Ligand-Switching and Counteranion-Induced Hierarchical Self-Assembly of Silver-NHC Complexes

Siping Wei, Xiyu Li, Zhuang Yang, Jingbo Lan, Ge Gao, Ying Xue, and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Hospital, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064 (PR China)

Fax: 86-28-85412203; E-mail: jsyou@scu.edu.cn

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I. General Remarks

$^1$H NMR spectra were obtained with a Bruker AV II-400 (400 MHz), a Varian Inova-400 (400 MHz) or a Bruker AV II-600 (600 MHz) spectrometer, while $^{13}$C NMR spectra were recorded with a Bruker AV II-400 (100 MHz) or a Bruker AV II-600 (150 MHz) spectrometer. $^{19}$F NMR spectra were recorded with a Bruker AV II-400 (376 MHz) spectrometer. ROESY and HMQC NMR spectra were obtained with a Bruker AV II-400 (400 MHz) spectrometer. The $^1$H and $^{13}$C NMR chemical shifts were recorded with TMS, CDCl$_3$, DMSO-$d_6$, or CD$_3$COCD$_3$ as the internal standard. Elemental analyses were performed with a Euro EA 3000 instrument. Mass spectra were obtained on a Waters Quattro Premier XE Mass spectrometer or a Finnigan-LCQDECA instrument. The ESI-TOF mass spectra were recorded with a Waters Q-Tof premier instrument. Transmission electron microscopy (TEM) studies were carried out on a Tecnai G2 F20 S-TWIN, operating at 200 kV, or a HITACHI H-600, operating at 75 kV. Scanning transmission electron microscope (STEM) studies were carried out on a Tecnai G2 F20 S-TWIN, operating at 200 kV. Circular Dichroism (CD) spectra were recorded on an Aviv Model 215 Circular Dichroism Spectrometer at 25 °C.

X-Ray single-crystal diffraction data were collected on an Oxford Diffraction Xcalibur Eos Gemini Diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) with $\omega$ scan mode. Empirical absorption correction using spherical harmonics was implemented in SCALE3 ABSPACK scaling algorithm. All the structures were solved by direct methods using the SHELXS SHELXS-97 program and refined by full-matrix least-squares methods with SHELXL-97. All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F.$^2$ Hydrogen atoms were included in calculated positions and refined with constrained thermal parameters riding on their parent atoms. Drawings were produced with Ortep, Diamod, and OLEX2.$^2$

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise indicated, all syntheses and manipulations were carried out under dry inert atmosphere. ($R$)-1·2HCl, ($S$)-2·2HCl, ($R$)-2·2HCl, and ($S$)-3·2HCl were prepared according to our previous report.$^3$

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II. Data of \((R)\)-2·2HCl

![Chemical Structure](image)

1,3-Bis\{\((R)\)-5-benzyl-6,8-dihydro-5H-[1,4]oxazino[2,1-c]-[1,2,4]triazol-2-ium-2-yl\}benzene dichloride \((R)\)-2·2HCl. The compound \((R)\)-2·2HCl was prepared according to our previous report.\(^3\) m.p \(> 300 \, ^\circ\)C. \([\alpha]_D^{20}\): \(-0.48\, \text{cm}^3\, \text{g}^{-1}\, \text{dm}^{-1}\) (c = 0.50 in CH\(_3\)OH). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 3.18 (dd, \(J = 10.4\, \text{Hz}, 10.4\, \text{Hz}, 2\, \text{H}\)), 3.56 (dd, \(J = 4.4\, \text{Hz}, 4.4\, \text{Hz}, 2\, \text{H}\)), 3.95-4.04 (m, 4\, \text{H}), 4.92-4.95 (m, 2\, \text{H}), 5.20 (dd, \(J = 16.4\, \text{Hz}, 16.4\, \text{Hz}, 4\, \text{H}\)), 7.39-7.45 (m, 10\, \text{H}), 8.10 (t, \(J = 8.0\, \text{Hz}, 1\, \text{H}\)), 8.21-8.23 (m, 2\, \text{H}), 8.56 (s, 1\, \text{H}), 11.34 (s, 2\, \text{H}) ppm. \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)): 37.9, 57.0, 61.9, 65.5, 113.3, 122.5, 128.0, 129.5, 129.9, 133.0, 135.4, 136.5, 136.6, 142.3, 150.6 ppm. HR-MS (ESI) calcd for [M - Cl]\(^+\): 541.2117, found. 541.2119. Anal. Calcd for C\(_{30}\)H\(_{30}\)Cl\(_2\)N\(_6\)O\(_2\): C, 62.39; H, 5.24; N, 14.55; Found: C, 62.61; H, 5.51; N, 14.39.

