Tris(triazolyl) Calix[6]arene-Based Zinc and Copper Funnel Complexes: Imidazole-like or Pyridine-like? A Comparative Study

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Experimental section

Safety Note. Caution! Although we have not encountered any problems, it is noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions. Identically, sodium azide and organic azides are potentially explosive and should be manipulated carefully.

General experimental methods. THF was dried over Na/benzophenone and distilled. Other solvents and chemicals were of reagent grade and were used without purification. Silica gel (230-400 mesh) was used for flash chromatography separations. NMR spectra were recorded on a Brucker ARX250 MHz spectrometer or an Advance 500 spectrometer. MS (ESI) analyses were obtained with a ThermoFinnigen LCQ Advantage spectrometer using methanol and dichloromethane as solvents. HRMS were performed at the Institut de Chimie des Substances Naturelles, France. IR spectra were obtained with a Perkin-Elmer Spectrum on FTIR spectrometer equipped with a MIRacleTM single reflection horizontal ATR unit (germanium crystal). EPR spectra were recorded using a Bruker Elexys spectrometer (X-band).

The electrochemical studies of the copper complexes were performed in a glovebox (Jacomex) (O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 1 ppm) with a home-designed 3-electrodes cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Ecochemie) potentiostat monitored by a computer. Anhydrous “extra-dry” dichloromethane (H<sub>2</sub>O < 30 ppm, Acros) and acetonitrile (99.9% BDH, VWR) were used as received and kept under N<sub>2</sub> in the glovebox. The supporting salt NBu<sub>4</sub>PF<sub>6</sub> was synthesized from NBu<sub>4</sub>OH (Fluka) and HPF<sub>6</sub> (Aldrich). It was then purified, dried under vacuum for 48 hours at 100° C, then kept under N<sub>2</sub> in the glovebox.
Calixarene 2:

Calixarene 1 (505 mg, 0.49 mmol) and Cs$_2$CO$_3$ (1.6 g, 4.9 mmol) are suspended in 10 mL of degassed and dry DMF under Ar. Propargyl bromide (500 μL, 4.5 mmol) is then added dropwise. The reaction mixture is heated at 150°C for 3 hours after which 5 more equiv of propargyl bromide are added. The reaction is heated for an additional 1h30. DMF is then evaporated (caution: volatiles have to be trapped in a liquid nitrogen trap) and the residue is taken in 20 mL of CH$_2$Cl$_2$ and 10 mL of water. The organic phase is extracted a second time with 10 mL of water and then dried over Na$_2$SO$_4$. After filtration and evaporation of the solvent, the residue is dissolved in 2 mL of CH$_2$Cl$_2$ and 20 mL of pentane are added. The solution is cooled at 4°C for a night. The solid is filtered off and the mother liquor is evaporated to dryness to afford a clear brown solid. The crude product is purified by chromatography on silica gel (CH$_2$Cl$_2$ as eluent) to afford calixarene 2 as a white solid (540 mg, yield = 97%).

$^1$H NMR (500 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 0.97 (t-Bu, s, 27H), 1.33 (t-Bu, s, 27H), 2.29 (C$_{sp}$-H, s, 3H), 2.56 (OCH$_3$, s, 9H), 3.97 (ArCH$_2$, s, 12H), 4.32 (OCH$_2$, s, 6H), 6.83 (H$_{Ar}$, s, 6H), 7.21 (H$_{Ar}$, s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 154.5, 151.9, 146.3, 145.8, 133.8, 133.0, 127.4, 124.7, 79.6, 74.9, 60.2, 60.1, 34.2, 34.1, 31.5, 31.2, 31.1.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz, 300K) of calixarene 2.

