A Novel $M_8L_6$ Cubic Cage That Binds Tetrapyridyl Porphyrins: Cage and Solvent Effects in Cobalt-Porphyrin-Catalyzed Cyclopropanation Reactions

Valentinos Mouarrawis, Eduard O. Bobylev, Bas de Bruin,* and Joost N. H. Reek*
General considerations

Chemicals and solvents

All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen using standard Schlenk and vacuum line techniques. Unless noted otherwise, all reagents were of commercial grade and used without further purification. Dry DMF was kept under N₂ over molecular sieves. Styrene was filtered over basic alumina prior to use.

NMR spectroscopy

¹H NMR spectra were recorded on a Bruker AMX 400, Varian Mercury 300, Bruker DRX 500, Bruker DRX 300 or spectrometer, and they are referenced to the solvent residual signal (5.32 ppm for CD₂Cl₂, 7.32 ppm for CDCl₃, 8.03 ppm for DMF-d₇, 1.32 ppm for CD₃CN and 2.08 ppm for toluene-d₈). The temperature and the magnetic gradient were calibrated prior the measurement for 2D ¹H-DOSY NMR.

Mass spectrometry

High-resolution mass spectra were recorded on a HR-ToF Bruker Daltonik Gmbh Impact II, as ESI-ToF MS capable of a resolution of at least 4000 FWHM, coupled to a Bruker cryospray unit. The detection was done in positive-ion mode and the source voltage was between 4 and 6 kV. The flow rate was 18 μL/hr. The machine was calibrated prior to every measurement via direct infusion of a TFA-Na solution.

DFT calculations

DFT geometry optimizations were performed on full structures without simplifications using TURBOMOLE 7.3[¹] coupled to the PQS Baker optimizer[²] via the BOpt package.[³] The calculations were performed at the BP86[⁴] /def2-TZVP[⁵] level of theory on an m4 grid, using Grimme’s version 3 (disp3, “zero damping”) dispersion corrections.[⁶] Energies were in Hartree and converted to kcal mol⁻¹ by multiplication with 627.509.

GFN2-XTB calculations

For geometry optimizations of cages and caged-catalysts, Grimme’s GFN2-xTB (Geometry, Frequency, Noncovalent, extended tight, binding) software was used.[⁷] Figures and images of the geometry-optimized structures were generated with UCSF Chimera software.

EPR spectroscopy

EPR spectra were recorded on a Bruker EMX X-band spectrometer equipped with an ER 4112HV-CF100 helium cryostat.
Synthesis and characterization of subcomponent Zn-L

Figure S1. Synthesis of the building block Zn-L.

A1 was synthesized according to a literature procedure.\cite{8}

A2: To a three-neck round bottom flask, A1 (2.9 g, 3.12 mmol), potassium carbonate (9.91 g, 72 mmol), and (4-aminophenyl)boronic (4.33 g, 25 mmol) acid were dissolved in 15:1 mixture of DMF and water (960 mL in total), and the resulting suspension was degassed by bubbling N\textsubscript{2} for 25 min. Then Pd(dppf)Cl\textsubscript{2} (0.23 mg, 0.31 mmol) was added and the mixture was stirred at 70 °C for 48 h, followed by cooling to room temperature. The reaction mixture was filtered through a Celite pad using a P\textsubscript{4} glass filter, and the solids were collected by washing the filter with DMF (200 mL). The purple filtrate was precipitated in water, filtered off, and washed thoroughly with water and methanol to yield A2, as a dark red solid (2.75 g, 90%). \textsuperscript{1}H-NMR (400 MHz, 298 K, DMSO-d\textsubscript{6}): $\delta$ = 8.78 (s, 8H), 7.98 (d, $J$ = 7.5 Hz, 8H), 7.80 (d, $J$ = 7.6 Hz, 8H), 7.60 (d, $J$ = 8.0 Hz, 8H), 6.78 (d, $J$ = 7.9 Hz, 8H), 5.35 (s, 8H), -2.84 (s, 2H); \textsuperscript{13}C-NMR (101 MHz, 298 K, DMSO-d\textsubscript{6}): $\delta$=149.20, 140.43, 138.86, 135.26, 127.92, 127.12, 124.12, 120.36, 114.95; HRMS (ESI): m/z calcd for C\textsubscript{68}H\textsubscript{50}N\textsubscript{8}: 979.4237 [M+H]\textsuperscript{+}, found: 979.4203.
Figure S2. $^1$H NMR (400 MHz, 298 K, DMSO-$d_6$) of subcomponent A2.

