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A Second-Generation Dendrimer with Six 2,9-Dimethyl-1,10-phenanthroline Units as Ligand for Copper-Catalyzed Reactions[‡]

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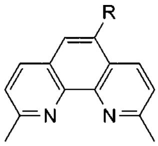
2,9-Dimethyl-1,10-phenanthroline (neocuproine, **1**) has been attached to dendritic structures through its 5-position providing a trimer **7** and the hexamers **11** and **12**. The copper-binding capability of the hexamer **12** has been studied, and the 6:1 complex has been used to catalyze the Cu^+-promoted substitution of an iodoarene **14** to give an aryl ether **15**.

Introduction

An effective and cheap synthesis should not only produce the desired compound in high yield, it must also provide an easy workup which includes the removal of reagents or catalysts from the product. Such a separation is facilitated if the reagents or catalysts are bound to a polymer because they can then be removed by filtration.[1,2] However, the polymeric backbone sometimes influences the outcome of a reaction, especially if the diffusion of substrates into the polymeric compound is uneven at different regions of a polymer. Dendrimers are a special class of polymers which combine two properties from polymer and non-polymer chemistry: they possess a high molecular weight but they are monodispers, well-defined molecules.[3,4] Therefore, the reactivity and selectivity of a catalyst bound to the surface of a dendrimer should be very similar to that of the non-polymeric analog.

Many catalytic systems consist of transition metal ions complexed to suitable ligands. Chelating ligands play an important role because their binding is stronger than that of the substrate to be altered. An important chelating ligand is 1,10-phenanthroline, and especially its 2,9-dimethyl derivative neocuproine (**1**).[5–7] In order to prevent interference with the metal ion bound to the nitrogen atoms of 1,10-phenanthroline, in a polymeric or dendritic scaffold, neocuproine should be connected by its backside, i.e. through positions 4, 5, 6 or 7. Recently, we developed an efficient route to 5-bromo-substituted neocuproines **2** and **3**,[8] which have proven to be good building blocks for 5-substituted derivatives.



1 R = H

2 R = Br

Results and Discussion

Crucial for the synthesis of **2** and **3** is the introduction of *tert*-butyldimethylsilyl (TBDMS) substituents at the methyl groups of the 2,9-dimethyl-1,10-phenanthroline system. This substitution protects the methyl groups from side reactions and drastically improves the solubility. After bromination, the bromine atom in 5-position can easily be replaced by a variety of substituents using palladium-catalyzed cross-coupling reactions. For example, the trimethylsilyl-protected ethynyl-neocuproine **4** has been synthesized from bromide **3** in 44% yield.[8] Treatment with tetrabutylammonium fluoride (TBAF) at –78 °C selectively desilylates the trimethylsilylethynyl group in compound **4** and produces the free alkyne **5** in 71% yield.

With the terminal alkyne functionality, again Sonogashira couplings are possible. Under standard Sonogashira conditions with additional use of ultrasound, three alkynes **5** can be coupled to triiodobenzene (**6**)[9] to give a symmetrical trimer **7** in 58% yield.

But the alkyne **5** can also be coupled to a branching unit **8**[10] possessing two iodide functionalities and one additional, trimethylsilyl-protected alkyne. By using more than 2 equiv. (2.5:1) of the alkyne **5** in the reaction with the diiodide **8**, a first-generation dendron **9** can be obtained in 56% yield under Sonogashira conditions with ultrasound. Again, the trimethylsilyl group can be removed with TBAF thereby setting free the alkyne **10** (81%).

With 3.3 equiv. of the dendron **10**, three branched units can then be connected to triiodobenzene (**6**)[9] to give 58%

