

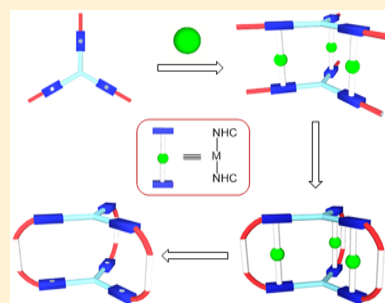
# Preparation and Post-Assembly Modification of Metallosupramolecular Assemblies from Poly(*N*-Heterocyclic Carbene) Ligands

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**ABSTRACT:** Although the coordination chemistry of *N*-heterocyclic carbenes (NHCs) with transition metals has been explored for half a century, only in the past ten years has the chemistry of metallosupramolecular assemblies based on poly-NHC ligands been studied more extensively. Remarkable discrete assemblies featuring poly-NHC ligands including two-dimensional metallacycles and three-dimensional metalprisms/cages have since emerged. These assemblies are mostly obtained starting from various imidazolium or benzimidazolium salts. Driven by the increasing interest in new supramolecular architectures from carbon donor ligands, design, and construction of poly-NHC metal assemblies has become a rapidly growing area of research. The metal–carbene bond length is fixed to approximately 2.0 Å in linear NHC–M–NHC complexes. This allows the use of such complexes bearing olefin-substituted NHC ligands as templates for subsequent photochemical [2 + 2] cycloaddition reactions. The postassembly modification of such assemblies has been actively explored in recent years. In this review, we focus on the synthetic methods, characterization, structural features, and postassembly modifications of metallosupramolecular assemblies obtained from poly-NHC ligands.



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## 1. INTRODUCTION

Over the past decades, the design and synthesis of metal-based, discrete polynuclear nanostructures has gained much attention, and various two-dimensional (2D) and three-dimensional (3D) supramolecular architectures have meanwhile been described.<sup>1–10</sup> These studies have been inspired by the use of metal-based supramolecular assemblies as a new generation of materials able to perform molecular recognition, catalysis, drug delivery, and sensing. It should be noted that this field of research is strongly dominated by Werner-type coordination complexes, wherein the metal ions are connected via oxygen donors from carboxylic acids and/or nitrogen donors from pyridyl-functionalized organic linkers, with only very few examples of assemblies bearing carbon donor ligands reported in the literature.<sup>11,12</sup>

Half a century ago, in 1968, the first examples of coordination compounds with N-heterocyclic carbenes (NHCs) were reported by Öfele<sup>13</sup> and Wanzlick.<sup>14</sup> This field of research has since witnessed a tremendous development and a large number of NHC complexes with transition metal and main group elements having meanwhile been synthesized and characterized.

The isolation and characterization of the first stable carbene was reported more than 20 years after the early studies of Öfele and Wanzlick. In their pioneering work of 1988, Bertrand and co-workers isolated a freely stable, uncoordinated [bis-(diisopropylamino)phosphino](trimethylsilyl)carbene, stabilized by phosphorus and silicon substituents adjacent to the carbene center.<sup>15</sup> Three years later, the isolation and characterization of 1,3-bis(adamantyl)imidazolin-2-ylidene by Arduengo and co-workers provided the first example for a free and stable N-heterocyclic carbene (NHC).<sup>16</sup> The application of NHC complexes in homogeneous catalysis, reported by Herrmann and co-workers,<sup>17</sup> kickstarted a strong interest in the design, synthesis, and characterization of novel NHCs and their metal complexes for catalytic applications in addition to theoretical studies.<sup>18</sup>

The coordination of NHCs to transition metals benefits from their strong  $\sigma$ -donor and (debatably) weak  $\pi$ -acceptor properties.<sup>19–22</sup> Compared to phosphines, NHCs are more electron-donating and the metal–ligand bonds thus formed are thermodynamically stronger. Due to rapid advances and the widespread interest in NHC coordination chemistry, the number of reviews covering the topic is growing rapidly. NHC complexes have been reported for all transition metals, alkali, alkaline earth, and *f*-block metals. A themed issue of *Chemical Reviews* entitled “Carbenes” was published in 2009.<sup>23–41</sup> Several

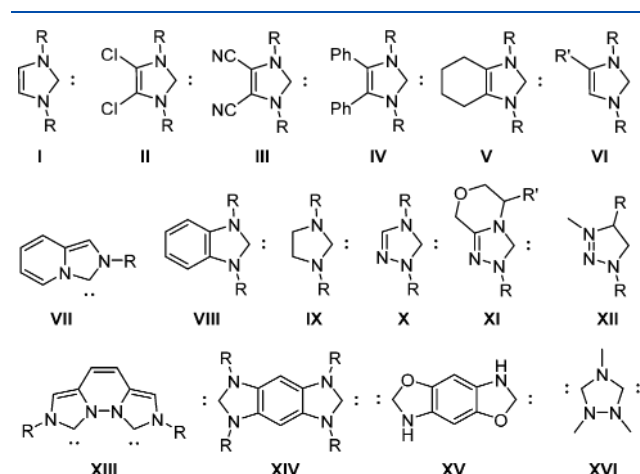
books<sup>42–44</sup> and a number of excellent reviews have also been published, providing further insight into different areas of the chemistry of NHC-metal complexes.<sup>18,45–54</sup> The attractive features of such complexes have led to various applications in areas ranging from homogeneous catalysis,<sup>55–61</sup> and metal-lodrugs,<sup>41,62–64</sup> to materials science.<sup>65–69</sup> Complexes of abnormal, mesoionic, and remote N-heterocyclic carbenes have also been reviewed.<sup>30,70</sup> The various synthetic routes to NHC precursors were reviewed in 2011.<sup>71</sup>

The number of metallosupramolecular assemblies featuring M–C<sub>NHC</sub> bonds has grown steadily over the last 20 years. The first review on complexes from poly-NHC ligands was published by Peris and co-workers in 2009.<sup>36</sup> In a recent account, Hahn and co-workers summarized their studies on the synthesis of metallosupramolecular assemblies using poly-NHC ligands.<sup>72</sup> An account of the synthesis and structural properties of dinuclear copper(I)–NHC complexes was published very recently.<sup>73</sup>

This review summarizes the developments in the areas of synthesis of poly-NHC precursors and discrete supramolecular assemblies obtained from poly-NHC ligands.

### 1.1. Types of NHC Donors, Poly-NHC Ligands, and Poly-NHC Supramolecular Assemblies

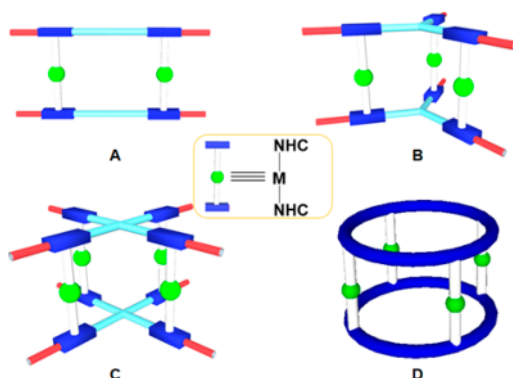
A large number of classes of cyclic singlet carbenes have been described in the literature.<sup>18,74</sup> However, only few of these have been used for the construction of supramolecular assemblies. Figure 1 depicts the known NHC frameworks that have been applied in the formation of discrete supramolecular metal-NHC assemblies.



**Figure 1.** Types of NHC donors that have been utilized for the construction of supramolecular metal-NHC assemblies and will be discussed in this review.

In this review, the term “poly-NHC ligand” refers to compounds containing more than one NHC donor.<sup>36</sup> Poly-NHC ligands can be, but are not limited to, bis-NHC, tris-NHC, tetrakis-NHC, and hexakis-NHC ligands, in addition to cyclophanes and calix[*n*]arenes incorporating more than one NHC donor. In the complexes of these poly-NHCs, the donor groups are normally restricted to carbene donors alone, although some exceptions are made. In addition to NHCs, additional donor groups such as nitrogen, oxygen, and phosphines can be present and selected complexes of such heterodonor ligands will also be considered. Among the known supramolecular assemblies, we will highlight two-dimensional molecular metal-

lacycles including di- and tetranuclear metallarectangles, tetranuclear metallasquares, and three-dimensional metallacages including tri-, tetra-, and hexanuclear metallaprisms/cylinders. Four representative types of supramolecular assemblies, (A) the dinuclear metallacycles, (B) the trinuclear metallacylinders, (C) the tetranuclear metallaprisms, and the (D) tetranuclear metallacylinders are shown in Figure 2.



**Figure 2.** Selected examples of metal-carbene supramolecular assemblies.

## 1.2. Post-Assembly Modification of Discrete Metallosupramolecular Assemblies

Compared to the established postsynthetic modification (PSM) of metal–organic frameworks (MOFs),<sup>75,76</sup> significantly less attention has been devoted to the postsynthetic modification of discrete metallosupramolecular assemblies, especially in solution. Due to their normally lower stability, discrete assemblies may decompose when they are covalently modified with new chemical functionalities if incompatible reagents or substrates are applied. However, some postassembly modification (PAM) reactions were found to be useful in the chemistry of selected metallosupramolecular assemblies.<sup>77,78</sup> For a PAM reaction to be useful for a discrete assembly, it should be highly efficient and proceed under mild conditions. In particular, it should not interfere with the metal–ligand coordination interactions, and the metallosupramolecular structure must be retained.<sup>78</sup> Two different methods, oxidation reactions and photochemical [2 + 2] cycloaddition reactions, have been successfully employed for the PAM of metal-NHC assemblies not only in the solid state but also in solution.

