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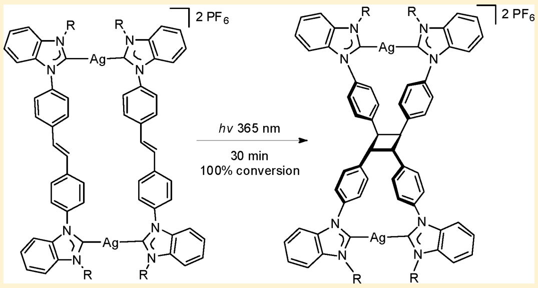
Photochemical Modification of Carbene-Based Metallacycles: A Facile Route to Polycarbene Complexes and Their Derivatives

Chun-Xiang Wang, Yang Gao, Yu-Xin Deng, Yue-Jian Lin, Ying-Feng Han,* and Guo-Xin Jin*

Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, 220 Handan Road, 200433 Shanghai, People's Republic of China

Supporting Information

ABSTRACT: The modification of dinuclear silver metallcycles via photochemical [2 + 2] cycloaddition is described. Reaction of benzimidazole with *trans*-4,4′-dibromostilbene gives *trans*-4,4′-bis(1*H*-benzo[*d*]imidazolyl)stilbene (**L**), which after subsequent dialkylation with alkyl bromides and anion exchange yields the corresponding dibenzimidazolium salts H_2-**1**$(PF_6)_2$ and H_2-**2**$(PF_6)_2$. The dibenzimidazolium salts react with Ag_2O to give the dinuclear silver(I) tetracarbene metallacycles Ag_2(**1**)$_2(PF_6)_2$ and Ag_2(**2**)$_2(PF_6)_2$ in high yield. Irradiation (UV light, λ 365 nm) of Ag_2(**1**)$_2(PF_6)_2$ and Ag_2(**2**)$_2(PF_6)_2$ in [D_6]DMSO resulted in rapid conversion into the corresponding dinuclear cyclobutane-carbene complexes Ag_2(**3**)$(PF_6)_2$ and Ag_2(**4**)$(PF_6)_2$ quantitatively. The cyclobutane-bridged polycarbene precursors were isolated in good yields as their tetrabenzimidazolium salts.



INTRODUCTION

In recent decades, metal−ligand-directed assemblies have played a prominent role in the design and construction of functional supramolecular architectures with a wide range of properties.[1] In contrast to the intense interest focused on the construction of typical Werner-type complexes, our knowledge of organometallic molecular assemblies (i.e., those containing metal−carbon bonds) is still somewhat underdeveloped.[2] N-heterocyclic carbene (NHC) ligands can form highly stable M−C_{NHC} bonds due to their strong electron-donor abilities to metal ions.[3] Metal−carbene complexes, formed from NHC ligands and metals, are an exciting class of structures with utility in catalysis,[4] medicine,[5] and functional materials.[6] Recently, intense research efforts have been directed toward the development of discrete organometallic assemblies based on poly-NHC ligands.[3,7] An efficient method to prepare such assemblies is silver(I)-mediated self-assembly. Such silver(I)−dicarbene complexes are usually obtained easily by reacting Ag_2O with the corresponding bis-imidazolium salts. Dinuclear silver(I)−NHC metallacycles have been reported with a variety of bridging motifs.[7,8] This method can also be used for the synthesis of three-dimensional metal−carbene assemblies.[9]

However, to the best of our knowledge, the functionalization of organometallic assemblies containing poly-NHC ligands has only been presented recently.[9] In previous work, we and others focused on template-designed photodimerization of olefins.[10] We found that a number of metallacycles can be used as organometallic templates to direct photochemical [2 + 2] cycloaddition reactions.[11] In general, [2 + 2] photodimerization occurs when the two olefinic groups lie approximately parallel and are separated by less than 4.2 Å. Photochemical [2 + 2] cycloaddition reactions have thereby provided an approach to postassembly modification and functionalization of target complexes in the solid state and in solution.[10−12]

Over the last two years, we have developed a photochemical modification method for dinuclear Ag^I and Au^I molecular rectangles featuring olefin-bridged dicarbene ligands.[13] The metallacycles $[M_2(\text{dicarbene})_2]^{2+}$ (M = Ag, Au) are good candidates for the photodimerization of olefinic double bonds within molecular rectangles. Following this strategy, a series of cyclobutane-based tetracarbene complexes were synthesized. In addition, a new method to polycarbene precursors has been developed by removal of metal centers. Building upon the successful modification of imidazolium-derived metallaycles by photochemical reaction, the photochemical modification of related benzimidazolium-derived metallacycles is an attractive goal in order to expand the possibilities for assembly and postassembly modification of new macromolecular carbene assemblies. In addition, cyclobutanes, the structural unit formed by photochemical [2 + 2] olefin dimerization, have attracted much attraction, in part because they are important in biology and biotechnology applications.[14]

Here we describe the preparation of dinuclear silver(I) dicarbene complexes from benzimidazolium salts featuring internal olefin groups. These metallacycles can be effectively modified by photochemical [2 + 2] cycloaddition reactions. The isolation of the cyclobutane-bridged tetracarbene precursors was subsequently realized by liberation of silver metals.

