color had disappeared. The mixture was dried over magnesium sulfate, filtered, and evaporated to give a solid. The crude product was recrystallized from cyclohexane to yield 138 mg (64%) of yellow crystals. − M.p. > 315 °C (decomp.). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.30−7.70 (m, 9 H), 7.86 (d, *J* = 8.3 Hz, 1 H, 3-H), 7.86−7.90 (m, 3 H, 8-H, 5-H, 6-H), 8.09 (d, 2 H), 8.18−8.22 (m, 2 H, 2′′-H, 6′′-H), 8.34 (d, *J* = 8.6 Hz, 1 H, 7-H), 8.43 (d, *J* = 8.3 Hz, 1 H, 4-H), 8.59 (s, 1 H, 10′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 120.4, 123.2, 125.1, 125.7, 125.8, 126.1, 126.6, 126.9, 127.8, 128.4, 128.6, 128.8, 129.1, 129.9, 130.4, 131.4, 135.9, 136.8, 139.6, 140.9, 146.3 (C-10a), 146.6 (C-1a), 157.3 (C-9), 158.3 (C-2). − IR (KBr): $\tilde{\nu}$ = 3042 cm^{-1} (m, C−H), 2923, (s, =C−H), 2845 (m), 1663 (w, C=C), 1587, 1542, 1483 (s, C=C), 1449 (w), 1356 (m), 1314, 1101, 1022, 886, 852 (s), 765, 732, 693 (vs), 615. − $C_{32}H_{20}N_2 \cdot 1H_2O$: calcd. C 85.31, H 4.92, N 6.37; found C 85.49, H 4.43, N 6.37.

Other examples of 2,9-substituted compounds were prepared by following the above procedure.

2-(9-Anthracenyl)-9-(1-naphthyl)-1,10-phenanthroline (3): Yield 25% of a yellow solid. − M.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23−7.53 (m, 8 H), 7.64 (d, *J* = 8.6 Hz, 2 H), 7.72 (d, *J* = 7.0 Hz, 1 H), 7.84−7.88 (br. s, 2 H, 5-H, 6-H), 7.86 (d, *J* = 8.3 Hz, 1 H, 3-H), 7.95 (d, *J* = 8.3 Hz, 1 H, 8-H), 8.05 (s, 1 H), 8.09 (d, *J* = 8.4 Hz, 2 H), 8.22 (d, *J* = 8.6 Hz, 1 H), 8.46 (d, *J* = 8.3 Hz, 1 H, 7-H), 8.53 (d, *J* = 8.3 Hz, 1 H, 4-H), 8.59 (s, 1 H, 10′-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 123.0, 124.8, 124.9, 125.2, 125.6, 125.9, 126.3, 126.4, 126.5, 126.9, 127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.4, 128.5, 129.3, 130.3, 131.4, 133.9, 135.6, 135.9, 136.4, 138.1, 140.6, 154.5, 158.4. − IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1} (w, =C−H), 1621 (m, C=C), 1577, 1550, 1499, 1442, 1402, 1351, 1136, 1015, 888 (s), 850 (s), 788 (w), 732 (s), 630. − $C_{36}H_{26}N_2 \cdot 0.5H_2O$: calcd. C 87.96, H 4.72, N 5.70; found C 88.41, H 4.82, N 5.69.

2,9-Bis(9-anthracenyl)-1,10-phenanthroline (4): Yield 21% of yellow crystals. − M.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.28−7.41 (m, 8 H), 7.83 (d, 4 H), 7.87 (d, *J* = 7.9 Hz, 2 H, 3-H, 8-H), 7.96 (d, 4 H), 8.07 (s, 2 H, 5-H, 6-H), 8.45 (s, 2 H, 10′-H), 8.50 (d, *J* = 7.9 Hz, 2 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 120.9, 123.5, 124.8, 125.3, 126.1, 126.3, 127.6, 128.1, 128.3, 128.6, 131.3, 138.0, 146.3 (C-1a, C-10a), 158.7 (C-2, C-9). − IR (KBr): $\tilde{\nu}$ = 3046 cm^{-1} (w, =C−H), 1618 (m, C=C), 1578, 1542, 1491, 1442, 1402, 1345, 1187, 1136, 1085, 1014, 886 (s), 845 (s), 788 (w), 732 (s), 628, 613. − $C_{40}H_{24}N_2 \cdot 2H_2O$: calcd. C 84.56, H 4.71, N 5.16; found C 84.48, H 4.96, N 4.93.

