Concurrent Base and Silver(I) Catalysis Pulsed by Fuel Acid

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1. Synthesis

1.1 General information.

All reagents were obtained from commercial suppliers and used without further purifications. Technical grade solvents were distilled prior to use. $^1$H-, $^{13}$C-, and $^1$H-$^1$H-COSY NMR spectra were recorded at 298 K using the deuterated solvent as the lock. The chemical shifts refer to the residual protiated fraction of the solvent (CHCl$_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.0$ ppm; CHDCl$_2$: $\delta_H = 5.32$ ppm, $\delta_C = 53.8$ ppm; CHD$_2$CN: $\delta_H = 1.94$ ppm, $\delta_C = 1.32, 118.3$ ppm). The following abbreviations are used in $^1$H NMR assignments to describe splitting patterns (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, td: triplet of doublets, ddd: doublet of doublet of doublets, brs: broad singlet, quint: quintet, m: multiplet), the value of coupling constant(s) is reported in Hertz (Hz) and the number of protons are implied. The numbering of carbon atoms is usually not in accordance with IUPAC nomenclature guidelines. Melting points were measured on a Büchi SMP-20 and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum-Two FT-IR spectrometer. UV-vis spectra were measured on a Cary Win 50. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. Column chromatography was performed on silica gel 60 (60–230 mesh). Thin Layer Chromatography (TLC) was performed on Merck silica gel (60 F254) or on neutral Al$_2$O$_3$ (150 F254) sheets. Compounds 1, $^1$2 $^2$ and 3 $^3$ were synthesized according to known protocols and in some cases modified. The spectral data of these compounds are in good agreement with those in the literature reports.

1.2 Ligands

![Chart 1. Structure of ligands 1,2 and fuel acid 3.](image-url)
1.3 Characterization of ligands

Characterization of literature-known ligand 1

\[
\begin{align*}
\text{Mp: } & 131 \, ^\circ\text{C. IR (KBr): } 3512, 3480, 2957, 2845, 2197, 1573, 1448, 1387, 1189, 954, 713, 679 \\
\text{cm}^{-1}. & 1^1 \text{H NMR (CD}_2\text{Cl}_2, \text{500 MHz): } \delta \text{ 1.52 (quint, } ^3J = 6.0 \text{ Hz, } 2\text{H, o-H)}, 1.82 \text{ (quint, } ^3J = 5.5 \text{ Hz, 2H, j-H)}, 1.98 \text{ (brs, } 3\text{H, q-, r-, s-H)}, 2.38-2.45 \text{ (m, 4H, g-, p-H)}, 2.56-2.63 \text{ (m, 6H, i/k-, l-, m-H)}, 2.68 \text{ (t, } ^3J = 8.1 \text{ Hz, 2H, h-H)}, 2.70-2.75 \text{ (m, 4H, k/-, n-H)}, 4.53 \text{ (s, 2H, f-H)}, 7.49 \text{ (td, } ^3J = 8.4 \text{ Hz, } ^4J = 1.4 \text{ Hz, 2H, c-H)}, 7.54 \text{ (td, } ^3J = 8.4 \text{ Hz, } ^4J = 1.4 \text{ Hz, 2H, d-H)}, 8.03 \text{ (d, } ^3J = 10.1 \text{ Hz, 2H, b-H)}, 8.45 \text{ (s, 1H, a-H)}, 8.57 \text{ (d, } ^3J = 10.1 \text{ Hz, 2H, e-H)} \text{ ppm.} \\
\text{ESI-MS: } m/z \text{ (\%)} = 391.5 \text{ (100) [1•H]^+.} 
\end{align*}
\]

Characterization of literature-known ligand 2

\[
\begin{align*}
\text{Mp: } & 82 \, ^\circ\text{C. IR (KBr): } 3077, 2858, 2791, 2191, 1605, 1518, 1473, 1436, 1390, 1347, 1285, 1255, 1191, 1119, 992, 938, 903, 876, 815, 753, 622, 602, 576, 536, 576 \text{ cm}^{-1}. & 1^2 \text{H NMR (CD}_2\text{Cl}_2, \text{400 MHz): } \delta \text{ 3.59 (s, 4H, 11-H)}, 3.63 \text{ (t, } ^3J = 6.0 \text{ Hz, 4H, 7-H)}, 3.64 \text{ (s, 8H, 9-, 10-H)}, 3.77 \text{ (t, } ^3J = 6.0 \text{ Hz, 4H, 8-H)}, 6.70 \text{ (d, } ^3J = 8.8 \text{ Hz, 2H, 6-H)}, 7.60-7.69 \text{ (m, 6H, 5-, 3-, 2-H)}, 8.52-8.58 \text{ (m, 2H, 4/1-H)}, 8.70-8.75 \text{ (m, 2H, 1/4-H)} \text{ ppm.} \\
\text{ESI-MS: } m/z \text{ (\%)} = 576.2 \text{ (100) [2•H]^+.} 
\end{align*}
\]