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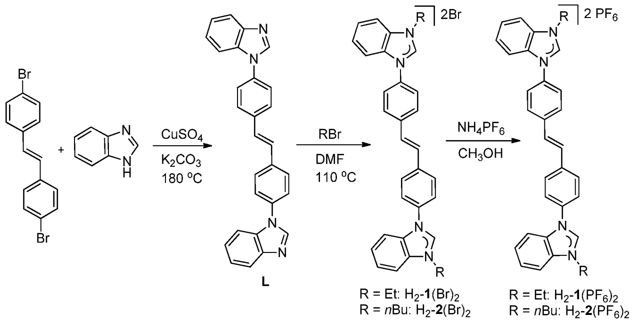
■ RESULTS AND DISCUSSION

trans-4,4′-Dibromostilbene was synthesized from 4-bromobenzaldehyde and 1-bromo-4-(bromomethyl)benzene according to a reported protocol.[15] As shown in Scheme 1, the dibenzoimidazolium salts H_2-**1**$(PF_6)_2$ and H_2-**2**$(PF_6)_2$ were prepared by a three-step procedure in good yields starting from *trans*-4,4′-dibromostilbene and benzimidazole. The ligand (*E*)-1,2-bis(4-(1H-benzo[*d*]imidazol-1-yl)phenyl)ethene (**L**) was synthesized by the solid-state reaction of *trans*-4,4′-dibromostilbene and 1*H*-benzo[*d*]imidazole in the presence of $CuSO_4 \cdot 5H_2O$ and K_2CO_3.

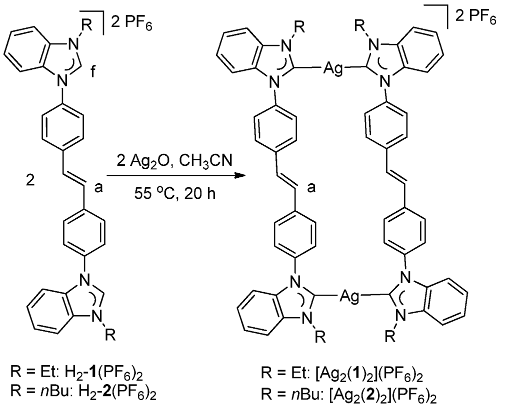
Scheme 1. Synthesis of the Ligand Precursors



The alkylation of **L** with ethyl bromide or *n*-butyl bromide gave the corresponding dibenzimidazolium salt H_2-**1**$(Br)_2$ or H_2-**2**$(Br)_2$. The bromide compounds H_2-**1**$(Br)_2$ and H_2-**2**$(Br)_2$ could be converted into H_2-**1**$(PF_6)_2$ and H_2-**2**$(PF_6)_2$ by anion exchange with ammonium hexafluorophosphate in methanol. The ^{1}H NMR spectra of H_2-**1**$(Br)_2$ and H_2-**2**$(Br)_2$ in $[D_6]$DMSO show characteristic resonances for the benzimidazolium C2−H protons at δ 10.28 and 10.30 ppm, respectively. The corresponding signals were observed upfield at δ 9.25 and 9.26 ppm for H_2-**1**$(PF_6)_2$ and H_2-**2**$(PF_6)_2$, which are consistent with previous observations upon anion exchange from bromide to hexafluorophosphate salts.[13] The typical olefinic resonance is observed at δ 7.67 (H_2-**1**$(PF_6)_2$) or 7.53 ppm (H_2-**2**$(PF_6)_2$).

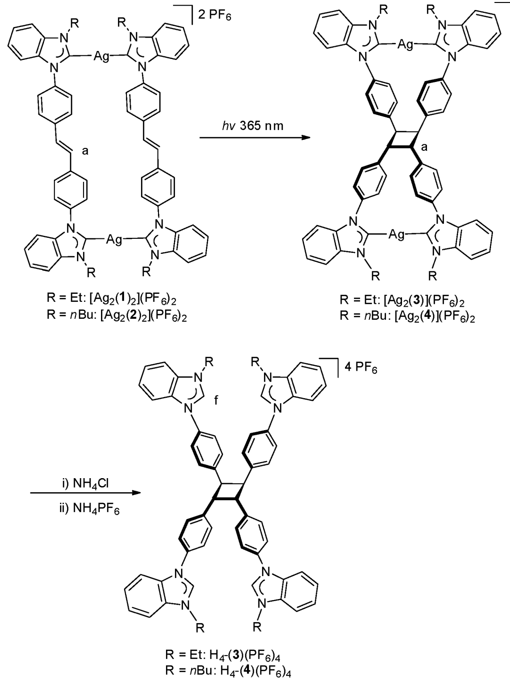
The reaction of H_2-**1**$(PF_6)_2$ or H_2-**2**$(PF_6)_2$ with Ag_2O, as shown in Scheme 2, afforded the desired disilver(I) tetracarbene complex Ag_2(**1**)$_2(PF_6)_2$ or Ag_2(**2**)$_2(PF_6)_2$ in high yield. Each reaction was complete after 20 h at 55 °C in acetonitrile. Successful formation of the carbene complexes was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Positive-ion electrospray ionization mass spectroscopic (ESI-MS) studies further supported the formation of discrete supramolecular rectangles. For example, the ESI-MS spectrum for Ag_2(**1**)$_2(PF_6)_2$ showed peaks at *m*/*z* 576.1379, corresponding to $[Ag_2(\mathbf{1})_2]^{2+}$ (calcd for $[Ag_2(\mathbf{1})_2]^{2+}$ *m*/*z* 576.1362), and *m*/*z* 1297.2386, attributed to $[Ag_2(\mathbf{1})_2(PF_6)]^+$ (calcd for $[Ag_2(\mathbf{1})_2(PF_6)]^+$ *m*/*z* 1297.2371). The ESI mass spectrum (positive ions) confirmed the formation of $[Ag_2(\mathbf{2})_2](PF_6)_2$ by exhibiting an intense peak at *m*/*z* 632.2006 (calcd for $[Ag_2(\mathbf{2})_2]^{2+}$ *m*/*z* 632.1989).