2,9-Bis(9-anthracenyl)-4,7-dichloro-3,8-di-*n*-hexyl-1,10-phenanthroline (5): Yield 59% of bright yellow crystals. − M.p. > 269 °C (decomp.). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.52−0.65 (m, 10 H, CH_3, CH_2), 0.70−0.86 (m, 8 H, CH_2), 1.08−1.30 (m, 4 H, CH_2), 2.50 (t, *J* = 8.0 Hz, 4 H, CH_2), 7.17−7.40 (m, 12 H, anthracenyl),

7.90 (d, J = 8.2 Hz, 4 H, 4′-H, 5′-H), 8.40 (s, 2 H, 10′-H), 8.62 (s, 2 H, 5-H, 6-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.8, 21.9, 28.5, 28.8, 30.6, 31.3, 123.9, 124.8, 125.6, 126.1, 126.3, 127.5, 128.3, 130.3, 131.2, 133.9, 137.2, 142.4, 145.2, 159.3. − IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (m, Ar−H), 2955, 2926, 2856 (s, C−H), 1604 (s), 1534 (w, arom. C=C), 1458 (s, C−H), 1140 (w), 1084 (s, Ar−Cl). − $C_{52}H_{46}Cl_2N_2$: calcd. C 81.13, H 6.02, N 3.64; found C 80.90, H 6.24, N 3.56.

2,4-Bis(9-anthracenyl)-1,10-phenanthroline (8): Yield 39% of yellow crystals. − M.p.: > 300 °C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.27 (d, J = 8.6 Hz, 1 H, 5-H), 7.35−7.56 (m, 8 H), 7.62 (d, J = 8.6 Hz, 1 H, 6-H), 7.57−7.64 (m, 2 H), 7.64 (dd, J = 7.7 Hz, J = 4.3 Hz, 8-H), 7.87−7.92 (m, 2 H), 7.94 (s, 1 H, 3-H), 8.04−8.16 (m, 4 H), 8.23 (dd, J = 7.7 Hz, J = 1.8 Hz, 1 H, 7-H), 8.56 (s, 1 H, 10′-H), 8.65 (s, 1 H, 10′′-H), 9.23 (dd, J = 4.3 Hz, J = 1.8 Hz, 1 H, 9-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 124.6, 125.0, 125.4, 125.9, 126.0 (2 ×), 126.4 (2 ×), 127.0, 127.7, 127.9, 128.0, 128.2, 128.5, 128.7, 129.0, 129.5, 130.3, 130.6, 131.5, 135.6, 135.9, 145.9, 146.0, 146.8 (C-10a), 147.1 (C-1a), 150.7 (C-9), 158.6 (C-2). − IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (m, =C−H), 1617 (m), 1577 (m), 1541 (s), 1480 (s), 1442 (m), 1375 (w), 1342 (w), 1013 (m), 888 (s), 832 (s), 788 (s), 730 (vs), 652 (m), 614 (m). − $C_{40}H_{24}N_2 \cdot 0.75H_2O$: calcd. C 87.82, H 4.72, N 5.12; found C 87.94, H 4.72, N 4.99.

Data for Homoleptic Complexes. − General Procedure for the Synthesis of the Homoleptic Cu^I Complexes