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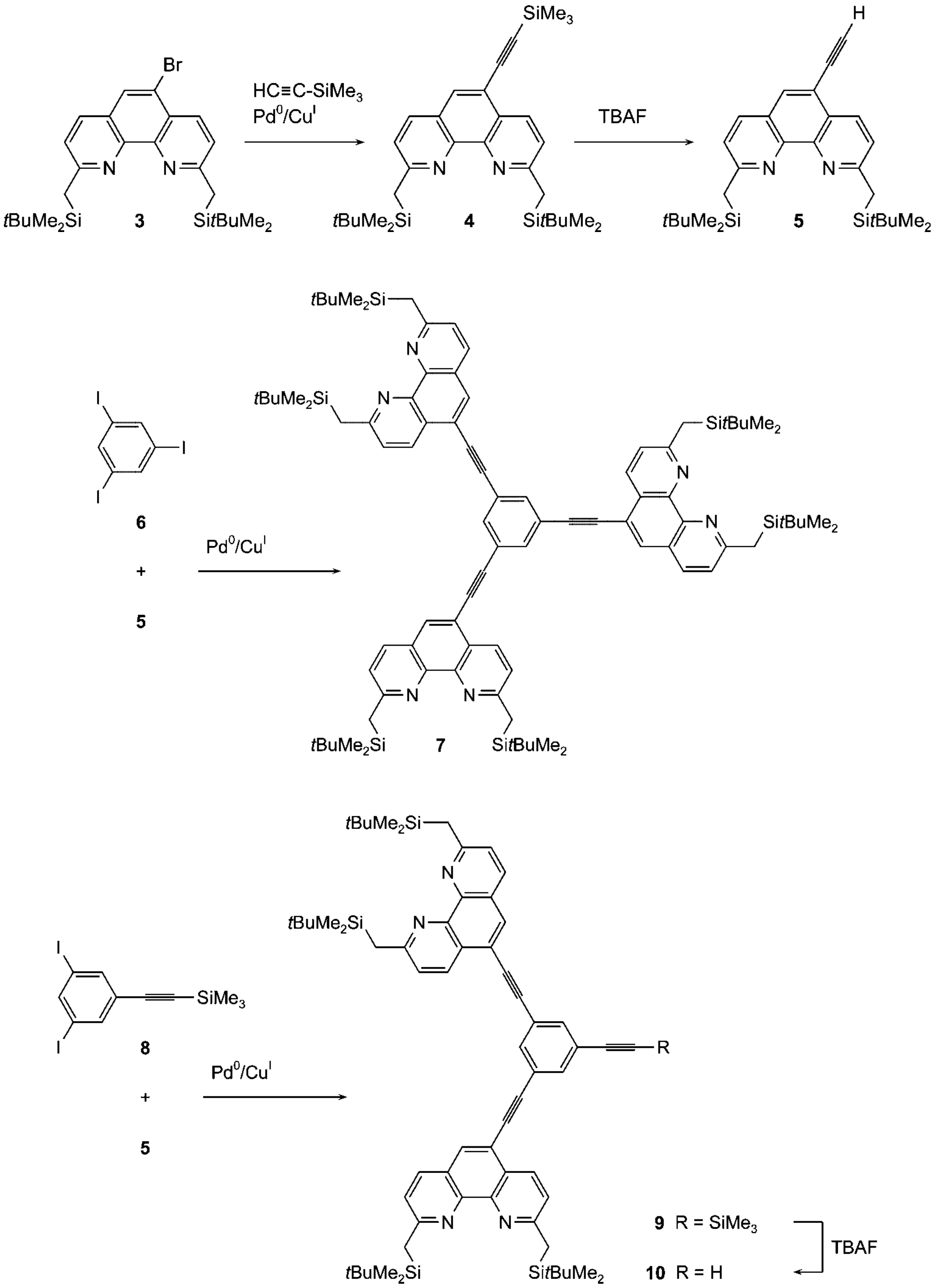
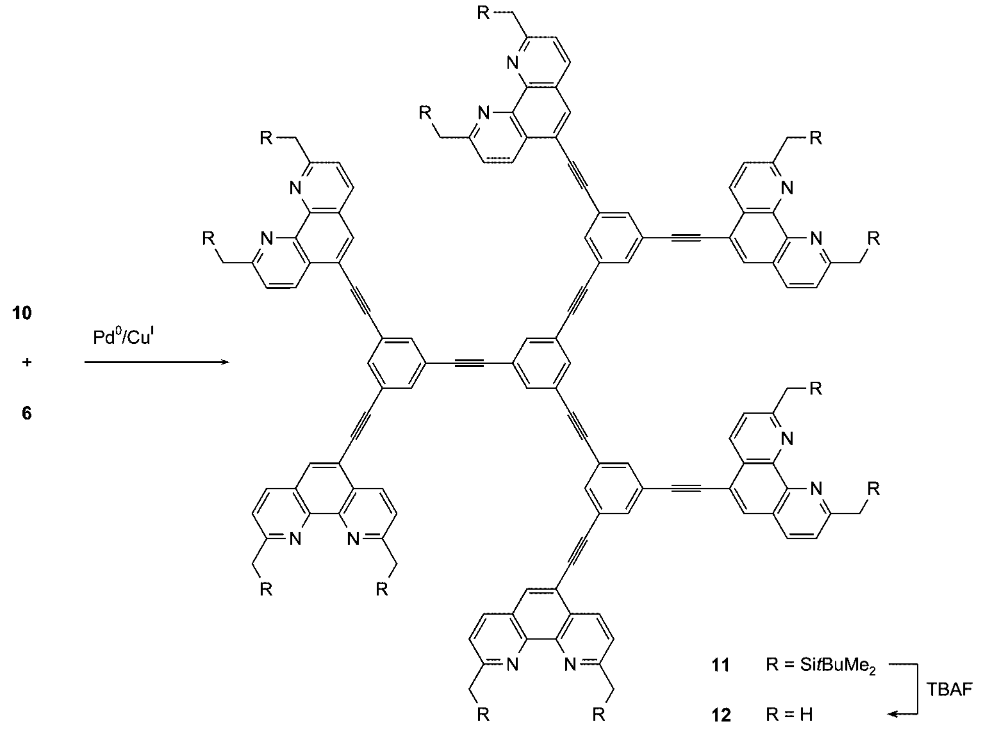


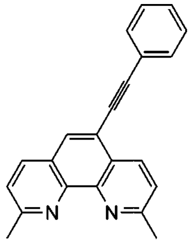
of a second-generation dendrimer **11**, decorated with six 1,10-phenanthroline units on the outside. In addition, the silyl groups in this dendrimer can be removed by reaction with tetrabutylammonium fluoride, thus generating the hexakis(neocuproine) dendrimer **12** (86%).

