Electronic Supplementary Information (ESI)

Clean formation and dynamic exchange reactions of a supramolecular equilateral triangle that is both heterometallic and heteroleptic

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Synthesis



Scheme S1. Synthesis of angular molecule 1.

All reagents were commercially available and used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use. Thin-layer chromatography (TLC) was performed using TLC plates from Merck (silica gel 60 F_{254}). Silica gel 60 was used for column chromatography. ¹H NMR and ¹³C NMR were recorded on Bruker Avance 400 MHz spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. The numbering of the carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signal and is not in

accordance with the IUPAC nomenclature rules. Electrospray ionisation mass spectra (ESI-MS) were recorded using a Thermo-Quest LCQ Deca. Differential pulse voltammetry (DPV) was measured on a Parstat 2273 in dry acetonitrile.

Phenanthrolines B, C and D were prepared according to known procedure¹
2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-3-trimethylsilanylethynyl-[1,10]phenanthroline
(B)



Yield 64%; mp 107 °C; ¹H NMR (400 MHz, CD₂Cl₂) δ 0.23 (s, 9 H, 3'-H), 1.53 (s, 18 H, *t*-Bu), 3.78 (s, 3 H, methoxy), 7.63 (dd, ³*J* = 8.0 Hz, ³*J* = 4.3 Hz, 1 H, 8-H), 7.78 (d, ³*J* = 8.8 Hz, 1 H, 6-H), 7.80 (d, ³*J* = 8.8 Hz, 1 H, 5-H), 7.91 (s, 2 H, 2''-, 6''-H), 8.26 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.6 Hz, 1 H, 7-H), 8.48 (s, 1 H, 4-H), 9.14 (dd, ³*J* = 4.3 Hz, ⁴*J* = 1.6 Hz, 1 H, 9-H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 0.2, 32.5, 36.5, 65.1,

101.5, 103.8, 118.1, 123.7, 126.1, 126.9, 127.4, 128.6, 130.0, 134.9, 136.5, 142.5, 143.6, 145.2, 146.7, 150.9, 160.4, 161.1; IR (KBr) v 2958, 2921, 2869, 2147, 1618, 1583, 1545, 1489, 1467, 1441, 1397, 1363, 1299, 1261, 1250, 1221, 1175, 1116, 1078, 1011, 916, 890, 854, 844, 774, 760, 738, 699, 637; ESI-MS m/z (%) 495.3 (100), [M + H]⁺. Anal. Calcd for C₃₂H₃₈N₂OSi 'H₂O: C, 74.96; H, 7.86; N, 5.46.Found: C, 74.83; H 7.70; N, 5.22.

$2, 9-Bis-(3, 5-di\ tert-butyl-4-methoxyphenyl)-3-trimethyl silanylethynyl-$

[1,10]phenanthroline (C)



Yield 78%; mp 120 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ 0.23 (s, 9 H, 3'-H), 1.52 (s, 18 H, 3'''-, 5'''- *t*-Bu), 1.53 (s, 18 H, 3''-, 5''- *t*-Bu), 3.74 (s, 3 H, 4'''-methoxy), 3.76 (s, 3 H, 4''-methoxy), 7.75 (d, ³J = 8.7 Hz, 1 H, 6-H), 7.82 (d, ³J = 8.7 Hz, 1 H, 5-H), 7.95 (s, 2 H, 2'''-, 6'''-H), 8.04 (d, ³J = 8.4 Hz, 1 H,