Scheme 2. Synthesis of Dinuclear Tetracarbene Metallacycles



Photolysis of the metallacyclic rectangles Ag_2(**1**)$_2(PF_6)_2$ and Ag_2(**2**)$_2(PF_6)_2$ was investigated (Scheme 3). The photochemical reaction was carried out at room temperature in a Pyrex tube with a 400 W high-pressure mercury lamp as a light source. Irradiation (Hg lamp, 365 nm) of Ag_2(**1**)$_2(PF_6)_2$ in degassed $[D_6]$DMSO resulted in rapid and practically complete conversion into the corresponding *rctt*-tetracarbene-substituted cyclobutane-bridged dinuclear silver complex Ag_2(**3**)$(PF_6)_2$. As judged by ^{1}H NMR, the [2 + 2] cycloaddition was complete in 30 min. Although the ^{1}H NMR resonances of Ag_2(**1**)$_2(PF_6)_2$ are slightly broadened, the corresponding peaks were found to be sharp after photoreaction. The ^{1}H NMR spectrum of Ag_2(**3**)$(PF_6)_2$ displayed a sharp singlet at 4.98 ppm corresponding to a single cyclobutane environment. The ^{13}C{^{1}H} NMR spectrum of Ag_2(**3**)$(PF_6)_2$ features a signal for the carbon nuclei of the cyclobutane ring at 44.39 ppm. Similarly, UV irradiation of Ag_2(**2**)$_2(PF_6)_2$ afforded the desired dimer product Ag_2(**4**)$(PF_6)_2$ in nearly quantitative conversion. As can be seen from Figure 1, the spectrum of the photoreaction product showed the disappearance of the olefin proton signal at 7.51 ppm and the appearance of the cyclobutane proton signal at 4.99 ppm (Figure 1b,c).

Scheme 3. Photochemical Reactions of Metallacycles and the Formation of the Polybenzimidazolium Salts



UV−vis measurements also clearly indicated that photodimerization had occurred (Figures S1 and S2 in the Supporting Information). In each case, the spectrum showed

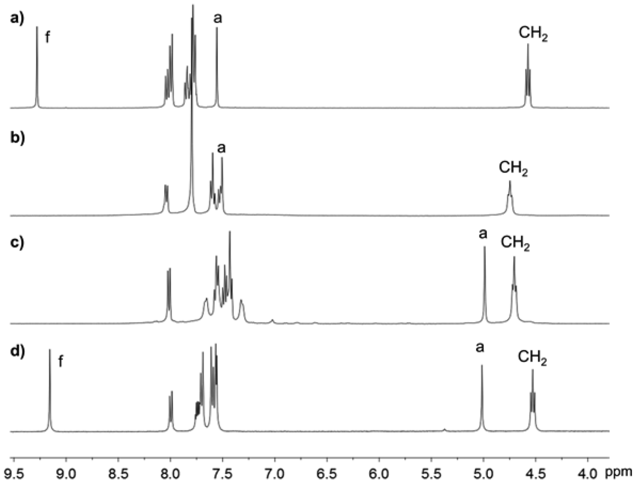


Figure 1. Partial ^{1}H NMR spectra (400 Hz, 300 K) of (a) H_2-**2**$(PF_6)_2$ in CD_3CN, (b) before and (c) after UV irradiation of Ag_2(**2**)$_2(PF_6)_2$ in [D_6]DMSO, and (d) H_4-**4**$(PF_6)_4$ in CD_3CN.

the disappearance of the absorption band around 320 nm after the photochemical reaction, which is consistent with the cycloaddition of two olefinic groups. Further fluorescence experiments also supported this conclusion (Figures S3 and S4 in the Supporting Information).

Although silver(I)−carbene complexes are often slightly sensitive to light, NMR spectroscopy indicated that no byproducts were formed during these processes. Attempts to investigate the photodimerization in the solid state failed because of the decomposition of silver−carbene complexes under UV irradiation.[13a]

Single-crystal X-ray structural analysis revealed the expected molecular structure containing a cyclobutane ring (Figure 2).[16] Metric parameters such as M−C_{NHC} bond lengths (2.080(7)−2.099(8) Å) and C_{NHC}−M−C_{NHC} angles (177.1(3) and 177.3(3)°) in the $[Ag_2(\mathbf{4})]^{2+}$ cation are in the ranges previously observed for linearly coordinated bis(NHC) silver complexes.