[Cu(6)$_2$]BF$_4$: $[Cu(MeCN)_4]BF_4$ (42.0 mg, 134 μmol) was dissolved in anhydrous acetonitrile (5 mL) under an inert atmosphere at room temperature. Upon addition of **6** (80.0 mg, 268 μmol) in anhydrous dichloromethane (5 mL) the solution immediately turned to a deep red hue. After 30 min of stirring at room temperature, the solvent was removed in vacuo. The solid was purified by recrystallization from CH_2Cl_2/cyclohexane to yield [Cu(**6**)$_2$]BF_4 as orange needles (84 mg, 84%). − M.p. > 300 °C. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 6.81 (d, J = 8.9 Hz, 2 H), 7.02−7.24 (m, 6 H), 7.07 (dd, J = 8.1 Hz, J = 4.6 Hz, 2 H, 8-H), 7.38−7.44 (m, 4 H), 7.57 (d, J = 8.5 Hz, 2 H), 7.65 (dd, J = 4.6 Hz, J = 1.5 Hz, 2 H, 9-H), 7.69 (d, J = 8.0 Hz, 2 H, 3-H), 7.78 (d, J = 8.5 Hz, 2 H), 7.80 (d, J = 9.2 Hz, 2 H, 5-H), 7.83 (s, 2 H), 7.90 (d, J = 9.2 Hz, 2 H, 6-H), 8.25 (dd, J = 8.1 Hz, J = 1.5 Hz, 2 H, 7-H), 8.33 (d, J = 8.0 Hz, 2 H, 4-H). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 125.3, 125.7, 125.9, 126.1 (2 ×), 126.3, 127.4, 127.5, 127.6, 128.2, 128.4, 129.1, 129.2, 129.3, 129.7, 130.1, 130.5, 131.0, 131.3, 132.6, 136.4, 137.9, 143.2, 144.2, 147.9 (C-9), 157.5 (C-2). − IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1}, 1705, 1654, 1618, 1560, 1508, 1489, 1444, 1408, 1383, 1357, 1356, 1221, 1198, 1142, 1054, 883, 844, 734, 662. − $C_{52}H_{32}N_4CuBF_4 \cdot 0.5H_2O$: calcd. C 70.88, H 3.89, N 6.36; found C 70.41, H 4.02, N 5.92.

[Cu(2)$_2$]PF$_6$: Reacting $[Cu(MeCN)_4]PF_6$ (23.0 mg, 62.0 μmol) with **2** (54.0 mg, 62.0 μmol) according to the above procedure yielded, after column chromatography with CH_2Cl_2/MeOH (R_f = 0.32), [Cu(**2**)$_2$]PF_6 (33 mg, 50%) as red crystals. − M.p. > 300 °C. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 6.48−6.57 (m, 6 H), 6.68−6.84 (m, 6 H), 7.05−7.11 (m, 2 H), 7.19−7.31 (m, 8 H), 7.39 (d, J = 8.3 Hz, 2H, 8-H), 7.63 (d, J = 8.6 Hz, 2 H), 7.67 (d, J = 8.3 Hz, 2 H, 3-H), 7.84 (d, J = 8.6 Hz, 2 H), 7.91 (d, J = 8.9 Hz, 2 H, 6-H), 7.97 (d, J = 8.9 Hz, 2 H, 5-H), 8.05 (s, 2 H, 10′-H), 8.26 (d, J = 8.3 Hz, 2 H, 7-H), 8.42 (d, J = 8.3 Hz, 2 H, 4-H). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 124.4, 124.5, 124.6, 125.0, 125.2, 125.3, 126.5, 126.6, 127.0, 127.3 (2 ×), 127.8, 127.9 (2 ×), 128.1, 128.4 (2 ×), 128.6, 128.9, 129.5, 129.7, 130.5, 132.2, 136.9, 137.4, 138.1, 142.6, 144.3, 155.4, 157.1. − IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2920, 1609, 1525, 1476, 1391, 1350, 1055, 900, 844, 800, 738. 620. − ESI-MS: calcd. for $C_{64}H_{40}N_4Cu^+$: m/z = 927.3, found m/z = 927.4. − $C_{64}H_{40}N_4CuPF_6 \cdot 1H_2O$: calcd. C 70.42, H 3.88, N 5.13; found C 70.11, H 3.92, N 5.04.