1.4 Synthesis and Characterization of complexes

Synthesis of complex [Ag(1)]^+

In an NMR tube, ligand 1 (357 µg, 913 nmol) was dissolved in 500 µL of CD₂Cl₂, then AgBF₄ (178 µg, 913 nmol) in CD₃CN (15.0 µL) was added and subsequently the NMR was recorded. Yield: Quantitative. MP: > 250 ºC. IR (KBr): 3677, 3342, 3124, 3011, 2305, 2263, 2198, 2092, 2004, 1752, 1682, 1387, 1189, 1036, 993, 954, 831, 713, 679 cm⁻¹. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.43 (brs, 2H, j-H), 1.59 (brs, 2H, o-H), 1.71 (brs, 3H, q-, r-, s-H), 1.89 (brs, 2H, p-H), 2.25 (brs, 2H, g-H), 2.46 (s, 4H, l-, m-H), 2.56 (brs, 4H, h-, n-H), 2.70 (brs, 4H, i-, k-H), 4.58 (brs, 2H, f-H), 7.50-7.55 (m, 2H, c-H), 7.62-7.68 (m, 2H, d-H), 8.07 (dd, ²J = 9.9 Hz, ⁴J = 1.5 Hz, 2H, b-H), 8.47 (brs, 1H, a-H), 8.50 (brs, 2H, e-H) ppm. ¹³C NMR (CD₂Cl₂, 125 MHz): δ 27.4, 28.3, 47.5, 48.0, 48.2, 48.3, 48.4 (2C), 51.6, 52.1, 52.3, 124.6, 125.4, 126.1, 128.4, 129.7, 130.3, 131.1, 131.5 ppm. ESI-MS: m/z (%) = 497.5 (100) [Ag(1)]^+ Elemental analysis: Calcd. for C₂₅H₃₄AgBF₄N₄•0.25CD₂Cl₂ •0.05C₅H₁₂: C, 50.20; H, 5.72; N, 9.16. Found: C, 50.48; H, 5.33; N, 8.78.
Synthesis of complex $1 \cdot H^+$

In an NMR tube, ligand 1 (357 µg, 913 nmol) was dissolved in 500 µL of CD$_2$Cl$_2$, then trifluoroacetic acid (TFA) (104 µg, 913 nmol) in CD$_2$Cl$_2$ (15.0 µL) was added and subsequently the NMR was recorded. **Yield:** Quantitative. **MP:** 122 °C.  **IR** (KBr): 3339, 2305, 2196, 1751, 1388, 954, 713, 679 cm$^{-1}$. **$^1$H NMR** (CD$_2$Cl$_2$, 500 MHz): $\delta$ 1.53 (brs, 2H, o-H), 1.62 (brs, 3H, q-, r-, s-H), 2.12 (brs, 2H, j-H), 2.58 (brs, 2H, p-H), 2.83 (t, $^3J = 6.9$ Hz, 2H, g-H), 2.93 (brs, 4H, l-, m-H), 3.02 (brs, 4H, h-, n-H), 3.11-3.34 (brs, 4H, i-, k-H), 4.75 (brs, 2H, f-H), 7.57 (t, $^3J = 10.1$ Hz, 2H, c-H), 7.67 (t, $^3J = 10.1$ Hz, 2H, d-H), 8.10 (d, $^3J = 10.1$ Hz, 2H, b-H), 8.46 (d, $^3J = 10.1$ Hz, 2H, e-H), 8.56 (s, 1H, a-H) ppm. **ESI-MS:** $m/z$ (%) = 391.5 (100) [1$\cdot$H$^+$].

