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Silver(I) Coordination Polymers Containing Heteroditopic Ureidopyridine Ligands: The Role of Ligand Isomerism, Hydrogen Bonding, and Stacking Interactions

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New silver (I) coordination polymers has been successfully designed and synthesized using heteroditopic ureidopyridine ligands **1** and **2** via a combination of coordinations bonds, hydrogen bonding, and π–π stacking interactions. This study shows an example of the orientation of the pyridine nitrogen relative to the urea moiety (4-substituted, **1**, or 3-substituted, **2**), used to control the packing of resulting crystalline coordination polymers. The ureidopyridine ligands present some flexibility because of the conformational rotation around the central urea moiety. The co-complexation of the silver(I) cation by two pyridine moieties and of the PF_6^- counteranion by the urea moiety results in the formation of discrete $[\mathbf{1}_2Ag]^+PF_6^-$, (**3**) and $[\mathbf{2}_2Ag]^+PF_6^-$, (**4**) complexes presenting restricted rotation around the central urea functionality. The geometrical information contained in the structures of ligands **1** and **2** and the heteroditopic complexation of silver hexafluorophosphate are fully exploited in an independent manner resulting in the emergence of quasi-rigidly preorganized linear and angular building blocks of **3** and **4**, respectively. Additional π–π stacking contacts involving interactions between the π-donor benzene and the π-acceptor pyridine systems reinforce and direct the self-assembly of the above-described combined structural motifs in the solid state. Accordingly, linear and tubular arrays of π–π stacked architectures are generated in the solid state by synergistic and sequential metal ion complexation, hydrogen bonding, and π–π stacking interactions

Introduction

Molecular construction in a bottom-up strategy and self-organization of new coordination polymers are the major facets of supramolecular chemistry and crystal engineering.[1,2] The design and construction of metal−organic coordination polymers has attracted intense interest not only for their potential applications as new functional materials but also for their fascinating structural and superstructural diversity. Crystal engineering of metal−organic networks via self-assembly of ligand "spacers" and metal "nodes" has attracted considerable interest because of the structural diversity in chemistry or material science. The path from molecular to large crystalline systems depends both on the nature of its constituents and on the interactions between them.[2−4] Among these interactions, noncovalent motifs such as metal−ligand coordination,[3] hydrogen bonding,[4] and $\pi-\pi$ stacking[5] have been used for the generation of a wide variety of such superstructures. In many previous examples, solvent molecules, anion templates or both were found to produce a dramatic effect on the extended structure of the network.[5,6] One approach to address this problem is to design molecular ligands built from binding subunits of different types to

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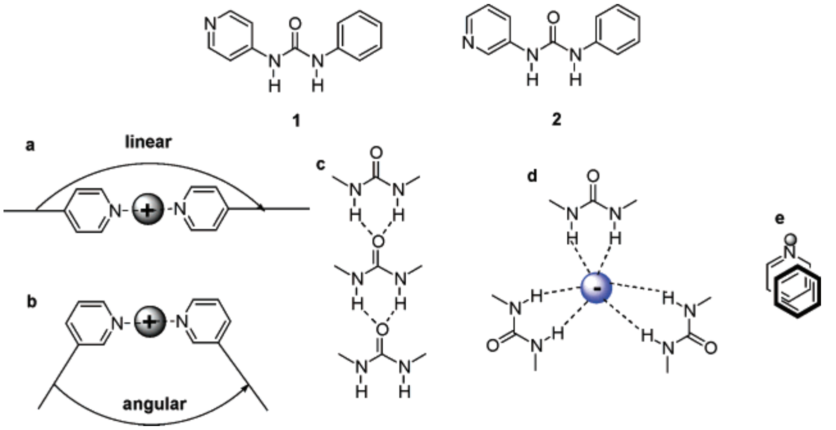

Figure 1. Concept and design of molecular precursors **1** and **2**. Drawings depict compounds **1** and **2** and show the (a) linear and (b) angular ion coordination directing structure scaffolds, the (c) urea head-to-tail and (d) anion urea hydrogen bonding, and the (e) $\pi-\pi$ stacking guiding interactions.

combine within their structures the information required for the processing of distinct noncovalent interactions leading to different supramolecular architectures.[6] Metal-directed self-assembly[3,6] or combined metal coordination, anion−hydrogen bonding (templating),[7] and $\pi-\pi$ stacking−metal coordination[5c,8] interactions have been extensively used as a powerful tools for the spontaneous generation of such crystalline coordination superstructures.