8-H), 8.09 (s, 2 H, 2''-, 6''-H), 8.29 (d, ${}^{3}J$ = 8.4 Hz, 1 H, 7-H), 8.49 (s, 1 H, 4-H) ; ${}^{13}C$ NMR (100 MHz, CD₂Cl₂) δ 0.2, 32.6, 32.7, 36.4, 36.5, 65.0, 65.1, 101.2, 104.2, 118.0, 121.5, 125.6, 126.8, 127.3 (2C), 128.7, 128.8, 134.9, 135.0, 137.2, 142.8, 143.5, 144.6, 145.4, 146.5, 158.8, 160.3, 161.1, 161.7; IR (KBr) v 2959, 2915, 2866, 2149, 1618, 1603, 1584, 1533, 1501, 1459, 1416, 1391, 1359, 1319, 1251, 1225, 1176, 1116, 1078, 1011, 915, 891, 865, 844, 760, 697,

641; ESI-MS *m*/*z* (%) 713.5 (100), [M + H]⁺. Anal. Calcd for C₄₇H₆₀N₂O₂Si: C, 79.16; H, 8.48; N, 3.93. Found: C, 79.15; H, 8.90; N, 3.50.

2,9-Bis-(3,5-di-*tert*-butyl-4-methoxyphenyl)-3-ethynyl-[1,10]phenanthroline (D)



Yield 94%; mp 212 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ 1.53 (s, 18 H, 3^{**}-, 5^{**}-*t*-Bu), 1.54 (s, 18 H, [3^{**}-, 5^{**}*t*-Bu), 3.45 (s, 1 H, 2^{*}-H), 3.75 (s, 3 H, 4^{***}-methoxy), 3.77 (s, 3 H, 4^{**}-methoxy), 7.76 (d, ³*J* = 8.7 Hz, 1 H, 6-H), 7.83 (d, ³*J* = 8.7 Hz, 1 H, 5-H), 8.01 (s, 2 H, 2^{***}-,6^{***}-H), 8.06 (d, ³*J* = 8.4 Hz, 1 H, 8-H), 8.11 (s, 2 H,

2''-,6''-H), 8.30 (d, ${}^{3}J$ = 8.4 Hz, 1 H, 7-H), 8.52 (s, 1 H, 4-H); ${}^{13}C$ NMR (100 MHz, CD₂Cl₂) δ 32.5, 32.6, 36.4, 36.5, 65.0 (2C), 83.0, 83.5, 116.9, 121.6, 125.6, 126.8, 127.2, 127.4, 128.7, 129.1, 134.6, 134.9, 137.2, 142.7, 143.6, 144.6, 145.8, 146.5, 158.8, 160.6, 161.1, 161.7; IR (KBr) v 3304, 2960, 2925, 2864, 1618, 1603, 1586, 1534, 1500, 1459, 1416, 1391, 1360, 1317, 1262, 1224, 1116, 1011, 891, 843, 648; ESI-MS *m*/*z* (%) 641.5 (100), [M + H]⁺. Anal. Calcd for C₄₄H₅₂N₂O₂: C, 82.46; H, 8.18; N, 4.37. Found: C, 82.84; H, 8.53; N, 3.88.

Compound 7



Compound **D** (0.50 g, 0.78 mmol) was dissolved in dry dichloromethane (25 mL) in a 50 mL two-necked round-bottomed flask under nitrogen. [Cu(MeCN)₄)]PF₆ (0.15 mg, 0.39 mmol) was added to the solution and the mixture was stirred at room temperature for 7 days. Then the solvent was removed under reduced pressure to afford a blackish solid. Small traces of the free ligand were separated off using column chromatography (SiO₂, DCM: EtOAc, 9:1). Yield 99%; mp > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ 0.90 (s, 36 H, 3""-,

5^{'''-*t*-Bu), 0.96 (s, 36 H, 3^{''-}, 5^{''-*t*-Bu), 3.11 (s, 6 H, 4^{'''-}methoxy), 3.21 (s, 6 H, 4^{''-}methoxy), 3.46 (s, 2 H, ethynyl-H), 7.48 (s, 4 H, 2^{''-}, 6^{''-}H) 7.52 (s, 4 H, 2^{''-}, 6^{''-}H), 7.91 (d, ${}^{3}J = 8.9$ Hz, 2 H, 6-H), 7.91 (d, ${}^{3}J = 8.6$ Hz, 2 H, 8-H), 8.01 (d, ${}^{3}J = 8.9$ Hz, 2 H, 5-H), 8.39 (d, ${}^{3}J = 8.6$ Hz, 2 H, 7-H), 8.60 (s, 2 H, 4-H); 13 C NMR (100 MHz, CD₂Cl₂) δ 31.6, 32.0,}}

