Postsynthetic Modification of Dicarbene-Derived Metallacycles via Photochemical [2 + 2] Cycloaddition

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S *Supporting Information*

ABSTRACT: Molecular squares obtained from two olefin-bridged bis(NHC) ligands, NHC−Ar−C═C−Ar−NHC, and two Ag^+ or Au^+ ions undergo postsynthetic modifications via a UV-irradiation-initiated [2 + 2] cycloaddition reaction to yield the corresponding cyclobutane-bridged dinuclear tetrakis(NHC) complexes. The tetrakis(NHC) ligand can be liberated from the Ag^I complexes as the tetraimidazolium salt. For the Au^I complexes, the substituents at N3 and N3′ of the dicarbene ligands determine the outcome of the reaction in the solid state.

Metal−ligand-directed assembly has led to a large number of metal−organic assemblies such as metal−organic frameworks (MOFs) and various metal−organic polyhedra. Until recently, only molecular architectures built from Werner-type complexes featuring oxygen or nitrogen donor atoms were known.[1] Recently, N-heterocyclic carbenes (NHCs)[2] have been used for the generation of organometallic molecular assemblies featuring a framework of metal−carbon bonds. Among others, silver(I)−NHC complexes have played an important role in this development because of their facile accessibility via the Ag_2O route, the stability of the Ag−C_{NHC} bond, and the possibility of transmetalating the NHC ligand to other metal centers.[3] Today, a number of molecular squares and rectangles,[4] cylinder-like structures,[5] and organometallic polymers[6] held together by M−C_{NHC} bonds are known.

The subsequent functionalization of organometallic polyhedra obtained from poly(NHC) ligands has not been described to date. Such postsynthetic modifications (PSMs) have been shown to be broadly applicable for the preparation of a variety MOFs that would be difficult to obtain via other synthetic protocols.[7] In addition, various postassembly modifications of discrete assemblies have also been reported.[8]

The photochemically induced [2 + 2] cycloaddition reaction constitutes a classical PSM of metal−organic polyhedra based on Werner-type ligands. This reaction, which leads to cyclobutanes, requires the presence of two properly aligned C═C double bonds (parallel arrangement, separation less than 4.2 Å). It has been performed in the solid state[9] and in solution[10] utilizing inclusion,[10] hydrogen-bonded,[11] or coordination-driven[12] molecular assemblies. The application of the [2 + 2] cycloaddition for PSM of NHC-based assemblies has not been demonstrated to date.

Here we report dinuclear Ag^I and Au^I molecular rectangles featuring olefin-bridged dicarbene ligands. These assemblies function as scaffolds for photodimerization of the olefinic bonds to yield cyclobutane units within the molecular rectangles both in solution (Ag^I and Au^I complexes) and in the solid state (Au^I complexes) (Scheme 1). The alignment of the C═C double

Scheme 1. Preparation and Reactions of Dicarbene-Bridged Molecular Rectangles
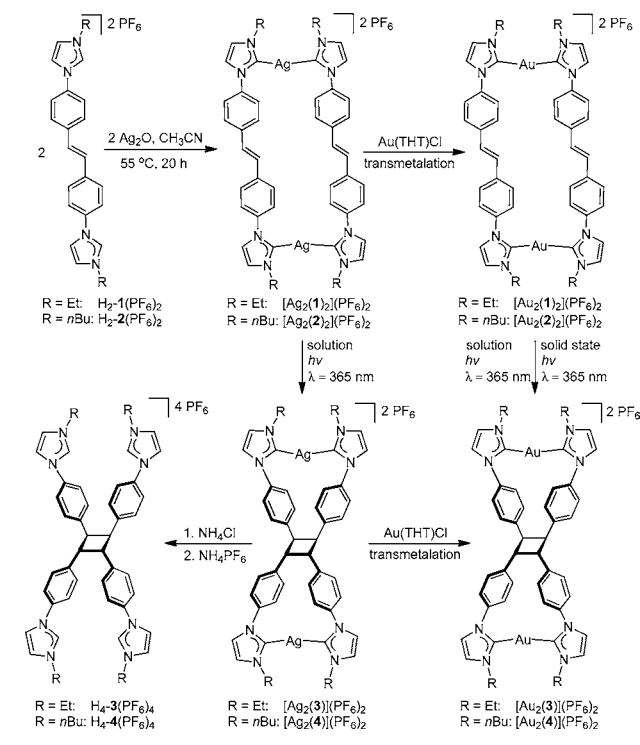
bonds and thus the speed of the cycloaddition reaction in the solid state are influenced by the substituents at N3 and N3′ of the dicarbene ligands.