In this paper we describe new silver (I) coordination polymers, which are built up through the combination of silver-coordination, anion−hydrogen bonding, and $\pi-\pi$ stacking interactions. We have designed two heteroditopic ureidopyridine ligands, **1** and **2**, which complex the silver hexafluorophosphate by using both metal-coordination (pyridine) and anion−hydrogen bonding (urea) events (Figure 1). This study shows an example of the orientation of the pyridine nitrogen relative to the urea moiety (4-substituted, **1**, or 3-substituted, **2**) used to control the packing of the resulting crystalline coordination polymers. The self-assembly of discrete $[\mathbf{1}_2Ag]^+PF_6^-$ (**3**) and $[\mathbf{2}_2Ag]^+PF_6^-$ (**4**) complexes, in the crystalline coordination polymers, relies on the use of linear and angular geometries by means of directional information encoded within the metal and ligand precursors.

Results and Discussions

Design Strategy. The systems mentioned in this paper operate under conditions in which distinct metal coordination, hydrogen bonding, and $\pi-\pi$ stacking interactions should be involved in independent binding events between the heteroditopic ligands **1** and **2** and $AgPF_6$.

The molecular information contained in the structure of the heteroditopic ligands **1** and **2** (Figure 1) should be exploited by the metal ion coordination, urea-self self-assembly[9a] or hydrogen bond−anion coordination (templating)[9b,c] interactions. Molecular heteroditopic ligands **1** and **2** were designed as precursors for coordination polymeric materials by combining silver-coordination and hexafluorophosphate hydrogen bonding events and were based on three encoded features. (i) The coordination sphere of silver(I) can adopt coordination numbers between two and six and various geometries, as a function of the nature of the used ligand.[6] According to the literature, the silver(I) cation prefers a linear two-coordinate coordination geometry with N-donor ligands[6a] generating a variety of discrete square macrocycles[6b,c] or 1D, 2D, and 3D coordination polymers,[6a,6d−f] as a function of the molecular information stored in the ligand. Assuming that the ureidopyridine ligands **1** and **2** coordinate to Ag^+ cations upon a linear coordination geometry, their subsequent substitution in para and meta positions with benzourea groups might be directed by the subsequent hydrogen bonding events to the linear (Figure 1a) and angular (Figure 1b) coordination polymers. (ii) Hydrogen bonding guiding interactions could be one of the following: (a) the urea head-to-tail motif (Figure 1c) which could generate hydrogen bond ribbons or (b) the anion assisted self-assembly generating scaffold specific geometries (Figure 1d) as function of the hydrogen bond geometry of the resulting anion−urea complex.[7] (iii) Additional $\pi-\pi$ stacking contacts involving interactions between the π-donor benzene and the π-acceptor pyridine systems (Figure 1e)

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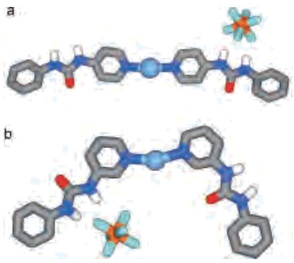


Figure 2. Crystal structure of silver complexes **3** and **4** indicating (a) a linear or (b) an angular relative disposition of phenylurea hydrogen bond directing substituents. The aromatic H atoms are omitted for clarity.

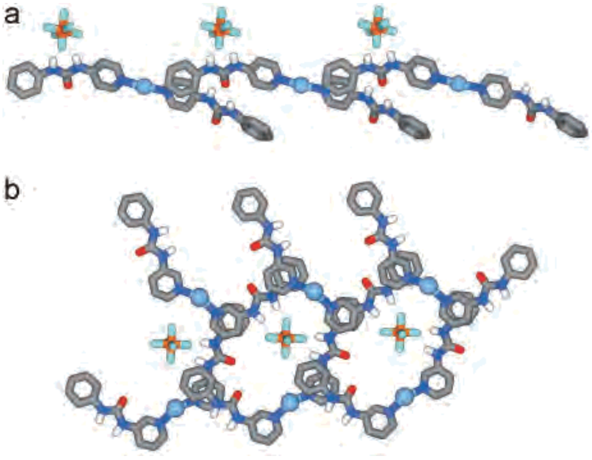


Figure 3. Stick representation of the crystal packing of silver complexes. They show (a) linear complex **3** and (b) the circular-type architecture of complex **4**. The aromatic H atoms are omitted for clarity.