Synthesis of complex$^2$ [Ag(2)]$^+$

In an NMR tube, ligand 2 (524 µg, 913 nmol) was dissolved in 500 µL of CD$_2$Cl$_2$, then AgBF$_4$ (178 µg, 913 nmol) in CD$_3$CN (15.0 µL) was added and subsequently the NMR was recorded. **Yield:** Quantitative. **MP:** > 250 °C. **$^1$H NMR** (CD$_2$Cl$_2$, 400 MHz): $\delta$ 3.54 (t, $^3J = 4.0$ Hz, 4H, 7-H), 3.66 (s, 4H, 11-H), 3.68 (s, 8H, 9-, 10-H), 3.72 (t, $^3J = 4.0$ Hz, 4H, 8-H), 7.05 (d, $^3J = 7.2$ Hz, 2H, 6-H), 7.63-7.69 (m, 4H, 2-, 3-H), 7.71 (d, $^3J = 7.2$ Hz, 2H, 5-H), 8.58-8.60 (m, 2H, 1/-4-H), 8.69-8.73 (m, 2H, 4/-1-H). **ESI-MS:** $m/z$ (%) = 682.2 (100) [Ag(2)]$^+$. 
Synthesis of complex [Ag(13)]⁺

In an NMR tube, ligand 13 (275 µg, 930 nmol) was dissolved in 500 µL of CD₂Cl₂, then AgBF₄ (181 µg, 930 nmol) in CD₃CN (15.0 µL) was added and subsequently the NMR was recorded. **Yield:** Quantitative. **MP:** > 250 °C. **IR** (KBr): 3653, 3055, 2987, 2576, 2306, 1786, 1650, 1422, 1265, 1217, 1172, 1026, 896, 740, 705, 533, 520 cm⁻¹. **¹H NMR (CD₂Cl₂, 500 MHz):** δ 3.39 (t, 3J = 6.5 Hz, 4H, 18-H), 3.59 (t, 3J = 6.5 Hz, 4H, 19-H), 3.63 (m, 12H, 20-, 21-, 22-H), 6.93 (t, 3J = 9.0 Hz, 1H, 15-H), 6.99 (d, 3J = 8.2 Hz, 2H, 17-H), 7.28 (ddd, 3J = 9.0 Hz, 2J = 8.2 Hz, 4J = 1.4 Hz, 2H, 16-H) ppm. **¹³C NMR (CD₂Cl₂, 125 MHz):** δ 56.1, 67.4, 69.4, 69.7, 69.9, 120.3, 122.8, 129.5, 148.6 ppm. **ESI-MS:** m/z (%) = 402.4 (100) [Ag(13)]⁺. **Elemental analysis:** Calcd. for C₁₆H₂₅AgBF₄NO₄•0.15CD₂Cl₂: C, 38.56; H, 5.01; N, 2.78. Found: C, 38.95; H, 4.62; N, 2.59.
1.5 Synthesis and characterization of NetStates-I and II

Synthesis of NetState-I  \( (= [\text{Ag}(1)]^+ + 2 \) )

\[
\begin{align*}
\text{[Ag(1)]}^+ & \quad \text{NetState I} \\
+ & \quad 2
\end{align*}
\]

In an NMR tube, ligand 1 (357 µg, 913 nmol) was dissolved in 500 µL of CD$_2$Cl$_2$, then AgBF$_4$ (178 µg, 913 nmol) in CD$_3$CN (15.0 µL) was added. After 1 min of mixing, ligand 2 (524 µg, 913 nmol) was added and subsequently the NMR was recorded. **Yield**: Quantitative; $^1$H NMR (CDCl$_3$, 500 MHz): 1.13-1.31 (m, 2H, j-H), 1.58 (brs, 2H, o-H), 1.68 (brs, 3H, q-, s-, r-H), 2.14 (brs, 2H, g-H), 2.33 (brs, 2H, p-H), 2.41 (brs, 4H, l-, m-H), 2.57 (brs, 4H, h-, n-H), 2.66 (brs, 4H, i-, k-H), 3.63 (s, 4H, 11-H), 3.65 (s, 4H, 7-H), 3.67 (s, 8H, 9-, 10-H), 3.79 (t, $^3J = 7.5$ Hz, 4H, 8-H), 4.58 (brs, 2H, f-H), 6.70 (d, $^3J = 10.5$ Hz, 2H, 6-H), 7.51 (t, $^3J = 10.2$ Hz, 2H, c-H), 7.56-7.64 (m, 6H, 2-, 3-, 5-H), 7.76 (brs, 2H, d-H), 8.07 (d, $^3J = 10.2$ Hz, 2H, b-H), 8.47 (s, 1H, a-H), 8.49 (d, $^3J = 10.2$ Hz, 2H, e-H), 8.53 (dd, $^3J = 9.6$ Hz, $^4J = 2.3$ Hz, 2H, 1/4-H), 8.09 (dd, $^3J = 9.6$ Hz, $^4J = 2.3$ Hz, 2H, 4/1-H) ppm.
Synthesis of NetState-II (= \(1\cdot\text{H}^+ + [\text{Ag}(2)]^+\))