Figure S3. $^{13}$C NMR spectrum (101 MHz, 298 K, DMSO-$d_6$) of subcomponent A2.
**A3: Zn-L** was synthesized via a modified literature procedure.\(^5\) **A2** (1 g, 1.02 mmol) was dissolved in a 3:1 mixture of CHCl\(_3\) and DMF (450 mL in total). A solution of zinc(II) acetate dihydrate (1.35 g, 6.12 mmol) in methanol (100 mL) was then added. The resulting solution was heated at reflux for 24 h, followed by cooling to room temperature. The reaction mixture was then filtered through a Celite pad using a P\(_4\) glass filter, and the solids were collected by washing the filter with DMF (200 mL). The green filtrate was precipitated in water. The solids were collected by filtration, and washed thoroughly with DCM and diethyl ether to yield **A3**, as a dark blue solid (1 g, 94%).

**\(^1\)HNMR** (500 MHz, 298 K, DMSO-\(d_6\)): \(\delta = 8.88\) (s, 8H), 8.16 (d, \(J = 7.4\) Hz, 8H), 7.94 (d, \(J = 7.8\) Hz, 8H), 7.69 (d, \(J = 8.0\) Hz, 8H), 6.80 (d, \(J = 7.2\) Hz, 8H), 5.34 (s, 8H); **\(^{13}\)C-NMR** (101 MHz, 298 K, DMSO-\(d_6\)) \(\delta = 149.84, 149.07, 140.54, 139.97, 135.27, 132.11, 127.93, 127.46, 123.92, 120.73, 114.97\);

HRMS (ESI): \(m/\text{z} \) calcd for C\(_{68}\)H\(_{48}\)N\(_8\)Zn: 1041.3372 \([\text{M}+\text{H}]^+\), found: 1041.3325.

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**Figure S4.** \(^1\)H NMR (500 MHz, 298 K, DMSO-\(d_6\)) of subcomponent **Zn-L**.
Figure S5. $^{13}$C NMR spectrum (126 MHz, 298 K, DMSO-d$_6$) of subcomponent Zn-L.

Synthesis and characterization of subcomponent 1

![Synthesis and characterization of subcomponent 1](image)

1: 5-hydroxypicolinaldehyde (0.8 g, 6.5 mmol), cesium carbonate (2.18 g, 6.5 mmol), and dry DMF (190 mL) were added to a Schlenk flask. The mixture was stirred at 100 °C for 1.5 h under N$_2$. 1-bromoicosane (2.35 g, 6.5 mmol) was added and the reaction mixture was heated at 100°C for 18 h, followed by cooling down to room temperature. The brown suspension was filtered and the DMF was removed under reduced pressure. The crude product was purified by flash column chromatography (SiO$_2$ hexane/DCM (100:0 to 100:50, v/v) which afforded the desired product 1 (2.23 g, 85%) as a white solid. $^1$H-NMR (400 MHz, 298 K, CDCl$_3$): δ=10.01 (s, 1H), 8.44 (d, J = 2.8 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.34 – 7.28 (m, 1H), 4.11 (t, J = 6.5 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.27 (s, 34H), 0.89 (t, J = 6.7 Hz, 3H); $^{13}$C-NMR (101 MHz, 298 K, CDCl$_3$) δ=192.05, 158.64, 146.10, 138.82, 123.38, 120.41, 68.92, 31.93, 29.71, 29.67, 29.65, 29.58, 29.53, 29.37, 29.30, 28.96, 25.87, 22.70, 14.12, 1.03; HRMS (ESI): m/z calcd for C$_{26}$H$_{45}$NO$_2$: 404.3529 [M+H]$^+$, found: 404.3540.
**Figure S6.** $^1$H NMR (500 MHz, 298 K, CDCl$_3$) of subcomponent 1.

**Figure S7.** $^{13}$C NMR spectrum (101 MHz, 298 K, CDCl$_3$) of subcomponent 1.
Synthesis and characterization of Fe₈(Zn-L∙1)₆.