We[4c,13a] and others[13b−e] have prepared dinuclear molecular rectangles of the form $[M_2(dicarbene)_2]^{2+}$ (M = Ag^I, Au^I). In the case of aryl-bridged dicarbenes, transannular separations as short as 3.6 Å[13b] have been observed, most likely caused by

$\pi\cdots\pi$ stacking interactions. This type of ring positioning and the M$-$C$_{NHC}$ bond lengths of $\sim$2.0 Å indicate the suitability of the [M$_2$(dicarbene)$_2$]$^{2+}$ scaffold for an intramolecular [2 + 2] cycloaddition provided that a suitable olefin-bridged dicarbene ligand can be introduced.

To achieve this goal, we prepared the structurally similar bis(imidazolium)-substituted stilbene derivatives H$_2$-1(PF$_6$)$_2$ and H$_2$-2(PF$_6$)$_2$ from *trans*-4,4′-dibromostilbene using reported precedures.[13] The reactions of equimolar amounts of Ag$_2$O with H$_2$-1(PF$_6$)$_2$ and H$_2$-2(PF$_6$)$_2$ in acetonitrile yielded the dinuclear silver tetracarbene complexes [Ag$_2$(1)$_2$](PF$_6$)$_2$ and [Ag$_2$(2)$_2$](PF$_6$)$_2$ in good yields of 92% and 90%, respectively (Scheme 1). The formation of the molecular rectangles was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (δ_{NCN} = 178.21 ppm for [Ag$_2$(1)$_2$](PF$_6$)$_2$ and 180.30 ppm for [Ag$_2$(2)$_2$](PF$_6$)$_2$) and electrospray ionization (ESI) or MALDI-TOF mass spectrometry [see the Supporting Information (SI)].

The metallacycles [Ag$_2$(1)$_2$](PF$_6$)$_2$ and [Ag$_2$(2)$_2$](PF$_6$)$_2$ were tested for postsynthetic modification via photochemically induced [2 + 2] cycloaddition. Irradiation (Hg lamp, 365 nm) of [Ag$_2$(1)$_2$](PF$_6$)$_2$ in DMSO-d_6 and [Ag$_2$(2)$_2$](PF$_6$)$_2$ in CD$_3$CN resulted in rapid conversion into the corresponding dinuclear *rctt*-cyclobutane$-$silver complexes [Ag$_2$(3)](PF$_6$)$_2$ and [Ag$_2$(4)](PF$_6$)$_2$. The [2 + 2] cycloadditions were complete after 2.5 h, and the conversions were essentially quantitative and stereospecific as judged by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Figure 1; also see the SI).
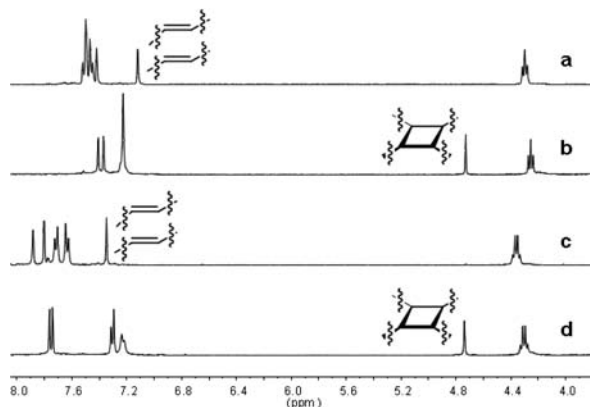

Figure 1. Partial ^{1}H NMR spectra (400 MHz, 300 K) of [Ag$_2$(2)$_2$](PF$_6$)$_2$ in CD$_3$CN (a) before and (b) after UV irradiation and of [Ag$_2$(1)$_2$](PF$_6$)$_2$ in DMSO-d_6 (c) before and (d) after UV irradiation.