Complexation Behaviour of the Dendrimer 12 and Its Use as Ligand in a Cu$^+$-Catalyzed Reaction

1,10-Phenanthrolines are good ligands for transition metal ions, and many of the resulting complexes are catalysts for a variety of reactions.[5–7] Therefore, the complex formation of the hexamer **12** has been studied. Cu$^+$ was chosen as metal ion, and the stoichiometry of the complex formation with **12** has been investigated by Job plots.[11,12] The experiments have also been carried out with 2,9-dimethyl-5-(phenylethynyl)-1,10-phenanthroline (**13**) for comparison (see Figure 1).

In contrast to monomer **13**, the Job plot for dendrimer **12** shows two separated maxima which correspond to Cu$^+$ ions bound to one or two 1,10-phenanthroline moieties. This double maximum indicates that depending on the molar ratio chosen, 2:1 or 1:1 complexes will predominantly exist for each Cu$^+$ ion. A 1:6 ratio of **12**/CuPF$_6$ corresponds to a situation in which each Cu$^+$ ion is bound to one neocuproine unit.





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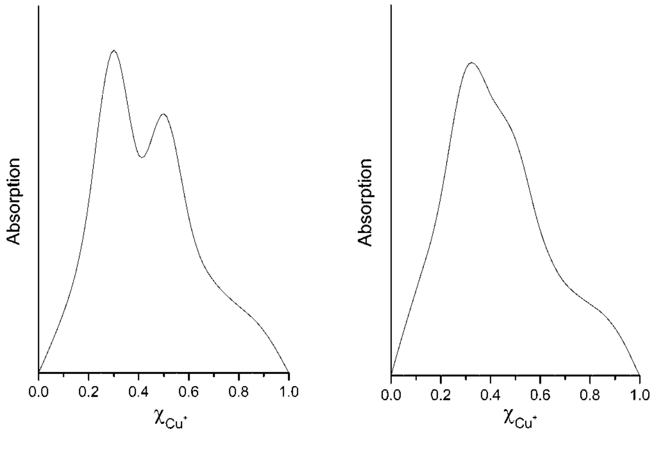
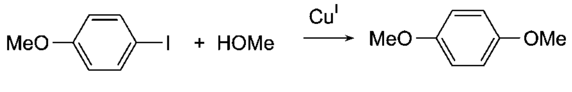


Figure 1. Normalized Job plots for mixtures of the hexamer **12** and $CuPF_6$ (left), and of the monomer **13** and $CuPF_6$ (right).

This should enable the resulting complex to coordinate additional molecules such as substrates. As a model reaction for catalytic activity of Cu^+ complexes of **12**, we checked the formation of dimethoxybenzene (**15**) from 4-iodoanisole (**14**). The nucleophilic substitution of halogen atoms by alkoxy groups (Ullmann reaction) can be catalyzed by copper salts under drastic conditions (high temperature, strong bases). Buchwald has developed a milder reaction using copper(I) triflate in the presence of cesium carbonate.[13] To avoid the use of the air-sensitive and expensive triflate, copper(I) iodide can be used if a suitable ligand is present, for instance unsubstituted 1,10-phenanthroline.[14] To allow a comparison with the dendrimer **12**, we have first checked this catalysis in the presence of 2,9-dimethyl-1,10-phenanthroline (**1**), and then applied the same conditions to dendrimer **12**. To promote the formation of the catalytically active 1:1 complexes, copper(I) iodide and the ligand were used in equal amounts. The reactions were carried out using 20 mol-% of the catalysts, calculated per 1,10-phenanthroline unit. Table 1 lists the results obtained with the monomeric neocuproine **1** and the dendritic hexamer **12**. Furthermore, reactions have been carried out which lacked the ligand or Cu^+ ions (see Table 1).



14 **15**

Table 1. Cu^+-catalyzed substitution of 4-iodoanisol (**14**) to give 1,4-dimethoxybenzene (**15**) using different ligands.

Ligand	Product **15**/anisol **14**
1	85:15
12	86:14
No ligand	35:65
No copper salt	11:89

With **1**, the reported yield was almost confirmed (88%[14]). The hexamer **12** gives nearly identical results. This proves that each Cu^+ center in the dendrimer complex operates separately and that the dendritic core has no influence on the reactivity of the metal ion complex.