Fe₈(Zn-L∙1)₆: Zn-L (0.110 g, 0.106 mmol) together with 5-(icosyloxy)picolinaldehyde (0.170 g, 0.422 mmol), iron(II) triflate (0.05 g, 0.141 mmol) and dry DMF (8.5 mL) were added to a Schlenk flask. The mixture was degassed by three cycles of freeze-pump-thaw, and heated at 70 °C for 18 h. The reaction mixture was cooled down to room temperature and stirred for 1 hour. The purple-red solution was passed through a short pad of celite and precipitated in diethyl ether. The precipitates were collected by filtration and washed with diethyl ether (10 mL) and CHCl₃(10 mL). The solids were washed with THF and the solvent was removed under reduced pressure afford Fe₈(Zn-L∙1)₆ as dark purple solid. (0.257 g, 80 %). ¹H-NMR (300 MHz, 298 K, Acetone-d₆) δ=9.32 (s, 24H), 8.93 – 8.87 (d, J = 6.0 Hz 24H), 8.86 – 8.76 (s, 48H), 8.47 – 7.88 (m, 168H), 7.61 – 7.43 (s, 24H), 5.93 (s, 48H), 4.33 (s, 48H), 1.86 (s, 62H), 1.45 – 1.25 (m, 802H), 0.86 (t, J = 6.0 Hz, 72H); ¹³C-NMR (126 MHz, 298 K, Acetone-d₆) δ=174.18, 146.6, 135.8, 131.8, 131.3, 128.52, 125.5, 123.5, 122.9, 70.6, 30.13, 29.36, 14.16.

Figure S8. ¹H NMR (300 MHz, 298 K, acetone-d₆) of Fe₈(Zn-L∙1)₆.
Figure S9. $^1$H-$^1$H COSY spectrum (500 MHz, 298 K, acetone-$d_6$) for Fe$_8$(Zn-L·1)$_6$.

Figure S10. $^1$H DOSY NMR spectrum (500 MHz, 298 K, acetone-$d_6$) of Fe$_8$(Zn-L·1)$_6$. 
Figure S11. $^1$H-$^{13}$C HSQC spectrum (500 MHz, 298 K, acetone-d$_6$) of Fe$_8$(Zn-L·1)$_6$.

ESI-MS characterization.

Figure S12. Full ESI-MS spectrum of Fe$_8$(Zn-L·1)$_6$ in acetone-d$_6$. 
Figure S13. ESI-MS peak for [(Fe₈L₆)(OTF)₉]⁷⁺ in acetone-d₆, m/z 2471.1516; calculated m/z 2471.1534.

Figure S14. ESI-MS peak for [(Fe₈L₆)(OTF)₈]⁸⁺ in acetone-d₆, m/z 2143.6330; calculated m/z 2143.6406.
Figure S15. ESI-MS peak for [(Fe₈L₆)(OTF)]²⁺ in acetone-d₆, m/z 1888.9055; calculated m/z 1888.9081.

Figure S16. ESI-MS peak for [(Fe₈L₆)(OTF)]¹⁰⁺ in acetone-d₆, m/z 1685.1187; calculated m/z 1685.1212.
Figure S17. ESI-MS peak for \([(\text{Fe}_8\text{L}_6)(\text{OTF})_5]^{11+}\) in acetone-\(d_6\), m/z 1518.3858; calculated m/z 1518.3878.

Figure S18. ESI-MS peak for \([(\text{Fe}_8\text{L}_6)(\text{OTF})_4]^{12+}\) in acetone-\(d_6\), m/z 1379.4420; calculated m/z 1379.4422.
Figure S19. ESI-MS peak for [(Fe₈L₆)(OTF)]¹³⁺ in acetone-d₆, m/z 1261.8748; calculated m/z 1261.8737.

Figure S20. ESI-MS peak for [(Fe₈L₆)(OTF)]¹⁴⁺ in acetone-d₆, m/z 1161.1038; calculated m/z 1161.1004.
Figure S21. ESI-MS peak for [(Fe₈L₆)(OTF)]⁺ in acetone-d₆, m/z 1073.6999; calculated m/z 1073.6962.

