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Dipyrromethene-Triazolylidene Silver Complexes: Synthesis, Structure and Opportunities

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Abstract: The synthesis and characterization of unusual silver triazolylidene-containing dipyrromethene complexes are described. The carbene **TAD-N₃C-H** obtained from its parent Triazole-Appended Dipyrromethene (**TAD-N₄**) is an excellent ligand for the complexation of silver, thanks to the proximity between the dipyrromethene scaffold and the triazolylidene. The effect of silver salt stoichiometry on the structure of the complexes was clearly evidenced by ¹H-NMR spectroscopy and mass spectrometry. Furthermore, an unexpected argentophilic interaction was proved by different analytical techniques, including X-Ray diffraction analysis and fluorescence spectroscopy. The potentiality of using the unprecedented DPM-triazolydene silver complexes for the preparation of dipyrromethene-based metallocomplexes displaying unusual coordination mode was further demonstrated with palladium.

Dipyrromethenes (DPM) have been studied in the literature.^[1] They constitute key building blocks in the synthesis of pyrrolic macrocycles.^[2] Also, their BF₂-complexes (BODIPYs) are well-known for their remarkable optical properties.^[3] DPMs present a strong affinity for a large variety of metals, and can be functionalized to afford metallocomplexes displaying original structures with applications in catalysis,^[4–8] luminescence^[9,10] or in the construction of supramolecular assemblies.^[11–13] Most commonly, phosphine^[14–16] and carbene^[17–21] ligands are used to synthesize silver complexes. In particular, they play a key role in transmetalation reactions. Unexpectedly, to the best of our knowledge, there is only one example of DPM-Ag complex, obtained by addition of a base and (Ph₃P)AgOTf on an azadipyrromethene solution.^[22] In these conditions, a trigonal

complex is isolated. Generally, the silver atom interacts with pyrrole double bonds through π interactions.^[23]

For several years, our group has been involved in the synthesis and the study of a family of functionalized dipyrromethenes, the Triazole-Appended Dipyrromethenes (**TADs**) (Figure 1). In particular, we have shown that the **TAD-N₄**-derived BODIPYs present excellent optical properties, both in organic and in aqueous solution.^[24] In addition, Zn-**TAD-N₄**-metallocomplexes have recently been proven efficient as catalyst for the carbonation of epoxides.^[25] In parallel, the corresponding triazolium salt **TAD-N₃C-H** has shown good promises in anion recognition, particularly with BF₄⁻.^[26]

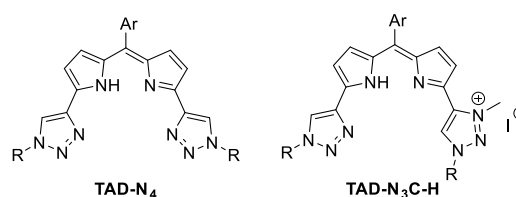


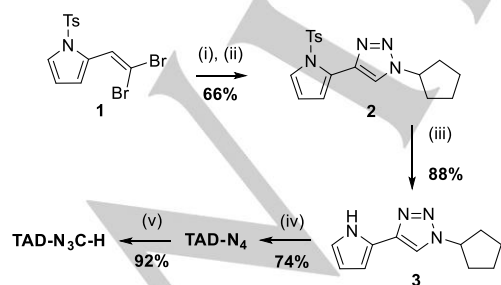
Figure 1. **TAD-N₄** and **TAD-N₃C-H** general structures

Among the large potential of this ligand, its easy conversion to the corresponding mesoionic carbene (MIC) after triazole salt deprotonation with a relatively weak base has caught our attention. Triazolylidenes have been described for the first time in 2008 by Albrecht and *coll.*^[27] and have been widely investigated since. Interestingly, they are obtained efficiently from the corresponding triazole, and can be easily functionalized. Many examples of triazolylidene-metal complexes have been described in the literature.^[28] They can be obtained by direct metalation, by free-