Conclusion

Therefore, dendritic neocuproines can be used as a substitute for the monomer with the potential of easy recovery. Dendrimers of higher generation should easily be separatable from the reaction mixture by ultrafiltration as shown for many other dendritic structures.[3,15]

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: bis(triphenylphosphane)palladium(II) dichloride (Fluka), 4-iodoanisol (Fluka), neocuproine (Chempur), tetrabutylammonium fluoride trihydrate (Fluka), tetrakis(acetonitrile)copper(I) hexafluorophosphate (Aldrich). 1,3,5-Triiodobenzene[9] and 1,3-diiodo-5-(trimethylsilylethynyl)benzene,[9] were prepared according to literature procedures. HPLC grade THF was used. Other dry solvents were obtained with suitable desiccants. Column chromatography was carried out on neutral alumina (Fluka) or silica gel (Macherey–Nagel). The chromatotron was model 7924T from Harrison Research. ^{1}H and ^{13}C NMR spectra were recorded with Bruker ARX 300 (300 MHz or 75 MHz) or DRX 500 (500 MHz or 125 MHz) instruments, using tetramethylsilane as internal standard. IR spectra were measured with a Perkin–Elmer 1600 instrument. Mass spectra were recorded with Finnigan MAT 8200 or 8230 instruments, a MALDI-TOF mass spectrometer Biflex III (Bruker-Daltonics; using 4-hydroxy-α-cinnamic acid as matrix), or an ESI mass spectrometer Esquire-LC (Bruker-Daltonics; using methanol/dichloromethane, 1:1, as solvent). UV/Vis spectra were recorded with a Lambda 14 instrument (Perkin–Elmer) at 25.0 ± 0.1 °C. Elemental analyses were carried out with a VarioEl instrument (Elementaranalysensysteme GmbH). Gas chromatography was performed with a 6890 N instrument (Agilent); injector: split/splitless, split ratio: 11:1, injector temp.: 250 °C, detector: FID, detector temp.: 300 °C.

2,9-Bis[(*tert*-butyldimethylsilyl)methyl]-5-ethynyl-1,10-phenanthroline (5): 2,9-Bis[(*tert*-butyldimethylsilyl)methyl]-5-[(trimethylsilyl)ethynyl]-1,10-phenanthroline (**4**, 107 mg, 200 µmol) was dissolved in dry THF (8 mL) and cooled to –78 °C. Then, tetra-*n*-butylammoniumfluoride trihydrate (TBAF·3H_2O, 63.1 mg, 200 µmol) dissolved in dry THF (1 mL) was added dropwise. After stirring for 1 h at –78 °C, deionized water (9 mL) was added, and after warming to room temp., the mixture was extracted with dichloromethane (2 × 10 mL), the organic layers were combined, washed with brine (10 mL), dried with sodium sulfate, and the solvents were evaporated in vacuo. Chromatography [chromatotron, neutral alumina, cyclohexane/ethyl acetate (20:1); DC (10:1), R_f = 0.43] yielded 65.0 mg (71%) of **5** as a colorless solid, m.p. 141 °C. IR (KBr): $\tilde{\nu}$ = 3138 (C≡C–H), 2951 (aliph. C–H), 2074 (C≡C), 1604 (arom. C=C), 1482 (aliph. C–H), 845 (arom. C–H) cm^{-1}. MS (EI = 70 eV): *m*/*z* (%) = 461 (100) $[M+H]^+$, 403 (42) $[M+H-t\text{Bu}]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, J = 8.4 Hz, 1 H, Phen-H^4), 7.96 (d, J = 8.3 Hz, 1 H, Phen-H^7), 7.90 (s, 1 H, Phen-H^6), 7.35 (d, J = 8.4 Hz, 1 H, Phen-H^3), 7.28 (d, J = 8.3 Hz, 1 H, Phen-H^8), 3.45 (s, 1 H, C≡CH), 2.78 (s, 2 H, PhenC^2-CH_2), 2.77 (s, 2 H, PhenC^9-CH_2), 0.94 [s, 9 H, PhenC^{2}CH$_2$SiC(CH_3)$_3$], 0.94 [s, 9 H, PhenC^{9}CH$_2$SiC(CH_3)$_3$], –0.01 [s, 12 H, PhenC^{2,9}CH$_2$Si(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.49 (Phen-C^9), 162.72 (Phen-C^2), 145.78 (Phen-C^{10a}), 145.17 (Phen-C^{10b}), 135.29 (Phen-C^7), 133.86 (Phen-C^4), 130.20 (Phen-C^6), 125.54 (Phen-C^{4a}), 124.94 (Phen-C^{6a}), 123.20 (Phen-$C^{3,8}$), 116.53 (Phen-C^5), 81.69 (Phen-C≡CH), 81.05 (Phen-C≡CH), 27.86 (PhenC^9-CH$_2$), 27.54 (PhenC^2-CH$_2$), 26.53 [PhenC^{2,9}CH$_2$SiC(CH$_3$)$_3$], 17.06 [PhenC^{2,9}CH$_2$SiC(CH$_3$)$_3$], –6.06 [PhenC^{2,9}CH$_2$Si(CH$_3$)$_2$] ppm. $C_{28}H_{40}N_2Si_2$ (460.27): calcd. C 72.98, H 8.75, N 6.08; $C_{28}H_{40}N_2Si_2\cdot0.2H_2O$ (463.87): calcd. C 72.41, H 8.77, N 6.03; found C 72.51, H 8.64, N 6.25. The product is sensible to acid and heat. It was stored under argon at –18 °C.