## 1.3. Scope of the Review

In this review, we will summarize the synthesis, the structural properties, and the postassembly modifications of discrete metallosupramolecular assemblies obtained from poly-NHC ligands. Where relevant, we will also describe details of the characterization and potential applications of a given assembly. The manuscript is organized into six major parts: (i) two-dimensional metallacycles, (ii) three-dimensional molecular cages, (iii) other structures, (iv) postassembly modifications, (v) potential applications of poly-NHC assemblies, and (vi) conclusions and outlook.

Almost all known metallosupramolecular assemblies derived from poly-NHC ligands are diamagnetic species. This allows the characterization of the metal-carbene assemblies by NMR spectroscopy (especially <sup>13</sup>C NMR spectroscopy). In addition, the <sup>107/109</sup>Ag and <sup>13</sup>C coupling constants are also a useful tool for the characterization of silver-NHC assemblies.

Poly-NHC ligands have also been extensively used for the synthesis of mononuclear chelate complexes. Such mononuclear complexes are not included in this review.

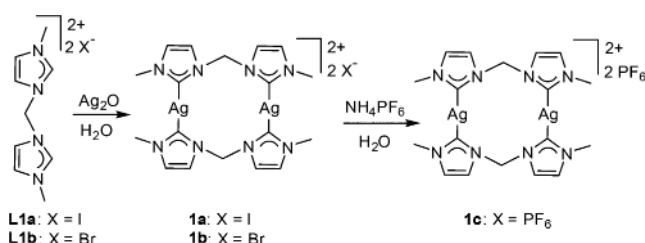
## 2. TWO DIMENSIONAL MOLECULAR METALLACYCLES

The most widely used method for the preparation of poly-NHC metallosupramolecular assemblies is the direct reaction of imidazolium/benzimidazolium salts with a metal source in the presence of a suitable base in one pot or in a stepwise procedure. Dinuclear metallacycles composed of two bis-NHC ligands belong to the earliest described assemblies. They are generally prepared from bisimidazolium or bisbenzimidazolium salts and suitable metal precursors under a range of different conditions. Dinuclear silver assemblies are good starting materials for transmetalation reactions of bis-NHC ligands. Such transmetalation reactions can be performed under rather mild conditions. Tetranuclear squares featuring four bridging Janus-type benzobisimidazolylienes and four metal vertices can be synthesized from the reaction of linear benzobisimidazolium salts with selected metal salts in the presence of a base in a one-pot multicomponent self-assembly reaction. The construction of related molecular squares linked by bis(NH,O-NHCs) has been achieved in metal template-controlled reactions.

### 2.1. Dinuclear Bis-NHC Metal Structures

**2.1.1. Dinuclear Silver(I) Assemblies.** In 2004, Youngs and co-workers reported an efficient method for the synthesis of disilver(I) tetracarbene complexes.<sup>79</sup> Reaction of methylene-linked bisimidazolium halide salts **L1a,b** with a slight excess of Ag<sub>2</sub>O in aqueous solution at room temperature resulted in the nearly quantitative formation of the complexes **1a,b** (Scheme 1).

**Scheme 1.** Synthesis of Complexes **1a–1c**



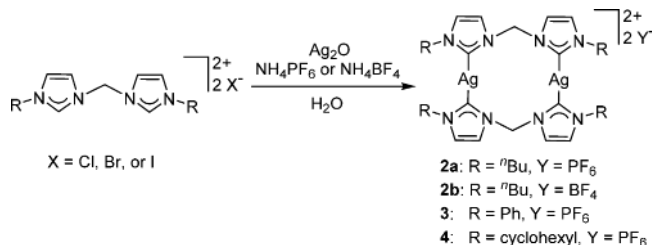
It should be noted that ligands of type **L1** can also form chelate complexes with transition metals if the NHC donors can coordinate to the metal center in cis-geometry. This coordination mode is impossible for silver(I) complexes where the metal prefers a linear coordination geometry, and thus the metallamacrocycles are obtained.

Complex **1a** is light-sensitive, and decomposition was observed in solution and in the solid state. An anion-exchange reaction of **1a** with NH<sub>4</sub>PF<sub>6</sub> afforded the air-stable hexafluorophosphate salt **1c** exhibiting in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the characteristic resonance for the C<sub>NHC</sub> carbon atom at δ 196.01 ppm. The facile synthesis of **1c** starting from the bromide salt of **1b** has been proposed as a potential laboratory experiment for undergraduate students.<sup>80</sup>

Following a similar procedure, complexes **2–4** were prepared from Ag<sub>2</sub>O and bis-NHC precursors featuring different counterions and N,N'-substituents of various size and geometry (Scheme 2).<sup>79,81–83</sup> An X-ray diffraction study with crystals of **2a** confirmed the formation of the dinuclear tetracarbene

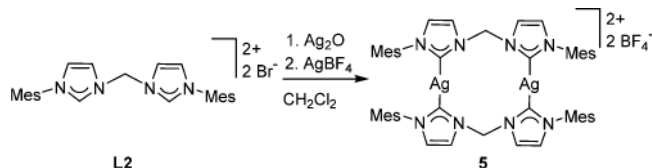


Scheme 2. Synthesis of Complexes 2–4



metallamacrocycle. The Ag–C<sub>NHC</sub> bond distances (for the two independent molecules in the asymmetric unit) fall in the range from 2.083(5) to 2.088(5) Å, and the silver atoms link the NHC ligands in an almost linear fashion, with C<sub>NHC</sub>–Ag–C<sub>NHC</sub> angles in the range from 169.7(2)° to 171.2(2)°. These are typical metric parameters for dinuclear metallacycles bearing two bis-NHC ligands.

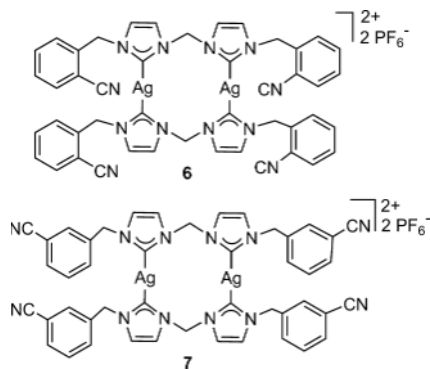
Even the bulky N,N′-substituted bisimidazolium salt **L2** can be employed for the preparation of the disilver tetracarbene metallacycle **5** (Scheme 3).<sup>84</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of

Scheme 3. Synthesis of Complex 5<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 84. Copyright 2004 American Chemical Society.

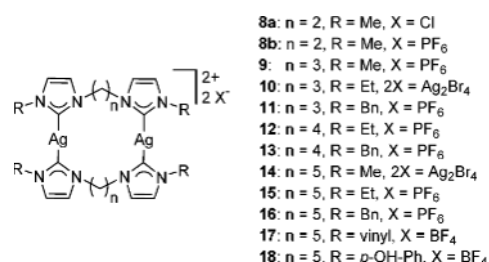
complex **5** exhibits a pair of doublets at  $\delta = 180.9$  ppm caused by Ag–C<sub>NHC</sub> coupling of  $^1J(\text{C},^{109}\text{Ag}) = 210$  Hz and  $^1J(\text{C},^{107}\text{Ag}) = 182$  Hz. This coupling is diagnostic for silver-carbene complex formation; however, it is not always observed. While equivalent parameters in **5** resemble those in **1–4**, compound **5** exhibits a rather short Ag⋯Ag contact of 3.2039(3) Å.

Additional metallamacrocycles featuring a methylene linker between the NHC donors and various N,N′-benzylidene substituted nitriles such as **6** and **7** have also been described (Figure 3).<sup>85–87</sup> The bioactivity of **6** against cancer cells was investigated. The nonhygroscopic complex **7** bearing an N,N′-*m*-benzylidene-substituted dicarbene ligand exhibited activity against two cancer cell lines, HCT 116 and MCF-7.<sup>87</sup>



**Figure 3.** Dinuclear complexes with N,N′-benzylidene substituted bis-NHC ligands.

Expansion of the linker between the NHC donors in the bis-NHC ligands led to the metallamacrocyclic complexes **8–18**. A range from C<sub>2</sub> to C<sub>5</sub> bridges between the NHC donors have been introduced (Figure 4).<sup>81,88–92</sup> With the exception of



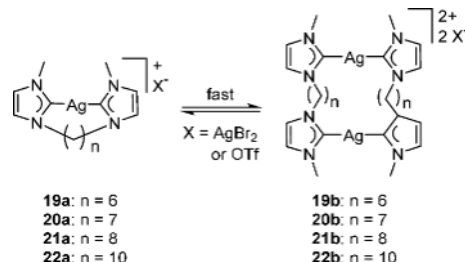
**Figure 4.** Dinuclear silver complexes **8–18**.

complexes **8a**,<sup>88</sup> **10**,<sup>89</sup> and **14**,<sup>91</sup> these complexes were found to be stable under ambient conditions in solution. However, both the type of counterion and the length of the alkyl linker influence the stability of the complexes.