might reinforce and direct the self-assembly of above-described combined structural motifs.[8]

Synthesis and Characterization of $[\mathbf{1}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$, 3 and $[\mathbf{2}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$, 4 Complexes. By following the above-mentioned strategy, we designed ligands **1** and **2**, which we prepared from phenyl isocyanate and 4- and 3-aminopyridine, respectively. Complexation studies revealed that the addition of $AgPF_6$ salt to acetonitrile suspensions of **1** or **2** (1/1, mol/mol) caused a rapid dissolution of the ligand to give colorless solutions, the quantitative result of which are complexes **3** and **4**. The ^{1}H NMR spectra of the complexes **3** and **4** were very sharp, indicating the formation of discrete metal complexes. They showed a deshielding of the pyridine protons, resulting from the silver complexation, and a deshielding of the N−H urea protons, resulting from the anion complexation. The positive electrospray mass spectra of the complexes **3** and **4** showed two peaksat 533.4 (100%) and 535.4 (100%), corresponding to isotopic species $[\mathrm{L}_2{}^{107}\mathrm{Ag}]^+$ and $[\mathrm{L}_2{}^{109}\mathrm{Ag}]^+$, of an almost equal abundance (L = **1** or **2**).

Crystal Structures of Linear $[\mathbf{1}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$ (3) and Tubular $[\mathbf{2}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$ (4) Architectures. Crystals of $[\mathbf{1}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$ (**3**) and $[\mathbf{2}_2\mathrm{Ag}]^+\mathrm{PF}_6^-$ (**4**) were obtained from acetonitrile/isopropyl ether (1/5, vol/vol) solutions at room temperature. The molecular structure and packing diagrams are presented in Figures 2−4. The crystal structure of Ag(I) complexes **3** and **4** revealed that these crystals are based on linear (Figure 2a) and angular (Figure 2b) elementary (monomeric) scaffolds.

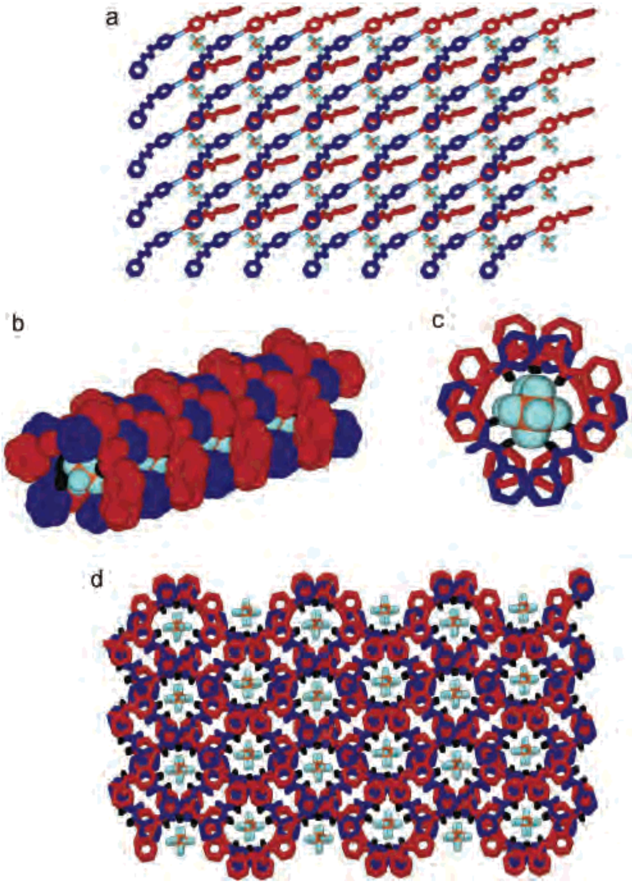


Figure 4. (a) Crystal packing of the linear supramolecular rods of complex **4**. (b) CPK representation along the axis of the stacks, (c) perpendicular stick representation (the PF_6^- are shown in CPK), and (d) crystal packing of the tubular bundles of complex **4**. The aromatic H atoms are omitted for clarity.