carbene generation followed by metal complexation or by transmetalation of a silver complex. The most common metals used for the transmetalation are palladium,^[29–32] iridium,^[33–35] rhodium,^[36–39] ruthenium,^[40–43] or gold.^[44–46] The corresponding complexes are commonly used as catalysts in various transformations such as cross-coupling,^[47–49] α -arylation,^[49] hydrogenation,^[35,40–42,50] or in the synthesis of oxazolines.^[44,51] Generally, the intermediate silver complexes are not isolated, the second source of metal being added in the reaction medium *in situ*. A few examples of silver-triazolylidene complexes have been described in the literature. For example, Heath *et al.* have reported on the formation of a linear triazolylidene-Ag-X complex with the addition of silver oxide onto the ligand.^[51] The dimer-complex can also be observed, with the coordination of the metal between two triazolylidene ligands.^[52] When the ligand incorporates other chelating sites, it is possible to obtain complexes displaying original structures with less common geometries, including Ag-Ag interactions.^[53]

Herein, we describe the synthesis and the metalation of the **TAD-N₃C-H** ligand with silver. The presence of the triazolylidene in α -dipyrrromethene position was proven to play a key role in the binding mode. The fine control of the amount of silver appeared essential for controlling the structure of the expected silver complexes.

The **TAD-N₄** ligand was synthesized in three steps from 2-dibromoethene-*N*-tosylpyrrole **1** according to the methodology developed in our group (Scheme 1).^[24] After a Corey-Fuchs reaction followed by a Huisgen cycloaddition, compound **2** was isolated in 66% yield. Next, the nitrogen atom deprotection afforded the “half” ligand **3** in 88% yield. After condensation and oxidation, the targeted **TAD-N₄** ligand was isolated in 74% yield. After mono-methylation of the **TAD-N₄** ligand with methyl iodide in toluene at 65 °C during 24 hours, the triazolium salt **TAD-N₃C-H** was obtained in 92% yield. Noticeably, no trace of the bis-methylated adduct was observed at this temperature.



Scheme 1. Synthesis of **TAD-N₄** and **TAD-N₃C-H** ligands. Reagents and conditions: (i) *n*-BuLi, THF, -78 °C, 4 h; (ii) azidocyclopentane, CuSO₄·5H₂O, sodium ascorbate, benzoic acid, t-BuOH/H₂O, rt, 12 h; (iii) 5M aq. NaOH, TBAB, dioxane/H₂O, reflux, 24 h; (iv) methyl 4-formylbenzoate, TFA, DCM, rt, 12 h then *p*-chloranil, 35 °C, 1 h; (v) MeI, toluene, 65 °C, 24 h.

Next, complexation with silver oxide was explored. This source of silver is commonly used in carbene chemistry. Indeed this salt offers the possibility to deprotonate and metalate at the same time without adding another base.

The **TAD-N₃C-H** ligand displays several acidic protons in different environments (Figure 2). The triazolium proton is the more acidic.^[54,55] However, the metalation of the DPM and the triazole can be considered, leading to the formation of different structures (Figure 2). Interestingly, the deprotonation-complexation sequence could easily be monitored by ¹H NMR as the acidic protons appear at different chemical shifts (Figure 3, a). Indeed, the triazole proton signal appears at $\delta = 8.70$ ppm (in blue) and the triazolium salt proton signal appears at $\delta = 10.25$ ppm (in orange).