X-ray diffraction experiments showed that the expansion of the length of the bridge between the NHC donors leads to either unsymmetrical or centrosymmetric molecular structures of the [Ag<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> cations in the solid state. The metric parameters around the silver atoms are not significantly influenced by this feature. Naturally, the Ag⋯Ag separation in the dinuclear complexes expands with the expansion of the alkyl linker, and Ag⋯Ag separations in the range from 4.773(4) Å to 9.394(2) Å were observed for **8–18**.

A further expansion of the length of the alkyl linker between the NHC donors enables the formation of both mononuclear chelate complexes and dinuclear metallamacrocycles. As illustrated with complexes **19–22**, alkyl linkers of 6 to 10 CH<sub>2</sub> groups were employed (Scheme 4).<sup>93</sup> Complexes **19–22** were

**Scheme 4.** Equilibria between Mononuclear (**19a–22a**) and Dinuclear (**19b–22b**) Silver(I) Complexes<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 93. Copyright 2013 American Chemical Society.

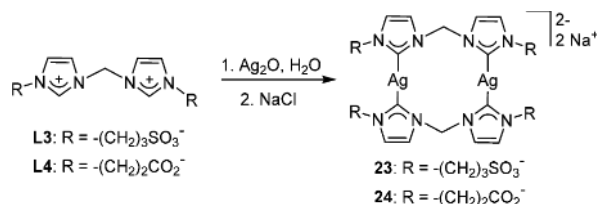
found to exist in an equilibrium between the mononuclear chelate complexes (**19a–22a**) and the dinuclear metallamacrocycles (**19b–22b**). The exchange process between the mononuclear and dinuclear species at ambient temperature is fast on the NMR time scale. If the number of carbon atoms in the bridge is greater than 7, the equilibrium shifts toward the mononuclear complexes in the order of **21a** > **22a** > **20a** (i.e.,  $n = 8 > 10 > 7$ ) indicating that the  $-(\text{CH}_2)_8-$  linker has the optimal length for a linear chelation of the silver atom. ESI-MS spectrometry also allowed the detection of the equilibria between the mononuclear and dinuclear complexes. Formation of the equilibria confirms the lability of the Ag–C<sub>NHC</sub> bond,

which allows formation of the thermodynamically most stable reaction product.

Water has attracted considerable attention as a cheap and nontoxic solvent, given its obvious environmental benefits and safety advantages. The development of water-soluble and -stable NHC complexes is therefore of great importance in catalysis research as well as for biomedical applications. Compared to phosphine complexes, NHC complexes generally exhibit a greater stability toward oxygen and moisture.

A synthetic pathway for the preparation of water-soluble silver complexes from sulfonate- or carboxylate-functionalized NHC ligands was reported in 2009.<sup>94</sup> Deprotonation of the zwitterionic NHC ligand precursors **L3** and **L4** with  $\text{Ag}_2\text{O}$  in degassed water led to the disilver(I) complexes **23** and **24** (Scheme 5). Of the prolignands, **L3** was found to be a

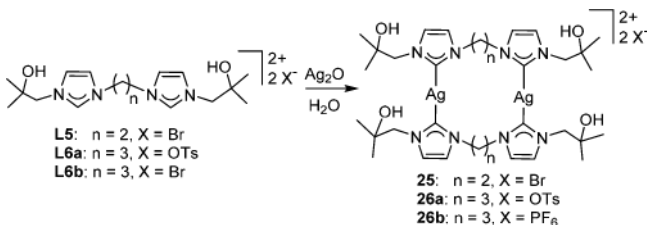
Scheme 5. Synthesis of Complexes **23** and **24**



hygroscopic solid, while the compound **L4** was obtained as a microcrystalline solid. The molecular structure of the digold(I) complex obtained by transmetalation of the dicarbene ligand from **24** to gold(I) was characterized by X-ray diffraction.<sup>95</sup>  $\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$  dicarbene chelate complexes were also prepared by transmetalation of the dicarbene ligand from **23** in water.<sup>96</sup>

Treatment of the alcohol-functionalized bisimidazolium salt **L5** with  $\text{Ag}_2\text{O}$  in water at 50 °C for 14 h yielded the dinuclear complex **25** (Scheme 6).<sup>95</sup> The  $\text{C}_3$ -bridged bisimidazolium salts **L6a** and **L6b** react analogously in the presence of molecular sieves to give complexes **26a** and, after anion exchange with  $\text{NH}_4\text{PF}_6$ , **26b**.<sup>97,98</sup>

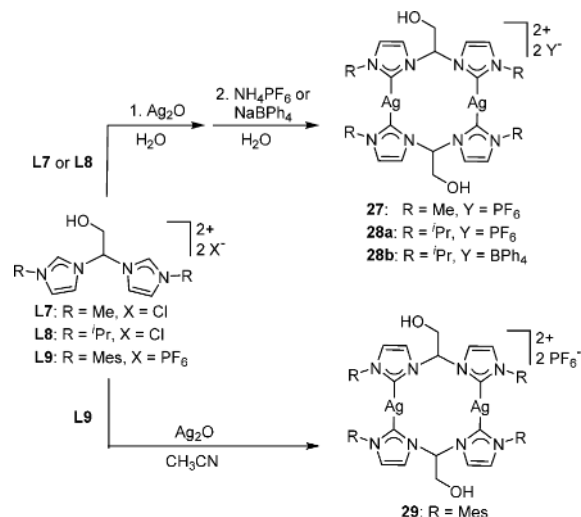
Scheme 6. Synthesis of Silver(I) Complexes **25** and **26a,b**



Complexes **26a** and **26b** bear the same ligands but feature different counterions. This led to two different conformations of the complexes in the solid state as revealed by X-ray diffraction analyses.<sup>97,98</sup>

A new type of methylene-bridged bisimidazolium salt bearing a central hydroxymethyl substituent was described in 2015.<sup>99</sup> Using the protocol developed for the synthesis of complexes of type **1** (Scheme 1), complex **27** was prepared by treatment of prolignand **L7** with  $\text{Ag}_2\text{O}$  in water (Scheme 7). An anti-configuration of the two hydroxymethyl groups was found by an X-ray diffraction study. Further studies of the spectroscopic properties revealed no influence of the hydroxymethyl substituent on the electronic properties of **27**.

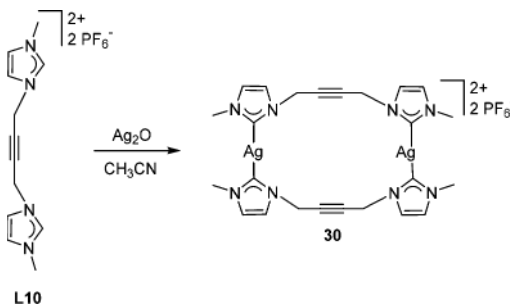
Scheme 7. Synthesis of Complexes **27–29**



In order to investigate the impact of different  $\text{N,N}'$ -substituents on the complexes obtained from hydroxymethyl bridged bisimidazolium salts, complexes **28a,b** and **29** were prepared from prolignands **L8** and **L9** (Scheme 7).<sup>100</sup> NMR spectroscopy and DFT calculations indicated the existence of various isomers (syn and anti, exo and endo orientation of the hydroxymethyl substituents) of the complexes in solution. Very recently, a hydroxymethyl-functionalized bisimidazolium salt with 2-pyridine substituents at the  $\text{N,N}'$ -positions and its silver carbene complex has also been described.<sup>101</sup>

The bisimidazolium prolignand ligand **L10**, featuring a rigid linear  $-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-$  linker, has been prepared and was reacted with  $\text{Ag}_2\text{O}$  to yield complex **30** (Scheme 8).<sup>102</sup> The

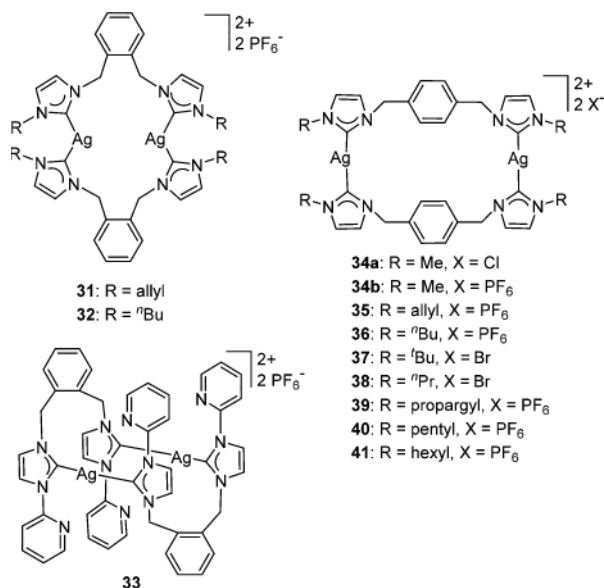
Scheme 8. Synthesis of Complex **30**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 102. Copyright 2008 Elsevier.

complex proved to be air stable and was not sensitive to light. An X-ray diffraction study revealed a coplanar arrangement of the two NHC donors coordinated to each silver atom and the two  $\text{NHC}-\text{Ag}-\text{NHC}$  planes are also coplanar. Due to the rigid linkers, the metallamacrocycle is twisted and a weak  $\text{Ag}\cdots\text{Ag}$  interaction of 3.252(1) Å was found.