In an NMR tube, ligand 1 (357 µg, 913 nmol) was dissolved in 500 µL of CD\(_2\)Cl\(_2\), then AgBF\(_4\) (178 µg, 913 nmol) in CD\(_3\)CN (15.0 µL) was added. After 1 min of mixing, first ligand 2 (524 µg, 913 nmol) and then TFA (104 µg, 913 nmol) in CD\(_2\)Cl\(_2\) (15.0 µL) were added, and subsequently the NMR was recorded. **Yield:** Quantitative; \(^1\text{H} \text{NMR (CDCl}_3, 500 \text{ MHz):} \) \(\delta\) 1.49 (brs, 2H, o-H), 2.15 (brs, 2H, j-H), 2.29 (brs, 3H, q-, s-, r-H), 2.59 (brs, 4H, l-, m-H), 2.88 (t, 3\(J = 6.5 \text{ Hz}, 2\text{H, g-H}\)), 2.96 (t, 3\(J = 6.5 \text{ Hz}, 2\text{H, p-H}\)), 3.09 (t, 3\(J = 6.5 \text{ Hz}, 4\text{H, h-, n-H}\)), 3.29 (brs, 4H, i-, k-H), 3.42 (brs, 4H, 7-H), 3.63-3.69 (m, 8H, 8-, 11-H), 3.73 (s, 8H, 9-, 10-H), 4.75 (brs, 2H, f-H), 7.05 (brs, 2H, 6-H), 7.50-7.74 (m, 10H, 2-, 3-, 5-, c-, d-H), 8.10 (d, 3\(J = 10.7 \text{ Hz}, 2\text{H, b-H}\)), 8.43 (d, 3\(J = 10.7 \text{ Hz}, 2\text{H, e-H}\)), 8.56 (s, 1H, a-H), 8.59 (d, 3\(J = 10.8 \text{ Hz}, 2\text{H, 1-/4-H}\)), 8.68 (d, 3\(J = 10.8 \text{ Hz}, 2\text{H, 4-/1-H}\)) ppm.
1.6 Synthesis and characterization of substrates and products of the catalysis

Synthesis of substrate 12

A solution of KOH (128 mg, 2.28 mmol) in deionized water (10 mL) was added to a solution of (E)-2-((trimethylsilyl)ethynyl)benzaldehyde oxime\textsuperscript{5} (248 mg, 1.14 mmol) in THF-MeOH (2:1, v/v, 60 mL). Then the reaction mixture was allowed to stir at rt for 5 h. After completion of the reaction that was followed by thin-layer chromatography (TLC), the solvent was evaporated and the remainder extracted with DCM (2 × 30 mL). The solution was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the solvent, purification by chromatography (silica gel, EtOAc/DCM = 1:5, \(R_t = 0.5\)) provided 136 mg of pure 12 (938 \(\mu\)mol, 82\%). **Mp:** 115-117 °C. **IR** (KBr): 3560, 3339, 3300, 3121, 2302, 2196, 1751, 1387, 954, 713, 679 cm\(^{-1}\). \(^1\)H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 500 MHz): \(\delta\) 3.43 (s, 1H, 41-H), 7.34-7.38 (m, 2H, 43-, 44-H), 7.52 (dd, \(^3\)J = 7.6 Hz, \(^4\)J = 1.6 Hz, 1H, 42-H), 7.85 (dd, \(^3\)J = 7.6 Hz, \(^4\)J = 1.6 Hz, 1H, 45-H), 8.22 (brs, 1H, 47-H), 8.63 (s, 1H, 46-H) ppm. \(^13\)C NMR (CD\textsubscript{2}Cl\textsubscript{2}, 125 MHz): \(\delta\) 80.7, 83.1, 125.4, 127.1, 129.5, 129.9, 133.4, 134.4, 148.8 ppm. **ESI-MS:** \(m/z\) (%) = 146.4 (100) [12•H]\(^+\). **Elemental analysis:** Calcd. for C\(_9\)H\(_7\)NO: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.51; H, 4.58; N, 9.39.
Synthesis of substrate 10