[Cu(3)$_2$]PF$_6$: Reacting $[Cu(MeCN)_4]PF_6$ (31.0 mg, 83.0 μmol) with **3** (80.2 mg, 166 μmol) yielded, after recrystallization from dichloromethane/pentane, [Cu(**3**)$_2$]PF_6 (82.0 mg, 85%) as orange crystals. − M.p. > 300 °C. − ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 6.15 (m, 2 H, 3′′-H), 6.64 (d, J = 8.0 Hz, 2 H, 4′′-H), 6.80 (dd, J = 6.3 Hz, J = 6.3 Hz, 2 H, 3′-H), 6.85 (m, 2 H, 4′-H), 6.89 (d, J = 7.6 Hz, 2 H, 5′′-H), 6.93 (m, 2 H, 2′-H), 7.01 (m, 4 H, 8′′-H, 6′-H), 7.13−7.17 (m, 4 H, 7′′-, 6′′-H), 7.27 (d, J = 8.3 Hz, 2 H, 8-H), 7.30 (m, 2 H, 7′-H), 7.38 (d, J = 8.6 Hz, 2 H, 5′-H), 7.45 (d, J = 6.8 Hz, 2 H, 2′′-H), 7.60 (d, J = 8.6 Hz, 2 H, 1′-H), 7.74 (d, J = 8.7 Hz, 2 H, 8′-H), 7.77 (d, J = 8.0 Hz, 2 H, 3-H), 7.87 (d, J = 8.9 Hz, 2 H, 5-H), 7.96 (d, J = 8.9 Hz, 2 H, 6-H), 7.97 (s, 2 H, 10′-H), 8.22 (d, J = 8.3 Hz, 2 H, 7-H), 8.42 (d, J = 8.0 Hz, 2 H, 4-H). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 122.6, 123.8, 124.0, 125.0 (2 ×), 125.1, 125.3 (2 ×), 125.8, 126.1, 126.7, 126.8 (2 ×), 127.2, 127.5 (2 ×), 127.9, 128.5 (2 ×), 128.6, 129.0, 129.3, 129.5 (2 ×), 129.7, 130.5, 132.0, 132.2, 134.5, 135.2, 137.6, 137.7, 143.4, 144.5, 154.8, 157.1. − IR (KBr): $\tilde{\nu}$ = 3044 cm^{-1}, 2915, 1623, 1498, 1357, 841, 777, 734, 619, 557. − ESI-MS: calcd. for $C_{72}H_{44}N_4Cu^+$: m/z = 1027.3, found m/z = 1027.2. − $C_{72}H_{44}N_4CuPF_6 \cdot 0.5H_2O$: calcd. C 73.12, H 3.84, N 4.74, found C 72.99, H 3.85, N 4.60.

[Cu(7)$_2$]PF$_6$: $[Cu(MeCN)_4]PF_6$ (34.0 mg, 108 μmol) was allowed to react with **7** (128 mg, 216 μmol) to yield, after filtration and recrystallization from dichloromethane/pentane, [Cu(**7**)$_2$]PF_6 (123 mg, 85%) as dark red crystals. − M.p. 212 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.46−0.71 (m, 16 H, CH_3, CH_2), 0.72−1.04 (m, 8 H, CH_3, CH_2), 1.04−1.50 (m, 18 H, CH_2), 2.10−2.30 (m, 4 H, CH_2), 2.35−2.52 (m, 2 H, CH_2), 2.85−3.05 (m, 2 H, CH_2), 3.63 (t, J = 6.4 Hz, 2 H, CH_2), 6.63 (d, J = 8.6 Hz, 2 H), 6.91 (m, 2 H), 7.10−7.31 (m, 6 H), 7.36−7.45 (m, 2 H), 7.42 (s, 2 H, 9-H), 7.55 (d, J = 8.7 Hz, 2 H), 7.80 (d, J = 8.7 Hz, 2 H), 7.89 (s, 2 H, 10′-H), 8.28 (d, J = 9.3 Hz, 2 H, 5-H), 8.36 (d, J = 9.3 Hz, 2 H, 6-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.5, 13.9, 14.9, 21.6, 22.4, 28.2, 28.6, 29.0, 30.2, 31.2, 31.3, 32.3, 122.4, 123.4, 124.2, 124.6 (2 ×), 124.8, 125.4, 125.7, 126.5, 126.9, 127.6, 127.7, 128.5, 128.7, 129.1, 129.8, 130.4, 130.5, 137.7, 139.0, 140.7, 141.2, 141.7, 143.4, 147.9, 156.9. − IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1}, 2953, 2926, 2855, 1609, 1545, 1466, 1391, 1348, 1084, 1055, 900, 844, 800, 738. − $C_{76}H_{76}BCl_4CuF_4N_4$: calcd. C 68.34, H 5.74, N 4.20; found C 67.84, H 5.49, N 3.92.