$^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 300K) of calixarene 2.
Synthesis of the ligands 3, 4 and 5. Calixarene 2 (50 mg, 0.43 mmol) and RN₃ (6 equiv) are dissolved in 1 mL of CH₂Cl₂. A solution of 1 mL of water containing CuSO₄·5H₂O (0.6 equiv) and sodium ascorbate (1.2 equiv) is added. The mixture is then vigorously stirred at room temperature during 48h. CH₂Cl₂ and a diluted aqueous solution of NH₄OH are used to separate the two phases. The organic layer is then washed with water and dried with Na₂SO₄. After filtration and evaporation of the solvent, the solid was triturated with pentane to afford the ligand (76 % yield for calixarene 3 and 87 % yield for calixarene 4). In the case of calixarene 5, the pure compound was obtained after chromatography on silica gel using CH₂Cl₂/CH₃OH (2%) as eluents (87 % yield).

Calixarene 3:

¹H NMR (500 MHz, CDCl₃, 300 K) δ (ppm): 0.83 (t-Bu, s, 27H), 1.39 (t-Bu, s, 27H), 2.20 (OCH₃, s, 9H), 2.35 (CH₃, s, 9H), 3.35 (ArCH₂, d, J = 15.2 Hz, 6H), 4.52 (ArCH₂, d, J = 15.2 Hz, 6H), 5.09 (NCH₂, s, 6H), 5.52 (OCH₂, s, 6H), 6.69 (HAr, s, 6H), 7.12 (Htol, d, J = 8.1 Hz, 6H), 7.18 (Htol, d, J = 8.1 Hz, 6H), 7.22 (HAr, s, 6H), 7.70 (Htri, s, 3H). ¹³C NMR (125 MHz, CDCl₃, 300 K) δ (ppm): 158.8, 152.9, 147.5, 147.2, 146.7, 139.9, 135.1, 134.4, 133.1, 131.2, 129.5, 129.4, 125.1, 124.2, 68.1, 61.5, 55.4, 35.6, 35.4, 33.0, 32.5, 31.2, 22.6. ES-MS (MeOH) m/z: 1570.7 (calcd for [M+H]+ 1571.0). High resolution ESMS: for C₁₀₂H₁₂₄N₉O₆ Calculated: 1570.9675 Found: 1570.9680
$^1$H NMR spectrum (CDCl$_3$, 500 MHz, 300K) of calixarene 3.

$^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 300K) of calixarene 3.
ESMS spectrum of calixarene 3.
IR spectrum of 3

Calixarene 4:

$^1$H NMR (250 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 0.82 (t-Bu, s, 27H), 1.37 (t-Bu, s, 27H), 2.25 (OCH$_3$, s, 9H), 3.42 (ArCH$_2$, d, $J = 15.2$ Hz, 6H), 3.86 (OCH$_3$, s, 9H), 4.60 (ArCH$_2$, d, $J = 15.2$ Hz, 6H), 5.16 (OCH$_2$, s, 6H), 6.70 (H$_{Ar}$, s, 6H), 7.00 (H$_{ArOMe}$, d, $J = 8.9$ Hz, 6H), 7.27 (H$_{Ar}$, s, 6H), 7.63 (H$_{ArOMe}$, d, $J = 8.9$ Hz, 6H), 8.10 (H$_{tria}$, s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 159.8, 154.4, 151.5, 146.2, 145.9, 145.4, 133.7, 132.9, 130.6, 128.0, 123.7, 122.3, 121.2, 114.7, 66.6, 60.2, 55.6, 34.2, 34.0, 31.6, 31.4, 31.2, 31.1, 29.8.

ES-MS (MeOH) $m/z$: 1576.7 (calcd for [M+H]$^+$ 1576.9). High resolution ESMS: for C$_{99}$H$_{138}$N$_9$O$_9$ Calculated: 1576.9053 Found: 1576.9038
$^1$H NMR spectrum (CDCl$_3$, 500 MHz, 300K) of calixarene 4.

