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

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Supporting Information Placeholder

ABSTRACT: Molecular squares obtained from two olefin substituted di(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 cyclobutane bridged dinuclear tetra(NHC) complexes. The tetra(NHC) ligand can be liberated from the Ag^I complexes as tetraimidazolium salt. For the Au^I complexes, the N3,N3' substituents 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 like metal-organic frameworks (MOFs) and different metal-organic polyhedra. Until recently, only molecular architectures build 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 played an important role in this development based on their facile accessibility via the Ag₂O route, the stability of the Ag-C_{NHC} bond and the possibility to transmetalate the NHC ligand to other metal centers.³ Today, a number of molecular squares and rectangles,⁴ cylinder-like structures⁵ and organometallic polymers⁶ held together by $M-C_{NHC}$ bonds is known.

The subsequent functionalization of organometallic polyhedra obtained from poly(NHC) ligands has not been described yet. Such postsynthetic modifications (PSM) have been shown to be broadly applicable for the preparation of a variety MOFs which would be difficult to obtain via other synthetic protocols.⁷ In addition, various post-assembly modification of discrete assemblies have also been reported.⁸

The photochemical induced [2+2] cycloaddition reaction constitutes a classical PSM of metal-organic polyhedra based on Werner type ligands. This reaction, leading 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 state⁹ and in solution¹⁰ utilizing inclusion,¹⁰ hydrogen bond¹¹ or coordination driven¹² molecular assemblies. The application of the [2+2] cycloaddition for the PSM of NHC based assemblies has not been demonstrated yet.

In this contribution we report dinuclear Ag^{I} and Au^{I} molecular rectangles featuring olefin bridged dicarbene ligands. These assemblies function as scaffolds for the photodimerization of the olefinic bonds to yield cyclobutane units within the molecular rectangles both in solution (Ag^{I} and Au^{I} complexs) and in the solid state (Au^{I} complexes) (Scheme 1). The alignment of the C=C double bonds and thus the speed of the cycloaddition reaction in the solid state are influenced by the N3,N3'-substituents of the dicarbene ligands.

Scheme 1. Preparation and Reactions of Dicarbene-Bridged Molecular Rectangles



 $We^{4c,13a}$ and others^{13b-e} have prepared dinuclear molecular rectangles of type $[M_2(dicarbene)_2]^{2+}$ (M = Ag^I, Au^I). In case of aryl bridged dicarbenes, transannular separations as short as

3.6 Å^{13b} have been observed, most likely caused by π ··· π stacking interactions. This type of ring positioning and the M–C_{NHC} bond lengths of about 2.0 Å indicate the suitability of the $[M_2(dicarbene)_2]^{2+}$ scaffold for an intramolecular [2+2] cycloaddition provided a suitable olefin bridged dicarbene ligand can be introduced.

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59 60 To achieve this goal we have prepared the structurally similar dimidazolium substituted stilbene derivatives H₂-1(PF₆)₂ and H₂-2(PF₆)₂ from *trans*-4,4'-dibromostilbene using reported precedures.¹³ The reaction of equimolar amounts of Ag₂O and H₂-1(PF₆)₂ or H₂-2(PF₆)₂ in acetonitrile yielded the dinuclear silver tetracarbene complexes [Ag₂(1)₂](PF₆)₂ and [Ag₂(2)₂](PF₆)₂ in good yields of 92% and 90%, respectively. Formation of the molecular rectangles was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy ($\delta_{NCN} = 178.21$ for [Ag₂(1)₂](PF₆)₂ and 180.30 for [Ag₂(2)₂](PF₆)₂) and by ESI or MALDI-TOF mass spectrometry [Scheme 1; 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 a photochemical induced [2+2] cycloaddition reaction. 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 CD₃CN result in a 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 completed after 2.5 h, and the conversions were essentially quantitative and stereospecific, as judged from ¹H and ¹³C{¹H} NMR spectroscopy (Figure 1; see also SI).



Figure 1. Section of the ¹H NMR spectra (400 MHz, 300K) of $[Ag_2(2)_2](PF_6)_2$ in CD₃CN before (a) and after (b) UV-irradiation and of $[Ag_2(1)_2](PF_6)_2$ in DMSO- d_6 before (c) and after (d) UV-irradiation.

The ¹HNMR 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 (Figure 1) instead of the resonances for the olefinic protons at 7.35 and 7.10 ppm, respectively. This observation is consistent with a previous report on the related tetra(pyridine)-substituted cyclobutane ligand 4,4'-tpcb (where 4,4'-tpcb = *rctt*-tetrakis-(4-pyridyl)cyclobutane).^{12c} The ¹³C {¹H} 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 (see also SI). The olefin complexes $[Ag_2(1)_2](PF_6)_2$ and $[Ag_2(2)_2](PF_6)_2$ can be isolated but attempts to characterize them by X-ray diffraction failed as UV-irradiation in addition to the light sensitivity of the compounds caused decomposition. This sensitivity, which was not observed in solution, also prevented us to study the singe-crystal to singe-crystal transformations $[Ag_2(1)_2](PF_6)_2 \rightarrow [Ag_2(3)](PF_6)_2$ and $[Ag_2(2)_2](PF_6)_2 \rightarrow$ $[Ag_2(4)](PF_6)_2$ in detail.