Under nitrogen atmosphere, 4-(2-bromophenyl)-2-methylbut-3-yn-2-ol (150 mg, 628 μmol) and compound 12 (181 mg, 1.25 mmol) were dissolved in 15 mL of dry THF and 15 mL of di-isopropylamine. Subsequently, the solution was deaerated by bubbling nitrogen through the solution for 15 min. Then the solution was charged with Pd(PPh₃)₄ (36.0 mg, 31.3 μmol) and heated at 85 °C for 24 h. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, EtOAc/DCM = 1:6, Rf = 0.4) providing 134 mg of 10 as brownish yellow solid (439 μmol, 70%). Mp: 73 °C. IR (KBr): 3945, 3758, 3692, 3614, 3054, 2987, 2686, 2522, 2411, 2305, 2126, 1553, 1422, 1264, 1156, 1048, 896, 737, 703 cm⁻¹. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.61 (s, 6H, 18-H), 3.18 (brs, 1H, 17-H), 7.33 (ddd, 3J = 8.4 Hz, 3J = 6.8 Hz, 4J = 1.6 Hz, 1H, 20-H), 7.34 (ddd, 3J = 8.6 Hz, 3J = 6.8 Hz, 4J = 1.4 Hz, 1H, 21-H), 7.39 (ddd, 3J = 8.4 Hz, 3J = 7.0 Hz, 4J = 1.6 Hz, 1H, 24-H), 7.41 (ddd, 3J = 8.2 Hz, 3J = 7.0 Hz, 4J = 1.4 Hz, 1H, 25-H), 7.48-7.52 (m, 1H, 19-H), 7.56-7.58 (m, 1H, 22-H), 7.60-7.63 (m, 1H, 23-H), 7.91 (dd, 3J = 8.2 Hz, 4J = 1.6 Hz, 1H, 26-H), 8.21 (brs, 1H, 28-H), 8.92 (s, 1H, 27-H) ppm. ¹³C NMR (CD₂Cl₂, 125 MHz): δ 31.6, 65.8, 80.8, 90.0, 93.9, 98.9, 123.3, 125.1, 125.5, 125.6, 128.5, 128.8, 129.2, 130.1, 132.5, 132.9, 133.0, 133.4, 149.8 ppm. ESI-MS: m/z (%) = 304.3 (100) [10•H]+. Elemental analysis: Calcd. for C₂₀H₁₇NO₂: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.04; H, 5.64; N, 4.45.
Synthesis of cyclization product 11

Compound 10 (100 mg, 330 μmol) was dissolved in 5 mL of DCM, then AgBF₄ (5.84 mg, 30.0 μmol, 10 mol%) in 100 μL of acetonitrile was added, and the mixture was heated for 5 h at 40 °C. The solvent was removed, and the residue was purified by chromatography (silica gel, MeOH/DCM = 1:10, Rf = 0.4) to furnish product 11 (91 mg, 300 μmol, 91%) as a brownish yellow solid. Mp: 143 °C. IR (KBr): 3944, 3757, 3691, 3611, 3054, 2987, 2831, 2685, 2521, 2410, 2305, 2197, 2054, 1604, 1551, 1422, 1265, 1157, 1048, 954, 896, 739, 706 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): 1.24 (s, 6H, 30-H), 7.45 (ddd, ³J = 8.6 Hz, ³J = 6.8 Hz, ⁴J = 1.4 Hz, 1H, 33-H), 7.46 (ddd, ³J = 8.4 Hz, ³J = 6.8 Hz, ⁴J = 1.6 Hz, 1H, 32-H), 7.54-7.57 (m, 2H, 31-, 34-H), 7.60 (dd, ³J = 7.9 Hz, ³J = 6.8 Hz, ⁴J = 1.4 Hz, 1H, 38-H), 7.62 (dd, ³J = 7.7 Hz, ³J = 6.8 Hz, ⁴J = 1.2 Hz, 1H, 37-H), 7.74 (dd, ³J = 7.9 Hz, ⁴J = 1.2 Hz, 1H, 39-H), 7.81 (dd, ³J = 7.7 Hz, ⁴J = 1.4 Hz, 1H, 36-H), 7.82 (s, 1H, 40-H), 8.86 (s, 1H, 35-H) ppm. ¹³C NMR (CD₂Cl₂, 125 MHz): δ 31.2, 65.2, 80.4, 98.5, 123.8, 124.9, 126.1, 126.9, 128.4, 129.0, 129.2, 129.4, 129.6, 129.7, 130.5, 132.2, 136.4, 136.8, 146.5 ppm. ESI-MS: m/z (%) = 304.5 (100) [11•H]⁺. Elemental analysis: Calcd. for C₂₀H₁₇NO₂: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.57; H, 5.49; N, 4.39.
Synthesis of catalysis product 9