1,3,5-Tris[2,9-(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolinyl-5-ethynyl]benzene (7): 1,3,5-Triiodobenzene[9] (**6**, 5.71 mg, 30.0 µmol) and 2,9-bis(*tert*-butyldimethylsilylmethyl)-5-ethynyl-1,10-phenanthroline (**5**, 184 mg, 400 µmol) were dissolved in a mixture of dry benzene (5 mL) and dry triethylamine (1 mL). After degassing in an ultrasound bath under a flow of argon for 30 min, copper(I) iodide (5.71 mg, 30.0 µmol) and bis(triphenylphosphane) palladium(II) dichloride (10.5 mg, 15.0 µmol) were added and the mixture was sonicated in an ultrasound bath at 50 °C (the heating was caused by the energy of the sonification) for 18 h. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane (5 mL) and the organic layer was washed with 0.1 M potassium cyanide solution (5 mL) and deionized water (5 mL). After drying with sodium sulfate, the solvent was evaporated in vacuo and the residue was purified by chromatography [chromatotron, neutral alumina, cyclohexane/ethyl acetate (10:1); R_f = 0.1] yielding 84.0 mg (58%) of **7** as a yellow solid, m.p. 222 °C. IR (KBr): $\tilde{\nu}$ = 2924 (aliph. C–H), 1602 (arom. C=C), 1483 (aliph. C–H), 843 (arom. C–H) cm^{-1}. MS (MALDI-TOF): *m*/*z* (%) = 1478 (26) $[M+Na]^+$, 1456 (100) $[M+H]^+$, 1341 (23) $[M+H-\text{TBDMS}]^+$. HRMS: $C_{90}H_{121}N_6Si_6$: found 1453.8377, calcd. 1453.8286 (–7.4 ppm); $C_{89}{}^{13}CH_{121}N_6Si_6$: found 1454.8303, calcd. 1454.8301 (–0.1 ppm). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, J = 8.3 Hz, 3 H, Phen-H^4), 8.02 (d, J = 8.4 Hz, 3 H, Phen-H^7), 7.99 (s, 3 H, Phen-H^6), 7.95 (s, 3 H, Ar-$H^{2,4,6}$), 7.43 (d, J = 8.4 Hz, 3 H, Phen-H^3), 7.32 (d, J = 8.3 Hz, 3 H, Phen-H^8), 2.82 (s, 6 H, PhenC^2-CH_2), 2.81 (s, 6 H, PhenC^9-CH_2), 0.97 [s, 54 H, PhenC^{2,9}CH$_2$SiC(CH_3)$_3$], 0.03 [s, 18 H, PhenC^{2}CH$_2$Si(CH_3)$_2$], 0.02 [s, 18 H, PhenC^{9}CH$_2$Si(CH_3)$_2$]. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.57 (Phen-C^9), 162.85 (Phen-C^2), 145.82 (Phen-C^{10a}), 145.33 (Phen-C^{10b}), 135.35 (Phen-C^7), 134.32 (Ar-$C^{2,4,6}$), 133.92 (Phen-C^4), 129.70 (Phen-C^6), 125.44 (Phen-C^{4a}), 125.19 (Phen-C^{6a}), 124.29 (Ar-$C^{1,3,5}$), 123.43 (Phen-C^8), 123.29 (Phen-C^3), 117.11 (Phen-C^5), 92.25 (Phen-C≡C), 88.42 (Phen-C≡C), 27.96 (PhenC^9-CH$_2$), 27.67 (PhenC^2-CH$_2$), 26.58 [PhenC^{9}CH$_2$SiC(CH$_3$)$_3$], 26.56 [PhenC^{2}CH$_2$SiC(CH$_3$)$_3$], 17.09 [PhenC^{9}CH$_2$SiC(CH$_3$)$_3$], 17.08 [PhenC^{2}CH$_2$SiC(CH$_3$)$_3$], –6.01 [PhenC^{2,9}CH$_2$Si(CH$_3$)$_2$] ppm.