[Cu(4)(CH$_3$CN)$_2$](BF$_4$): Reacting $[Cu(MeCN)_4]PF_6$ (16.6 mg, 53.0 μmol) with **4** (56.0 mg, 105 μmol) yielded, after recrystallization from dichloromethane/pentane, [Cu(**4**)$(CH_3CN)_2$](BF_4) as yellow crystals (56.0 mg, 69%). − M.p. > 300 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.30−7.49 (m, 12 H), 8.05 (bd, J = 8.1 Hz, 4 H), 8.20 (bd, J = 8.4 Hz, 2 H, 8-H, 3-H), 8.37 (s, 2 H, 5-H, 6-H), 8.59 (s, 2 H, 10′-H), 8.90 (bd, J = 8.4 Hz, 2 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 114.6, 125.1, 125.3, 126.5, 127.2, 128.3, 128.5, 128.7, 129.9, 130.9, 132.9, 138.7, 144.6 (C-1a, C-10a), 158.2 (C-2, C-9). − IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (w, =C−H), 2926 (w), 1618 (m, C=C arom.), 1578, 1507, 1443, 1406, 1355, 1059 (br. s, B−F), 879 (m), 789 (m), 732 (s), 628. − ESI-MS: calcd. for $C_{40}H_{24}N_2Cu^+$: m/z = 595.3, found m/z = 595.3. − $C_{44}H_{30}BCuF_4N_4 \cdot 1H_2O$: calcd. C 67.58, H 4.12, N 7.15; found C 67.42, H 3.90, N 6.60.

General Procedure for the Synthesis of Heteroleptic Cu^I Complexes: One equivalent of $[Cu(MeCN)_4]PF_6$ or $[Cu(MeCN)_4]BF_4$ was dis-

solved in dry dichloromethane under an inert atmosphere. One equivalent of the sterically hindered 2,9-substituted phenanthroline **4** or **5** was added, resulting in a yellowish solution. After 5 min stirring at room temperature one equivalent of 4,7-substituted phenanthroline was added and a deep red solution formed immediately. The mixture was stirred for another 30 min, and the solvent was removed in vacuo. The red solids were purified by column chromatography (silica gel, dichloromethane/methanol = 10:1) to remove traces of additional ligands and copper salts.

Data for Heteroleptic Cu^{I} Complexes

[Cu(4)(9)]BF$_4$: [Cu(MeCN)$_4$]BF$_4$ (34.5 mg, 110 μmol) was allowed to react with **4** (34.5 mg, 110 μmol) and **9** (58.5 mg, 110 μmol) to yield, after filtration and recrystallization from dichloromethane/cyclohexane, [Cu(**4**)(**9**)]BF$_4$ (99.0 mg, 88%) as orange crystals. − M.p. > 300 °C. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 6.59 (d, J = 5.0 Hz, 2 H, 3′′-H, 8′′-H), 6.92−7.13 (m, 8 H, anthracenyl), 7.14 (d, J = 5.0 Hz, 2 H, 2′′-H, 9′′-H), 7.23 (bd, J = 8.4 Hz, 4 H, anthracenyl), 7.31 (bd, J = 7.7 Hz, 4 H, anthracenyl), 7.41 (s, 2 H, 10′-H), 7.45 (s, 2 H, 5′′-H, 6′′-H), 7.57−7.68 (m, 10 H, phenyl), 8.27 (d, J = 8.0 Hz, 2 H, 3-H, 8-H), 8.46 (s, 2 H, 5-H, 6-H), 8.97 (d, J = 8.0 Hz, 2 H, 4-H, 7-H). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 125.3, 125.9, 126.6 (2 ×), 127.0, 128.0, 128.7, 129.1, 129.5, 129.8, 130.4, 130.8, 131.0, 131.2, 131.4, 132.0, 136.0, 138.6, 139.0, 143.5, 146.1, 148.0, 148.9, 158.7. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 1654, 1618, 1560, 1492, 1421, 1354, 1059, 875, 845, 767, 734, 703, 628. − ESI-MS: calcd. for $C_{64}H_{40}N_4Cu^+$: m/z = 927.3, found m/z = 927.4. − $C_{64}H_{40}N_4CuBF_4 \cdot H_2O$: calcd. C 74.38, H 4.10, N 5.42; found C 74.21, H 4.15, N 5.12.