III. Preparation and characterization of silver- and gold-NHC complexes

1. Preparation and characterization of \([((R)-1\cdot Ag])_2(BF_4)(Cl)\)

Bis-triazolium salt \((R)-1\cdot 2\text{HCl}\) (110 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and NaBF\(_4\) (24 mg, 0.22 mmol) were added to CH\(_2\)Cl\(_2\) (5 mL) under argon. The mixture became gray after being stirred for 10 h at room temperature, and the solvent was then removed in vacuo at room temperature to give a gray solid, followed by extraction with hot DMSO (2~3 mL). The colorless
crystalline product was prepared by slow diffusion of ethyl ether into the solution of crude product in DMSO at room temperature in ca. 80 % yield. Colorless block crystals \([((R)-1\cdot Ag)_2(BF_4)(Cl)]\) suitable for X-ray analysis were obtained by slow diffusion of ethyl ether into the DMSO solution at ambient temperature through several days. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 3.97\) (dd, \(J = 6.0\) Hz, 6.0 Hz, 4H), 4.32 (dd, \(J = 4.4\) Hz, 4.4 Hz, 4H), 5.23 (d, \(J = 15.6\) Hz, 4H), 5.40 (d, \(J = 16.0\) Hz, 4H), 5.94 (s, 4H), 6.47 (t, \(J = 7.2\) Hz, 4H), 6.56 (t, \(J = 7.2\) Hz, 8H), 6.96 (d, \(J = 7.2\) Hz, 8H), 7.44 (s, 2H), 7.88 (t, \(J = 8.4\) Hz, 2H), 8.00 (d, \(J = 8.0\) Hz, 4H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta 59.0, 62.3, 69.7, 110.5, 121.8, 127.6, 128.1, 128.6, 131.9, 137.9, 139.2, 150.6, 178.7\) (dd, \(^1J^{107}\text{Ag} = 189.4\) Hz, \(^1J^{109}\text{Ag} = 214.2\) Hz, carbene N-C-N) ppm. \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \(\delta -148.2\) (s, BF\(_4\)) ppm. Anal. Calcd for C\(_{56}\)H\(_{48}\)Ag\(_2\)BClF\(_4\)N\(_{12}\)O\(_4\): C, 52.10; H, 3.75; N, 13.02; Found: C, 51.87; H, 4.03; N, 12.71. ESI-TOF found: \(m/z = 583.10\) (calcd for \([((R)-1\cdot Ag]^+] 583.10\)); \(m/z = 1203.17\) (calcd for \([[((R)-1\cdot Ag)_2Cl]^+] 1203.17\)); \(m/z = 1255.20\) (calcd for \([[((R)-1\cdot Ag)_2(BF_4)]^+] 1255.19\)).

2. Preparation and characterization of \([((R)-1\cdot Ag)_2(PF_6)_2]\)

Bis-triazolium salt \((R)-1\cdot 2\text{HCl}\) (110 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and KPF\(_6\) (40.5 mg, 0.22 mmol) were added to CH\(_2\)Cl\(_2\) (5 mL) under argon. The mixture became gray after being stirred for 10 h at room temperature, and the solvent was then removed in vacuo at room temperature to give a gray solid, followed by extraction with hot DMSO (2~3 mL). The crystalline product was prepared by slow diffusion of ethyl ether into the solution of crude product in DMSO at ambient temperature in ca. 85 % yield. Colorless block crystals \([((R)-1\cdot Ag)_2(PF_6)_2]\) suitable for X-ray analysis were obtained by slow diffusion of ethyl ether into the corresponding DMSO solution at room temperature through several days. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta 3.97\) (dd, \(J = 6.8\) Hz, 6.8 Hz, 4H), 4.32 (dd, \(J = 4.8\) Hz, 4.8 Hz, 4H), 5.25 (d, \(J = 15.6\) Hz, 4H), 5.41 (d, \(J = 16.0\) Hz, 4H), 5.77 (t, \(J = 5.6\) Hz, 4H), 6.47 (t, \(J = 7.2\) Hz, 4H), 6.56 (t, \(J = 7.6\) Hz, 8H), 6.94 (d, \(J = 7.6\) Hz, 8H), 7.38 (s, 2H), 7.90 (t, \(J = 8.4\) Hz, 2H), 8.02-8.05 (m, 4H) ppm. \(^{13}\)C NMR (100 MHz,
DMSO-d$_6$: $\delta$ 59.3, 62.3, 69.7, 110.3, 121.9, 127.6, 128.2, 128.6, 132.1, 137.8, 139.0, 150.8, 178.0 (dd, $^{1}J^{^{107}}\text{Ag} = 188.86$ Hz, $^{1}J^{^{109}}\text{Ag} = 214.7$ Hz, carbene N-C-N) ppm. $^{19}$F NMR (376 MHz, DMSO-d$_6$): $\delta$ -69.2 (d, $J = 756$ Hz, PF$_6$) ppm. Anal. Calcd for C$_{56}$H$_{48}$Ag$_2$F$_{12}$N$_{12}$O$_4$P: C, 46.11; H, 3.32; N, 11.52; Found: C, 45.79; H, 3.63; N, 11.75. ESI-TOF found: $m/z = 583.10$ (calcd for [(R)-1·Ag]$^+$ 583.10); $m/z = 1313.17$ (calcd for [[(R)-1·Ag]$_2$(PF$_6$)$_2$]$^+$ 1313.17).