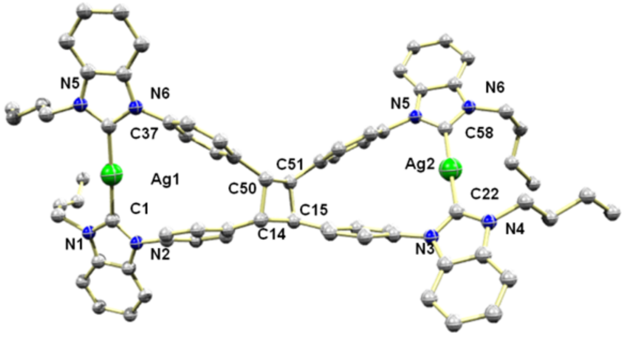


Figure 2. Crystallographically derived molecular structure of the dication $[Ag_2(\mathbf{4})]^{2+}$ (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag(1)−C(37) 2.080(7), Ag(1)−C(1) 2.093(6), Ag(2)−C(58) 2.098(8), Ag(2)−C(22) 2.099(8), N(1)−C(1) 1.353(8), N(2)−C(1) 1.351(8), N(3)−C(22) 1.353(10), N(4)−C(22) 1.346(9), N(5)−C(37) 1.371(9), N(6)−C(37) 1.386(10), N(7)−C(58) 1.370(10), N(8)−C(58) 1.349(9), C(14)−C(15) 1.541(10), C(14)−C(50) 1.574(10), C(15)−C(51) 1.586(10), C(50)−C(51) 1.551(11); C(37)−Ag(1)−C(1) 177.1(3), C(58)−Ag(2)−C(22) 177.3(3), C(15)−C(14)−C(50) 89.1(5), C(14)−C(15)−C(51) 87.8(5), C(51)−C(50)−C(14) 87.9(5), C(50)−C(51)−C(15) 88.3(6).

The addition of ammonium chloride successfully resulted in removal of the silver cations by the precipitate of AgCl from the solution (Scheme 3). The formed chloride salts were then converted to the hexafluorophosphate salts H_4-**3**$(PF_6)_4$ and H_4-**4**$(PF_6)_4$ by reactions with NH_4PF_6 in MeOH. In all cases, the only product observed was the stereospecific tetrabenzimidazolium salt. Compounds H_4-**3**$(PF_6)_4$ and H_4-**4**$(PF_6)_4$ exhibit typical NMR spectra for highly symmetrical structures in solution. All of the proton and carbon signals were fully assigned by 2D NMR measurements (H−H COSY, HSQC, and HMBC). For example, in H_4-**4**$(PF_6)_4$, two sharp singlets were observed at 9.11 and 4.99 ppm in a 1:1 ratio as expected, identical with the signals for the C2−H benzimidazolium and cyclobutane ring protons, respectively. ESI-MS data provided further evidence for the formation of the tetrabenzimidazolium salt. For example, the ESI mass spectrum for H_4-**4**$(PF_6)_4$ showed isotopically resolved peaks at *m*/*z* 671.2748 and 1487.5113, due to $[H_4\text{-}\mathbf{4}(PF_6)_2]^{2+}$ and $[H_4\text{-}\mathbf{4}(PF_6)_3]^{+}$, respectively.

Single crystals of the tetrabenzimidazolium hexafluorophosphate salts were obtained by slow diffusion of diethyl ether into saturated acetonitrile solutions of H_4-**3**$(PF_6)_4$ at ambient temperature. The X-ray crystal structure analysis of H_4-**3**$(PF_6)_4$ shows the presence of cyclobutylene-bridged tetrabenzimidazolium ligands (Figure 3). The C−C single bonds of the bridging four-membered carbocycle amount to 1.559(4) Å (C14−C15) and 1.572(4) Å (C14−C15A).

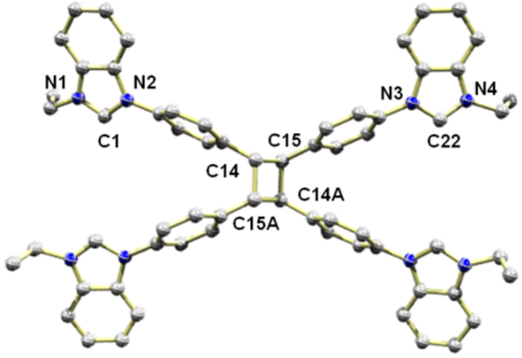


Figure 3. Crystallographically derived molecular structure of the cation $[H_4\text{-}\mathbf{3}]^{4+}$ in H_4-**3**$(PF_6)_4$ crystals (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): N(1)−C(1) 1.322(4), N(2)−C(1) 1.335(4), C(14)−C(15) 1.559(4), C(14)−C(15A) 1.572(4); N(1)−C(1)−N(2) 110.3(3), N(3)−C(22)−N(4) 110.3(3), C(15)−C(14)−C(15A) 90.0(2), C(14)−C(15)−C(14A) 90.0(2).