[Cu$_2$(5)$_2$(13)](BF$_4$)$_2$: [Cu(MeCN)$_4$]BF$_4$ (26.5 mg, 84.4 μmol) was allowed to react with **5** (64.9 mg, 84.8 μmol) and 4,4′-bipyridine (**13**) (6.50 mg, 42.0 μmol) in dichloromethane. After stirring for 2 h the product was precipitated by adding pentane. After filtration and washing with pentane the product was obtained as red crystals (34.1 mg, 49%). − M.p. > 120−135 °C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55 (t, J = 7.5 Hz, 12 H, CH_3), 0.65−0.95 (m, 12 H, CH_2), 1.25−1.43 (m, 12 H, CH_2), 2.60−2.75 (m, 8 H, CH_2), 3.65 (m, 8 H, CH_2), 5.96−6.10 (m, 4 H, 3′′-H, 5′′-H), 6.60−6.75 (m, 4 H, 2′′-H, 6′′-H), 7.10−7.20 (m, 12 H, anthracenyl), 7.20−7.35 (m, 12 H, anthracenyl), 7.85−7.95 (m, 8 H, anthracenyl), 8.43 (s, 4 H, 10′-H), 8.77 (s, 4 H, 5-H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.3, 23.7, 30.2, 30.7, 32.4, 33.8, 114.2, 126.7, 126.9, 127.2, 128.6, 129.3, 130.6, 130.7, 131.5, 132.7, 133.9, 142.4, 144.6, 146.6, 159.8, 159.9, 160.7. − IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (m, Ar−H), 2955 (s), 2927 (s), 2856 (s, C−H), 1604 (s), 1534 (w, arom. C=C), 1458 (m, C−H), 1410 (w), 1084 (vs, B−F), 819 (m), 800 (m), 738 (s). − ESI-MS: calcd. for $C_{114}H_{100}N_6Cl_4Cu_2 \cdot CH_3CN^{2+}$: m/z = 931.8, found m/z = 932.0. − $C_{114}H_{100}N_6Cl_4Cu_2B_2F_8 \cdot 1CH_3CN \cdot 1CH_2Cl_2$: calcd. C 66.21, H 4.99, N 4.62; found C 66.31, H 5.26, N 4.98.

[Cu(5)(9)]PF$_6$: Reaction of [Cu(MeCN)$_4$]PF$_6$ (18.6 mg, 50.0 μmol) with **5** (38.5 mg, 50.0 μmol) and **9** (16.6 mg, 50.0 μmol) yielded [Cu(**5**)(**9**)]PF$_6$ (58.0 mg, 88%) as a red powder. − M.p. > 170 °C (decomp.). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.51 (t, J = 6.9 Hz, 6 H, CH_3), 0.73−0.96 (m, 12 H, CH_2), 1.36−1.42 (m, 4 H, CH_2), 2.73−2.77 (m, 4 H, CH_2), 6.60 (d, J = 4.9 Hz, 2 H, 3′-H, 8′-H), 6.91−6.95 (m, 4 H, anthracenyl), 7.03 (d, J = 4.9 Hz, 2 H, 2′-H, 9′-H), 7.08−7.17 (m, 12 H, anthracenyl), 7.43 (s, 2 H, 10′-H), 7.44 (s, 2 H, 5′-H, 6′-H), 7.58−7.66 (m, 10 H, phenyl), 8.78 (s, 2 H, 5-H, 6-H). − ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 13.6, 21.8, 28.7, 28.9, 30.6, 31.2, 123.3, 124.3, 124.5, 124.6, 124.9 (2 ×), 125.7, 126.6 (2 ×), 127.1, 127.5, 129.0, 129.2 (2 ×), 129.9, 133.2, 136.7, 139.8, 141.3, 142.8, 143.0, 146.4, 146.6, 157.5. − IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1}, 2956, 2927, 2866, 2856, 1622, 1560, 1457, 840, 738, 557. − ESI-MS: calcd. for $C_{76}H_{62}N_4Cl_2Cu^+$: m/z = 1165.8, found m/z = 1165.9. − $C_{76}H_{62}N_4Cl_2CuPF_6 \cdot 1.5H_2O$: calcd. C 68.24, H 4.90, N 4.19; found C 68.18, H 4.40, N 4.20.