The Ag^+ ions are coordinated by two pyridine units situated in an almost planar arrangement (average Ag−N bond length is 2.15 Å), presenting a linear coordination geometry. Subsequent substitution of pyridine moieties in the 4 and 3 positions induced a linear or an orthogonal (inner angle between nitrogen mean lines of about 165° and 85°, respectively) relative disposition of the phenylurea hydrogen bond-directing phenylurea moieties.

PF_6^- counteranions were chosen for their strong F···H−N hydrogen bonding and their hydrophobic properties.[6] In both **3** and **4** monomeric complexes, the PF_6^- counteranion is hydrogen bonded to one urea moiety and the F···H−N hydrogen bond lengths fall within the range of 2.04−2.28 Å (Figure 2). This would result in the emergence of quasi-rigidly preorganized linear and angular building blocks of **3** and **4**, respectively.

The urea head-to-tail or anion−template hydrogen bonding interactions (Figure 1 panels c and d) could in principle yield a set of interconverting complexes in solution[10] and lead to a preferential expression of a specific member in the solid state.

The two independent hydrogen bonding interactions are expressed in an independent manner in the structure of complex **3** (Figure 3a). Both urea moieties of ligand **1** are connected by head-to-tail hydrogen bonds with one urea moiety of two neighboring molecules of **1** (average N−H−O distance is 3.01 Å, consistent with other urea systems[9]) which are each and successively bonded by a PF_6^- counteranion (Figure 3a). This results the urea−urea−PF_6^- hydrogen bonded triads, which developed in a parallel fashion. They are assisted by favorable $\pi-\pi$ stacking interactions between neighboring π-donor benzene molecules and π-acceptor pyridine rings (centroid−centroid distance of 3.98 Å, corresponding to van der Waals contact).

The solid-state architecture of **3** that resulted from the combination of these heterocomplexation processes is a linear coordination polymer with hydrogen bonded anions filling the voids between the parallel rods (Figure 4a).

The relative crystal packing of angular complex **4** is different from that of complex **3** and deserves some comment. In the solid-state structure of **4**, the urea−anion hydrogen bonding is preferred to the urea head-to-tail interaction and is favored by the relative angular disposition of the donor urea moieties (Figure 3b). This conformation allows considerable overlap between all of the aromatic pyridine−benzene pairs of the neighboring angular monomers of **4** (average $\pi-\pi$ stacking centroid−centroid distance of 3.65 Å, Figure 3b). Accordingly, tubular arrays of $\pi-\pi$ stacked columnar architectures of about 15 Å external diameter are generated in the solid state (Figure 4 panels b−d). The synergistic effect of the silver(I) metal−ion complexation, the anion−hydrogen bond templating, and the large stacking interactions result in the formation of a regulated polytubular bundle-type architecture in which the anions are arranged into an approximately linear array, tightly fitting into a polar N−H surrounded central cavity of about 8.40 Å diameter. One may point out that the role of the stacking interaction in the present tubular superstructure is related to that previously described for organic nanotubes[11] or artificial mono[12] and double helix supramolecular architectures.[8,13]

Conclusion

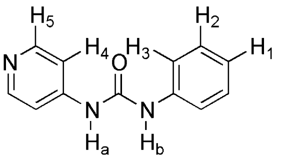
In conclusion, new silver(I) coordination polymers have been successfully designed and synthesized using heteroditopic ureidopyridine ligands **1** and **2** via the combination of silver(I) coordination, hydrogen bonds, and $\pi-\pi$ stacking interactions. Although many coordination polymers[2,6] have been widely studied on the basis of coordination bonds, a smaller number of examples focus on the combination of coordination bond and multi-supramolecular interactions. Generally, control over the self-assembly process is achieved by using a structurally rigid species.[14] The heteroditopic ureidopyridine ligands have some flexibility because of the conformational rotation around the central urea moiety. The co-complexation of the silver(I) cation by two pyridine moieties and the co-complexation of the PF_6^- counteranion by the urea moiety results in the formation of discrete $[\mathbf{1}_2Ag]^+PF_6^-$ **(3)** and $[\mathbf{2}_2Ag]^+PF_6^-$ (**4**) complexes with restricted rotation around the central urea functionality. The geometrical information contained in the structure of ligands **1** and **2** and the heteroditopic complexation of silver hexafluorophosphate are fully exploited in a independent way resulting in the emergence of quasi-rigidly preorganized linear and angular building blocks of **3** and **4**, respectively. Additional $\pi-\pi$ stacking contacts reinforce and direct the self-assembly of the above-described combined structural motifs in the solid state. Accordingly, the linear and tubular arrays of $\pi-\pi$ stacked architectures are generated in the solid state by synergistic and sequential metal ion complexation, hydrogen bonding, and $\pi-\pi$ stacking interactions