36.0, 36.2, 64.9, 65.5, 81.2, 86.3, 121.4, 126.3, 126.4, 126.9, 128.0, 128.2, 128.5, 129.6, 132.3, 133.4, 137.2, 142.3, 143.1, 143.5, 144.1, 144.3, 158.1, 158.9, 161.5, 162.8; IR (KBr) v 3308, 3279, 2963, 2871, 1620, 1580, 1543, 1501, 1458, 1406, 1392, 1360, 1319, 1256, 1223, 1113, 1004, 921, 842, 648; ESI-MS m/z (%) 1344.7 (100), [M]⁺. Anal. Calcd for C₈₈H₁₀₄CuF₆N₄O₄P·EtOAc: C, 70.01; H, 7.15; N, 3.55. Found: C, 70.20; H, 7.00; N, 3.63.

Angular Molecule 1



3-(4-Iodo-2,3,5,6-tetramethyl-phenylethynyl)-[1,10]phenanthroline (0.11 mg, 0.23 mmol), 7 (0.15 g, 0.10 mmol), TBAF.3H₂O (0.48 g, 1.5 mmol) and PdCl₂(PPh₃)₂ (14 mg, 20 µmol) were combined in a 25 mL side-armed test tube under N2 atmosphere. The solid mixture was stirred at 80 °C for 12 h. Then it was cooled, dissolved with dichloromethane (50 mL) and washed w successively ith aqueous KOH (50 mL) and water (50 mL). After drying over Na₂SO₄ the organic solvent was removed under reduced pressure. The crude product was purified using column chromatography (SiO₂). First separation was run using a 1:1 mixture of dichloromethane and ethyl acetate as eluent. Finally the target compound was obtained using 1:10 mixture of methanol and dichloromethane. Yield 60%; mp > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂):δ 0.70 (s, 18 H, [3" or 5"]-t-Bu), 0.91 (s, 36 H, 3" -, 5" -t- Bu) 1.16 (s, 18 H, [3" or 5"]-t-Bu), 1.99 (s, 12 H, a-H), 2.47 (s, 12 H, b-H), 3.06 (s, 6 H, 4" -methoxy), 3.22 (s, 6 H, 4"- methoxy), 7.23 (s, 2 H, [2" or 6"]-H), 7.50 (s, 4 H, 2"-, 6"-H), 7.61 (s, 2 H, [2" or 6'']-H), 7.65 (dd, ${}^{3}J = 8.1$ Hz, ${}^{3}J = 4.3$ Hz, 2 H, 8'-H), 7.80 (d, ${}^{3}J = 8.8$ Hz, 2 H, 6'-H), 7.87 (d, ${}^{3}J = 8.8$ Hz, 2 H, 5'-H), 7.93 (d, ${}^{3}J = 8.8$ Hz, 2 H, 6-H), 7.94 (d, ${}^{3}J = 8.5$ Hz, 2 H, 8-H), 8.03 (d, ${}^{3}J = 8.8$ Hz, 2 H, 5-H), 8.29 (dd, ${}^{3}J = 8.1$ Hz, ${}^{4}J = 1.7$ Hz, 2 H, 7'-H), 8.40 (d, ${}^{4}J = 2.0$ Hz 2 H, 4'-H), 8.43(d, ${}^{3}J$ = 8.5 Hz, 2 H, 7-H), 8.61 (s, 2 H, 4-H), 9.14 (dd, ${}^{3}J$ = 4.3 Hz, ${}^{4}J$ = 1.7 Hz, 2 H, 9'-H), 9.21 (d, ${}^{4}J$ = 2.0 Hz, 2 H, 2'-H); ${}^{13}C$ NMR (100 MHz, CD₂Cl₂) δ 18.1, 18.7, 31.6, 31.8, 32.3, 36.0, 36.3, 65.0, 65.8, 92.8, 95.5, 96.2, 97.2, 120.2, 123.1, 123.7, 123.8, 124.1, 126.2, 126.5 (2C), 126.6, 127.0, 128.0, 128.1, 128.5, 128.6, 128.8, 129.3, 129.7, 132.4, 133.5, 133.6, 136.4, 136.6, 136.7, 137.2, 138.2, 139.5, 142.2, 143.0, 144.3, 145.4, 146.6, 151.0, 152.1, 158.3, 159.7, 161.1, 163.1; IR (KBr) v 3411, 2960, 2920, 2868, 2202, 1617, 1579, 1541, 1502, 1447, 1421, 1408, 1391, 1360, 1255, 1222, 1113, 1003, 909, 848, 733; ESI-MS m/z (%) 2012.8 (100), [M]⁺. Anal. Calcd for C₁₃₆H₁₄₀CuF₆N₈O₄P . 2CH₂Cl₂: C, 71.17; H, 6.23; N, 4.81. Found: C, 71.59; H, 6.34; N, 4.89.