A series of *ortho*- and *para*-xylylene-bridged bisimidazolium salts have been employed for the preparation of disilver(I) complexes **31** and **32**,<sup>103,104</sup> **33**,<sup>105</sup> and **34–41**.<sup>103,104,106–108</sup> (Figure 5). The introduction of pyridyl wingtips in complex **33** led to a boxlike conformation with two silver ions separated by 3.257 Å. Weak interactions between the pyridine nitrogen and the silver atoms were also observed in the solid state.

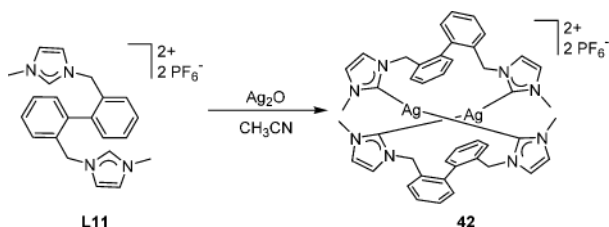


**Figure 5.** Dinuclear silver metallamacrocycles obtained from xylene-bridged bis-NHC ligands.

At ambient temperature, complex **34b** exhibited a flexible conformation in solution, as was observed by <sup>1</sup>H NMR spectroscopy.<sup>106</sup> It is worth noting that only mononuclear complexes were obtained from the reaction of *meta*-xylene-bridged bisimidazolium salts with Ag<sub>2</sub>O. This arrangement of the donors is apparently suitable for the formation of silver chelate complexes with a linearly coordinated silver atom.<sup>107</sup>

The bisimidazolium salt **L11** was used for the preparation of complex **42** (Scheme 9).<sup>109</sup> A variety of analytical methods were

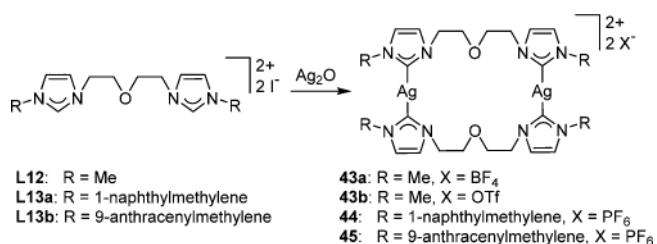
#### Scheme 9. Synthesis of Dinuclear Silver(I) Complex 42



used to characterize this complex, including NMR spectroscopy and X-ray crystallography. Due to the twisted nature of the biphenyl moiety, a helical structure was found, presumably stabilized by the intramolecular Ag...Ag contact of 3.2918(5) Å.

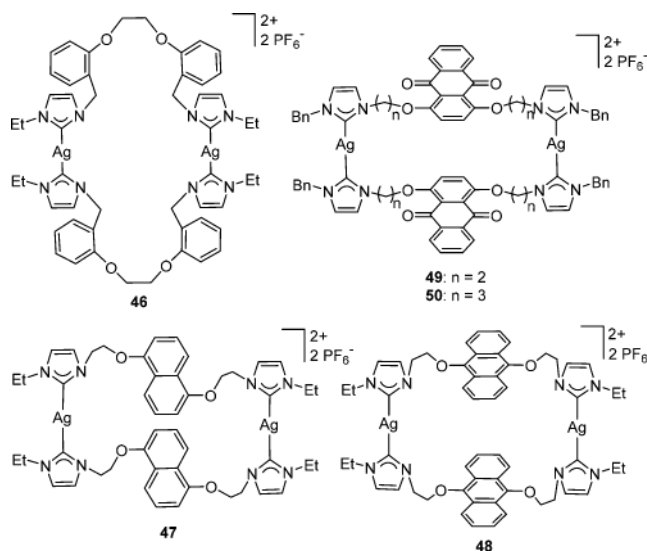
The first bisimidazolium salt bridged by an ether-linker **L12** was used by Cavell and co-workers for the preparation of the dinuclear metallacycles **43a** and **43b** (Scheme 10).<sup>91,110</sup> In order to study the impact of the N,N'-wingtips on the coordination

#### Scheme 10. Synthesis of Silver(I) Complexes 43–45



geometry at the silver atoms, complexes **44** and **45** bearing large N,N'-substituents were subsequently prepared from **L13a** and **L13b**.<sup>111</sup> As confirmed by X-ray diffraction studies, the overall conformation of the complexes, but not the coordination geometry of the silver ions, changed upon modification of the N,N'-wingtips.

As shown in Figure 6, among these was the 30-membered disilver(I) macrocycle **46**.<sup>112</sup> A similar linker was employed for

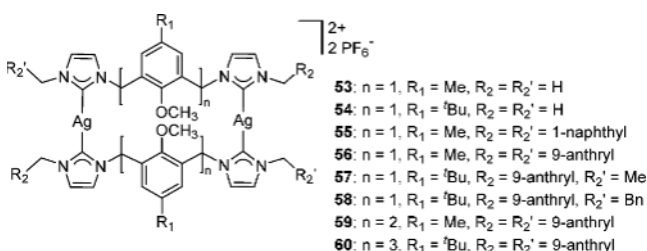
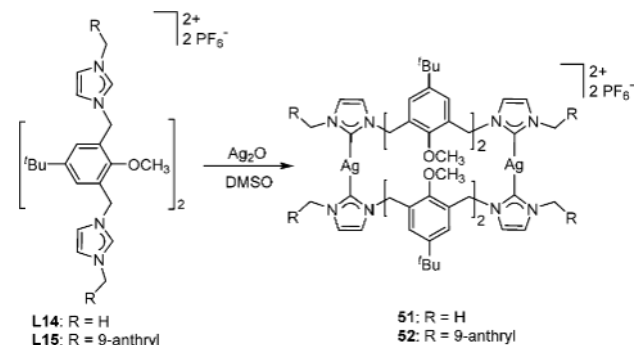


**Figure 6.** Dinuclear silver tetracarbene complexes obtained from ether-linked bisimidazolium salts.

the synthesis of complex **47**.<sup>113</sup> Metallamacrocycle **47** proved efficient in the recognition of *p*-phenylenediamine in acetonitrile. Complex **48** was prepared using a bisimidazolium salt featuring a diether linker derived from anthracene (Figure 6).<sup>114</sup> An X-ray diffraction study revealed two parallel anthracene rings with  $\pi \cdots \pi$  stacking interactions. In addition, an anthraquinone building block was used for the preparation of two bisimidazolium salts and their dinuclear metallacycles **49** and **50**.<sup>115</sup> These complexes were shown to be light-stable in the solid state but slightly light-sensitive in solution. The two anthraquinone moieties in **49** were found to be arranged in a parallel fashion forming  $\pi \cdots \pi$  interactions, while in complex **50** the anthraquinone rings were offset from one another, with  $\pi \cdots \pi$  interactions formed between imidazolin-2-ylidene and anthraquinone rings.

Calix[*n*]arene-like metallamacrocycles **51** and **52** have been obtained from bisimidazolium salts **L14** and **L15** modified with calixarene fragments (Scheme 11).<sup>116</sup> Complexes **51** and **52** each contain two identical bis-NHC ligands coordinated to two silver centers. In complex **52**, the four *tert*-butyl moieties adopted a heavily twisted 1,2-alternating conformation, and the four anisole groups are disposed toward the center of the cavity. This complex also shows a strong tendency to complex [60]fullerene, with a large stability constant ( $K_s = 348\,000\text{ M}^{-1}$ ).

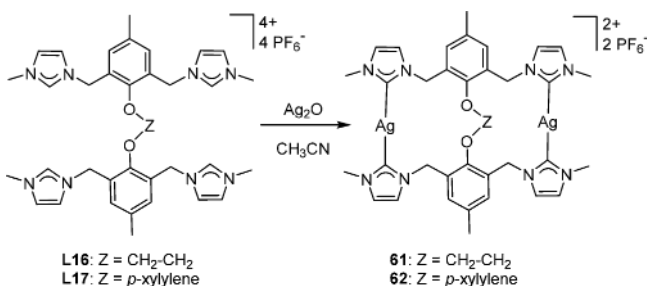
Subsequently, a series of calix[*n*]arene analogs **53–60** were prepared (Figure 7).<sup>117,118</sup> As confirmed by X-ray diffraction structure analysis, complex **54** with *tert*-butyl groups adopts a cone-conformation due to strain caused by the *tert*-butyl groups, while **53**, **55**, and **56**, containing smaller methyl substituents, form rectangular cavities.<sup>117</sup> Complex **56** has been applied as a fluorescence chemosensor for *p*-benzoquinone. In addition,

Scheme 11. Synthesis Calix[*n*]arene Analogs 51 and 52Figure 7. Calix[*n*]arene analogue complexes 53–60.

fluorescence quenching behavior was observed for **59** and **60** when interacting with C<sub>60</sub> or C<sub>70</sub> fullerenes.

The reaction of unsymmetrical bisimidazolium salts with Ag<sub>2</sub>O in acetonitrile produced the dinuclear complexes **57** and **58**.<sup>118</sup> Complex **57** was investigated by X-ray diffraction showing that only one of the bulky-substituted NHC donors from each ligand coordinates to each silver atom, while the other possible isomer was not mentioned by the authors.