Experimental Section

General Methods. All reagents were obtained from commercial suppliers and used without further purification. Acetonitrile was distilled over CaH_2. All organic solutions were routinely dried using sodium sulfate (Na_2SO_4). Column chromatography was carried out on Merck alumina activity II−III.

^1H and ^{13}C NMR and COSY and ROESY spectra were recorded on an ARX 250 MHz Bruker spectrometer in CD_3CN. Mass spectrometric studies were performed using a quadrupole mass spectrometer (Micromass). The microanalyses were carried out at Service de Microanalyses, CNRS, Lyon, France.

General Procedure for the Synthesis of Compounds 1 and 2. Compounds **1** and **2** were prepared by adding phenyl isocyanate to the corresponding 4- and 3-aminopyridine (1.5/1 mol/mol) in benzene, and reaction was refluxed under Ar for 5 h. After the solvent was removed, the residue was subjected to recrystallization from acetonitrile to produce **1** and **2** as colorless crystals.



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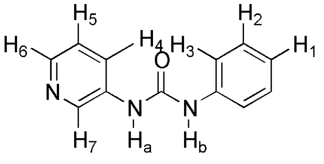

2

1-Phenyl-3-pyridine-4-yl-urea (1). Yield: 85%. ^1H NMR (CH_3CN): δ 7.1 (t, J = 6.95 Hz, 1H, H_1), 7.28 (m, 6H, H_2 H_3, H_4), 8.1 (s, 1H, H_b), 8.4 (d, J = 6.03 Hz, 2H, H_5), 8.8 (s, 1H, H_a). ^{13}C NMR ($CDCl_3$): δ 113.6, 120.7, 124.6, 129.6, 138.0, 147.7, 150.2, 153.0. ES-MS: m/z [M + H^+] 214 (100). Anal. Calcd for $C_{12}H_{11}N_3O$ (213.2 g/mol): C, 67.59; H, 5.20; N, 19.71. Found: C, 67.49; H, 5.33; N, 19.10.

1-Phenyl-3-pyridine-3-yl-urea (**2**). Yield: 80%. ^1H NMR (CH_3CN): δ 7.1 (t, J = 6.95 Hz, 1H, H_1), 7.26 (m, 6H, H_2 H_3, H_4, H_7), 8.2 (s, 1H, H_b), 8.3 (d, J = 6.03 Hz, 1H, H_5), 8.53 (d, J = 6.03 Hz, 1H, H_6), 8.9 (s, 1H, H_a). ^{13}C NMR($CDCl_3$): δ 120.7, 124.6, 129.6,

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(10) In particular, a dynamic library of such hydrogen bond complexes can be generated from which a preferential expression could be extracted by crystallization. For example, see: (a) Baxter, P. W. N.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.*−*Eur J.* **2000**, 6, 4510−4517. (b) Baxter, P. W. N.; Khoury, R. G.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.*−*Eur J.* **2000**, *6*, 4140−4148.

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138.0, 139.4, 147.7, 150.2, 153.0. ES-MS: m/z [M + H$^+$] 214 (100). Anal. Calcd for $C_{12}H_{11}N_3O$ (213.2 g/mol): C, 67.59; H, 5.20; N, 19.71. Found: C, 67.12; H, 5.44; N, 19.80.