3. Preparation and characterization of [(S)-2·Ag]$_3$(BF$_4$)$_3$

Bis-triazolium salt (S)-2·HCl (116 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and NaBF$_4$ (24 mg, 0.22 mmol) were added to CH$_2$Cl$_2$ (5 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from CHCl$_3$/EtOAc to afford a colorless crystalline product in 95% yield. Colorless block crystals [(S)-2·Ag]$_3$(BF$_4$)$_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding CHCl$_3$/EtOAc solution at ambient temperature through several days.

In addition, [(S)-2·Ag]$_3$(BF$_4$)$_3$ could also be prepared by anion-exchange reaction of [(S)-2·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$) with NaBF$_4$ (~ 3.3 equiv) in CH$_2$Cl$_2$ for 24 h at room temperature. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.84-2.97 (m, 12H$_g$), 3.70 (dd, $J = 11.2$ Hz, 12.0 Hz, 12H$_h$), 3.98 (t, $J = 7.6$ Hz, 6H$_d$), 4.62 (d, $J = 15.6$ Hz, 6H$_d$), 5.02 (d, $J = 16.0$ Hz, 6H$_d$), 6.45 (d, $J = 7.2$ Hz, 12H$_b$), 7.03 (t, $J = 7.2$ Hz, 12H$_b$), 7.08 (t, $J = 7.2$ Hz, 6H$_b$), 7.87 (d, $J = 7.6$ Hz, 6H$_b$), 8.00 (t, $J = 8.0$ Hz, 3H$_c$) 8.50 (s, 3H$_a$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 40.5, 57.0, 62.1, 65.4, 120.1, 125.6, 127.2, 129.0, 130.7, 136.0, 141.4, 148.6, 148.7 ppm (Note: the carbene resonance of [(S)-2·Ag]$_3$(BF$_4$)$_3$ was inconspicuous). $^{18}$F NMR (376 MHz, CDCl$_3$): $\delta$ -154.2 (s, 8F), -150.7 (s, 4F) ppm. Anal. Calcd for C$_{90}$H$_{84}$Ag$_3$N$_{18}$O$_6$B$_3$F$_{12}$: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.72; H, 4.21; N, 12.43. ESI-TOF found: $m/z = 611.11$ (calcd for [(S)-2·Ag]$^+$ 611.13); $m/z = 2012.41$ (calcd for [[(S)-2·Ag]$_3$(BF$_4$)$_3$]$^+$ 2012.41).
Figure S1. The HMQC and ROESY NMR of [(S)-2·Ag]3(BF₄)₃ in CDCl₃.
4. Preparation and characterization of \([((S)-2\cdot Ag]_3(PF_6)_3\)

Bis-triazolium salt \((S)-2\cdot2HCl\) (58 mg, 0.1 mmol), silver oxide (23 mg, 0.1 mmol), and KPF₆ (20 mg, 0.11 mmol) were added to CH₂Cl₂ (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to afford a white solid, which was recrystallized from CHCl₃/EtOAc to afford a colorless crystalline product in 75% yield.

In addition, \([((S)-2\cdot Ag]_3(PF_6)_3\) could also be prepared by anion-exchange reaction of \([((S)-2\cdot Ag]_3(X)_3\) (X = Cl and/or AgCl₂) with KPF₆ (~3.3 equiv) in CH₂Cl₂ for 24 h at room temperature. ¹H NMR (400 MHz, CDCl₃): \(\delta\) 2.85-2.98 (m, 12H), 3.70 (dd, \(J = 12.0\) Hz, 11.2 Hz, 12H), 3.98 (t, \(J = 7.6\) Hz, 6H), 4.63 (d, \(J = 16.0\) Hz, 6H), 5.02 (d, \(J = 16.0\) Hz, 6H), 6.45 (d, \(J = 7.2\) Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, \(J = 8.0\) Hz, 6H), 8.00 (t, \(J = 8.0\) Hz, 3H) 8.51 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): \(\delta\) 40.0, 57.0, 62.2, 65.2, 117.5, 122.2, 122.6, 126.5, 128.4, 129.8, 130.2, 130.3, 136.1, 140.5, 147.7 ppm (Note: the carbene resonance of \([((S)-2\cdot Ag]_3(PF_6)_3\) was inconspicuous). ¹⁹F NMR (376 MHz, CDCl₃): \(\delta\) -72.4 (d, \(J = 840\) Hz, 6F), -71.5 (d, \(J = 840\) Hz, 12F). Anal. Caled for C₉₀H₄₄Ag₃N₁₈O₆P₃F₁₈: C, 47.57; H, 3.73; N, 11.10; Found: C, 48.22; H, 4.19; N, 11.37. ESI-TOF found: \(m/z\) = 611.12 (calcd for \([((S)-2\cdot Ag]_3^+\) 611.13); \(m/z\) = 2125.24 (calcd for \([((S)-2\cdot Ag]_3(PF_6)_2]_{}^+\) 2125.33).