**Synthesis and characterization of Zn-G@Fe₈(Zn-L-1)₆.**

The encapsulation of Zn-G in the preformed cage Fe₈(Zn-L-1)₆ was unsuccessful, as MS spectrometry and ¹H-NMR spectroscopy only showed empty cage. The one-pot reaction of Zn-L, 1, iron (II) triflate and Zn-G led to the selective formation of the host-guest complex (Zn-G@Fe₈(Zn-L-1)₆).

**Zn-G@Fe₈(Zn-L-1)₆:** To an oven-dried Schleck flask under nitrogen atmosphere were added Zn-G (0.012 g, 0.018 mmol), Zn-L (0.110 g, 0.106 mmol), 1 (0.170 g, 0.422 mmol), iron (II) triflate (0.05 g, 0.141 mmol) and dry DMF (8.5 mL). The mixture was degassed by three cycles of freeze-pump-thaw, and heated at 70 °C for 18 h. The reaction mixture was cooled down to room temperature and stirred for 1 hour. The purple-red solution was passed through a short pad of celite and precipitated in diethyl ether. The precipitates were collected by filtration and washed with diethyl ether (10 mL), CHCl₃ (10 mL). The remaining solids on the filter were collected by washing with DCM. The solvent was removed under reduced pressure to afford Zn-G@Fe₈(Zn-L-1)₆ as a dark purple solid (0.276 g, 83 %). **¹H-NMR** NMR (400 MHz, Acetone-d₆) δ=9.34 (s, 24H), 8.98 (m, 52H), 8.62 (s, 12H), 8.40 – 7.91 (m, 176H), 7.51 (s, 24H), 6.38 (s, 8H), 5.85 (s, 48H), 5.59 (s.8H), 4.31 (s, 48H), 2.56 (s, 8H), 1.84 (s, 48H), 1.29 (s, 816H), 0.87 – 0.83 (m, 72H).
**Figure S22.** $^1$H NMR (400 MHz, 298 K, acetone-$d_6$) of Zn-G@Fe₈(Zn-L·1)$_6$.

**Figure S23.** $^1$H-$^1$H COSY (400 MHz, 298 K, acetone-$d_6$) of Zn-G@Fe₈(Zn-L·1)$_6$. 
Figure S24. $^1$H DOSY NMR spectrum (500 MHz, 298 K, acetone-$d_6$) of Zn-G@Fe$_8$(Zn-L·1)$_6$. Guest peaks are indicated with a circle.

Figure S25. $^{19}$F NMR (282 MHz, acetone-$d_6$) of Zn-G@Fe$_8$(Zn-L·1)$_6$. 
ESI-MS characterization.

Figure S26. Full ESI-MS spectrum of Zn-G@Fe₈(Zn-L·1)₆ in acetone-d₆.

Figure S27. ESI-MS peak for [(Zn-G@Fe₈L₆)(OTF)₆]⁺ in acetone-d₆, m/z 2228.8967; calculated m/z 2228.9083.
**Figure S28.** ESI-MS peak for \([\text{Zn-G@Fe}_8\text{L}_6](\text{OTF})_2]^{2+}\) in acetone-\(d_6\), m/z 1964.6964; calculated m/z 1964.7016.

**Figure S29.** ESI-MS peak for \([\text{Zn-G@Fe}_8\text{L}_6](\text{OTF})_6]^{10+}\) in acetone-\(d_6\), m/z 1753.3299; calculated m/z 1753.3353.
**Figure S30.** ESI-MS peak for [(Zn-G@Fe₈L₆)(OTF)₅]¹⁺ in acetone-d₆, m/z 1580.3978; calculated m/z 1580.4008.

**Figure S31.** ESI-MS peak for [(Zn-G@Fe₈L₆)(OTF)₄]²⁺ in acetone-d₆, m/z 1436.2848; calculated m/z 1436.2881.
Figure S32. ESI-MS peak for [(Zn-G@Fe₈L₆)(OTF)₃]₁³⁺ in acetone-d₆, m/z 1314.3481; calculated m/z 1314.3463.

Figure S33. ESI-MS peak for [(Zn-G@Fe₈L₆)(OTF)₂]₁⁴⁺ in acetone-d₆, m/z 1209.7527; calculated m/z 1209.7533.
Figure S34. ESI-MS peak for $[(\text{Zn-G@Fe}_8\text{L}_6)(\text{OTF})_1]^{15+}$ in acetone-d$_6$, m/z 1119.1763; calculated m/z 1119.1727.