[Cu(5)(10)]PF$_6$: [Cu(MeCN)$_4$]PF$_6$ (18.6 mg, 50.0 μmol) was allowed to react with **5** (38.5 mg, 50.0 μmol) and 4,7-diethynylphenyl-3,8-di-*n*-hexyl-1,10-phenanthroline (**10**) (27.4 mg, 50.0 μmol) to afford [Cu(**5**)(**10**)]PF$_6$ (37.8 mg, 49%) as a dark red powder. − M.p. 146−148 °C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.49 (t, J = 6.9 Hz, 6 H, CH_3), 0.76−0.83 (m, 8 H, CH_2), 0.95 (t, J = 6.9 Hz, 6 H, CH_3), 1.29−1.56 (m, 24 H, CH_2), 2.44 (m, 4 H, CH_2), 2.63 (m, 4 H, CH_2), 6.98−7.03 (m, 4 H, anthracenyl), 7.10−7.24 (m, 12 H, anthracenyl), 7.36 (s, 2 H, 10′-H), 7.41 (s, 2 H, 2′-H, 9′-H), 7.60−7.71 (m, 6 H, phenyl), 7.75 (m, 4 H, phenyl), 8.08 (s, 2 H, 5′-H, 6′-H), 8.79 (s, 2 H, 5-H, 6-H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.6, 14.0, 21.7, 22.6, 28.4, 28.7, 29.7, 30.0, 30.4, 31.6, 31.7, 32.8, 83.0, 104.1, 121.8, 124.1, 124.5, 124.6, 124.8, 126.1, 126.3, 127.0, 127.1 (2 ×), 127.8, 128.8 (2 ×), 129.7, 129.9, 131.9, 132.7, 139.2, 139.4, 139.7, 142.7, 143.2, 147.1, 157.4. − IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1}, 2953, 2924, 2854, 2208, 1620, 1558, 1539, 1506, 1457, 840, 756, 737, 557. − ESI-MS: calcd. for $C_{92}H_{86}N_4Cl_2Cu^+$: m/z = 1382.2, found m/z = 1382.0. − $C_{92}H_{86}N_4Cl_2CuPF_6$: calcd. C 72.36, H 5.68, N 3.67; found C 72.08, H 5.80, N 3.75.

X-ray Crystallographic Study: Red squares were grown from a dichloromethane solution of **5**. − Data were collected with a STOE IPDS (Imaging Plate Diffraction System) diffractometer at 203(2) K with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). No. of reflns. collected: 18670, No. of unique reflns: 8618, merging factor: R(int) = 0.06671, $2\theta_{max}$ = 28.18°. − Crystal data: empirical formula $C_{52}H_{46}Cl_2N_2$, molecular mass = 769.81, a = 9.314(2) Å, b = 16.469(3) Å, c = 26.486(5) Å, α = 90°, β = 92.31 (3)°, γ = 90°, Z = 4, V = 4059.4(14) Å^3, μ = 0.199 mm^{-1}, F(000) = 1624, $\rho_{calcd.}$ =1.260 mg/m^3, monoclinic, space group $P2_1/n$, final R indices [$I > 2\sigma(I)$]: R1 = 0.0494, wR2 = 0.1536; R indices (all data): R1 = 0.0661, wR2 = 0.1803. − Structure solution and refinement: direct methods, programs Siemens SHELXTL-Ver.5.03. The structure was refined anisotropically against F^2 (full-matrix least squares) for the non-hydrogen atoms. Hydrogens were included at calculated positions using a riding model.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150120. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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