The ^{1}H NMR spectra of [Ag$_2$(3)](PF$_6$)$_2$ and [Ag$_2$(4)](PF$_6$)$_2$ displayed sharp singlets at 4.74 and 4.73 ppm corresponding to a single cyclobutane environment instead of the resonances for the olefinic protons at 7.35 and 7.10 ppm, respectively (Figure 1). This observation is consistent with a previous report on the related tetrapyridine-substituted cyclobutane ligand *rctt*-tetrakis(4-pyridyl)cyclobutane.[12c] The ^{13}C{^{1}H} NMR spectra of [Ag$_2$(3)](PF$_6$)$_2$ and [Ag$_2$(4)](PF$_6$)$_2$ also feature the typical signals[12c] for the cyclobutane carbon atoms at 43.89 and 45.54 ppm, respectively (see the SI).

The olefin complexes [Ag$_2$(1)$_2$](PF$_6$)$_2$ and [Ag$_2$(2)$_2$](PF$_6$)$_2$ were isolated, but attempts to characterize them by X-ray diffraction failed because UV irradiation in addition to the light sensitivity of the compounds caused decomposition. This

sensitivity, which was not observed in solution, also prevented us from studying the single-crystal to single-crystal transformations [Ag$_2$(1)$_2$](PF$_6$)$_2$ → [Ag$_2$(3)](PF$_6$)$_2$ and [Ag$_2$(2)$_2$]-(PF$_6$)$_2$ → [Ag$_2$(4)](PF$_6$)$_2$ in detail.

X-ray diffraction analysis of crystals of [Ag$_2$(4)]-(PF$_6$)$_2$·2MeCN confirmed the formation of the cyclobutane ring (Figure 2). The [Ag$_2$(4)]$^{2+}$ cation resides on a crystallo-
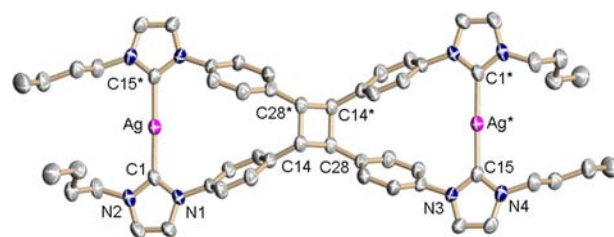

Figure 2. Molecular structure of the [Ag$_2$(4)]$^{2+}$ cation (50% probability ellipsoids, H atoms omitted for clarity; the cation resides on a crystallographic inversion center). Selected bond lengths (Å) and angles (deg): Ag$-$C1, 2.082(3); Ag*$-$C15, 2.084(3); N1$-$C1, 1.357(3); N2$-$C1, 1.353(3); N3$-$C15, 1.359(3); N4$-$C15, 1.349(3); C14$-$C28, 1.551(3); C14$-$C28*, 1.583(4); C1$-$Ag$-$C15*, 177.09(10); N1$-$C1$-$N2, 104.1(2); N3$-$C15$-$N4, 104.0(2); C28$-$C14$-$C28*, 89.4(2); C14$-$C28$-$C14*, 90.6(2).

graphic inversion center. The metric parameters [Ag$-$C$_{NHC}$ = 2.082(3) and 2.084(3) Å; C$_{NHC}$$-Ag-C_{NHC}$ = 177.09(10)°] fall in the ranges previously observed for linearly coordinated bis(NHC)silver complexes.[3,5a,c$-$e,13] The cyclobutane ring features typical single-bond C$-$C distances but strongly distorted C$-$C$-$C angles of $\sim$90°.