$^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 300K) of calixarene 4.
ESMS spectrum of calixarene 4.
Calixarene 5:

$^1$H NMR (250 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 0.90 (t-Bu, s, 27H), 1.29 (t-Bu, s, 27H), 2.37 (OCH$_3$, s, 9H), 3.44 (ArCH$_2$, d, $J = 15.2$ Hz, 6H), 4.56 (ArCH$_2$, d, $J = 15.2$ Hz, 6H), 5.08 (OCH$_2$, s, 6H), 6.79 (H$_{Ar}$, s, 6H), 7.20 (H$_{Ar}$, s, 6H), 8.01 (H$_{ArNO_2}$, d, $J = 9.1$ Hz, 6H), 8.39 (H$_{tria}$, s, 3H), 8.40 (H$_{ArNO_2}$, d, $J = 9.1$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 155.6, 152.8, 148.6, 147.9, 147.8, 147.5, 142.6, 134.9, 134.2, 129.1, 126.9, 125.7, 122.6, 122.0, 67.6, 61.8, 35.6, 35.5, 33.0, 32.9, 32.7, 32.6, 31.4 ES-MS (MeOH) $m/z$: 1621.5 (calcd for [M+H]$^+$ 1621.8). **High resolution ESMS:** for C$_{96}$H$_{109}$N$_{12}$O$_{12}$ Calculated: 1621.8288 Found: 1621.8293

IR spectrum of 4
$^1$H NMR spectrum (CDCl$_3$, 500 MHz, 300K) of calixarene 5.

$^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 300K) of calixarene 5.
ESMS spectrum of calixarene 5.
Synthesis of the zinc complexes. The ligand (15 mg) is dissolved in THF (0.5 mL) and Zn(H₂O)₆(ClO₄) (1 equiv) is added. The solution is stirred at room temperature for one hour after which pentane (5 mL) is added. After centrifugation, the solid is dried under vacuum to quantitatively yield the zinc complex.

Complex [Zn₃(H₂O)](ClO₄)₂:

\(^1\)H NMR (500 MHz, CDCl₃, 300 K) \(\delta\) (ppm): 0.81 (t-Bu, s, 27H), 1.37 (t-Bu, s, 27H), 2.30 (CH₃, s, 9H), 3.17 (OCH₃, s, 9H), 3.35 (ArCH₂, d, \(J = 15.2\) Hz, 6H), 4.05 (ArCH₂, d, \(J = 15.2\) Hz, 6H), 4.89 (NCH₂, s, 6H), 5.59 (OCH₂, s, 6H), 6.54 (HAr, s, 6H), 7.13 (Htol, m, 12H), 7.27 (HAr, s, 6H), 8.31 (Htria, s, 3H). Elementary analysis for [Zn₃(H₂O)](ClO₄)₂.₃H₂O: Calcd: C 64.23%; H 6.92%; N 6.61% Found C 64.28%; H 6.88%; N 7.00%. 

IR spectrum of 5
IR Spectrum of [Zn.3.(H2O)](ClO4)2

Complex [Zn.4.(H2O)](ClO4)2:

$^1$H NMR (500 MHz, CDCl3, 300 K) $\delta$ (ppm): 0.78 ($t$-Bu, s, 27H), 1.39 ($t$-Bu, s, 27H), 3.21 (OCH3, s, 9H), 3.42 (ArCH2, d, $J = 15.2$ Hz, 6H), 3.86 (OCH3, s, 9H), 4.25 (ArCH2, bs, 6H), 5.37 (OCH2, s, 6H), 6.51 (HAr, s, 6H), 7.10 (HArOMe, bs, 6H), 7.29 (HAr, s, 6H), 7.80 (HArOMe, bs, 6H), 9.03 (Htria, s, 3H).
Preparation of the copper(I) complexes. The ligand (15 mg) and Cu(CH₃CN)₄PF₆ (1 equiv) are placed in a vial under argon. Dry and degassed THF (0.5 mL) is added. The solution is stirred at room temperature for one hour. During this period, a precipitate is formed. After centrifugation, the solid is dried under vacuum to yield the copper complex.