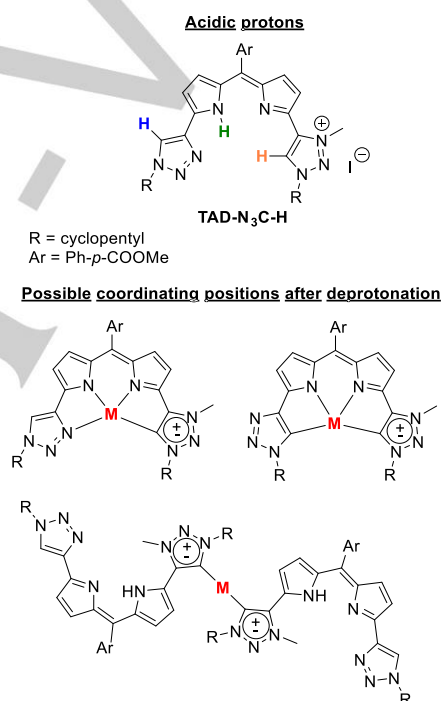


Figure 2. **TAD-N₃C-H**-acidic protons and possible coordination modes

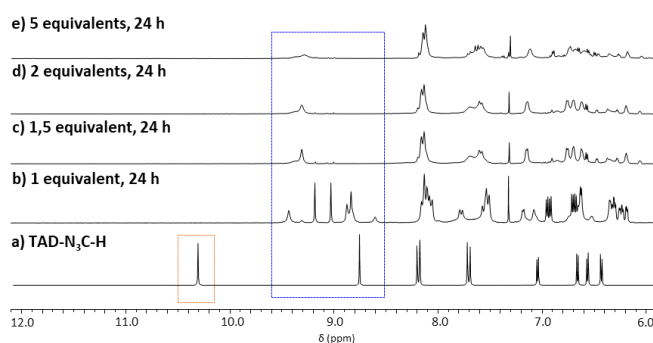
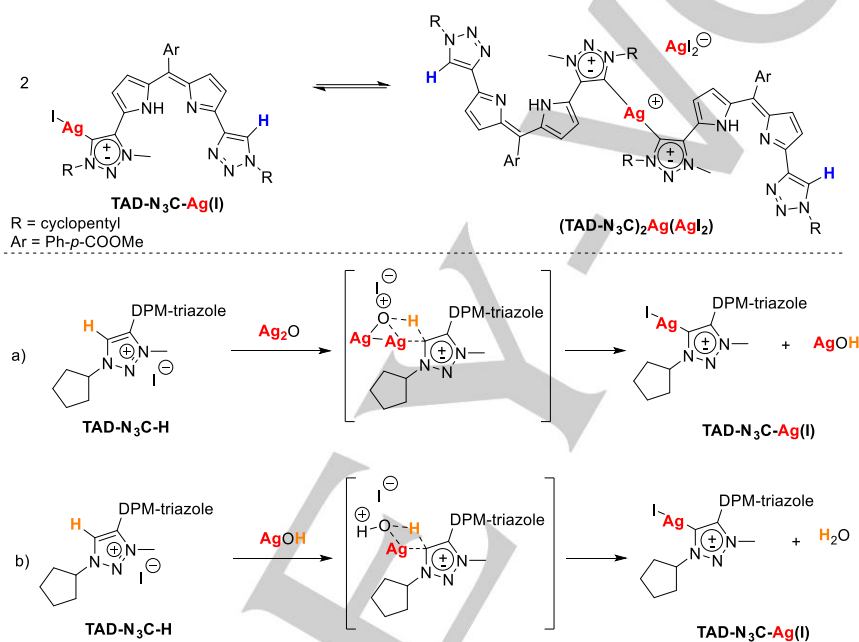


Figure 3. *In situ* ¹H NMR spectra (300 MHz, CD₂Cl₂) of the silver complex obtained after 24 h at 40 °C with different silver amounts.

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The complexation was carried out at 40 °C in deuterated dichloromethane. After the addition of one equivalent of silver oxide to a solution of **TAD-N₃C-H** (Figure 3, b), the ¹H NMR spectrum displayed two well-defined signals in the triazole proton area at δ = 9.04 and 9.19 ppm. At 8.84, 8.88 ppm and 9.44 ppm, three broader signals were observed but it was not possible to assign them unambiguously to any structure. However, on the basis of precedents from the literature^[28] and mass spectrometry analyses (see *Supplementary Information*), it is likely that those signals reveal an equilibrium between the neutral **TAD-N₃C-Ag(I)** and the cationic **(TAD-N₃C)₂**Ag(AgI₂) forms of the silver-TAD complexes (Scheme 2). Noticeably, the silver-carbene complexes

were proven very stable in solution even after ageing. Indeed, after 6 months, the mass spectrum of the sample revealed the presence of **(TAD-N₃C)₂**Ag(AgI₂) as the only remaining product in solution. Inspired by the work of Hayes *et al.*^[56], the following mechanism (Scheme 2) is proposed for explaining the formation of the two complexes. Firstly, Ag₂O deprotonates the triazolium and coordinates to the newly formed carbene affording the first neutral complex **TAD-N₃C-Ag(I)** and silver hydroxide (Scheme 2, a). The release of AgOH allows a second deprotonation/complexation sequence on an additional molecule of **TAD-N₃C-H** with water release (Scheme 2, b).