Since the [2 + 2] cycloaddition could not be studied in the solid state with the silver complexes [Ag$_2$(1)$_2$](PF$_6$)$_2$ and [Ag$_2$(2)$_2$](PF$_6$)$_2$, we searched for more stable molecular rectangles bridged by the olefin-bridged bis(NHC) ligands 1 and 2. The dinuclear silver complexes [Ag$_2$(1)$_2$](PF$_6$)$_2$ and [Ag$_2$(2)$_2$](PF$_6$)$_2$, like many other silver$-$NHC complexes, underwent transmetalation with [Au(THT)Cl] (THT = tetrahydrothiophene)[5d,e] to give the corresponding gold complexes in 75% and 68% yield, respectively, with retention of the two-dimensional structure (Scheme 1; also see the SI). The gold(I) complexes [Au$_2$(1)$_2$](PF$_6$)$_2$ and [Au$_2$(2)$_2$](PF$_6$)$_2$ were fully characterized by NMR spectroscopy and mass spectrometry. Subsequent photochemically induced [2 + 2] cycloaddition reactions in CD$_3$CN solution (UV, λ = 365 nm) produced the desired dinuclear *rctt*-cyclobutane$-$gold(I) complexes [Au$_2$(3)](PF$_6$)$_2$ and [Au$_2$(4)](PF$_6$)$_2$ in quantitative yield, as established by NMR spectroscopy (Scheme 1; also see the SI). Complexes [Au$_2$(3)](PF$_6$)$_2$ and [Au$_2$(4)](PF$_6$)$_2$ were also obtained from the silver(I) complexes [Ag$_2$(3)](PF$_6$)$_2$ and [Ag$_2$(4)](PF$_6$)$_2$, respectively, by transmetalation reactions in acetonitrile. Yields of $\sim$90% and retention of the metallosupramolecular scaffold were observed in these transmetalation reactions.

Surprisingly, the intramolecular [2 + 2] cycloaddition reactions of [Au$_2$(1)$_2$](PF$_6$)$_2$ and [Au$_2$(2)$_2$](PF$_6$)$_2$ in the solid state proceeded with different results. When a powdered crystalline sample of [Au$_2$(1)$_2$](PF$_6$)$_2$ was irradiated with a mercury lamp (λ = 365 nm) for 12 h, the [2 + 2] cycloaddition readily proceeded, and the cyclobutane derivative [Au$_2$(3)]-(PF$_6$)$_2$ was obtained in quantitative yield. NMR spectroscopy confirmed that no byproducts were formed (see Figure S65 in the SI). In contrast to this, the [2 + 2] cycloaddition of the *n*-

butyl-substituted derivative $[Au_2(2)_2](PF_6)_2$ in the solid state was quite slow, and only a 25% yield of $[Au_2(4)](PF_6)_2$ together with unreacted $[Au_2(2)_2](PF_6)_2$ was obtained after UV irradiation of a powdered crystalline sample of $[Au_2(2)_2]$-$(PF_6)_2$ for 72 h. This low yield indicated that the alignment of the C=C double bonds in $[Au_2(2)_2](PF_6)_2$ in the solid state might not be suitable for the cycloaddition reaction. An X-ray diffraction study of crystals of $[Au_2(2)_2](PF_6)_2$ (Figure 3, top)

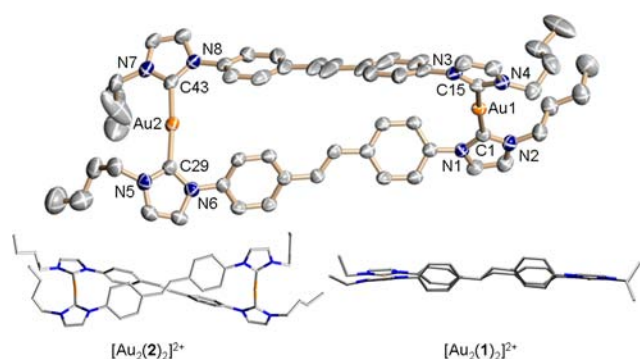**Figure 3.** (top) Molecular structure of the $[Au_2(2)_2]^{2+}$ cation (H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1−C1, 2.022(5); Au1−C15, 2.027(5); Au2−C29, 2.025(5); Au2−C43, 2.020(5); N1−C1, 1.357(6); N2−C1, 1.347(6); N3−C15, 1.351(7); N4−C15, 1.354(6); N5−C29, 1.341(6); N6−C29, 1.361(6); N7−C43, 1.343(6); N8−C43, 1.356(7); C1−Au1−C15, 174.2(2); C29−Au2−C43, 173.8(2); N1−C1−N2, 104.7(4); N3−C15−N4, 104.5(4); N5−C29−N6, 105.0(4); N7−C43−N8, 104.4(4). (bottom) Views of the arrangement of the C=C double bonds in cations $[Au_2(2)_2]^{2+}$ (left) and $[Au_2(1)_2]^{2+}$ (right).