Figure S35. ESI-MS peak for $[(\text{Zn-G@Fe}_8\text{L}_6)(\text{OTF})_0]^{16+}$ in acetone-d$_6$, m/z 1039.9167; calculated m/z 1039.9149.
Synthesis and characterization of Co-G@Fe₈(Zn-L·1)₆.

Co-G@Fe₈(Zn-L·1)₆: To an oven-dried Schleck flask under nitrogen atmosphere were added Co-G (0.014 g, 0.02 mmol), Zn-L (0.130 g, 0.125 mmol), 1 (0.202 g, 0.5 mmol), iron (II) triflate (0.059 g, 0.17 mmol) and dry DMF (12 mL). The mixture was degassed by three cycles of freeze-pump-thaw, and heated at 70 °C for 18 h. The reaction mixture was cooled down to room temperature and stirred for 1 h. The purple-red solution was passed through a short pad of celite and precipitated in diethyl ether. The precipitates were collected by filtration and washed with diethyl ether (10 mL), and CHCl₃ (10 mL). The remaining solid was dissolved in DCM. The solvent was removed under reduced pressure to afford Co-G@Fe₈(Zn-L·1)₆ as a dark purple solid. (0.341 g, 86 %).

ESI-MS characterization.

Figure S36. Full ESI-MS spectrum of Co-G@Fe₈(Zn-L·1)₆ in acetone-d₆.
Figure S37. ESI-MS peak for \([\text{Co-G@Fe}_8\text{L}_6]\text{(OTF)}_8\)^{10+} in acetone-d$_6$, m/z 2228.1667; calculated m/z 2228.1589.

Figure S38. ESI-MS peak for \([\text{Co-G@Fe}_8\text{L}_6]\text{(OTF)}_7\)^{11+} in acetone-d$_6$, m/z 1964.0402; calculated m/z 1964.0355.
Figure S39. ESI-MS peak for \([\text{Co-G@Fe}_8\text{L}_6\text{(OTF)}_6]^{10+}\) in acetone-d$_6$, m/z 1752.6373; calculated m/z 1752.6358.

Figure S40. ESI-MS peak for \([\text{Co-G@Fe}_8\text{L}_6\text{(OTF)}_6]^{11+}\) in acetone-d$_6$, m/z 1579.7648; calculated m/z 1579.7646.
Figure S41. ESI-MS peak for [(Co-G@Fe₈L₆)(OTF)₄]^{12+} in acetone-d₆, m/z 1435.7042; calculated m/z 1435.7044.

Figure S42. ESI-MS peak for [(Co-G@Fe₈L₆)(OTF)₃]^{13+} in acetone-d₆, m/z 1313.8089; calculated m/z 1313.8081.
**Figure S43.** ESI-MS peak for [(Co-G@Fe₈L₆)(OTF)]^{14+} in acetone-d₆, m/z 1209.3271; calculated m/z 1209.3251.

**Figure S44.** ESI-MS peak for [(Co-G@Fe₈L₆)(OTF)]^{15+} in acetone-d₆, m/z 1118.7708; calculated m/z 1118.7730.
Figure S45. ESI-MS peak for [(Co-G@Fe₈L₆)(OTF)₅]^{16+} in acetone-d₆, m/z 1039.6008; calculated m/z 1039.6031.
EPR spectroscopy

Co-catalyst was dissolved in a toluene:DMF mixture (100:1) in a N₂-filled glovebox and the solution was directly transferred to an EPR tube. The sample was frozen in liquid N₂ before recording the X-band EPR spectra on a Bruker EMX spectrometer at 20 K. The EPR spectrum of Co-G@Fe₈(Zn-L∙1)_₆ is similar to a previously reported S= ½ (por)Co system encapsulated in a different cage and it shows a somewhat larger g-anisotropy and more defined hyperfine structure (Figure S46, top) than the free Co-G (Figure S46, bottom).[10]

Figure S46. EPR spectrum of Co-G@Fe₈(Zn-L∙1)_₆ (top) and Co-G (bottom) recorded in frozen toluene:DMF mixture (100:1) at 20 K (microwave frequency: 9.357052 GHz; microwave power 0.63 mW; modulation amplitude: 4 Gauss).
Co-G@Fe₈(Zn-L·1)₆-carbene EPR characterization.