Heterometallic Triangle T₁



Bisphenanthroline 2a (4.25 mg, 3.73 µmol) was loaded into a NMR tube and was dissolved in CD₂Cl₂ (0.15 mL). AgPF₆ (1.89 mg, 7.46 µmol), dissolved in CD₃CN (0.45 mL), was added to the bisphenanthroline solution leading to a light yellow hue. Finally, 1 (8.05 mg, 3.73 μ mol) was added to the mixture furnishing a yellowish-black solution. T₁ was received in quantitative yield. mp > 300 °C; ¹H NMR (400 MHz, CD₃CN/CD₂Cl₂, 3:1): δ 0.59 (s, 18 H, [3" or 5"]-t-Bu), 0.86 (s, 36 H, 3" -, 5" -t-Bu), 1.19 (s, 18 H, [3" or 5"]-t-Bu), 1.25-2.03 (m, 54 H, methyl, a-H), 2.39 (s, 12 H, b-H), 3.00 (s, 6 H, 4"-methoxy), 3.20 (s, 6 H, 4"methoxy), 6.21-6.48 (m, 4 H, mes-H), 6.96 (s, 4 H, c-H), 7.16 (s, 2 H, [2" or 6"]-H), 7.50 (s, 4 H, 2^{'''}-, 6^{'''}-H), 7.56 (s, 2 H, [2^{''} or 6^{''}]-H), 7.80 (dd, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 4.4$ Hz, 2 H, 8[']-H), 7.95-8.07 (m, 12 H, 5-, 5'-, 6-, 6'-, 8-, 8''''-H), 8.19 (d, ${}^{3}J = 8.8$ Hz, 2 H, 6''''-H), 8.26 (d, ${}^{3}J$ $= 8.8 \text{ Hz}, 2 \text{ H}, 5^{\circ}, 4^{\circ}, 4^{\circ}$ 7'-, 7'''', 9'-H); ¹³C NMR (100 MHz, CD₃CN/CD₂Cl₂, 3:1): δ 18.0, 18.5, 18.8, 20.3, 20.6 (2C), 31.4, 31.6, 32.3, 35.9, 36.2, 65.2, 66.1, 88.4, 94.5, 95.1, 96.0, 96.1, 96.5, 121.2, 121.5, 123.1 (2C), 123.3, 123.9, 125.3, 126.2, 126.8, 126.9 (2C), 127.0, 127.6, 128.1, 128.3, 128.5, 128.6 (2C), 128.9, 129.0 (2C), 129.3, 129.7, 130.1, 132.1, 132.2, 133.6, 133.7, 134.2, 135.9, 136.8, 137.0, 137.9, 138.7, 138.8 (2C), 139.1, 139.4, 139.9, 140.3, 140.4 (2C), 141.0 (2C), 141.3, 142.2, 142.4, 142.5, 144.2 (2C), 144.3, 151.4, 151.7, 157.9, 159.4, 161.0, 161.6, 162.3, 163.3; IR (KBr) v 3427, 2957, 2920, 2868, 2203, 1617, 1580, 1544, 1503, 1449, 1426, 1408, 1390, 1361, 1297, 1256, 1222, 1113, 1004, 911, 843, 727, 557; ESI-MS m/z (%) 1123.4