In conclusion, we have demonstrated the synthesis of two new dibenzimidazolium salts containing internal olefinic groups. Reactions of the obtained dibenzimidazolium salts with Ag_2O yield the corresponding rectangular dinuclear disilver(I) carbene complexes. Irradiation of Ag_2(**1**)$_2(PF_6)_2$ or Ag_2(**2**)$_2(PF_6)_2$ in solution resulted in rapid conversion into the corresponding dinuclear *rctt*-cyclobutane−carbene complex Ag_2(**3**)$(PF_6)_2$ or Ag_2(**4**)$(PF_6)_2$. After removal of the metal centers, the cyclobutane-bridged polycarbene precursors were isolated as their tetrabenzimidazolium salts. This method demonstrates the feasibility of utilizing photochemical [2 + 2] cycloaddition reactions at active olefinic groups within metal−carbene metallacycles. This work presented here also provides a new entry to the synthesis of potentially very useful

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polycarbene precursors. The application of the new cyclobutane-bridged tetrabenzimidazolium salts is the subject of current research in our laboratory.

■ EXPERIMENTAL SECTION

Description of Synthetic Procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Glassware was oven-dried at 130 °C prior to use. Solvents were freshly distilled by standard procedures prior to use. ^{1}H, ^{13}C{^{1}H}, and 2D NMR spectra were recorded on Bruker AVANCE I 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. Coupling constants are expressed in hertz. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen, Germany) spectrometers. UV–vis spectra were obtained using an Agilent 8453 spectrophotometer. Fluorescence emission spectra were obtained using a Cary Eclipse spectrofluorophotometer (Varian). Elemental analyses were performed on an Elementar Vario EL III analyzer. *trans*-4,4′-Dibromostilbene[17] was synthesized according to reported procedures. All other chemicals were purchased from commercial sources and used as received.

Synthesis of (*E*)-1,2-Bis(4-(1*H*-benzo[*d*]imidazol-1-yl)-phenyl)ethene (L). Samples of *trans*-4,4′-dibromostilbene (0.34 g, 1.0 mmol), benzoimidazole (0.47 g, 4.0 mmol), K_2CO_3 (0.55 g, 4.0 mmol) and $CuSO_4\cdot5H_2O$ (0.02 g, 0.08 mmol) were mixed in a 50 mL round-bottom flask, and this mixture was heated under an argon atmosphere for 24 h to 180 °C. The reaction mixture was cooled to ambient temperature and washed three times with hot water. The solid residue was extracted with dichloromethane (120 mL). The solution was brought to dryness and then was washed with methanol. The solid was dried under vacuum to give a colorless product. Yield: 0.35 g (0.85 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 (s, 2H, NCHN), 7.91 (d, 4H, *J* = 8.32 Hz, Ar–H), 7.80 (d, 2H, *J* = 7.68 Hz, Ar–H), 7.74 (d, 4H, *J* = 8.32 Hz, Ar–H), 7.69 (d, 2H, *J* = 7.68 Hz, Ar–H), 7.50 (s, 2H, CH═CH), 7.35 (m, 4H, Ar–H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 143.86, 143.20, 136.32, 135.20, 132.98, 128.23, 128.06, 123.82, 123.50, 122.49, 119.97, 110.77 ppm. Anal. Calcd for $C_{28}H_{20}N_4$ (412.17): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.46; H, 4.95; N, 13.24.

Synthesis of H_2-1(Br)$_2$. A Schlenk flask was charged with *trans*-4,4′-bis(1-benzoimidazolyl)stilbene (0.41 g, 1.0 mmol) and an excess of ethyl bromide (0.44 g, 4.0 mmol). To this mixture was added DMF (5 mL), and the reaction mixture was heated to 110 °C for 24 h. During this time a white compound precipitated, which was filtered off, washed with diethyl ether, and dried under vacuum to give H_2-**1**(Br)$_2$ as a white solid. Yield: 0.60 g (0.95 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.28 (s, 2H, NCHN), 8.24 (d, ^{3}J = 7.9 Hz, 2H), 8.05 (d, 4H, ^{3}J = 8.4 H), 7.92 (m, 6H), 7.74–7.82 (m, 4H), 7.67 (s, 2H, CH═CH), 4.65 (q, 4H, CH$_2$), 1.65 ppm (t, 6H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 142.3, 138.7, 132.5, 131.0 (br, two carbon signals), 129.2, 128.3, 127.4, 126.9, 125.5, 114.0, 113.6, 42.5 (CH$_2$), 14.0 ppm (CH$_3$). Anal. Calcd for $C_{32}H_{30}Br_2N_4$ (628.08): C, 60.97; H, 4.80; N, 8.89. Found: C, 60.79; H, 4.63; N, 8.74.

Synthesis of H_2-1(PF$_6$)$_2$. H_2-**1**(Br)$_2$ was converted to H_2-**1**(PF$_6$)$_2$ by adding a solution of NH_4PF_6 (0.36 g, 2.2 mmol) in methanol (8 mL) to a methanolic solution of H_2-**1**(Br)$_2$ (0.63 g, 1.0 mmol in 50 mL of methanol). The white hexafluorophosphate salt H_2-**1**(PF$_6$)$_2$ precipitated immediately. The precipitated solid was collected by filtration, washed with small portions of cold methanol and diethyl ether, and dried under vacuum. Yield: 0.65 g (0.85 mmol, 85%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 9.25 (s, 2H, NCHN), 7.96–8.02 (m, 6H), 7.74–7.84 (m, 10H), 7.53 (s, 2H, CH═CH), 4.60 (q, 4H, CH$_2$), 1.69 ppm (t, 6H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 141.4, 140.4, 133.5, 132.8, 130.4, 129.5, 128.8, 128.4, 126.6, 118.3, 114.7, 114.7, 44.1 (CH$_2$), 14.4 ppm (CH$_3$). Anal. Calcd for $C_{32}H_{30}F_{12}N_4P_2\cdot H_2O$: C, 49.37; H, 4.14; N, 7.20. Found: C, 49.24; H, 3.97; N, 7.35.