Scheme 2. Mechanistic proposition for the complexation with one equivalent of silver oxide

The reaction was repeated with 1.5 equivalent of silver oxide. Under these conditions, the ¹H NMR revealed the formation of another compound (Figure 3, c) in 70% NMR yield. The latter could be crystallized by slow diffusion of pentane in the CD₂Cl₂ NMR solution. The X-ray diffraction analysis (CCDC number: 1997118) revealed a dimer structure with the chelation of a silver atom by the dipyrromethene, the triazolylidene and a Ag-Ag bond (Figure 4). On the dipyrromethene scaffold, planar distortions of the pyrroles of 25.5° and 21.0° respectively were observed for the two ligands. The N1-Ag2 and N10-Ag1 distances were similar (2.16 and 2.18 Å, respectively) whereas the N2-Ag2 and N9-Ag1 bonds were longer (2.56 and 2.47 Å, respectively). An argentophilic interaction was observed, with a Ag1-Ag2 distance of 2.97 Å. Hence, each silver atom sits in a deformed triangular-based pyramidal environment. Such an environment and the interatomic distances are comparable with those described by

Wagner *et al.* in the case of a imidazolylidene-silver-pyridine dimer complex,^[57] where the Ag-Ag distance reached 2.89 Å. It is also similar with the complex described by Cai *et al.* where the distance Ag-Ag was 2.84 Å.^[53] The C26-Ag1 and C58-Ag2 bonds are similar (~ 2.10 Å), which is common for a carbene-silver bond.

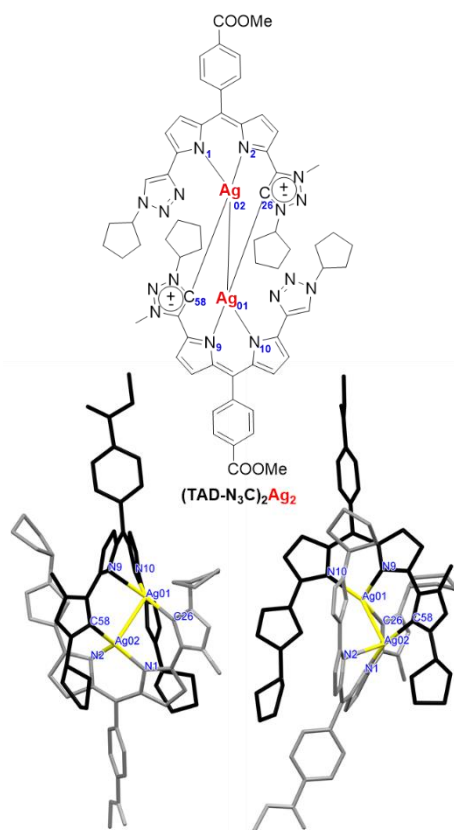


Figure 4. Different views of $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$ molecular structure - all hydrogen atoms were omitted for clarity

To confirm the existence of $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$, several analyses were carried out. The molecular ion observed in the MS spectrum confirmed the existence of the $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$ complex ($m/z = 1337$ uma for $[\text{M}+\text{H}]^+$). Argentophilic interactions, as well as aurophilic interactions, display specific features. In particular, LMCT (Ligand to Metal Charge Transfer) transitions are observed in a silver complex without any Ag-Ag interaction. Conversely, LMMCT transitions (Ligand to Metal-Metal Charge Transfer) reveal Ag-Ag interactions.^[58–60] Particularly, it is possible to

observe large bands related to the Ag-Ag interactions leading to the formation of a Ag-Ag* excimer under irradiation. Consequently, the stabilization induced by the Ag-Ag bond results in a smaller HOMO-LUMO gap allowing a radiative relaxation of the complex. Fluorescence measurements (Figure 5) of the silver complex solution confirmed the existence of the $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$ dimer. Unfortunately, in agreement with precedents from the literature,^[57] the life time of the excimer was too short to be measured. Noticeably, the Stokes shift was about 42 nm which is lower than what it is generally observed.