Colorless block crystals \([((S)-2\cdot Ag]_3(PF_6)_3\) suitable for X-ray analysis were obtained by slow evaporation of the corresponding dichloromethane/ethyl acetate solution at ambient temperature through several days. Because the counteranions and solvent molecules could not be precisely located from the difference maps due to their high thermal disorder, these counteranions and solvent molecules were omitted by Squeeze program, and the Squeeze results were appended to the CIF file.
The crystal structure of [(S)-2·Ag]₃(PF₆)₃ was shown in Figure S2. The dihedral angle between the two NHC rings connected by a 1,3-phenylene unit was 82.73°, which was close to that in [(S)-2·Ag]₃(BF₄)₃ (82.81°).

![Figure S2](image)

**Figure S2.** The crystal structure of [(S)-2·Ag]₃(PF₆)₃ viewed along the c axis. The counteranions and solvent molecules were omitted by Squeeze program. Hydrogen atoms have been omitted for clarity. Atom color code: C (gray), N (blue), O (red), and Ag (orange).

5. Preparation and characterization of [(S)-2·Au]₃(BF₄)₃

[(S)-2·Ag]₃(BF₄)₃ (63 mg, 0.03 mmol) and (dimethylsulfide)gold(I) chloride [AuCl(Me₂S)] (29.5 mg, 0.1 mmol, 3.3 equiv) were added to CHCl₃ (10 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The filtrate was washed with water (5 mL), and the solvent was then removed in vacuo at room temperature to give a white solid, which was recrystallized from CHCl₃/EtOAc to afford colorless crystals (43 mg, ~ 60% yield). Colorless block crystals [(S)-2·Au]₃(BF₄)₃ suitable for X-ray analysis were obtained by slow evaporation of the corresponding chloroform/ethyl acetate solution at ambient temperature through several days. ¹H NMR (400 MHz, CDCl₃): δ 2.84-2.98 (m, 12H), 3.70 (dd, J = 12.0 Hz, 11.2 Hz, 12H), 3.98 (t, J =
7.6 Hz, 6H), 4.63 (d, J = 15.6 Hz, 6H), 5.02 (d, J = 15.6 Hz, 6H), 6.45 (d, J = 7.6 Hz, 12H), 7.03-7.12 (m, 18 H), 7.88 (d, J = 7.6 Hz, 6H), 8.00 (t, J = 8.0 Hz, 3H) 8.51 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 40.5, 57.0, 62.1, 65.3, 120.1, 125.5, 127.2, 129.0, 130.7, 136.0, 141.4, 148.8, 148.7, 181.2 (dd, J = 60 Hz, 60 Hz, carbene N-C-N) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): 150.7 (s, 8F), 154.1 (s, 4F). Anal. Calcd for C$_{90}$H$_{84}$Au$_3$N$_{18}$O$_6$B$_3$F$_{12}$: C, 45.71; H, 3.58; N, 10.66; Found: C, 45.36; H, 3.93; N, 10.29. ESI-TOF found: m/z = 701.19 (calcd for [(S)-2·Au]$^+$ 701.19); m/z = 2277.57 (calcd for [(S)-2·Au$_3$(BF$_4$)$_2$]$^+$ 2277.59).

6. Preparation and characterization of [(R)-2·Ag]$_3$(BF$_4$)$_3$

Bis-triazolium salt (R)-2·2HCl (58 mg, 0.1 mmol), NaBF$_4$ (12 mg, 0.11 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH$_2$Cl$_2$ (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from CHCl$_3$/EtOAc to afford a colorless crystalline product in 90% yield. Colorless block crystals [(R)-2·Ag]$_3$(BF$_4$)$_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding dichloromethane/ethyl acetate solution at ambient temperature through several days. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.85-2.98 (m, 12H), 3.71 (dd, J = 11.2 Hz, 12.0 Hz, 12H), 3.98 (t, J = 7.6 Hz, 6H), 4.63 (d, J = 15.6 Hz, 6H), 5.02 (d, J = 15.6 Hz, 6H), 6.45 (d, J = 7.6 Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, J = 7.6 Hz, 6H), 8.00 (t, J = 8.0 Hz, 3H) 8.54 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 40.5, 57.0, 62.1, 65.3, 125.5, 127.2, 129.0, 129.0, 130.7, 136.0, 141.4, 148.8 ppm (Note: the carbene resonance of [(R)-2·Ag]$_3$(BF$_4$)$_3$ was inconspicuous). Anal. Calcd for C$_{90}$H$_{84}$Ag$_3$N$_{18}$O$_6$B$_3$F$_{12}$: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.63; H, 4.27; N, 12.08. ESI-TOF found: m/z = 611.12 (calcd for [(R)-2·Ag]$^+$ 611.13); m/z = 2012.40 (calcd for [(R)-2·Ag]$_3$(BF$_4$)$_2$]$^+$ 2012.41).
7. Preparation and characterization of silver-NHC complexes through the reaction of Ag₂O and the mixture of (S)-2·2HCl and (R)-2·2HCl at a 1:1 ratio