Co-G@Fe₈(Zn-L·1)₆ was dissolved in toluene:DMF mixture (100:1) under N₂ at −20 °C. After that ethyl diazoacetate (50 equiv.) was added and the mixture was directly transferred to an EPR tube. The sample was kept frozen in liquid N₂ before recording the X-band EPR spectra on a Bruker EMX spectrometer at 20 K. EPR was recorded at different times after the addition of EDA, shortly warming-up the sample to thaw the frozen solution before refreezing the sample again.

The spectra (Figures S47) show disappearance of Co-G@Fe₈(Zn-L·1)₆ in time (black arrows), appearance and disappearance of signals characteristic for a carbene radicals species formed as a short-lived intermediate (red arrows, up and down) and appearance of a signal characteristic for an organic radical (single red arrows). The latter presumably stems from an organic radical trapped in the cage formed by HAT from solvent or EDA to the carbene radical. After a longer period the latter signal also starts to decrease in time.
Figure S47. Top: Reaction as followed by EPR spectroscopy. Middle: EPR spectrum of Co-G@Fe₈(Zn-L·1)₆ after adding ethyl diazoacetate (50 equiv.) in frozen toluene:DMF mixture (100:1) at 20 K (microwave frequency: 9.357052 GHz; microwave power 0.63 mW; modulation amplitude: 4 Gauss). Black arrows represent decrease of the signals of Co-G@Fe₈(Zn-L·1)₆. Red arrows up+down show formation and disappearance of the short-lived carbene radical intermediate. Single red arrows show appearance of a free organic radical, presumably trapped inside the cage. Bottom: Zoom of the organic radical signal.

Density Functional Theory Calculations

Absolute and relative energies for all DFT optimized structures were obtained using the BP86 functional. Table S1 shows the relevant absolute energies for all compounds. Table S2 shows the relative Gibbs free energies for all relevant intermediates.

Table S1. Calculated <s2> and energies (in Hartree) for all relevant compounds.

<table>
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<tr>
<th>Compound + spin state</th>
<th>&lt;s2&gt;</th>
<th>SCF</th>
<th>ZPE Correction</th>
<th>Enthalpy Correction 298K</th>
<th>Entropy Correction 298K</th>
<th>ΔG°298K</th>
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<tr>
<td><strong>EDA Adducts A</strong></td>
<td></td>
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<tr>
<td>CoTPP (doublet)</td>
<td>0.76330</td>
<td>-3712.77518</td>
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<td>0.73233</td>
<td>0.59934</td>
<td>-3712.17584</td>
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<td>CoTPP-O-DMF (doublet)</td>
<td>0.7669</td>
<td>-3961.42854</td>
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<td>CoTPP-N-DMF (doublet)</td>
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<tr>
<td>CoTPP-H₂O (doublet)</td>
<td>0.7652</td>
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<td>0.75902</td>
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<td><strong>Carbene radical B</strong></td>
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<td>0.67302</td>
<td>0.71967</td>
<td>0.58941</td>
<td>-3602.59710</td>
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Calculations were performed at the BP86/def2-TZVP/disp3/m4-grid level of theory. Conversion from Hartree to kcal mol\(^{-1}\) can be achieved by multiplication with 627.509.

**Table S2.** Absolute and relative Gibbs free energies for EDA adduct \(A\), Carbene radical \(B\) and \(C\), and the respective transition states. The relative energies are calculated with respect to CoTPP-EDA adduct \(A\). The activation energies of \(\text{TS1}\) and \(\text{TS2}\) for every intermediate are shown in parenthesis.

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>Gibbs free energy of formation at 298K (kcal mol(^{-1}))</th>
<th>(\Delta G^{\circ, 298K}) (kcal mol(^{-1}))</th>
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<tr>
<td><strong>EDA adduct (A)</strong></td>
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<tr>
<td>CoTPP</td>
<td>-2329423.749</td>
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<td>CoTPP-H(_2)O</td>
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<tr>
<td><strong>Carbene radical (B)</strong></td>
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<td>CoTPP</td>
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<td><strong>Transition state 1 ((\text{TS1}))</strong></td>
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<tr>
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<tr>
<td>CoTPP-H(_2)O</td>
<td>-2377392.012</td>
<td>13.89 (14.71)</td>
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</table>
Table S3. Graphical representation of the geometry optimized structures of EDA adducts A (CoTPP, CoTPP-O-DMF, CoTPP-N-DMF, and CoTPP-H$_2$O) showing the interaction of A with DMF and H$_2$O.
Solubility study of Zn-G@Fe₈(Zn-L∙1)₆ in different solvents