![Image of compound 9]

Compound 7 (186 mg, 1.25 mmol) and 8 (82.5 mg, 1.25 mmol) were dissolved in 25 mL of DCM. Then the solution was charged with cyclam (12.5 mg, 62.5 μmol) and stirred at rt for 5 min. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, EtOAc/n-Hexane = 1:5, $R_f = 0.4$) providing 134 mg of 9 as colorless solid (193 mg, 72%). 

**Mp:** 119-121 °C. ¹H NMR (CD₂Cl₂, 400 MHz): $\delta$ 4.10-4.17 (m, 1H, 51-H), 4.47 (d, $^3J = 7.1$ Hz, 1H, 53-H), 4.93-5.06 (m, 2H, 52-H), 7.38-7.42 (m, 2H, 50-H), 7.49-7.53 (m, 3H, 48-, 49-H) ppm.
2. NMR spectra: $^1$H, $^{13}$C, $^1$H-$^1$H COSY

2.1 NMR spectra of ligands: $^1$H, $^{13}$C, $^1$H-$^1$H COSY

Figure S1. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of ligand 1.

Figure S2. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of ligand 1.
Figure S3. $^{1}$H-$^{1}$H COSY NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of ligand 1.
2.2 NMR spectra of complexes: $^1$H, $^{13}$C, $^1$H-$^1$H COSY

Figure S4. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex [Ag(I)]$^+$.  

Figure S5. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of complex [Ag(I)]$^+$.  

S15
Figure S6. $^1$H-$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex [Ag(1)]$^+$. 

Figure S7. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex 1·H$^+$. 

S16
Figure S8. $^1$H-$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex 1$\cdot$H$^+$. 

Figure S9. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex [Ag(13)]$^+$. 
Figure S10. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of complex [Ag(13)]$^+$. 

Figure S11. $^1$H-$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of complex [Ag(13)]$^+$. 
2.3 $^1$H NMR spectra of Networking States

Figure S12. $^1$H NMR spectrum (CDCl$_3$, 500 MHz, 298 K) of NetState-I.
Figure S13. ¹H NMR spectrum (CDCl₃, 500 MHz, 298 K) of NetState-II.
2.4 NMR spectra of substrate and product of the model catalysis: $^1$H, $^{13}$C, $^1$H-$^1$H COSY

Figure S14. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of substrate 10.

Figure S15. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of substrate 10.
Figure S16. $^1$H–$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of substrate 10.

Figure S17. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of compound 12.
Figure S18. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of compound 12.

Figure S19. $^1$H-$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of compound 12.
Figure S20. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of cyclization product 11.

Figure S21. $^{13}$C NMR spectrum (CD$_2$Cl$_2$, 125 MHz, 298 K) of cyclization product 11.
Figure S22. $^1$H-$^1$H COSY spectrum (CD$_2$Cl$_2$, 500 MHz, 298 K) of cyclization product 11.
3. ESI-MS spectra

Figure S23. ESI-MS spectrum of complex 1•H⁺ in DCM.

Figure S24. ESI-MS spectrum of complex [Ag(1)]⁺ in DCM.
Figure S25. ESI-MS spectrum of complex $\text{12} \cdot \text{H}^+$ in DCM.

Figure S26. ESI-MS spectrum of complex $\text{10} \cdot \text{H}^+$ in DCM.
Figure S27. ESI-MS spectrum of complex 11•H⁺ in DCM.

Figure S28. ESI-MS spectrum of complex [Ag(2)]⁺ in DCM.
Figure S29. ESI-MS spectrum of complex [Ag(13)]⁺ in DCM.
4. Fluorescence spectra

**Figure S30.** Emission spectra ($\lambda_{\text{exc}} = 350$ nm) of ligand 1 (green), complex [Ag(1)]$^+$ (red) and complex (1)H$^+$ (blue).