A mixture of bis-triazolium salts (S)-2·2HCl and (R)-2·2HCl (at a 1:1 ratio) (116 mg, 0.2 mmol), NaBF₄ (24 mg, 0.22 mmol), and silver oxide (46 mg, 0.2 mmol) were added to CH₂Cl₂ (4 mL) under argon. The suspension became clear after being stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid (135 mg, 96% yield). ^1H NMR (400 MHz, CDCl₃): δ 2.85-2.98 (m, 12H), 3.70 (dd, J = 11.2 Hz, 12.0 Hz, 12H), 3.98 (t, J = 7.6 Hz, 6H), 4.63 (d, J = 15.6 Hz, 6H), 5.02 (d, J = 15.6 Hz, 6H), 6.45 (d, J = 7.6 Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, J = 8.0 Hz, 6H), 8.00 (t, J = 7.6 Hz, 3H), 8.53 (s, 3H) ppm. ^13C NMR (100 MHz, CDCl₃): δ 40.0, 57.0, 62.2, 65.2, 117.5, 122.7, 126.5, 128.4, 129.9, 130.1, 136.0, 140.5, 147.7 ppm (Note: the carbene resonances of the mixture were inconspicuous). 

Anal. Calcd for C₉₀H₈₄Ag₃N₁₈O₆B₃F₁₂: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.07; H, 3.64; N, 11.75. ESI-TOF found: m/z = 611.13 (calcd for [2·Ag]$^+$ 611.13); m/z = 2012.44 (calcd for [(2·Ag)$_3$(BF₄)$_2$]$^+$ 2012.41).

8. Preparation and characterisation of [(S)-3·Ag]₃(PF₆)₂(Cl)

Bis-triazolium salt (S)-3·2HCl (48.5 mg, 0.1 mmol), KPF₆ (20 mg, 0.11 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH₂Cl₂ (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from CHCl₃/EtOAc to afford a colorless crystalline product (41 mg, ~65% yield). ^1H NMR (400 MHz, CDCl₃): δ 0.56 (d, J = 6.8 Hz, 12H), 0.74 (d, J = 7.2 Hz, 12H), 0.84 (s, 6H), 0.95 (s, 6H), 2.22 (d, J = 4.8 Hz, 4H), 2.38 (s, 2H), 3.76 (d, J = 9.2 Hz, 6H), 4.02 (t, J = 11.6 Hz, 6H), 4.22 (d, J = 12.8 Hz, 3H), 4.51 (s, 2H), 4.68 (d, J = 15.6...
Hz, 4H), 4.84 (d, \(J = 16.0\) Hz, 3H), 4.99 (dd, \(J = 2.8\) Hz, 2.8 Hz, 6H), 7.59 (t, \(J = 8.0\) Hz, 1 H), 7.73-7.78 (m, 6H), 7.85 (d, \(J = 7.6\) Hz, 2H), 8.67 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 17.3, 17.7, 19.3, 19.8, 29.7, 33.1, 59.7, 59.8, 61.7, 61.9, 63.5, 64.4, 119.0, 125.2, 130.6, 131.3, 134.0, 141.3, 149.7, 149.9 ppm (Note: the carbene resonances in \([\text{(S-3-Ag)}_3\text{(PF}_6)_2\text{(Cl)}]\) were inconspicuous). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -71.43 (d, 1012 Hz, PF\(_6\)) ppm. Anal. Calcd for C\(_{66}\)H\(_{84}\)Ag\(_3\)N\(_{18}\)O\(_6\)P\(_2\)F\(_{12}\)Cl: C, 42.29; H, 4.52; N, 13.45; Found: C, 42.01; H, 4.25; N, 13.17. ESI-TOF found: \(m/z = 515.11\) (calcd for \([\text{(S-3-Ag)}]^+ 515.13\)); \(m/z = 1582.37\) (calcd for \([\text{[(S-3-Ag)}_3\text{Cl}]]^2+ 1582.37\)).

Colorless block crystals \([\text{(S-3-Ag)}_3\text{(PF}_6)_2\text{(Cl)(CHCl}_3)(EtOAc)}\) suitable for X-ray analysis were obtained by slow evaporation of the corresponding chloroform/ethyl acetate solution at ambient temperature through several days. The crystal structure of \([\text{(S-3-Ag)}_3\text{(PF}_6)_2\text{(Cl)(CHCl}_3)(EtOAc)}\) viewed from different angles are shown in Figure S3.