The solubility study was done by dissolving an equal amount of Zn-G@Fe₈(Zn-L∙1)₆ in 1 mL of deuterated solvent. Although, the ¹H-NMR in THF, DCM and toluene is very broad, the cage is completely soluble in all of the solvents, and the broadness of ¹H-NMR increases as the polarity of the solvent decreases (Figure S48). In toluene, the aromatic region is almost flat, indicating a high degree of aggregation whereas in a 100:1 mixture of toluene:DMF there is a lower degree of aggregation (Figure S49), as the ¹H NMR spectrum is less broad. This suggests that DMF disrupts the cage aggregates, as evidenced by the relatively sharper ¹H NMR spectrum in pure DMF (Figure S49).

Figure S48. ¹H-NMR of Zn-G@Fe₈(Zn-L∙1)₆ in different solvents.

Figure S49: ¹H-NMR of Zn-G@Fe₈(Zn-L∙1)₆ in toluene (top), 100:1 mixture of toluene DMF (middle) and pure DMF (bottom).
Stability of the Zn-G@Fe₈(Zn-L·1)₆ under aerobic conditions

Zn-G@Fe₈(Zn-L·1)₆ (15 mg) was dissolved in 1 mL of acetone-d₆ and left at room temperature in the presence of oxygen for 2 weeks. Based on ¹H NMR the cage was intact after 2 weeks, showing that the cage (Zn-G@Fe₈(Zn-L·1)₆) is stable under aerobic conditions.

Figure S50. ¹H-NMR of Zn-G@Fe₈(Zn-L·1)₆ the first day (top) and ¹H-NMR of Zn-G@Fe₈(Zn-L·1)₆ after 15 days (bottom).
UV-Vis in different solvents

Spectra were measured in double-beam mode using only the (front) analyte beam to record spectra, with the used solvent in the reference path. A background spectrum of the solvent was recorded prior to each experiment. $\text{Zn-G@Fe}_8(\text{Zn-L·1})_6$ and $\text{Zn-L}$ were measured at 1 μM concentrations in the desired solvent. $\text{Zn-L}$ is only soluble in DMF (green solution). UV-vis shows that $\text{Zn-G@Fe}_8(\text{Zn-L·1})_6$ is soluble and stable in acetone, THF, DCM, toluene and DMF.

Figure S51. The stock solutions of $\text{Zn-G@Fe}_8(\text{Zn-L·1})_6$ in different solvents and $\text{Zn-L}$ in DMF (top). UV-vis spectrum of $\text{Zn-G@Fe}_8(\text{Zn-L·1})_6$ in different solvents (red line) and of $\text{Zn-L}$ in DMF (green line).
Figure S52. Enlarged initial part of the reaction profile for the formation of P1 using [Co(TPP)], monitored by $^1$H NMR (top) and the corresponding initial TOF (TOF$_{ini}$) estimation (bottom).
Figure S53. Reaction profile for the formation of P1 using Co-G@Fe₆(Zn-L·1)₆, monitored by ¹H NMR (top) and the corresponding initial TOF (TOFₗⁱ) estimation (bottom).
Procedure for the catalytic cyclopropanation experiments

To an oven-dried Schlenk flask were added the cobalt-catalyst (0.0025 eq.), deuterated solvent (1.5 mL/mmol S1), and S1 (2.0 eq.) under nitrogen. The mixture was degassed for 10 minutes by bubbling nitrogen and then stirred for 30 min, after which degassed S2 (1.0 eq.) was added. The reaction mixture was stirred for 30 h at 40 °C, followed by cooling to room temperature. The yield and the conversion were determined by directly measuring $^1$H-NMR of the reaction mixture in the presence of 1,3,5-trimethoxybenzene as an internal standard. $^1$H-NMR data of the obtained products were in agreement with published data.$^{[11]}$
Substrate scope for the catalytic cyclopropanation reaction