An X-ray diffraction analysis with crystals of $[Ag_2(4)](PF_6)_2 \cdot 2MeCN$ confirmed the cyclobutane formation (Figure 2). The cation $[Ag_2(4)]^{2+}$ resides on a crystallographic inversion center. The metric parameters $(Ag-C_{NHC} 2.082(3)$ and 2.084(3) Å, C_{NHC} -Ag- $C_{NHC} 177.09(10)^{\circ}$) fall in the ranges previously observed for linearly coordinated di(NHC) silver complexes.^{3,5a,5c,5d,5e,13} The cyclobutane ring features typical single bond C-C distances but strongly distorted C-C-C angles of about 90°.



Figure 2. Molecular structure of the dication $[Ag_2(4)]^{2+}$ (50% probability ellipsoids, hydrogen atoms have been 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).

Since the [2+2] cycloaddition could not be studied in the solid state with the silver olefin 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 functionalized di(NHC) ligands 1 or 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, undergo transmetalation with [Au(THT)Cl] (THT = tetrahydrothiophene)^{5d,e} to give the corresponding gold complexes with retention of the two-dimensional structure in 75% and 68% yield respectively (Scheme 1; see also 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. A subsequent photolysis reactions in CD₃CN solution (UV, $\lambda = 365$ nm) produced the desired dinuclear *rctt*-cyclobutane gold(I) complexes $[Au_2(3)](PF_6)_2$ and $[Au_2(4)](PF_6)_2$ in quantitatively yields as established by NMR spectroscopy (Scheme 1; see also SI). Alternatively, complexes [Au₂(3)](PF₆)₂ and [Au₂(4)](PF₆)₂ can be obtained from the silver(I) complexes [Ag₂(**3**)](PF₆)₂ and [Ag₂(**4**)](PF₆)₂ by a transmetalation reaction in acetonitrile. Yields of about 90% and retention of the metallosupramolcular scaffold were observed in these transmetalation reactions.

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Surprisingly, the intramolecular [2+2] cycloaddition reaction 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 ($\lambda = 365$ 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 SI, Figure S65). In contrast to this, the [2+2] cycloaddition of the N-butyl substituted derivative $[Au_2(2)_2](PF_6)_2$ in the solid states was quite slow and only 25% of $[Au_2(4)](PF_6)_2$ together with unreacted $[Au_2(2)_2](PF_6)_2$ were 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 with crystals of $[Au_2(2)_2](PF_6)_2$ (Figure 3, top) revealed that interactions of 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 $[Au_2(1)_2]^{2+1}$ (for full details of the molecular structure determination of $[Au_2(1)_2](ClO_4)_2$ see SI) are oriented in a parallel fashion thus enabling the observed rapid [2+2] cycloaddition.



Figure 3. Molecular structure of the dication $[Au_2(2)_2]^{2^+}$ (top, hydrogen atoms have been omitted for clarity) and view of the arrangement of the C=C double bonds in cations $[Au_2(2)_2]^{2^+}$ (bottom left) and $[Au_2(1)_2]^{2^+}$ (bottom right). 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).

The cyclobutane-bridged tetacarbene ligands from the silver complexes $[Ag_2(3)](PF_6)_2$ and $[Ag_2(4)](PF_6)_2$ can be liberated as the tetrakis(imidazolium) salts by reaction of the complexes with NH₄Cl in MeOH. The initially formed chloride salts have been converted into H₄-3(PF₆)₄ and H₄-4(PF₆)₄ by reactions of with NH₄PF₆ in MeOH (total yield 705 and 68% respectively). In both cases, only one tetrakis(imidazolium) salt was observed which was confirmed by NMR spectroscopy. The ¹H NMR spectra feature sharp singlets (ratio 1:1) at 8.77 [H₄- $3(PF_4)_4$] and 8.76 ppm [H₄-4 (PF₆)₄] for the four imidazolium C2-H protons and at 4.80 ppm for the four cyclobutane protons. ESI-MS spectrometry provided further evidence for the formation of the tetraimidazolium salts (see also SI).

The silver(I) complexes $[Ag_2(1)](PF_6)_2-[Ag_2(2)](PF_6)_2$, but not the analogous gold(I) complexes are sensitive to light. In no case have we observed retrocyclization. The cyclobutanebridged 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 up to 60 °C without any sign of retrocyclization. The same is true for the cyclobutane-linked tetraimidazolium salts H₄-**3**(PF₆)₄ and H₄-**4**(PF₆)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 olefine bridged dicarbene ligands as well as the cyclobutane bridged tetracarbene ligands can be transmetalated from Ag¹ to Au¹, a feature which 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 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 in progress is directed to expand this approach to more than two reaction centers and higher dimensional olefins.

ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds and X-ray crystallographic files for compounds $[Ag_2(4)](PF_6)_2 \cdot 2CH_3CN$, $[Au_2(1)_2](CIO_4)_2$, and $[Ag_2(2)_2](PF_6)_2 \cdot CH_3CN$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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