Synthesis of H_2-2(Br)$_2$. By a procedure similar to that for the synthesis of H_2-**1**(Br)$_2$, H_2-**2**(Br)$_2$ was obtained as a white solid from *trans*-4,4′-bis(1-benzoimidazolyl)stilbene and *n*-butyl bromide as starting materials. Yield: 0.62 g (0.90 mmol, 90%). ^{1}H NMR (400 MHz, DMSO-*d6*): δ 10.30 (s, 2H, NCHN), 8.26 (d, ^{3}J = 8.1 Hz, 2H), 8.05 (d, ^{3}J = 8.5 Hz, 4H), 7.92 (m, 6H), 7.73–7.82 (m, 4H), 7.66 (s, 2H, CH═CH), 4.61 (t, 4H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.01 (m, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.46 (m, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.98 ppm (t, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d6*): δ 142.4, 138.7, 132.4, 131.3, 131.0, 129.2, 128.3, 127.4, 127.0,125.6, 114.1, 113.6, 46.8 (CH$_2$CH$_2$CH$_2$CH$_3$), 30.5 (CH$_2$CH$_2$CH$_2$CH$_3$), 19.2 (CH$_2$CH$_2$CH$_2$CH$_3$), 13.4 ppm (CH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{36}H_{38}Br_2N_4$ (684.15): C, 62.98; H, 5.58; N, 8.16. Found: C, 62.51; H, 5.86; N, 7.92.

Synthesis of H_2-2(PF$_6$)$_2$. The bromide salt from the previous reaction was converted to H_2-**2**(PF$_6$)$_2$ by adding a solution of NH_4PF_6 (0.36 g, 2.2 mmol) in methanol (8 mL) to a methanolic solution of H_2-**2**(Br)$_2$ (0.69 g, 1.0 mmol in 10 mL of methanol). The white hexafluorophosphate salt H_2-**2**(PF$_6$)$_2$ precipitated immediately. The precipitated solid was collected by filtration, washed with small portions of cold methanol and diethyl ether, and dried under vacuum. Yield: 0.65 g (0.80 mmol, 80%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 9.26 (s, 2H, NCHN), 7.96–8.02(m, 6H), 7.73–7.84 (m, 10H), 7.53 (s, 2H, CH═CH), 4.55 (t, 4H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.05 (m, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.52 (m, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.02 ppm (t, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 141.6, 140.4, 133.5, 132.8, 132.7, 130.4, 129.5), 128.8,128.5, 126.7, 114.8, 48.5 (CH$_2$CH$_2$CH$_2$CH$_3$), 31.6 (CH$_2$CH$_2$CH$_2$CH$_3$), 20.4 (CH$_2$CH$_2$CH$_2$CH$_3$), 13.8 ppm (CH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{36}H_{38}F_{12}N_4P_2$ (816.24): C, 52.95; H, 4.69; N, 6.86. Found: C, 53.14; H, 4.62; N, 6.39.

Synthesis of [Ag$_2$(1)$_2$](PF$_6$)$_2$. A sample of H_2-**1**(PF$_6$)$_2$ (76 mg, 0.1 mmol) was dissolved in 10 mL of CH$_3$CN, and to this solution was added Ag$_2$O (26 mg, 0.11 mmol). The resulting suspension was heated to 55 °C for 20 h under exclusion of light. After it was cooled to ambient temperature, the obtained suspension was filtered slowly through Celite to give a clear solution. The filtrate was concentrated to 3 mL, and diethyl ether (20 mL) was added. This led to the precipitation of a white solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 64 mg (0.045 mmol, 89%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (m, 8H), 7.79–7.83 (m, 8H), 7.48–7.62 (m, 20H), 4.77 (m, 8H, CH$_2$), 1.66 ppm (t, 12H, CH$_3$). ESI-MS (positive ions) for [Ag$_2$(**1**)$_2$](PF$_6$)$_2$ ($C_{64}H_{56}Ag_2F_{12}N_8P_2$): *m*/*z* 576.1379 (calcd for [Ag$_2$(**1**)$_2$]$^{2+}$ 576.1362), 1297.2386 (calcd for [Ag$_2$(**1**)$_2$(PF$_6$)]$^{+}$ 1297.2371). Anal. Calcd for $C_{64}H_{56}Ag_2F_{12}N_8P_2\cdot2CH_3CN$: C, 53.56; H, 4.10; N, 9.19. Found: C, 53.41; H, 3.96; N, 9.27.