Table S4. Substrate scope of alkenes for the $[\text{Co(TPP)}]$- and $\text{Co-G@Fe}_8(\text{Zn-L-1})_6$-catalyzed cyclopropanation reaction with ethyl diazoacetate.$^{[a],[b]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>alkene</th>
<th>Conversion [%]</th>
<th>Cyclopropane [%]</th>
<th>P2 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[\text{Co(TPP)}]$</td>
<td></td>
<td>74</td>
<td>74</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Co-G@Fe}_8(\text{Zn-L-1})_6$</td>
<td></td>
<td>97</td>
<td>87</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>$[\text{Co(TPP)}]$</td>
<td></td>
<td>70</td>
<td>69</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Co-G@Fe}_8(\text{Zn-L-1})_6$</td>
<td></td>
<td>92</td>
<td>80</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>$[\text{Co(TPP)}]$</td>
<td></td>
<td>65</td>
<td>64</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Co-G@Fe}_8(\text{Zn-L-1})_6$</td>
<td></td>
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<td>76</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>$[\text{Co(TPP)}]$</td>
<td></td>
<td>68</td>
<td>68</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>$\text{Co-G@Fe}_8(\text{Zn-L-1})_6$</td>
<td></td>
<td>90</td>
<td>79</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>$[\text{Co(TPP)}]$</td>
<td></td>
<td>7</td>
<td>5</td>
<td>2</td>
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<tr>
<td>10</td>
<td>$\text{Co-G@Fe}_8(\text{Zn-L-1})_6$</td>
<td></td>
<td>13</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

$^{[a]}$ Reaction conditions: Catalyst (0.25 mol %) with respect to $\text{S2}$, alkene ($\text{S3-7}$, 0.16 mmol), ethyl diazoacetate ($\text{S2}$, 0.08 mmol) in DMF-d$_7$ (1.5 mL/$\text{S3-7}$ mmol), 30 h under N$_2$ atmosphere. $^{[b]}$ Conversion of $\text{S2}$ and yields with respect to $\text{S2}$ were determined by $^1$H NMR spectroscopy, using 1,3,5-trimethoxybenzene as internal standard.
Synthesis of P3

\[
\text{S3} + \text{S2} \xrightarrow{\text{Co-catalyst (0.25 mol %)}} \text{P3} + \text{P4}
\]

Solvent, 40 °C 30 h

The cobalt-catalyst (0.0025 eq.), DMF-d\text{7} (1.5 mL/S3 mmol), S3 (2 eq.) and S2 (1 eq.) were handled according to the generalized procedure described above for the catalytic cyclopropanation experiments to give P3 and P2. Data for cyclopropane P3 were in agreement with published data.\[^{12}\]

Synthesis of P4

\[
\text{S4} + \text{S2} \xrightarrow{\text{Co-catalyst (0.25 mol %)}} \text{P4} + \text{P2}
\]

Solvent, 40 °C 30 h

The cobalt-catalyst (0.0025 eq.), DMF-d\text{7} (1.5 mL/S4 mmol), S4 (2 eq.) and S2 (1 eq.) were handled according to the generalized procedure described above for the catalytic cyclopropanation experiments to give P4 and P2. Data for cyclopropane P4 were in agreement with published data.\[^{12}\]
Synthesis of P5

The cobalt-catalyst (0.0025 eq.), DMF-d₇ (1.5 mL/S₅ mmol), S₅ (2 eq.) and S₂ (1 eq.) were handled according to the generalized procedure described above for the catalytic cyclopropanation experiments to give P₅ and P₂. Data for cyclopropane P₅ were in agreement with published data.¹³

Synthesis of P6

The cobalt-catalyst (0.0025 eq.), DMF-d₇ (1.5 mL/S₆ mmol), S₆ (2 eq.) and S₂ (1 eq.) were handled according to the generalized procedure described above for the catalytic cyclopropanation experiments to give P₆ and P₂. Data for cyclopropane P₆ were in agreement with published data.¹⁴
Synthesis of P7

The cobalt-catalyst (0.0025 eq.), DMF-d7 (1.5 mL/S7 mmol), S7 (2 eq.) and S2 (1 eq.) were handled according to the generalized procedure described above for the catalytic cyclopropanation experiments to give P7 and P2. Data for cyclopropane P7 were in agreement with published data.\[15\]

References in the supporting information


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