(100), $[M - 3PF_6]^{3+}$, 1757.5 (10), $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{208}H_{200}Ag_2Br_2CuF_{18}N_{12}O_4P_3\cdot 4CH_2Cl_2$: C, 61.42; H, 5.06; N, 4.05. Found: C, 61.21; H, 5.32; N, 3.94.

Homometallic Triangle T₂



Bisphenanthroline 2a (4.01 mg, 3.51 µmol) and Cu(MeCN)₄PF₆ (2.62 mg, 7.03 µmol) were put into a NMR tube and were dissolved with CD₂Cl₂ furnishing a yellow solution. After addition of 1 (7.59 mg, 3.51 μ mol) a color change to dark red occurred. T₂ was received in quantitative yield. mp > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ 0.62 (s, 18 H, [3" or 5"]-t-Bu), 0.88 (s, 36 H, 3", 5"-t-Bu) 1.20 (s, 18 H, [3" or 5"]-t-Bu), 1.26-1.88 (m, 42 H, methyl), 1.95 (s, 12 H, a-H), 2.38 (s, 12 H, b-H), 3.01 (s, 6 H, 4"-methoxy), 3.21 (s, 6 H, 4"methoxy), 5.77-6.24 (m, 4 H, mes-H), 6.93 (s, 4 H, c-H), 7.15 (s, 2 H, [2" or 6"]-H), 7.48 (s, 4 H, 2^{'''}-, 6^{'''}-H), 7.55 (s, 2 H, [2^{''} or 6^{''}]-H), 7.76 (dd, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 4.4$ Hz, 2 H, 8[']-H), 7.88-7.95 (m, 10 H, 5'-, 6-, 6'-, 8-, 8''''-H), 8.02 (d, ${}^{3}J$ = 8.8 Hz, 2 H, 5-H), 8.21 (d, ${}^{3}J$ = 8.8 Hz, 2 H, 6^{'''}-H), 8.27 (d, ${}^{3}J$ = 8.8 Hz, 2 H, 5^{'''}-H), 8.41 (d, ${}^{3}J$ = 8.4 Hz, 2 H, 7-H), 8.46 (d, ${}^{3}J = 8.0$ Hz, 2 H, 7'-H), 8.50-8.55 (m, 6 H, 2'-, 4'-, 9'-H), 8.63 (s, 2 H, 4-H), 8.72 (d, ${}^{3}J = 8.0$ Hz, 2 H, 7['], H), 8.82 (s, 2 H, 4['], H); ¹³C NMR (100 MHz, CD₂Cl₂): δ 18.2, 18.5, 18.7, 18.9, 20.1, 20.3, 20.6 (2C), 20.8, 31.5, 31.8, 32.4, 36.0, 36.2, 65.1, 65.9, 87.8, 94.5, 95.2, 95.8, 96.8, 97.0, 122.1, 122.7, 123.0, 123.1, 123.5, 123.9, 125.4, 126.1, 126.5, 126.6, 126.8, 127.1, 127.4, 127.6 (2C), 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 128.9, 129.2, 129.3, 129.5, 132.0, 132.2, 132.3, 133.0, 133.4, 133.5 (2C), 134.2, 135.0, 135.4, 136.7, 136.8, 137.0, 137.2, 137.9 (2C), 138.1, 138.4, 139.4, 139.7, 141.6, 142.2, 142.5, 143.0, 143.1, 144.2, 144.3 (2C), 148.6, 149.4, 158.2, 159.7, 160.0, 160.9, 161.3, 163.3; IR (KBr) v 3428, 2957, 2921, 2867, 2203, 1618, 1578, 1547, 1502, 1449, 1426, 1409, 1390, 1361, 1295, 1256, 1222, 1113, 1004, 912, 842, 723, 557; ESI-MS m/z (%) 1094.1 (100), $[M - 3PF_6]^{3+}$, 1713.5 (10), $[M - 2PF_6]^{2+}$. Anal. Calcd for C₂₀₈H₂₀₀Br₂Cu₃F₁₈N₁₂O₄P₃·4CH₂Cl₂: C, 62.76; H, 5.17; N, 4.14. Found: C, 62.63; H, 5.43; N, 4.14.