![Figure S3](image_url)

**Figure S3.** The crystal structure of \([\text{(S-3-Ag)}_3\text{(PF}_6)_2\text{(Cl)(CHCl}_3)(EtOAc)}\) viewed from different angles. Hydrogen atoms and solvents have been omitted for clarity. Atom color code: C (gray), N (blue), O (red), Ag (dark gray), Cl (bottle green), P (cyan), and F (green).

9. **Preparation and characterization of \([\text{(S-2-Ag)}_3\text{(X)}_3\) (X = Cl and/or AgCl\(_2\))**
Bis-triazolium salt ([S]-2·2HCl (58 mg, 0.1 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH₂Cl₂ (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a grey solid. The solid was then dissolved in CHCl₃, followed by addition of activated carbon. The mixture was refluxed under argon for 15 min, and then filtered through Celite. The filtrate was concentrated to ca. 5 mL, and then added to ethyl ester (50 mL) under stirring at room temperature to afford a white solid in 95% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.54 (t, J = 12.0 Hz, 6H₉), 3.52 (d, J = 12.4 Hz, 6H₈), 3.68 (dd, J = 4.4 Hz, 4.0 Hz, 6H₆), 3.78 (d, J = 12.4 Hz, 6H₇), 4.70 (s, br, 6H₅), 4.70 (d, J = 15.4 Hz, 6H₄), 5.01 (d, J = 16.0 Hz, 6H₃), 7.11 (s, 12H₉ and 6H₈), 7.29 (s, 12H₈), 7.58 (s, 3H₇), 7.80 (d, J = 7.6 Hz, 6H₆), 9.49 (s, 3H₅) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 39.9, 57.0, 62.2, 65.1, 117.5, 122.6, 126.5, 128.4, 128.9, 129.9, 130.1, 136.1, 140.5, 147.7 ppm (Note: the carbene resonances in [(S)-2·Ag]₃(X)₃ (X = Cl and/or AgCl₂) were inconspicuous). ESI-TOF found: m/z = 611.13 (calcd for [(S)-2·Ag]⁺ 611.13); m/z = 1905.97 (calcd for [(S)-2·Ag]₃Cl₂]⁺ 1905.33); m/z = 2049.08 (calcd for [(S)-2·Ag]₃Cl(AgCl₂)]⁺ 2049.20). Anal. calcd found: C, 51.01; H, 4.51; N, 12.39. It is difficult to calculate the relative amounts of anions (Cl⁻ and AgCl₂⁻) from the elemental analysis data of [(S)-2·Ag]₃(X)₃ (X = Cl and/or AgCl₂).
Figure S4. The HMQC and ROESY NMR of [(S)-2·Ag]_3(X)_3 (X = Cl and/or AgCl_2) in CDCl_3.
10. Preparation and characterization of \([\text{(S)}-2\cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_3\)

\([\text{(S)}-2\cdot \text{Ag}]_3(\text{X})_3\) (X = Cl and/or AgCl₂) (62 mg, ~ 0.03 mmol) and silver acetate (17 mg, 0.1 mmol, 3.3 equiv) were added to CHCl₃ (10 mL) under argon. The mixture was stirred for 10 h at room temperature, followed addition of activated carbon. The resulting mixture was stirred at 30 °C for 15 min, and then filtered through a Celite. The filtrate was washed with water (5 mL), concentrated to ca. 4 mL, and then added to ethyl ester (50 mL) under stirring to afford a white solid (56 mg, 94% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.05 (s, 9H, CH₃CO₂), 3.17 (t, J = 12.4 Hz, 6H₂), 3.58 (dd, J = 4.4 Hz, 4.4 Hz, 6H₂), 3.79 (d, J = 10.8 Hz, 6H₂), 4.11 (d, J = 12.4 Hz, 6H₂), 4.70 (s, br, 6H₂), 4.83 (d, J = 16.4 Hz, 6H₂), 5.13 (dd, J = 16.0 Hz, 6H₂), 7.28 (t, J = 4.0 Hz, 6H₂), 7.34-7.35 (m, 12H₃ and 12H₄), 7.58 (t, J = 7.6 Hz, 3H₃), 8.01 (d, J = 8.0 Hz, 6H₃) 8.68 (s, 3H₄) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 22.8, 40.0, 57.7, 62.2, 65.6, 116.3, 122.5, 127.5, 129.1, 129.8, 130.1, 135.5, 140.0, 148.6, 178.9 ppm (Note: the carbene resonance of \([\text{(S)}-2\cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_3\) was inconspicuous). Anal. Calcd for C₉₆H₉₃Ag₃N₁₈O₁₂: C, 57.24; H, 4.65; N, 12.52; Found: C, 57.65; H, 4.88; N, 12.28; ESI-TOF found: m/z = 611.10 (calcd for \([\text{(S)}-2\cdot \text{Ag}]^+\) 611.13); m/z = 1954.41 (calcd for \([\text{(S)}-2\cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_2]^+\) 1954.43); m/z = 2014.40 (calcd for \([\text{(S)}-2\cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_3 + \text{H}]^+\) 2014.45).
**Figure S5.** The HMOC and ROESY NMR of [(S)-2·Ag]₃(CH₃CO₂)₃ in CDCl₃.
11. Preparation and characterization of \([\text{(S)}-\text{2-Ag}]_3(\text{CF}_3\text{CO}_2)_3\)