Complex [Cu₃(CO)]PF₆:

$^1$H NMR (250 MHz, CDCl₃, 300 K) δ (ppm): 0.73 ($t$-Bu, s, 27H), 1.37 ($t$-Bu, s, 27H), 2.33 (CH₃, s, 9H), 3.18 (OCH₃, s, 9H), 3.26 (ArCH₂, d, $J = 15.2$ Hz, 6H), 4.20 (ArCH₂, d, $J = 15.2$ Hz, 6H), 4.68 (NCH₂, s, 6H), 5.48 (OCH₂, s, 6H), 6.47 (H₆Ar, s, 6H), 7.12 (H₆tol, d, $J = 8.1$ Hz, 6H), 7.18 (H₆tol, d, $J = 8.1$ Hz, 6H), 7.25 (H₆Ar, s, 6H), 7.75 (H₆tri₅, s, 3H).
Complex \([\text{Cu.4.}(\text{CO})]\text{PF}_6\):  
\(^1\text{H NMR (250 MHz, CDCl}_3\text{, 300 K) }\) \(\delta\) (ppm): 0.78 (t-Bu, s, 27H), 1.44 (t-Bu, s, 27H), 3.28 (OCH\text{3}, s, 9H), 3.38 (ArCH\text{2}, d, J = 15.2 Hz, 6H), 3.88 (OCH\text{3}, s, 9H), 4.40 (ArCH\text{2}, d, J = 15.2 Hz, 6H), 5.09 (OCH\text{2}, s, 6H), 6.53 (HAr, s, 6H), 7.07 (HAr\text{OMe}, d, J = 8.9 Hz, 6H), 7.32 (HAr, s, 6H), 7.70 (HAr\text{OMe}, d, J = 8.9 Hz, 6H), 8.34 (H\text{tria}, s, 3H).

Complex \([\text{Cu.5.}(\text{CO})]\text{PF}_6\):  
\(^1\text{H NMR (250 MHz, CDCl}_3\text{, 300 K) }\) \(\delta\) (ppm): 0.74 (t-Bu, s, 27H), 1.40 (t-Bu, s, 27H), 3.20 (OCH\text{3}, s, 9H), 3.36 (ArCH\text{2}, d, J = 15.2 Hz, 6H), 4.30 (ArCH\text{2}, d, J = 15.2 Hz, 6H), 5.04 (OCH\text{2}, s, 6H), 6.50 (HAr, s, 6H), 7.30 (HAr, s, 6H), 8.00 (HAr\text{NO2}, d, J = 9.1 Hz, 6H), 8.37 (HAr\text{NO2}, d, J = 9.1 Hz, 6H), 8.65 (H\text{tria}, s, 3H).

Synthesis of the copper(II) complex \([\text{Cu.3.}(\text{H}_2\text{O})_2\text{]}(\text{ClO}_4)_2\): Ligand 3 (15 mg) is dissolved in THF (0.5 mL) and Cu(H\text{2O})\text{6}(\text{ClO}_4) (1 equiv) is added. The solution is stirred at room temperature for one hour after which pentane (5 mL) is added. After centrifugation, the solid is dried under vacuum to quantitatively yield the copper complex \([\text{Cu.3.}(\text{H}_2\text{O})_2\text{]}(\text{ClO}_4)_2\).