3,5-Bis[2,9-bis(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-ylethynyl]-1-(trimethylsilylethynyl)benzene (9): Under argon, 2,9-bis(*tert*-butyldimethylsilylmethyl)-5-ethynyl-1,10-phenanthroline (**5**, 340 mg, 738 µmol) was added to a solution of 1,3-diiodo-5-(trimethylsilylethynyl)benzene[10] (**8**, 126 mg, 295 µmol) in a mixture of dry benzene (10 mL) and dry triethylamine (2 mL). The mixture was degassed by sonication in an ultrasound bath using an argon flow for 20 min. Copper(I) iodide (11.4 mg, 60.0 µmol) and bis(triphenylphosphane)palladium(II) dichloride (21.1 mg, 30.0 µmol) were added, and the mixture was sonicated in an ultrasound bath at 50 °C (the heating was caused by the energy of the sonification) for 18 h. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane (10 mL) and the organic layer was washed with 0.1 M potassium cyanide solution (10 mL) and deionized water (10 mL). After drying with sodium sulfate, flash chromatography (neutral alumina, cyclohexane/ethyl acetate (10:1); DC (5:1), $R_f = 0.44$) gave 181 mg (56%) of **9** as colorless solid, m.p. 254–259 °C. IR (KBr): $\tilde{\nu}$ = 2950 (aliph. C–H), 1603 (arom. C=C), 1483 (aliph. C–H), 882, 843 (arom. C–H) cm^{-1}. MS (ESI): *m*/*z* (%) = 1092 (100) $[M+H]^+$, 1020 (14) $[M+H-TMS]^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.58 (d, J = 8.4 Hz, 2 H, Phen-H^4), 7.99 (d, J = 8.3 Hz, 2 H, Phen-H^7), 7.94 (s, 2 H, Phen-H^6), 7.86 (t, J = 1.6 Hz, 1 H, Ar-H^4), 7.76 (d, J = 1.6 Hz, 2 H, Ar-$H^{2,6}$), 7.40 (d, J = 8.4 Hz, 2 H, Phen-H^3), 7.30 (d, J = 8.3 Hz, 2 H, Phen-H^8), 2.81 (s, 4 H, PhenC^2-CH_2), 2.79 (s, 4 H, PhenC^9-CH_2), 0.96 [s, 18 H, PhenC^{2}CH$_2$SiC(CH_3)$_3$], 0.96 [s, 18 H, PhenC^{9}CH$_2$SiC(CH_3)$_3$], 0.30 [s, 9 H, C≡CSi(CH_3)$_3$], 0.01 [s, 12 H, PhenC^{2}CH$_2$Si(CH_3)$_2$], 0.01 [s, 12 H, PhenC^{9}CH$_2$Si(CH_3)$_2$]. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 163.50 (Phen-C^9), 162.80 (Phen-C^2), 145.80 (Phen-C^{10a}), 145.31 (Phen-C^{10b}), 135.34 (Phen-C^7), 134.68 (Ar-$C^{2,6}$), 134.27 (Ar-C^4), 133.92 (Phen-C^4), 129.60 (Phen-C^6), 125.43 (Phen-C^{4a}), 125.18 (Phen-C^{6a}), 124.24 (Ar-C^1), 124.00 (Ar-$C^{3,5}$), 123.26 (Phen-C^3), 123.23 (Phen-C^8), 117.15 (Phen-C^5), 103.15 (Ar-*C*≡CTMS), 96.24 (Ar-C≡*C*TMS), 92.25 (Phen-*C*≡C), 88.17 (Phen-C≡*C*), 27.93 (PhenC^9-*C*H$_2$), 27.64 (PhenC^2-*C*H$_2$), 26.56 [PhenC^{9}CH$_2$SiC(*C*H$_3$)$_3$], 26.55 [PhenC^{2}CH$_2$SiC(*C*H$_3$)$_3$], 17.09 [PhenC^{9}CH$_2$Si*C*(CH$_3$)$_3$], 17.08 [PhenC^{2}CH$_2$Si*C*(CH$_3$)$_3$], –0.10 [Si(*C*H$_3$)$_3$], –6.01 [PhenC^{2,9}CH$_2$Si(*C*H$_3$)$_2$] ppm. $C_{67}H_{90}N_4Si_5$ (1090.60): calcd. C 73.70, H 8.31, N 5.13; $C_{67}H_{90}N_4Si_5 \cdot 0.7H_2O \cdot 0.5C_6H_{12}$ (1145.26): calcd. C 73.32, H 8.56, N 4.89; found C 73.32, H 8.59, N 4.96. The product is sensitive to acid and heat. It was stored under argon at –18 °C.