\([(\text{S})-\text{2-Ag}]_3(\text{X})_3 (\text{X} = \text{Cl and/or AgCl}_2) (62 \text{ mg}, \sim 0.03 \text{ mmol}), \text{ and silver trifluoroacetate (22.1 mg, 0.1 \text{ mmol}, 3.3 equiv) were added to CHCl}_3 (10 \text{ mL}) under argon. The mixture was stirred for 10 h at room temperature, and activated carbon was added. The mixture was stirred for 15 min at 30 °C, and then filtered through a Celite. The filtrate was washed with water (5 mL), concentrated to ca. 4 mL, and then added to ethyl ester (50 mL) under stirring to afford a white solid (55 mg, 85% yield).

\(^1\text{H NMR (400 MHz, CDCl}_3\): \(\delta 3.08 \text{ (d, } J = 11.2 \text{ Hz, 6H}_g\), 3.31 (s, 6H\(_g\)), 3.82 (d, } J = 11.2 \text{ Hz, 6H}_e\), 4.02 (d, } J = 11.2 \text{ Hz, 6H}_i\), 4.76 (s, br, 3H\(_f\)), 4.80 (d, } J = 16.0 \text{ Hz, 6H}_d\), 4.80 (d, } J = 16.0 \text{ Hz, 6H}_d\), 7.06-7.16 (m, 12H\(_h\), 12H\(_i\) and 6H\(_j\)), 7.38 (s, 3H\(_c\)), 7.92 (d, } J = 6.8 \text{ Hz, 6H}_b\), 8.64 (s, 3H\(_a\)) ppm. \(^{13}\text{C NMR (100 MHz, CDCl}_3\): \(\delta 40.4, 57.2, 57.2, 62.1, 62.1, 65.8, 65.8, 112.9, 115.9, 117.1, 118.8, 121.7, 123.0, 127.3, 129.0, 129.5, 130.6, 135.7, 140.4, 148.9, 161.2, 161.5, 181.6 ppm. \(^{19}\text{F NMR (376 MHz, CDCl}_3\): \(\delta 74.0 \text{ (s, CF}_3\) ppm. Anal. Calcd for C\(_{96}\text{H}_{84}\text{Ag}_3\text{N}_{18}\text{O}_{12}\text{F}_9\): C, 52.98; H, 3.89; N, 11.58; Found: C, 53.25; H, 4.22; N, 11.24. ESI-TOF found: \(m/z = 611.13 \text{ (calcd for } [(\text{S})-\text{2-Ag}]^+ 611.13); m/z = 2062.36 \text{ (calcd for } [(\text{S})-\text{2-Ag}]_3(\text{CF}_3\text{CO}_2)_3)]^{2+} 2062.37).
Figure S6. The HMQC and ROESY NMR of [(S)-2·Ag]₃(CF₃CO₂)₃ in CDCl₃.
IV. Crystal parameters and refinement results of \([\text{(R)-1·Ag}]_2(\text{PF}_6)_2\), \([\text{(R)-1·Ag}]_2(\text{BF}_4)(\text{Cl})\), \([\text{(S)-2·Ag}]_3(\text{PF}_6)_3\), \([\text{(S)-2·Ag}]_3(\text{BF}_4)_3\), \([\text{(S)-2·Au}]_3(\text{BF}_4)_3\), \([\text{(R)-2·Ag}]_3(\text{BF}_4)_3\), and \([\text{(S)-3·Ag}]_3(\text{PF}_6)_2(\text{Cl})\cdot(\text{CHCl}_3)\cdot(\text{EtOAc})\).

Table S1. Crystal Parameters and Refinement Results of \([\text{(R)-1·Ag}]_2(\text{PF}_6)_2\), \([\text{(R)-1·Ag}]_2(\text{BF}_4)(\text{Cl})\), \([\text{(S)-2·Ag}]_3(\text{PF}_6)_3\), \([\text{(S)-2·Ag}]_3(\text{BF}_4)_3\), \([\text{(S)-2·Au}]_3(\text{BF}_4)_3\), \([\text{(R)-2·Ag}]_3(\text{BF}_4)_3\), and \([\text{(S)-3·Ag}]_3(\text{PF}_6)_2(\text{Cl})\cdot(\text{CHCl}_3)\cdot(\text{EtOAc})\)

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Calculated density (g cm⁻³) 1.443 1.621 1.433 1.625
μ (mm⁻¹) 0.674 4.526 0.681 0.936
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Independent reflections 6563 6306 6407 12951

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ε The counteranions (PF₆⁻) in [(S)-2·Ag₃(PF₆)₃ were omitted by Squeeze program.