ES-MS (MeOH) m/z: 1632.8 (calcd for [M-2H\text{2O-2ClO}_4]^+ 1632.9). UV-vis: in CH\text{2Cl}_2/CH\text{3CN} (14:1 v/v) (300 K), \(\lambda_{\text{max}} = 655\text{ nm, } \varepsilon = 130\text{ L.mol}^{-1}.\text{cm}^{-1}\). EPR (100K): in CH\text{2Cl}_2: \(A_{\parallel} = 164\text{ G, } g_{\parallel} = 2.31, g_{\perp} = 2.07\), in CH\text{3CN} \(A_{\parallel} = 166\text{ G, } g_{\parallel} = 2.29, g_{\perp} = 2.07\).
**Figures SI.**

**Figure S1.** $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) spectra of complex [Zn.3](ClO$_4$)$_2$ in anhydrous CDCl$_3$ (bottom) and after addition of ca. 2 equiv of water (estimated with integration) (top).
Figure S2. $^1$H NMR (CDCl$_3$, 500 MHz) spectra of [Zn$_3$(ClO$_4$)$_2$] at 300 K (bottom) and 265K (top).

Figure S3. $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) spectra of complex [Zn$_4$(ClO$_4$)$_2$] (the C$_{3v}$ complex is marked with *).
Figure S4. $^1$H NMR (CDCl$_3$, 500 MHz) spectra of complex [Zn.4](ClO$_4$)$_2$ at 265 K.

Figure S5. $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) spectra of complex [Cu.3](PF$_6$) before (bottom) and after (top) addition of CH$_3$CN.
Figure S6. $^1$H NMR (CDCl$_3$, 500 MHz) spectra of complex [Cu.3](PF$_6$) after addition of CH$_3$CN at 300 K (bottom) and 260 K (top).
Figure S7. $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) spectra of complex [Cu.5](PF$_6$) before (bottom) and after (top) addition of CH$_3$CN.
Figure S8. UV-vis spectra $[\text{Cu(II).}(\text{3}.\text{H}_2\text{O})_2](\text{ClO}_4)_2 \ (8.0 \times 10^{-4} \text{ mmol})$ in 0.7 mL CH$_2$Cl$_2$ (blue) and after addition of 50μL CH$_3$CN (red).

Figure S9. EPR spectra of $[\text{Cu(II).}(\text{3}.\text{H}_2\text{O})_2](\text{ClO}_4)_2$ in CH$_2$Cl$_2$ (blue) and in CH$_3$CN (red) at 100 K.
Electrochemical data.

- Addition of CO

**Figure S10.** Cyclic voltammogram ($v = 0.1 \text{ V.s}^{-1}$) at a vitreous carbon electrode of [Cu(I)4]PF6 (1 mM) in CH2Cl2 + NBut4PF6 0.1 M a) under Ar (plain line) and b) under CO (dashed line).

**Figure S11.** Cyclic voltammogram ($v = 0.1 \text{ V.s}^{-1}$) at a vitreous carbon electrode of [Cu(I)5]PF6 (1 mM) in CH2Cl2 + NBut4PF6 0.1 M a) under Ar (plain line) and b) under CO (dashed line).
Figure S12. Cyclic voltammogram ($v = 0.1 \text{ V.s}^{-1}$) at a vitreous carbon electrode of $[\text{Cu(I}.(\text{Imme}_3)]PF_6$ (1 mM) in CH$_2$Cl$_2$ + NBu$_4$PF$_6$ 0.1 M a) under Ar (plain line) and b) under CO (dashed line).

Figure S13. Cyclic voltammogram ($v = 0.1 \text{ V.s}^{-1}$) at a vitreous carbon electrode of $[\text{Cu(I}.(\text{Pic}_3)]PF_6$ (1 mM) in CH$_2$Cl$_2$ + NBu$_4$PF$_6$ 0.1 M a) under Ar (plain line) and b) under CO (dashed line).
- Addition of CH$_3$CN

**Figure S14.** Cyclic voltammograms ($v = 0.1$ V.s$^{-1}$) at a vitreous carbon electrode in CH$_2$Cl$_2$ + NBu$_4$PF$_6$ 0.1 M of [Cu(I).4]PF$_6$ (1 mM) A) before (a) and after (b) addition of the complex; B) before (a) and after addition of 75 equiv CH$_3$CN. [Intermediate curves: 15; 30 equiv]