Synthesis of [Ag$_2$(3)](PF$_6$)$_2$ (Photochemistry in Solution). A solution of [Ag$_2$(**1**)$_2$](PF$_6$)$_2$ (20 mg, 0.014 mmol) in DMSO-d_6 (0.6 mL) or CD$_3$CN (0.6 mL) in an NMR tube was irradiated with a Philips mercury high-pressure lamp (125 W) at ambient temperature for 30 min. The conversion to [Ag$_2$(**3**)](PF$_6$)$_2$ was quantitative. The solids were obtained by removal of CD$_3$CN. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02 (d, ^{3}J = 8.20 Hz, 4H), 7.43–7.58 (m, 28H), 4.98 (s, 4H, H$_{\text{cycobutane}}$), 4.74 (m, 8H, CH$_2$), 1.66 ppm (t, 12H, CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 188.8 (C$_{\text{carbene}}$), 141.2, 135.8, 133.9, 132.8, 125.9, 124.9, 124.6, 112.3, 111.9, 44.4 (C$_{\text{cycobutane}}$), 44.1 (CH$_2$), 16.13 ppm (CH$_3$). ESI-MS (positive ions) for [Ag$_2$(**3**)](PF$_6$)$_2$ ($C_{64}H_{56}Ag_2F_{12}N_8P_2$): *m*/*z* = 576.1381 (calcd for [Ag$_2$(**3**)]$^{2+}$ 576.1362), 1297.2373 (calcd for [Ag$_2$(**3**) (PF$_6$)]$^{+}$ 1297.2371). Anal. Calcd for $C_{64}H_{56}Ag_2F_{12}N_8P_2$: C, 53.28; H, 3.91; N, 7.77. Found: C, 53.07; H, 3.98; N, 7.82.

Synthesis of [Ag$_2$(2)$_2$](PF$_6$)$_2$. A sample of H_2-**2**(PF$_6$)$_2$ (82 mg, 0.1 mmol) was dissolved in 10 mL of CH$_3$CN, and to this solution was added Ag$_2$O (0.026 g, 0.11 mmol). The resulting suspension was heated to 55 °C for 20 h with the exclusion of light. After it was cooled to ambient temperature, the obtained suspension was filtered slowly through Celite to give a clear solution. The filtrate was concentrated to 3 mL, and diethyl ether (20 mL) was added. This led to the precipitation of a white solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield: 71 mg (0.045 mmol, 91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (d, ^{3}J = 8.20 Hz, 4H), 7.80 (m, 16H), 7.51–7.61 (m, 16H), 4.75 (t, 8H,

$CH_2CH_2CH_2CH_3$), 2.05 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.51 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.00 ppm (t, 12H, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 188.9 ($C_{carbene}$), 137.4, 136.58, 133.5, 133.0, 128.8, 128.1, 125.8, 125.0, 124.9, 112.6, 112.4, 112.3, 49.2 ($CH_2CH_2CH_2CH_3$), 32.6 ($CH_2CH_2CH_2CH_3$), 19.9 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$). ESI-MS (positive ions) for $[Ag_2(\mathbf{2})_2](PF_6)_2$ ($C_{72}H_{72}Ag_2F_{12}N_8P_2$): *m/z* 632.2006 (calcd for $[Ag_2(\mathbf{2})_2]^{2+}$ 632.1989). Anal. Calcd for $C_{72}H_{72}Ag_2F_{12}N_8P_2$ (1552.33): C, 55.61; H, 4.67; N, 7.21. Found: C, 55.33; H, 4.71; N, 7.15.

Synthesis of $[Ag_2(4)](PF_6)_2$ (Photochemistry in Solution). A solution of $[Ag_2(\mathbf{2})_2](PF_6)_2$ (20 mg, 0.013 mmol) in DMSO-d_6 (0.6 mL) or CD_3CN (0.6 mL) in an NMR tube was irradiated with a Philips mercury high-pressure lamp (125 W) at ambient temperature for 30 min. The conversion to $[Ag_2(\mathbf{4})](PF_6)_2$ was quantitative. The solids were obtained by removal of CD_3CN. ^1H NMR (400 MHz, DMSO-d_6): δ 8.01 (d, 4H), 7.32−7.65 (m, 28H), 4.99 (s, 4H, $H_{cyclobutane}$), 4.70 (t, 8H, $CH_2CH_2CH_2CH_3$), 2.03 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.50 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.01 ppm (t, 12H, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 189.3 ($C_{carbene}$), 141.2, 135.5, 134.0, 133.1, 131.6, 127.7, 125.9, 124.9, 124.6, 112.5, 111.9, 49.0 ($CH_2CH_2CH_2CH_3$), 44.3 ($C_{cycobutane}$), 32.6 ($CH_2CH_2CH_2CH_3$), 19.9 ($CH_2CH_2CH_2CH_3$), 13.7 ppm ($CH_2CH_2CH_2CH_3$). ESI-MS (positive ions) for $[Ag_2(\mathbf{4})](PF_6)_2$ ($C_{72}H_{72}Ag_2F_{12}N_8P_2$): *m/z* 632.2002 (calcd for $[Ag_2(\mathbf{4})]^{2+}$ 632.1989).