Metal Exchange Study

Metal exchange study with the heterometallic triangle T_1 was carried out according to Scheme S2. [Cu(MeCN)₄]PF₆ (1.0 eq. with respect to Ag⁺ ions in T_1) in dichloromethane was added solution of heterometallic triangle T_1 in DCM-MeCN (0.745 mM) at room temperature. The resulting solution was checked by ESI-MS within 5 min after the addition of Cu⁺.



Scheme S2. Metal exchange reaction.



Figure S1. ESI-MS of a solution of T_1 in DCM-MeCN after addition of $[Cu(MeCN)_4]PF_6$ (1.0 eq. with respect to Ag⁺ ions in T_1). Time after mixing until the ESI-MS was recorded: 5 min. Only signals of the homometallic triangle T_2 were detected.

Ligand Exchange Study

Ligand exchange study was carried out according to Scheme S3. To a solution of T_2 in dichloromethane (72 μ M), solid bisphenanthroline **2b** (1.0 eq. with regard to T_2) was added at room temperature. The resulting solution was checked by ESI-MS within 5 min after the addition of **2b**..



Scheme S3. Ligand exchange study.



Figure S2. ESI-MS of a solution of T_2 in DCM after addition of 2b (1.0 eq. with respect to T_2). Time after mixing until the ESI-MS was recorded: 5 min. Only signals of the mixture of the homometallic triangles T_2 and T_2' were detected. Experimental isotopic distributions (black lines) for the 3+ and 2+ charged species along with its calculated one (red lines) for T_2' are depicted.



Figure S4. ¹³C NMR spectrum of B

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Figure S10. ¹³C NMR spectrum of 7





Figure S13. Part of the ¹H NMR spectrum of complexes **7** and **1**. Due to steric effects of the duryl group, *ortho*-protons and *tert*-butyl protons of the aromatic substituent at the 2-position of the phenanthroline split into two different sets in **1**.



Figure S14. ¹H NMR spectrum of heterometallic triangle T₁



Figure S15. ¹H NMR spectrum of homometallic triangle T₂.



Figure S16. Absorption spectra of heterometallic triangle T_1 and homometallic triangle T_2



Figure S17. ESI-MS of homometallic triangle T_2 and the experimental isotopic distributions (black lines) for the 3+ and 2+ charged species along with their calculated ones (red lines).



Figure S18. DOSY NMR of homometallic triangle T₂



Figure S19. Differential pulse voltammetry (DPV) of homometallic triangle T_2 . The experiment was carried out in acetonitrile with 0.1 M nBu_4NPF_6 as electrolyte against a Ag wire as a quasi-reference electrode and 2,4,6-triphenylpyrylium tetrafluoroborate as internal standard (scan rate of 20 mVs⁻¹ and a pulse height of 2 mV).

References

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