V. Circular dichroism (CD) spectrum investigation of the silver NHC complexes

**Figure S7.** CD spectra of the silver NHC complexes at a concentration of 0.1 mg mL⁻¹ in CHCl₃. A (black line): [(S)-2·Ag₃(BF₄)₃; B (red line): [(R)-2·Ag₃(BF₄)₃; C and D (blue and cyan line): two typical CD spectra of the randomly picked bulk single crystals obtained from recrystallization of the rude mixture of the reaction of Ag₂O and the mixture of (S)-2·2HCl and (R)-2·2HCl at a 1:1 ratio; E (tan line): CD spectrum of the rude mixture of the reaction of Ag₂O and the mixture of (S)-2·2HCl and (R)-2·2HCl at a 1:1 ratio (before recrystallization).
VI. $^1$H NMR spectral changes of [(S)-2·Ag]$_3$(BF$_4$)$_3$ upon addition of 10 equiv TBACl in CDCl$_3$

![Figure S8](image)

Figure S8. $^1$H NMR spectra (400 MHz, CDCl$_3$) of a) [(S)-2·Ag]$_3$(BF$_4$)$_3$; and b) upon addition of 10 equivalents of tetrabutylammonium chloride (TBACl) to a CDCl$_3$ solution of [(S)-2·Ag]$_3$(BF$_4$)$_3$ at 20 °C.

VII. Influence of the counteranions of [(S)-2·Ag]$_3$(X)$_3$ on the hierarchical self-assemblies

The compound [(S)-2·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, or CF$_3$CO$_2$) was dispersed in 1 mL of solvent in a test tube. The resulting suspension was transferred to translucent gel after heating. The gel was simply confirmed by the “stable to inversion of a test tube” method. The results of gelation test in different solvents were summarized in Table S2.

Table S2. Gelation Test of Silver NHC Complexes (2 wt%) in Different Solvents

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<th>Solvent</th>
<th>[(S)-2·Ag]$_3$(Cl and/or AgCl)$_3$</th>
<th>[(S)-2·Ag]$_3$(CH$_3$CO$_2$)$_3$</th>
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<td>CHCl$_3$/EtOAc (~ 1/10 v/v)</td>
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<td>G</td>
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<td>CHCl$_3$&quot;</td>
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Higher concentrations (~ 50%) of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$) at 0 °C. S: solution; G: steady gel; G$_p$: partial gel; P: precipitate.

VIII. Morphology analysis of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$)

The morphologies of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$) were investigated using transmission electron microscope (TEM) and scanning transmission electron microscope (STEM). The TEM and STEM specimens were prepared by gently placing a carbon-coated copper grid on a surface of the sample. The grid was removed, stained with phosphotungstic acid aqueous solution (1 wt%) for $[\text{(S)-2·Ag\text{]}_3(\text{BF}_4)_3]$ and $[\text{(S)-2·Ag\text{]}_3(\text{CF}_3\text{CO}_2)_3]$, BaCl$_2$ aqueous solution (1 wt%) for $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = Cl and/or AgCl$_2$), and uranyl acetate aqueous solution (1%) for $[\text{(S)-2·Ag\text{]}_3(\text{CH}_3\text{CO}_2)_3]$ (or unstained), dried for 10 min at room temperature, and then subjected to observation.

IX. $^1$H NMR spectrum studies of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$)

The proton assignment of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, and CF$_3$CO$_2$) was confirmed by HMQC and ROESY NMR experiments in CDCl$_3$ (Figure S1, S4-S6). Compared with the $^1$H NMR spectrum of $[\text{(S)-2·Ag\text{]}_3(\text{BF}_4)_3]$, the chemical shifts of H$_a$, H$_h$, and H$_f$ of $[\text{(S)-2·Ag\text{]}_3(X)_3]$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, and CF$_3$CO$_2$) downfielded significantly, and the signals of H$_c$ were distinctly upfield shifted (Figure S9). These observations suggested significant differences in cation-anion interactions and noncovalent interactions of neighboring cation frameworks.
Figure S9. $^1$H NMR spectra (400 MHz, CDCl$_3$) of (a) [(S)-2·Ag]$_3$(BF$_4$)$_3$; (b) [(S)-2·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$); (c) [(S)-2·Ag]$_3$(CH$_3$CO$_2$)$_3$; and (d) [(S)-2·Ag]$_3$(CF$_3$CO$_2$)$_3$.

X. References


XI. Copies of $^1$H, $^{13}$C, and $^{19}$F NMR spectra
[(S)-2-Ag]_3(CF_3CO_2)_3