The tetrakisimidazolium proligands **L16** and **L17**, featuring an additional linker between two bisimidazolium units, were employed for the preparation of the disilver complexes **61** and **62** (Scheme 12).<sup>118</sup>

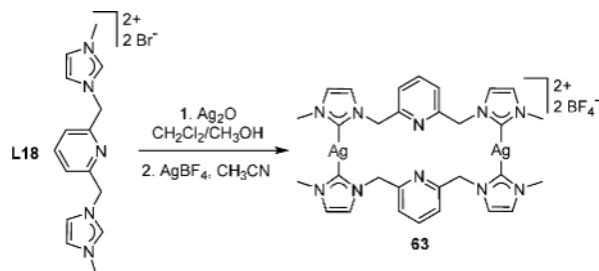
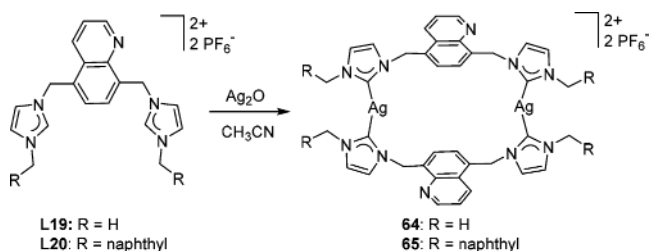
Scheme 12. Synthesis of Silver(I) Complexes 61 and 62<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 118. Copyright 2015 Elsevier Ltd.

The light gray complex **63**, with a 2,6-pyridine bridge between the NHC donors, was synthesized in high yield from proligand **L18** (Scheme 13).<sup>119</sup> The nitrogen atoms of the pyridyl groups remained uncoordinated.

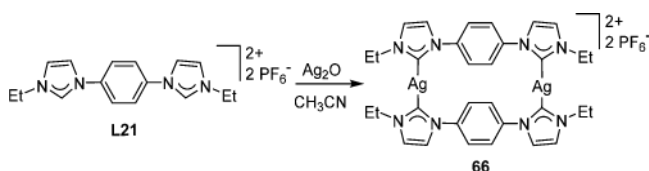
Two quinoline-bridged imidazolium precursors, **L19** and **L20**, have been used for the synthesis of metallamacrocycles **64** and **65** (Scheme 14).<sup>120</sup> The 22-membered metallamacrocycle in **64** forms a rectangular cavity as shown by X-ray diffraction. A simple *p*-benzene-linked bisimidazolium salt **L21** was used for the preparation of the dinuclear complex **66** (Scheme 15).<sup>121</sup>

Scheme 13. Synthesis of Dinuclear Silver(I) Complex 63

Scheme 14. Synthesis of Silver(I) Complexes 64 and 65<sup>a</sup>

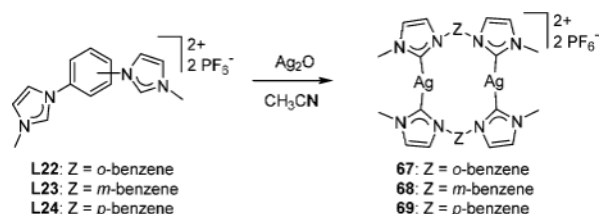
<sup>a</sup>Adapted with permission from ref 120. Copyright 2013 Wiley-VCH.

The molecular rectangle obtained featured two central benzene rings which were not arranged in a coplanar fashion.

Scheme 15. Synthesis of Dinuclear Silver(I) Complex 66<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 121. Copyright 2011 American Chemical Society.

The procedure used for the preparation of **66** was also employed for the preparation of the metallamacrocycles **67**–**69** from the bisimidazolium proligands **L22**–**L24** featuring *o*-, *m*-, and *p*-benzene bridges (Scheme 16).<sup>122</sup> The complexes were

Scheme 16. Synthesis of Silver(I) Complexes 67–69<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 122. Copyright 2016 Royal Society of Chemistry.

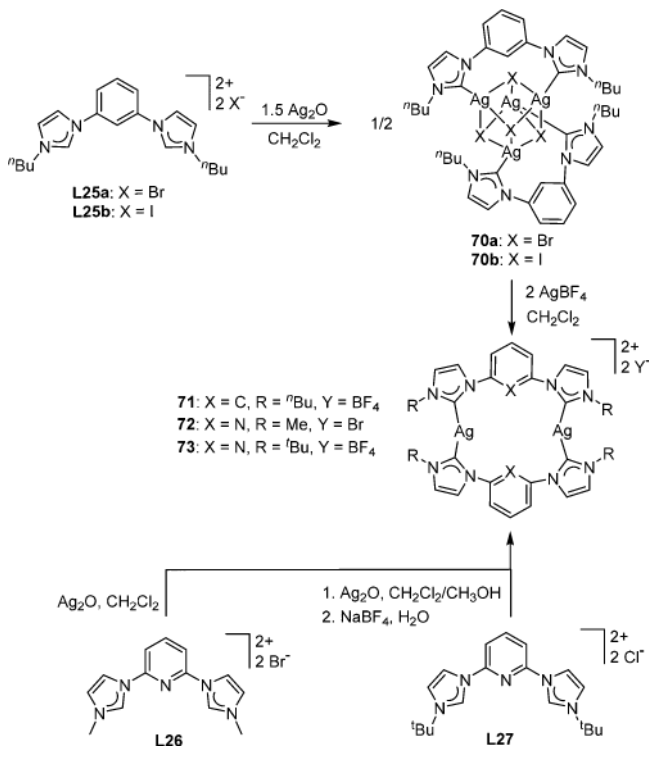
characterized by spectroscopic techniques, including NMR spectroscopy and ESI-MS spectrometry. The type of linker present in the bis-NHC ligands appears to influence the chemical shift of the C<sub>NHC</sub> resonance slightly ( $\delta$  = 186.7 ppm for **67**;  $\delta$  = 181.7 ppm for **68**; and  $\delta$  = 180.0 ppm for **69**).

When the bisimidazolium salts **L25a,b** were reacted with 1.5 equiv of Ag<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>, both NMR data and ESI-MS



spectrometry combined with single-crystal X-ray diffraction analysis confirmed that the resulting complexes **70a,b** contained a central cubane-type moiety (Scheme 17, top).<sup>123</sup> The subsequent reaction with 2.0 equiv of  $\text{AgBF}_4$  in dichloromethane cleanly provided the dinuclear metallamacrocycle **71** in good yield.

Scheme 17. Synthesis of Silver(I) Complexes **71**–**73**

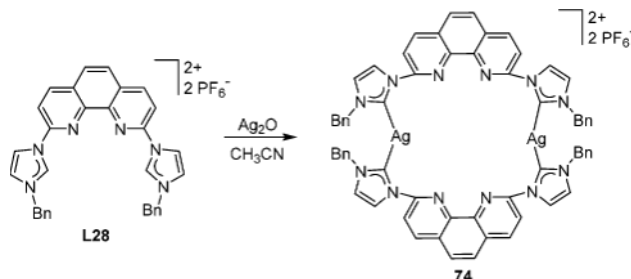


Mixing of **L26** with  $\text{Ag}_2\text{O}$  in dichloromethane resulted in the formation of the silver carbene complex **72** (Scheme 17, bottom). Complex **72** showed anti-HIV activity at low concentrations.<sup>124</sup> Similarly, complex **73**, bearing the related 2,6-bis(3-*tert*-butylimidazolin-2-ylidene)pyridine ligands, was prepared in good yield from the reaction of imidazolium precursor **L27** and  $\text{Ag}_2\text{O}$  in  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  (1/10) as shown in Scheme 17.<sup>125</sup> A variety of analytical methods including X-ray crystallographic studies were used to characterize complex **73**. The X-ray diffraction data showed that the two carbene ligand strands are intertwined and surround the silver ions in a double helical fashion. The  $\text{Ag}\cdots\text{Ag}$  distance [3.0251(14) Å in **73**] indicated the existence of argentophilic interactions. Interestingly, a weak interaction between the nitrogen atoms of bridging pyridine and the silver atoms [2.922(10) Å] was found in **73**.

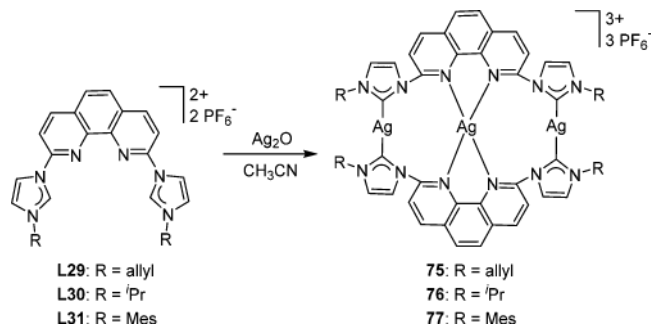
The helical macrocyclic structure **74** was obtained from the reaction of **L28**, bearing *N*-benzyl groups, with 1.5 equiv of  $\text{Ag}_2\text{O}$  in acetonitrile (Scheme 18).<sup>126</sup> The complex was obtained as part of a mixture of several complexes which could not be separated. Only a few crystals of complex **74** were isolated. A single-crystal X-ray diffraction study revealed that **74** is a classical dinuclear tetracarbeno metallamacrocycle.

The related phenanthroline-bridged dicarbene precursors **L29**–**L31**, bearing different *N,N'*-substituents, were shown to react with  $\text{Ag}_2\text{O}$  to give the trinuclear complexes **75**–**77** (Scheme 19).<sup>126</sup> In these complexes, the nitrogen atoms of the phenanthroline bridge coordinate to a third silver atom, leading to  $\text{C}_{\text{NHC}}^-$  and  $\text{N}_{\text{phen}}^-$ -metalated ligands.