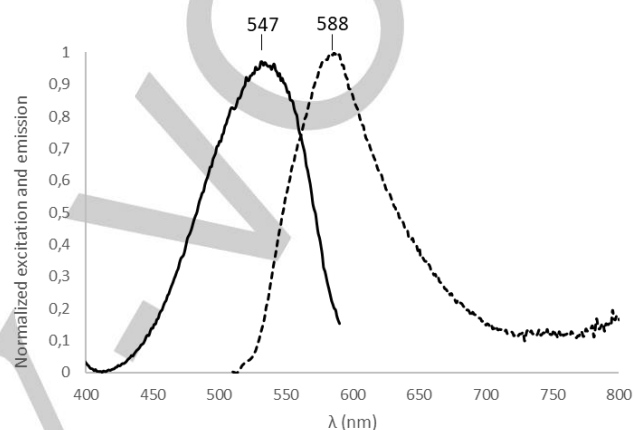
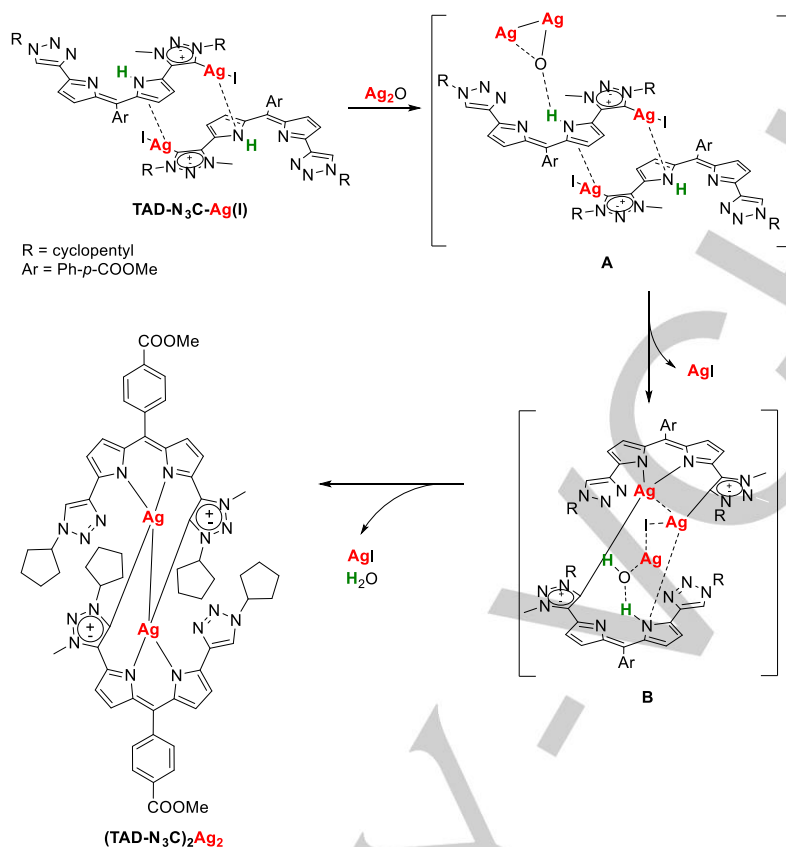


Figure 5. Normalized absorption (plain line) and emission (dotted line) of $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$ in DCM