revealed that interactions between the *n*-butyl substituents of the NHC donors enforced a rotation of one $\{Au(NHC)_2\}$ unit relative to the other one. As a consequence, the two C=C double bonds in cation $[Au_2(2)_2]^{2+}$ are oriented almost perpendicular to each other (Figure 3, bottom left), while the C=C bonds in the sterically less encumbered cation $[Au_2(1)_2]^{2+}$ (see the SI for full details of the molecular structure determination of $[Au_2(1)_2](ClO_4)_2$) are oriented in a parallel fashion, thus enabling the observed rapid [2 + 2] cycloaddition.

The cyclobutane-bridged tetracarbene ligands in the silver complexes $[Ag_2(3)](PF_6)_2$ and $[Ag_2(4)](PF_6)_2$ were liberated as the tetraimidazolium salts by reacting the complexes with NH₄Cl in MeOH. The initially formed chloride salts were converted into H_4-$3(PF_6)_4$ and H_4-$4(PF_6)_4$ by reaction with NH₄PF₆ in MeOH in overall yields of 70% and 68%, respectively. In both cases, only one tetraimidazolium salt was observed, as confirmed by NMR spectroscopy. The ¹H NMR spectra feature sharp singlets (1:1 ratio) at 8.77 [H_4-$3(PF_4)_4$] and 8.76 ppm [H_4-4 $(PF_6)_4$] for the four imidazolium C2−H protons and at 4.80 ppm for the four cyclobutane protons. ESI mass spectrometry provided further evidence for the formation of the tetraimidazolium salts (see the SI).

The silver(I) complexes $[Ag_2(3)](PF_6)_2$ and $[Ag_2(4)](PF_6)_2$, but not the analogous gold(I) complexes, are sensitive to light. In no case did we observe retrocyclization. The cyclobutane-bridged silver(I) and gold(I) complexes are stable in acetonitrile solution for weeks [under exclusion of light for the silver(I) complexes], and such solutions can be heated to 60 °C without any sign of retrocyclization. The same is true for the cyclobutane-linked tetraimidazolium salts H_4-$3(PF_6)_4$ and

H_4-$4(PF_6)_4$, which are stable for weeks in MeOH or DMSO solution or in the solid state without any signs of retrocyclization.

In summary, we have demonstrated that photochemical [2 + 2] cycloaddition reactions can be effectively used to modify metallacycles with bridging dicarbene ligands featuring internal olefin groups. Both the olefin-bridged dicarbene ligands and the cyclobutane-bridged tetracarbene ligands can be transmetalated from Ag^I to Au^I, a feature that is generally not available for polydentate Werner-type ligands bridged by olefins or cyclobutane. After the [2 + 2] cycloaddition, the generated cyclobutane-bridged tetracarbene ligands can be liberated from the silver(I) complexes as their tetraimidazolium salts, and this type of reaction might find applications in organic synthesis for the preparation of polyimidazolium salts. Finally, we have demonstrated that the N3,N3′ substitution pattern of the olefin-bridged NHCs can influence the outcome of the [2 + 2] cycloaddition in the solid state. Work to expand this approach to more than two reaction centers and higher-dimensional olefins is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details of the synthesis of all compounds, NMR and mass spectra, and X-ray crystallographic data (CIF) for $[Ag_2(4)](PF_6)_2$·2CH₃CN, $[Au_2(1)_2](ClO_4)_2$, and $[Au_2(2)_2]$-$(PF_6)_2$·CH₃CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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