Scheme 18. Synthesis of Dinuclear Silver(I) Complex **74**

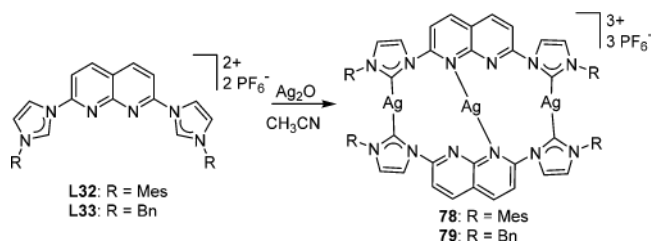


Scheme 19. Synthesis of Trinuclear  $\text{Ag}^{\text{I}}$  Complexes **75**–**77**



The naphthyridine-bridged bisimidazolium precursors **L32** and **L33** were also prepared.<sup>127</sup> The bisimidazolium salts contain pendant mesityl or benzyl units. Reaction of **L32** or **L33** with  $\text{Ag}_2\text{O}$  in acetonitrile yielded complexes **78** and **79** (Scheme 20).<sup>127</sup> An X-ray diffraction study showed that in **79**, the

Scheme 20. Synthesis of Trinuclear  $\text{Ag}^{\text{I}}$  Complexes **78**–**79**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 127. Copyright 2008 Elsevier.

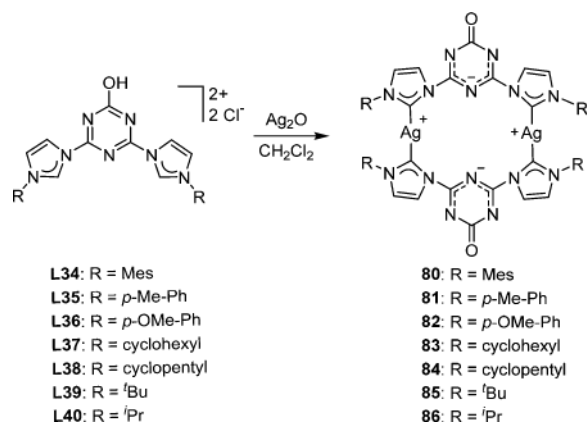
nitrogen atoms of the linker also participate in metal coordination, but due to steric constraints only one silver ion binds in a diagonal fashion to two of the bridge's nitrogen atoms, leading to trinuclear assemblies with an almost linear  $\text{Ag}_3$  core.

A series of unusual neutral dinuclear silver assemblies bearing anionic triazine-bridged bis-NHC ligands **80**–**86** were obtained from the reaction of bis(imidazolium) proligands **L34**–**L40** with  $\text{Ag}_2\text{O}$  (Scheme 21),<sup>128</sup> as was confirmed by multinuclear NMR spectroscopy and mass spectrometry in combination with X-ray crystallography for complexes **80**, **81**, **83**, **84**, and **86**. The core structure is the same for all complexes. Coordination of two ligand strands leads to the formation of *P*- and *M*-helical assemblies. All complexes are sensitive toward acids (protonation of the oxygen atom).

Apart from differently bridged linear dicarbene, macrocyclic cyclophane derivatives have also been used for the construction of dinuclear tetracarbeno metallamacrocycles. A first example for this approach was presented by Youngs and co-workers in 2001 (Scheme 22).<sup>129</sup> Reaction of cyclophane dicarbene proligand

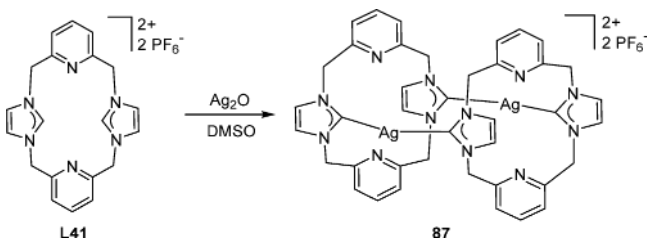


**Scheme 21. Synthesis of Neutral Dinuclear Silver(I) Complexes 80–86<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 128. Copyright 2011 American Chemical Society.

**Scheme 22. Synthesis of Dinuclear Silver(I) Complex 87 from Cyclophane Proligand L41**

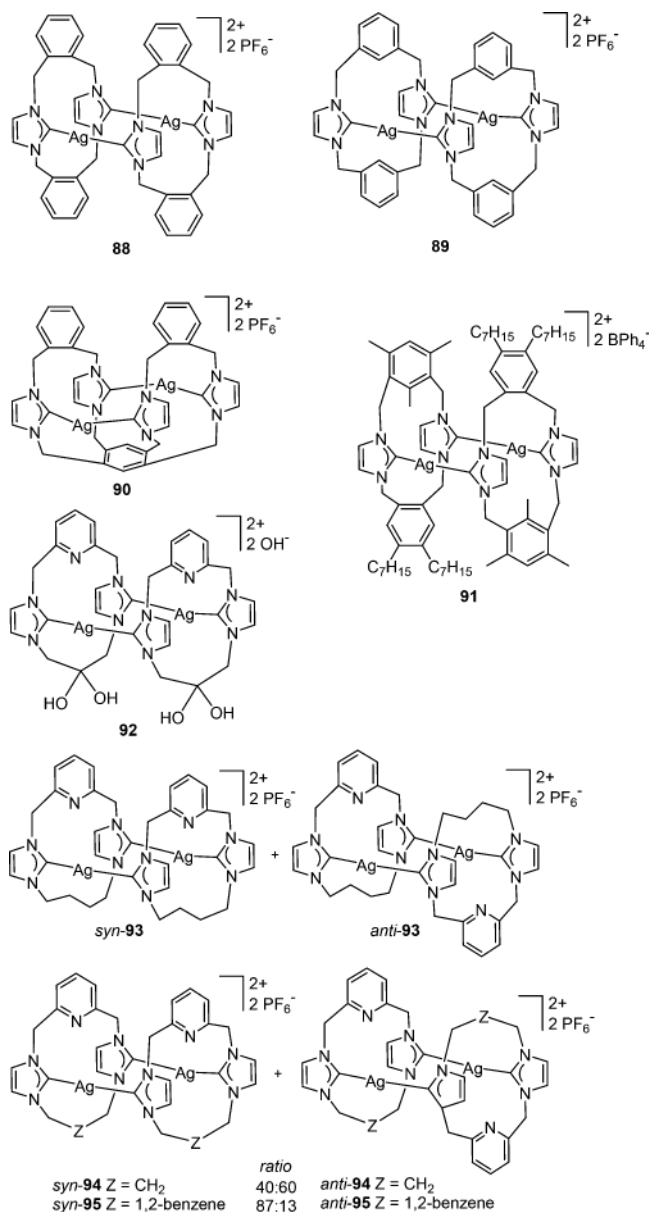


**L41** with  $\text{Ag}_2\text{O}$  in DMSO yielded the tetranuclear metal-lamacrocycle **87**. The cyclophane ligands in this complex are arranged in the form of a molecular box with an eclipsed alignment of the NHC donors. The same group later described an alternative synthesis of **87** by reacting prolignand **L41** with four equivalents of  $\text{Ag}_2\text{O}$  to obtain a complex featuring a central  $\text{Ag}_4$  core. This complex can be photolyzed to cleanly yield **87**.<sup>130</sup>

Subsequently, several cyclophane-type bisimidazolium salts featuring two identical or nonidentical linkers between the imidazolium groups have been prepared. They were used for the synthesis of dinuclear silver(I) metallacycles **88**,<sup>131</sup> **89**,<sup>131</sup> **90**,<sup>109</sup> **91**,<sup>131</sup> **92**,<sup>132</sup> **93**,<sup>133</sup> **94**, and **95**.<sup>134</sup> (Figure 8).

The synthesis of complexes **88** and **89** proceeded smoothly. Dinuclear complex **90** bears a tetracarbene ligand. The complex adopts a basketlike shape with a short nonbonding  $\text{Ag}\cdots\text{Ag}$  separation of 3.0460(4) Å. Complex **90** also exhibited significant antimicrobial activity. Complex **91** with an unsymmetrically bridged cyclophane-type bis-NHC ligand could form different geometrical isomers featuring *syn* and *anti* orientation of the ligands toward each other, and *exo* and *endo* orientation of the aromatic rings toward or away from the  $\text{Ag}_2\text{C}_2$  plane. However, only the *anti*-*endo*-*exo* isomer was detected by NMR spectroscopy (only one set of resonances) and by X-ray crystallography. A different observation was made for complex **92**, also bearing an unsymmetrically bridged cyclophane-type bis-NHC ligand. Here only the formation of complex *syn*-**92** was observed.