X-ray Crystallographic Data for Complexes 3 and 4. X-ray diffraction data for silver complexes **3** and **4** were collected with monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) on an Xcalibur diffractometer (Oxford Diffraction) equipped with a CCD camera. Data were reduced using the Crysalis RED software. The structures were determined using direct methods and refined by the full-matrix least-squares methods (CRYSTALS[15]). All data were used for the refinements except for **4** where only data with $I > 2\sigma(I)$ were used. Data for the latter compound were particularly weak because of the size of the selected crystal. Non-hydrogen atoms were refined anisotropically, except for **4**. For this compound, the PF_6^- counterions were refined as a rigid body. Hydrogen atoms were generally found using the Fourier difference maps and were allowed to ride on their parent atoms.

$[\mathbf{1}_2Ag]^+PF_6^-$ (3). Compound **3** was formed from ligand **1** (3 mg, 14.0 mmol) and $AgPF_6$ (18 mg, 7.0 mmol) in CD_3CN at room temperature. ^{1}H NMR (CH_3CN): δ 7.1 (t, $J = 6.95$ Hz, 1H, H_1), 7.26 (m, 4H, H_2, H_3), 8.1 (t, $J = 6.03$ Hz, 1H, H_5), 8.3 (d, $J = 6.03$ Hz, 2H, H_4), 8.53 (d, $J = 6.03$ Hz, 2H, H_6), 8.7 (s, 1H, H_b), 9.1 (s, 1H, H_a). ES-MS: m/z 533.4 (100%) $[\mathbf{1}_2{}^{107}Ag]^+$, 535.4 (100%) $[\mathbf{1}_2{}^{109}Ag]^+$. X-ray crystallographic data: $C_{24}H_{22}AgF_6N_6O_2P$; crystal dimensions: 0.40 × 0.20 × 0.09 mm; cell dimensions $a = 9.5870(7)$ Å, $b = 11.7012(8)$ Å, $c = 12.0765(7)$ Å, $\alpha = 109.30(1)°$, $\beta = 90.750(8)°$, $\gamma = 89.690(9)°$, $V = 1278.4(2)$ Å^3; triclinic; space group $P\bar{1}$; $Z = 2$; $\rho_{calcd} = 1.765$ gcm^{-3}; $\mu = 0.931$ mm^{-1}; 23558 measured reflections, 14350 unique, 2794 with $I > 2\sigma(I)$; final R factors, $R_1 = 0.1186$ and $R_2 = 0.0759$ ($R_1 = 0.0347$ and $R_2 = 0.0447$ for data $I > 2\sigma(I)$); 361 parameters. Maximal residual electron density: 1.460 eÅ^{-3}.

$[\mathbf{2}_2Ag]^+PF_6^-$ (4). Compound **4** was formed from ligand **2** (3 mg, 14.0 mmol) and $AgPF_6$ (18 mg, 7.0 mmol) in CD_3CN at room temperature. ^{1}H NMR (CH_3CN): δ 7.1 (t, $J = 6.95$ Hz, 1H, H_1), 7.26 (m, 4H, H_2, H_3), 8.3 (d, $J = 6.03$ Hz, 2H), 8.53 (t, $J = 6.03$ Hz,1H), 8.73 (d, $J = 6.03$ Hz,1H, H_2, H_3), 8.9 (s, 1H, H_a), 9.2 (s, 1H, H_2, H_b). ES-MS: m/z 533.4 (50%) $[2_2{}^{107}Ag]^+$, 535.4 (50%) $[2_2{}^{109}Ag]^+$. X-ray crystallographic data: $C_{26}H_{25}AgF_6N_7O_2P$; crystal dimensions 0.10 × 0.08 × 0.05 mm; cell dimensions $a = 10.907(1)$ Å, $b = 20.387(1)$ Å, $c = 13.286(2)$ Å, $\alpha = 90°$, $\beta = 106.19(2)°$, $\gamma = 90°$, $V = 2837.1(6)$ Å^3; monoclinic; space group $P2_1/c$; $Z = 4$; $\rho_{calcd} = 1.686$ gcm^{-3}; $\mu = 0.845$ mm^{-1}; 53888 measured reflections, 9604 unique, 716 with $I > 2\sigma(I)$; final R factors, $R_1 = 0.1171$ and $R_2 = 0.1342$; 153 parameters. Maximal residual electron density: 1.860 eÅ^{-3}.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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