3,5-Bis[2,9-bis(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-ylethynyl]-1-ethynylbenzene (10): A solution of tetrabutylammoniumfluoride trihydrate (TBAF·3H$_2$O, 80.0 mg, 254 μmol) in dry THF (4 mL) was added dropwise to a solution of 3,5-bis[2,9-(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-ylethynyl]-1-(trimethylsilylethynyl)benzene (**9**, 277 mg, 254 μmol) in dry THF (20 mL). After stirring for 1 h, deionized water (25 mL) and dichloromethane (25 mL) were added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 25 mL), the organic layers were combined, washed with brine (25 mL) and dried with sodium sulfate. Evaporation of the solvent in vacuo yielded 210 mg (81%) of **10** as a yellowish solid. IR (KBr): $\tilde{\nu}$ = 2925 (aliph. C–H), 2154 (C≡C), 1602 (arom. C=C), 1483 (aliph. C–H), 842 (arom. C–H) cm^{-1}. MS (ESI): *m*/*z* (%) = 1020 (100) $[M+H]^+$, 510 (53) $[MH_2]^{2+}$. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.58 (d, J = 8.4 Hz, 2 H, Phen-H^4), 8.00 (d, J = 8.3 Hz, 2 H, Phen-H^7), 7.95 (s, 2 H, Phen-H^6), 7.89 (t, J = 1.6 Hz, 1 H, Ar-H^4), 7.77 (d, J = 1.6 Hz, 2 H, Ar-$H^{2,6}$), 7.40 (d, J = 8.4 Hz, 2 H, Phen-H^3), 7.30 (d, J = 8.3 Hz, 2 H, Phen-H^8), 3.20 (s, 1 H, C≡C*H*), 2.81 (s, 4 H, PhenC^2-CH_2), 2.79 (s, 4 H, PhenC^9-CH_2), 0.96 [s, 18 H, PhenC^{2}CH$_2$SiC(CH_3)$_3$], 0.96 [s, 18 H, PhenC^{9}CH$_2$SiC(CH_3)$_3$], 0.01 [s, 24 H, PhenC^{2,9}CH$_2$Si(CH_3)$_2$]. ^{13}C NMR (125 MHz, CDCl$_3$): 163.55 (Phen-C^9), 162.83 (Phen-C^2), 145.82 (Phen-C^{10a}), 145.32 (Phen-C^{10b}), 135.34 (Phen-C^7), 134.82 (Ar-$C^{2,6}$), 134.65 (Ar-C^4), 133.88 (Phen-C^4), 129.67 (Phen-C^6), 125.42 (Phen-C^{4a}), 125.17 (Phen-C^{6a}), 124.15 (Ar-C^1), 123.28 (Ar-$C^{3,5}$), 123.23 (Phen-$C^{3,8}$), 117.05 (Phen-C^5), 92.07 (Phen-C≡*C*H), 88.37 (Phen-*C*≡CH), 81.94 (Ar-C≡*C*H), 78.76 (Ar-*C*≡CH), 27.94 (PhenC^9-*C*H$_2$), 27.65 (PhenC^2-*C*H$_2$), 26.57 [PhenC^{9}CH$_2$SiC(*C*H$_3$)$_3$], 26.55 [PhenC^{2}CH$_2$SiC(*C*H$_3$)$_3$], 17.09 [PhenC^{9}CH$_2$Si*C*(CH$_3$)$_3$], 17.08 [PhenC^{2}CH$_2$Si*C*(CH$_3$)$_3$], –6.01 [PhenC^{2,9}CH$_2$Si(*C*H$_3$)$_2$] ppm. $C_{64}H_{82}N_4Si_4$ (1018.56): calcd. C 75.38, H 8.10, N 5.49; $C_{64}H_{82}N_4Si_4 \cdot 0.4H_2O \cdot 0.4C_6H_{12}$ (1059.40): calcd. C 75.19, H 8.33, N 5.28; found C 75.17, H 8.44, N 5.38. The product is sensitive to acid and heat. It was stored under argon at –18 °C. The sample used for elemental analysis was purified by chromatography (neutral alumina, cyclohexane/ethyl acetate (10:1); DC (5:1), $R_f = 0.32$).

1,3,5-Tris{3,5-bis[2,9-bis(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-yl-ethynyl]phenylethynyl}benzene (11): 1,3,5-Triiodobenzene[9] (**6**, 5.95 mg, 12.6 μmol) and 3,5-bis[2,9-bis(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-yl-ethynyl]ethynylbenzene (**10**, 44.0 mg, 41.9 μmol) were dissolved in dry toluene (2 mL) and dry triethylamine (3 mL). After degassing in an ultrasound bath under a flow of argon for 30 min, copper(I) iodide (95.0 μg, 5.00 μmol) and bis(triphenylphosphane)palladium(II) dichloride (1.76 mg, 2.50 μmol) were added and the mixture was sonicated in an ultrasound bath at 50 °C (the heating was caused by the energy of the sonification) for 18 h. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane (5 mL) and the organic layer was washed with 0.1 M potassium cyanide solution (5 mL) and deionized water (5 mL). After drying with sodium sulfate, the solvent was evaporated in vacuo and the residue was purified by chromatography [neutral alumina, cyclohexane/ethyl acetate (5:1); $R_f = 0.17$] yielding 23.0 mg (58%) of **11**, m.p. 283 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.62 (d, J = 8.4 Hz, 6 H, Phen-H^4), 8.10 (d, J = 8.2 Hz, 6 H, Phen-H^7), 8.07 (s, 6 H, Phen-H^6), 7.92 (s, 3 H, Ar^1-$H^{2,4,6}$), 7.89 (t, J = 1.5 Hz, 3 H, Ar^2-H^4) 7.81 (d, J = 1.5 Hz, 6 H, Ar^2-$H^{2,6}$), 7.42 (d, J = 8.4 Hz, 6 H, Phen-H^3), 7.33 (d, J = 8.1 Hz, 6 H, Phen-H^8), 2.94 (s, 12 H, PhenC^2-CH_2), 2.88 (s, 12 H, PhenC^9-CH_2), 0.98 [s, 54 H, PhenC^{2}CH$_2$SiC(CH_3)$_3$], 0.96 [s, 54 H, PhenC^{9}CH$_2$SiC(CH_3)$_3$], 0.02 [s, 36 H, PhenC^{2,9}CH$_2$Si(CH_3)$_2$] ppm.