An unsymmetrical butyl/pyridyl-bridged bisimidazolium salt reacted with  $\text{Ag}_2\text{O}$  to give a mixture of complexes *syn*-**93** and *anti*-**93** in a ratio of 2:1 as shown by NMR spectroscopy.<sup>133</sup> The major isomer *syn*-**93** was characterized by X-ray diffraction analysis. Similar observations were made with related complexes



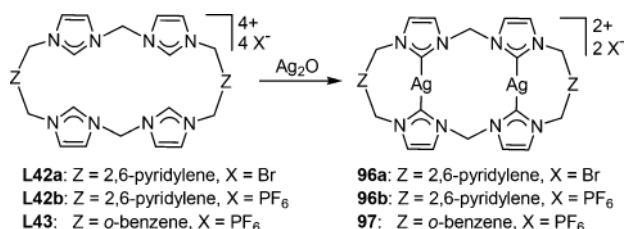
**Figure 8.** Dinuclear metallamacrocycles obtained from cyclophane-type bisimidazolium salts.

which, however, featured either a shorter (**94**) or longer bridge (**95**) as linkers. Both complex **94** and **95** form mixtures of *syn* and *anti* isomers. The major isomer of **94**, *anti*-**94**, was characterized by X-ray diffraction. Extension of the linker in **95** led to the preferred formation of *syn*-**95**.<sup>134</sup> The higher flexibility of the linker possibly allows the formation of  $\pi$ -stacking interactions between the aromatic rings.

The coordination chemistry of an unusual cyclophane-type bisimidazolium salt featuring a pyridine and an *N*-methylpyrrole linker between the NHC donors has also been described.<sup>135</sup> Upon deprotonation, two bis-NHC ligands assemble around a central  $\text{Ag}_4$  core with metalation of the  $\text{C}_{\text{NHC}}$  carbon and nitrogen atoms.

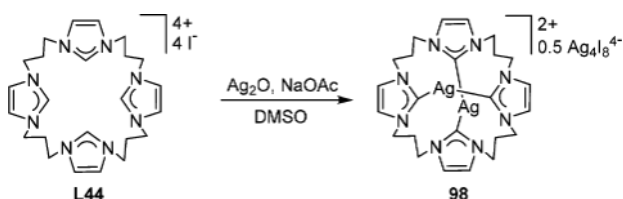
Disilver(I) complexes of cyclic tetrakis-NHC ligands have been prepared by metalation of the tetrakisimidazolium salts **L42a,b** with  $\text{Ag}_2\text{O}$  in good yields (Scheme 23).<sup>136</sup> Complex **96b**, containing the  $\text{PF}_6^-$  counterion, was found to be more stable than **96a**, with a bromide counterion.<sup>136</sup> Monometalation of

Scheme 23. Synthesis of Dinuclear Silver(I) Complexes from Cyclic Tetrakisimidazolium Salts



**L42a,b**, with just one silver atom being coordinated inside the macrocycle in a diagonal fashion, was also observed. Introduction of the *o*-xylylene bridges in **L43** reduced the size of the macrocycle by two atoms relative to **L42a,b**. Upon deprotonation of **L43**, the tetracarbene macrocycle (**97**) can accommodate two silver ions, but for steric reasons, the C<sub>NHC</sub>–Ag–C<sub>NHC</sub> angles have to adopt small values of around 160°. Coordination of only one silver atom in a diagonal, strain-free, and linear fashion is therefore preferred. The two remaining imidazolium groups of the monosilver macrocycle can be deprotonated, and reaction of this dicarbene metalloligand with additional silver ions then led to a tetranuclear assembly of two monometalated macrocycles bridged by two intermolecular C<sub>NHC</sub>–Ag–C<sub>NHC</sub> bonds (*vide infra*).<sup>137</sup>

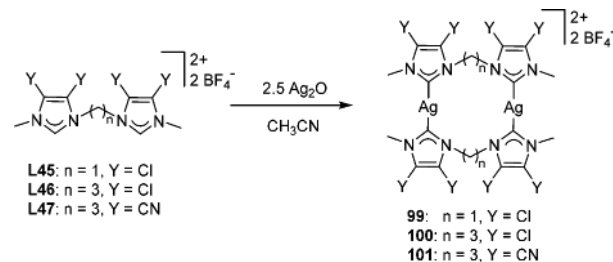
Furthermore, symmetrically bridged cyclic tetrakisimidazolium salts such as **L44** have been prepared (Scheme 24).<sup>138</sup> Iodo

Scheme 24. Synthesis of Disilver(I) Complex 98<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 138. Copyright 2007 Wiley-VCH.

salt **L44** reacted with Ag<sub>2</sub>O in the presence of NaOAc to give the disilver complex **98**. A molecular structure determination revealed that the silver atoms bind to alternate NHC donors in the macrocycle, which results in a mutually orthogonal orientation of the two C<sub>NHC</sub>–Ag–C<sub>NHC</sub> axes. While the macrocycle is flexible, it also constrains the silver atoms to be in close proximity to each other, resulting in a rather short Ag...Ag separation of 2.8349(6) Å. Complex **98** crystallizes with the remarkable (Ag<sub>4</sub>I<sub>8</sub>)<sup>4−</sup> tetraanion.

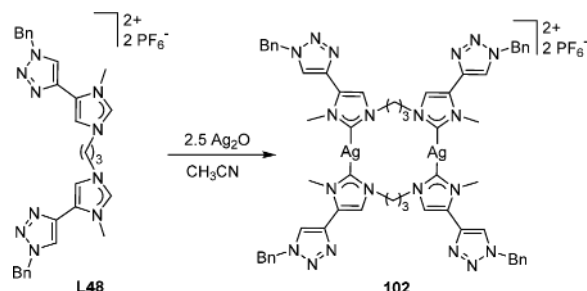
An interesting example of the synthesis of silver NHC complexes starting from less electron-donating NHC ligands has been reported by Tubaro, Biffis, and co-workers.<sup>139</sup> Electron-withdrawing groups such as chloride or cyanide were placed at the 4 and 5 positions of the imidazolium rings in **L45**–**L47**. As shown in Scheme 25, dinuclear silver complexes **99**–**101** were prepared from these bisimidazolium salts and an excess of Ag<sub>2</sub>O in acetonitrile. Due to the presence of electron-withdrawing substituents on the NHC backbone, the complexes were less stable than classical silver-NHC complexes and were therefore only characterized by NMR spectroscopy and ESI-MS spectrometry. The <sup>13</sup>C NMR resonance for the C<sub>NHC</sub> carbon atom of complex **101** was recorded at δ = 187.8 ppm, indicative of the electron-withdrawing influence of the cyanide sub-

Scheme 25. Synthesis of Silver(I) Complexes 99–101<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 139. Copyright 2015 Wiley-VCH.

stituents. The C<sub>NHC</sub> resonance for complex **100** was detected upfield relative to **101** at δ = 181.1 ppm.

A rare example of a disilver(I) complex bearing triazole-substituted dicarbene ligands was also reported. Complex **102** was prepared from proligand **L48** and Ag<sub>2</sub>O in acetonitrile (Scheme 26).<sup>140</sup> The bis-NHC ligand features a C<sub>3</sub> alkyl linker

Scheme 26. Synthesis of Complex 102 from a Ditrizole-Functionalized Bis-NHC Ligand<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 140. Copyright 2014 Elsevier.

and the triazole units were generated by copper-catalyzed “click” chemistry from the alkynyl-functionalized bisimidazolium ligand precursor. Due to the fluxional behavior of complex **102** in solution, the resonance for the C<sub>NHC</sub> carbon atom was not to be observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. However, formation of complex **102** was unambiguously confirmed by ESI-MS spectrometry and by microanalytical data. Complex **102** showed high in vitro antiproliferative activity, albeit with limited discrimination regarding cell line types.

In addition to poly-NHC ligands obtained from polyimidazolium salts, various polybenzimidazolium salts have been prepared and used as precursors for poly-NHC-metal assemblies. The propylene-bridged bisbenzimidazolium salts **L49a** and **L50** were used for the preparation of disilver complexes **103** and **104** using Ag<sub>2</sub>CO<sub>3</sub> as a metal source in the presence of 4 Å molecular sieves (Scheme 27).<sup>89</sup> Due to the fluxional behavior of the complexes, the resonances for the C<sub>NHC</sub> carbon atoms were not detected. However, both complexes were characterized by X-ray diffraction analyses. In addition, complexes **105**–**107**, bearing bis-NHCs with Et, <sup>n</sup>Pr, and pentyl wingtips, were prepared from proligands **L51**–**L53** (Scheme 27).<sup>141</sup>

In analogy to metallamacrocycles obtained from *o*-xylylene-bridged bisimidazolium salts (Figure 5), some *m*-<sup>142–144</sup> and *p*-xylylene-bridged<sup>145–148</sup> bisbenzimidazolium salts have also been prepared and used for the synthesis of dinuclear metallamacrocycles **108**–**121** using Ag<sub>2</sub>O as metal source (Figure 9).