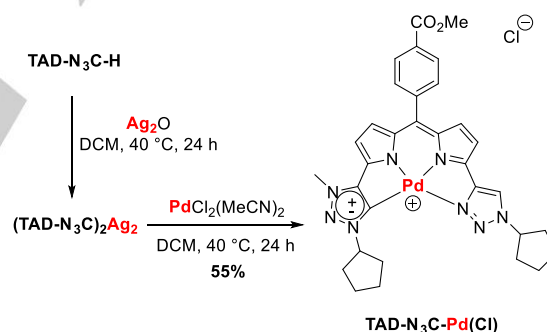
On the basis of the solid state and solution analyses, the following mechanism explaining the formation of the $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$ complex is proposed (Scheme 3). First, in the presence of Ag_2O , the DPM core undergoes a silver-assisted (intermediate **A**) deprotonation allowing the formation of the silver complex **B** and AgI which precipitates in the reaction medium. Similarly to Ag_2O , AgOH can deprotonate the complex **B** affording $(\text{TAD-N}_3\text{C})_2\text{Ag}_2$, H_2O and AgI .



Scheme 3. Mechanistic proposition for the formation of **(TAD-N₃C)₂Ag₂**

In the presence of larger amounts of Ag₂O (*i.e.* 2 or 5 equivalents; Figure 3, d-e), the signal at 9.05 ppm assigned to the triazole C-H tends to disappear. Hence, the excess Ag₂O is able to deprotonate the triazole C-H affording the corresponding triazolide that can further bind to silver. While a coordination of the triazolide to the DPM bound-silver atom was expected, the formation of oligomers (or short polymers) was evidenced by MS analyses. Unfortunately, the structure of resulting coordination-polymer could not be totally elucidated, even if the UV-Vis analyses confirmed that the Ag-DPM bonds remained ($\lambda_{\text{max}} = 551$ nm with 5 equivalents of Ag vs $\lambda_{\text{max}} = 547$ nm with 1.5 equivalent of Ag and $\lambda_{\text{max}} = 534$ nm for the ligand).

Next, the possibility to transmetalate the silver DPM-carbene with palladium was attempted. In the presence of an excess of PdCl₂(MeCN)₂, the *in-situ* generated **(TAD-N₃C)₂Ag₂** complex was converted to the corresponding **TAD-N₃C-Pd(Cl)** complex in 55% yield after purification on alumina (Scheme 4). Hence, the possibility to transmetalate the silver complexes was proven. Work is currently ongoing in our laboratory to investigate further this strategy and allow the preparation of unprecedented DPM-metallocomplexes.



Scheme 4. Transmetalation with palladium

This work clearly demonstrates that it is possible to form silver complexes from **TAD-N₃C-H** and possibly transmetalate the corresponding silver complexes to afford new DPM complexes. In the presence of one equivalent of silver oxide, an equilibrium between two triazolylidene-silver complexes was obtained without any contribution of the DPM scaffold. Interestingly, with 1.5 equivalent of silver oxide, a dimer was isolated. The X-Ray diffraction analysis of the dimer revealed the involvement of the DPM scaffold in the coordination of silver and the existence of an argentophilic interaction, which was further confirmed by fluorescence analysis, with the observation of a characteristic band for the Ag-Ag bond. In the presence of larger amounts of Ag₂O, a coordination polymer was obtained but it could not be

fully characterized. Interestingly, a preliminary test revealed that the silver ions could transmetalate with palladium affording an unprecedented Pd-DPM complex that could not be prepared directly. Further investigations will be needed to further understand the intrinsic potentialities of the silver complexes as key intermediates for the preparation of new metallocomplexes.

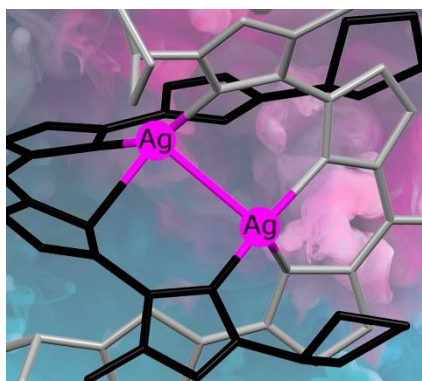
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Keywords: Carbene ligands • Metal-metal interactions • N ligands • Neighboring-group effects • Silver

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Entry for the Table of Contents**Key topic: Silver carbene complexes**

An unexpected silver-triazolylidene-dipyrromethene complex is described. Through this example, we evidence the crucial role of the stoichiometry in silver to afford unprecedented dipyrromethene silver complexes.