**Figure S31.** Emission spectra ($\lambda_{\text{exc}} = 350$ nm) of ligand 2 (blue) and complex [Ag(2)]$^+$ (red).
5. Fluorescence spectra of chemical fuel driven metal translocation cycle.

![Fluorescence spectra](image)

**Figure S32.** a) The second cycle of the fuel-driven metal translocation; b) change of the intensity of emission versus time at 554 nm during the second cycle; c) the third cycle of the fuel-driven metal translocation; and d) change of the intensity of emission versus time at 554 nm during the third cycle. Addition of 3 triggers rapid translocation of Ag⁺ ions from [Ag(1)]⁺ to 2 furnishing [Ag(2)]⁺. The reverse translocation of Ag⁺ ions was completed over the course of 150 min and 158 min, respectively.
6. $^1$H NMR spectra of chemical fuel driven metal translocation cycle

**Figure S33.** Translocation of Ag$^+$ ions driven by chemical fuel 3. $^1$H NMR recorded 5 min after addition of 3 and the reverse translocation of Ag$^+$ ions was completed over the course of 120 minutes. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) spectra after: a) 5 min; b) 8 min; c) 12 min; d) 16 min; e) 20 min; f) 24 min; g) 28 min; h) 32 min; i) 36 min; j) 40 min; k) 45 min; l) 50 min; m) 55 min; n) 60 min; o) 65 min; p) 70 min; q) 75 min; r) 80 min; s) 85 min; t) 90 min; u) 95 min; v) 100 min; w) 105 min; x) 110 min; y) 120 min. Marked signals are assigned to protons using the following symbols: Red star: f-H of [Ag(1)]$^+$; red rectangle: f-H of 1•H$^+$; blue star: 6-H of 2; blue rectangle: 6-H of [Ag(2)]$^+$; green star: peak of ligand 6 (chemical fuel waste); green rectangle: peak of ligand 3 (chemical fuel); purple star: peak of ligand 6 (chemical fuel waste); purple rectangle: peak of ligand 3 (chemical fuel).
7. Measurements of binding constants

The UV-vis titration technique was used to measure binding constants of complexes. The full data of a selected wavelength region was analyzed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA).

![UV-vis spectra](image)

**Figure S34.** UV-vis spectra of 1 ($c = 1.54 \times 10^{-5}$ M) in CH$_2$Cl$_2$ (2 mL) upon addition of AgBF$_4$ ($3.85 \times 10^{-3}$ M) in CH$_3$CN at 298 K to afford the complex [Ag(I)]$^+$. The wavelength region 325-425 nm was analyzed.

Result: $\log K = 8.43 \pm 0.41$. 
8. Fluorescence spectra of chemical fuel waste 6 addition into NetState-I

**Figure S35.** Fluorescence spectra of a) NetState-I ($c = 7.69 \times 10^{-6}$ M) in CH$_2$Cl$_2$ (2 mL) upon addition of chemical fuel waste 6 ($c = 1.54 \times 10^{-3}$ M) in CH$_2$Cl$_2$ at 298 K. b) 10 µL, c) 20 µL, d) 30 µL, e) 40 µL, f) 45 µL, g) 50 µL, h) 55 µL added.

Conclusion: Formation of waste 6 leads to a decrease of the fluorescence intensity of NetState-I.
9. Catalysis of NetState-I and II in presence of chemical fuel

Figure S36. Both Michael addition and the oxime cyclization reactions are ON after addition of 3 over 120 minutes in first cycle. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) yields for Michael addition and oxime cyclization are: a) 9% for both reactions after 5 min; b) 41% and 64% after 20 min; c) 55% and 99% after 50 min; d) 58% and 99% after 90 min; e) 60% and 99% after 120 min, respectively.
Figure S37. After first cycle had been completed (120 min), consumed amounts of reactants were added to NetState-I that was kept at rt over 100 min. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) spectra show that there is no product formation during NetState-I (2. cycle) after a) 20 min; b) 40 min; c) 60 min; d) 80 min; e) 100 min.
Figure S38. Both Michael addition and the oxime cyclization reactions are ON after addition of 3 over 120 minutes in NetState-II (second cycle). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) yields for Michael addition and oxime cyclization generated in cycle two: a) 10% and 13% after 5 min; b) 38% and 53% after 20 min; c) 50% and 99% after 50 min; d) 56% and 99% after 90 min; e) 57% and 99% after 120 min, respectively.
Figure S39. After the second cycle had been completed (120 min), consumed amounts of reactants were added to NetState-I (3. cycle) that was kept at rt over 100 min. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) spectra show that there is no product formation in NetState-I (3. cycle) after a) 20 min; b) 40 min; c) 60 min; d) 80 min; e) 100 min.
**Figure S40.** Both Michael addition and the oxime cyclization reactions are ON after addition of 3 over 120 min in NetState-II (third cycle). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) yields for Michael addition and oxime cyclization generated in cycle three: a) 6% and 7% after 5 min; b) 34% and 59% after 20 min; c) 43% and 89% after 50 min; d) 50% and 98% after 90 min; e) 52% and 99% after 120 min, respectively.
10. Control experiments: Base-catalyzed Michael addition