Synthesis of Ligand H_4-3$(PF_6)_4$. A sample of $[Ag_2(\mathbf{3})](PF_6)_2$ (72 mg, 0.05 mmol) was dissolved in a mixture of MeOH (5 mL) and DMSO (1 mL). To this solution was added NH_4Cl (11 mg, 0.2 mmol). White solid AgCl precipitated immediately. The resulting suspension was filtered through Celite to give a clear solution. The solvent was removed to give a white solid. The white solid was dissolved in MeOH (5 mL), and a solution of NH_4PF_6 (36 mg, 0.22 mmol) in methanol (3 mL) was added. The mixture was stirred at ambient temperature for 2 h. After this period a white solid precipitated, which was isolated by filtration, washed with diethyl ether, and dried under vacuum. Yield: 55 mg (0.036 mmol, 72%). ^1H NMR (400 MHz, CD_3CN): δ 9.11 (s, 4H), 7.97 (d, 4H), 7.67−7.72 (m, 12H), 7.54−7.59 (m, 16H), 4.99 (s, 4H, $H_{cyclobutane}$), 4.56 (d, 8H), 1.65 ppm (t, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 143.75, 141.3, 132.8, 132.3, 131.3, 128.7, 128.4, 125.9, 114.7, 114.3, 47.2, 44.0 (CH_2), 14.4 ppm (CH_3). Anal. Calcd for $C_{64}H_{60}F_{24}N_8P_4$ (1520.35): C, 50.54; H, 3.98; N, 7.37. Found: C, 49.97; H, 4.12; N, 7.12. Anal. Calcd for $C_{72}H_{72}Ag_2F_{12}N_8P_2$ (1552.33): C, 55.61; H, 4.67; N, 7.21. Found: C, 55.27; H, 4.52; N, 7.01.

Synthesis of Ligand H_4-4$(PF_6)_4$. A sample of $[Ag_2(\mathbf{4})](PF_6)_2$ (77 mg, 0.05 mmol) was dissolved in a mixture of MeOH (5 mL) and DMSO (1 mL). To this solution was added NH_4Cl (11 mg, 0.2 mmol). White solid AgCl precipitated immediately. The resulting suspension was filtered through Celite to give a clear solution. The solvent was removed to give a white solid. The white solid was dissolved in MeOH (5 mL), and a solution of NH_4PF_6 (36 mg, 0.22 mmol) in methanol (3 mL) was added. The mixture was stirred at ambient temperature for 2 h. After this period a white solid precipitated, which was isolated by filtration, washed with diethyl ether, and dried under vacuum. Yield: 46 mg (0.035 mmol, 70%). ^1H NMR (400 MHz, CD_3CN): δ 9.13 (s, 4H, NCHN), 7.67 (d, 4H), 7.67−7.74 (m, 12H), 7.53−7.59 (m, 16H), 4.99 (s, 4H, $H_{cyclobutane}$), 4.51 (t, 8H, $CH_2CH_2CH_2CH_3$), 2.01 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.47 (m, 8H, $CH_2CH_2CH_2CH_3$), 0.99 ppm (t, 12H, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 143.8, 141.5, 132.8, 132.5, 132.3, 131.3, 128.7, 128.4, 125.9, 114.7, 114.4, 48.4 ($CH_2CH_2CH_2CH_3$), 47.2 ($C_{cyclobutane}$), 31.6 ($CH_2CH_2CH_2CH_3$), 20.4 ($CH_2CH_2CH_2CH_3$), 13.7 ppm ($CH_2CH_2CH_2CH_3$). ESI-MS (positive ions) for H_4-$\mathbf{4}(PF_6)_4$ ($C_{72}H_{76}F_{24}N_8P_4$): *m/z* 671.2748 (calcd for $[H_4\text{-}\mathbf{4}(PF_6)_2]^{2+}$ 671.2733), 1487.5138 (calcd for $[H_4\text{-}\mathbf{4}(PF_6)_3]^+$ 1487.5118). Anal. Calcd for $C_{72}H_{76}F_{24}N_8P_4$ (1632.48): C, 52.95; H, 4.69; N, 6.86. Found: C, 52.46; H, 4.74; N, 6.93.

X-ray Crystallography. Diffraction data of $Ag_2(\mathbf{4})(PF_6)_2$ were collected at T = 203(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo Kα radiation (λ = 0.71073 A).[18] Diffraction measurement of H_4-$\mathbf{3}(PF_6)_4$ was carried out at T = 293(2) K on an Agilent SuperNova AtlasS2 diffractometer equipped with Cu X-ray source (Cu Kα 1.54184 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97 package using direct methods and were refined with SHELXL-97 against $|F^2|$ values of all data using first isotropic and later anisotropic thermal parameters (for exceptions see a description of the individual molecular structures).[19] Hydrogen atoms were added to the structure models in calculated positions. For crystallographic data, see the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00977.

UV−vis, fluorescence, and NMR (^1H, $^{13}C\{^1H\}$ and 2D) spectra (PDF)

Crystallographic data for $Ag_2(\mathbf{4})(PF_6)_2$ (CIF)

Crystallographic data for H_4-$\mathbf{3}(PF_6)_4$ (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for Y.-F.H.: yfhan1980@fudan.edu.cn.
*E-mail for G.-X.J.: gxjin@fudan.edu.cn.

Notes

The authors declare no competing financial interest.

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