1,3,5-Tris{3,5-bis[2,9-dimethyl-1,10-phenanthrolin-5-yl-ethynyl]-phenylethynyl}benzene (12): A solution of tetrabutylammonium fluoride (25.4 mg, 80.5 μmol) in dry THF (1 mL) was added dropwise to a solution of 1,3,5-tris{3,5-bis[2,9-bis(*tert*-butyldimethylsilylmethyl)-1,10-phenanthrolin-5-yl-ethynyl]phenylethynyl}-benzene (**11**, 21.0 mg, 6.71 μmol) in dry THF (3 mL). After stirring for 1 h, deionized water (3 mL) and dichloromethane (3 mL) were added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 3 mL), the organic layers were combined, washed with brine (3 mL) and dried with sodium sulfate. Evaporation of the solvent in vacuo yielded 10.1 mg (86%) of **12** as a colorless solid. MS (MALDI-TOF): 891 $[M+Na]^{2+}$. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.71 (d, J = 8.3 Hz, 6 H, Phen-H^4), 8.14 (d, J = 8.2 Hz, 6 H, Phen-H^7), 8.07 (s, 6 H, Phen-H^6), 7.92 (s, 3 H, Ar^1-$H^{2,4,6}$), 7.89 (t, J = 1.5 Hz, 3 H, Ar^2-H^4) 7.81 (d, J = 1.5 Hz, 6 H, Ar^2-$H^{2,6}$), 7.63 (d, J = 8.3 Hz, 6 H, Phen-H^3), 7.54 (d, J = 8.0 Hz, 6 H, Phen-H^8), 2.99 (s, 18 H, PhenC^2-CH_3), 2.97 (s, 18 H, PhenC^9-CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 160.68 (Phen-C^9), 160.09 (Phen-C^2), 145.38 (Phen-C^{10a}), 145.07 (Phen-C^{10b}), 139.46 (Ar^1-$C^{2,4,6}$), 139.46 (Ar^2-C^4), 136.22 (Phen-C^7), 134.80 (Ar^2-$C^{2,6}$), 134.56 (Phen-C^4), 130.42 (Phen-C^6), 126.37 (Phen-C^{4a}), 126.14 (Phen-C^{6a}), 124.09 (Ar^1-$C^{1,3,5}$), 124.09 (Ar^2-$C^{1,3,5}$), 123.98 (Phen-C^3), 123.98 (Phen-C^8), 118.07 (Phen-C^5), 94.22 (Phen-*C*≡C), 92.62 (Phen-C≡*C*), 78.54 (Ar^1-C≡*C*–Ar^2), 78.41 (Ar^1-*C*≡CAr^2), 29.71 (PhenC^{2,9}-*C*H$_3$).

UV/Vis Studies of the Complex Formation of 12 with Cu$^+$: 100 μM solutions of neocuproine **1** and tetrakis(acetonitrile)copper(I) hexafluorophosphate $[(CH_3CN)_4Cu]PF_6$ and a 16.7 μM solution of **12** in 1:1 mixtures of chloroform/acetonitrile were prepared. At 25 °C, aliquots of the ligand and the Cu$^+$ solutions were mixed in various ratios $(10-n):n$ in the range n = 0–10, i.e. the total volume always was identical (Job plot[11,12]). The spectra between 225 and 500 nm were recorded and the data were analyzed as Job plots at different wavelengths. Representatively, one plot is shown in Figure 1.

Cu$^+$-Catalyzed Formation of 4-Methoxyanisol from 4-Iodoanisol: 4-Iodoanisol (**14**, 23.4 mg, 100 µmol), copper(I) iodide (4.00 mg, 20.0 µmol), cesium carbonate (45.6 mg, 140 µmol), and the ligand [(i) 1,3,5-tris{3,5-bis[2,9-dimethyl-1,10-phenanthrolin-5-yl-ethynyl]-phenylethynyl}benzene (**12**, 5.87 mg, 3.33 µmol), or (ii) neocuproine (**1**, 4.17 mg, 20.0 µmol), or (iii) no ligand] were mixed with methanol (0.3 mL) in a vial (ca. 10 cm long) sealed with a teflon cap. The resulting mixture was heated to 110 °C for 24 h. After evaporation of the solvent, the residue was dissolved in diethyl ether (5 mL) and filtered through silica gel. After evaporation of the solvent, solutions with a concentration of 2 mg/mL were prepared, and 0.5 mL of these solutions were mixed with 0.5 mL of a solution of *n*-dodecane (c = 1 mg/mL), and the mixture was analyzed by GC [column: HP5, 30 m, flow (N_2): 20 mL/min, start at 100 °C, hold for 5 min, then 3 °C/min until 250 °C are reached. r_t: 4-iodoanisol: 4.88 min; 1,4-dimethoxybenzene: 2.43; *n*-dodecane as internal standard: 2.85 min].

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