10.1. Control experiments in presence of various additives: Ligand 3, TFA, 1·(2H)²⁺, 1·(3H)³⁺, 1·(4H)⁴⁺, 1·(2H)⁺, and ligand 1.

Figure S41. ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of ligand 3 (10 mol%) at 25 °C after a) 5 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min. No product was obtained.
Figure S42. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of TFA (10 mol%) at 25 °C after a) 5 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min. No product was obtained.
Figure S43. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of 1·(2H)$_2^+$ (10 mol%) at 25 °C after a) 5 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min. No product was obtained.
Figure S44. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of 1-1(3H)$^3+$ (10 mol%) at 25 °C after a) 5 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min. No product was obtained.
Figure S45. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of 1·(4H)$^{4+}$ (10 mol%) at 25 °C after a) 5 min, b) 30 min, c) 60 min, d) 90 min, e) 120 min. No product was obtained.
Figure S46. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of 1-H$^+$ (10 mol%) at 25 °C. a) After 5 min: 12% yield; b) after 15 min: 38% yield; c) after 30 min: 66% yield; d) after 45 min: 73% yield; e) after 60 min: 78% yield; f) after 75 min: 81% yield; g) after 90 min: 85% yield; h) after 120 min: 89% yield of 9.
Figure S47. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition reaction between substrates 7 and 8 in presence of 1 (10 mol%) at 25 °C. a) After 1 min: 59% yield; b) after 2 min: 78% yield; c) after 3 min: 89% yield; d) after 4 min: 95% yield; e) after 5 min: 98% yield.
10.2. Control experiments in presence of the “catalyst control system” (CCS)

The CCS consists of 1 equiv of $\text{1} \cdot \text{H}^+$ and 7 equiv of $[\text{Ag(13)}]^+$. The theory behind this experiment is: Generation of free and catalytically active 1 should be suppressed by excess of silver(I) ions contained in $[\text{Ag(13)}]^+$ (7 equiv) as immediate formation of the catalytically inactive $[\text{Ag(1)}]^+$ is warranted by the binding constants. If the yields of 9 in the Michael addition catalyzed by $\text{1} \cdot \text{H}^+$ and CCS are similar, then formation of free 1 during the fuelling should play no role.

The Michael addition between trans-$\beta$-nitrostyrene (7) and malononitrile (8) was performed in presence of 10 mol% of the CSS at 25 °C for 2 h. Figure S48 shows the resulting $^1\text{H}$ NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K). Results in presence of the Catalyst control system (CCS) (10 mol%) and $\text{1} \cdot \text{H}^+$ (10 mol%) are in good agreement with each other (Table S1). This experiment thus suggests that the base-catalyzed Michael addition reaction was run by the mono-protonated cyclam $\text{1} \cdot \text{H}^+$, and not by the free ligand 1.

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<tr>
<th>Time (min)</th>
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<td>$\text{1} \cdot \text{H}^+$</td>
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Table S1. Yields of the Michael addition reaction between substrates 7 and 8 in presence of CCS (10 mol%) and $\text{1} \cdot \text{H}^+$ (10 mol%) at 25 °C.
Figure S48. $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of the Michael addition between substrates 7 and 8 in presence of CCS (10 mol%) at 25 °C. a) After 5 min: 11% yield; b) after 15 min: 39% yield; c) after 30 min: 65% yield; d) after 45 min: 72% yield; e) after 60 min: 78% yield; f) after 75 min: 82% yield; g) after 90 min: 86% yield; h) after 120 min: 90% yield of 9.
11. References