Scheme 27. Synthesis of Silver(I) Complexes 103–107

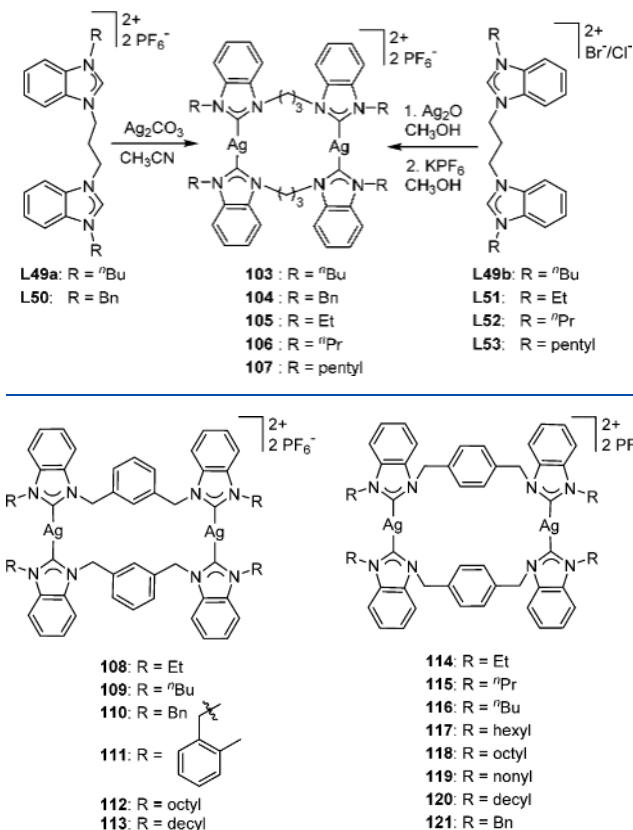
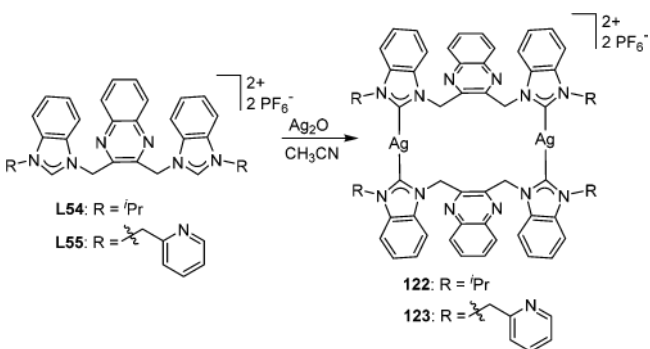


Figure 9. Dinuclear silver metallamacrocycles obtained from xylene-bridged bis-NHC ligands.

Additional bridges for the linkage of two benzimidazolin-2-ylidene donors have been employed. The bis-NHC proligands **L54** and **L55**, for example, feature quinoxaline bridges and react with  $\text{Ag}_2\text{O}$  to give the disilver(I) complexes **122** and **123** (Scheme 28).<sup>149</sup> X-ray diffraction analyses revealed that the

Scheme 28. Synthesis of Silver(I) Complexes 122 and 123



complexes adopt boxlike structures with the quinoxaline bridges being superimposed. The use of **122** and **123** as chemosensors for the recognition of  $\text{Cu}^{2+}$  ions via  $\text{Cu}\cdots\pi$  interactions has been investigated.

Metallamacrocycles with ether bridges between the benzimidazolin-2-ylidene donors **124**–**126** (Figure 10)<sup>113,115</sup> have been prepared in analogy to the related imidazolin-2-ylidene derivatives (Figure 6). Intramolecular  $\pi\cdots\pi$  interactions were observed between the two anthraquinone moieties in **125** and

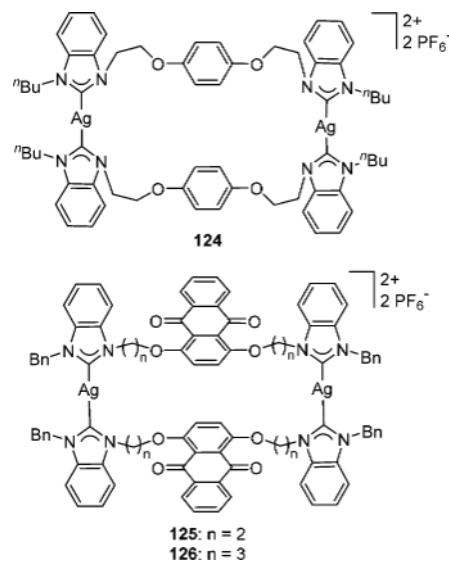
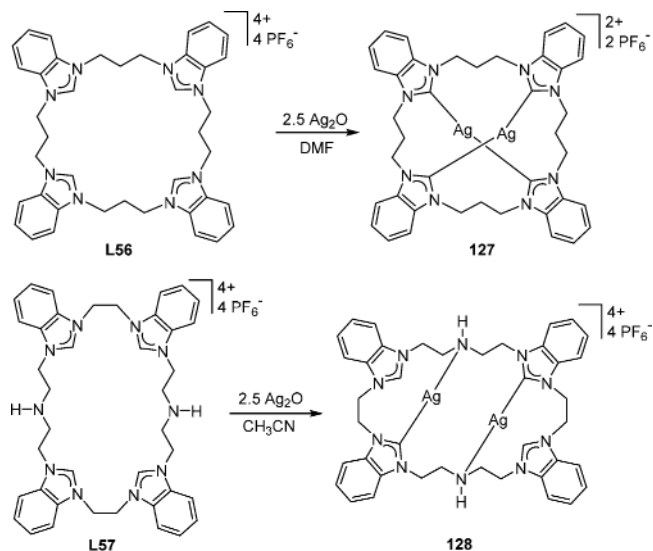


Figure 10. Metallamacrocycles obtained from ether-linkered bisbenzimidazolium salts.

**126**.<sup>115</sup> Owing to the large cavity formed by complex **124**, this complex was found to act as a receptor for *p*-phenylenediamine (PDA) molecules.

Cyclic tetrakisbenzimidazolium salts have also been prepared and used for the synthesis of disilver(I) complexes. The symmetrical propylene-bridged tetrakisbenzimidazolium salt **L56** is an analog of the imidazolium derivative **L44** (Scheme 24). It reacts with  $\text{Ag}_2\text{O}$  to give the cyclic disilver(I) complex **127** (Scheme 29, top).<sup>150</sup> A single-crystal X-ray structure

Scheme 29. Dinuclear Silver Complexes of Cyclic Tetrakisbenzimidazolin-2-ylidene Ligands



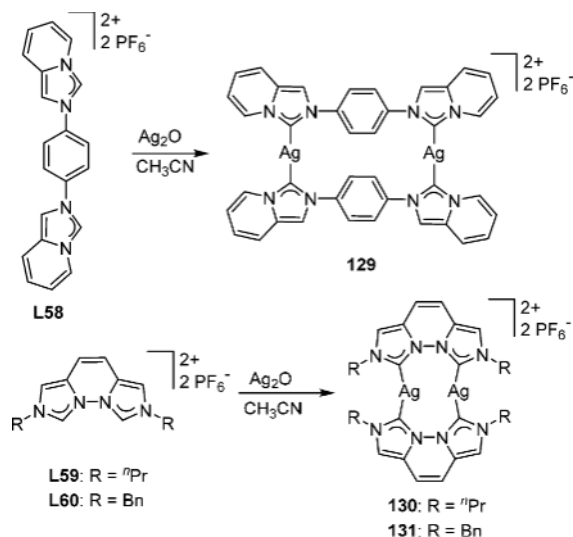
analysis revealed the essentially linear coordination of the two silver atoms by NHC donors in opposite positions of the macrocycle. The two  $\text{C}_{\text{NHC}}\text{--Ag--C}_{\text{NHC}}$  groups cross in an approximately orthogonal mode with a short  $\text{Ag}\cdots\text{Ag}$  separation of only 2.7826(6) Å, which is shorter than the  $\text{Ag}\cdots\text{Ag}$  separation in the cyclic tetrakisimidazolium derivative **98**.

Benzimidazolium precursor **L57** features bridges of differing lengths and types. It reacts with 2.5 equiv of  $\text{Ag}_2\text{O}$  to give the

dinuclear complex **128** with metalated NHC and amine donors (Scheme 29, bottom).<sup>151a</sup> Alternatively, the reaction of **L57** with only one equivalent of Ag<sub>2</sub>O yielded a mononuclear complex with metalation of only two NHC donors in opposite positions within the macrocycle, while the other two benzimidazolium groups remained protonated. The subsequent metalation of such unreacted azolium groups by a second type of metal with formation of heterobimetallic complexes has also been demonstrated.<sup>151b</sup>

A different mode of annulation of an imidazolium group, as seen in **L58** used for the preparation of metallamacrocycle **129**, has also been described (Scheme 30, top).<sup>152</sup> Some interesting

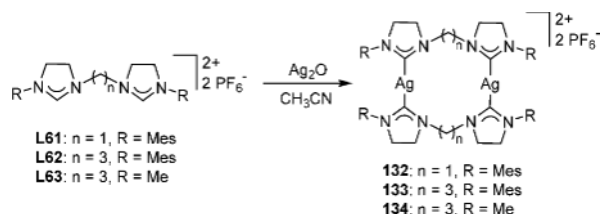
Scheme 30. Synthesis of Dinuclear Complexes 129–131



bisimidazolium salts **L59** and **L60** were prepared based on a central pyridazine building block. These bis-NHC ligand precursors were metalated by routine procedures to give complexes **130** and **131** (Scheme 30, bottom).<sup>153,154</sup> The specific linkage of the NHC donors forces the silver atoms into close proximity, leading to a very short Ag...Ag separation of only 2.741 Å in **130**.

Saturated bisimidazolidinium salts featuring  $-(\text{CH}_2)_n-$  bridges of varying lengths (**L61**–**L63**) have been used for the preparation of disilver metallamacrocycles **132**–**134** (Scheme 31).<sup>155,156</sup> The major difference exhibited by these complexes in

Scheme 31. Dinuclear Silver(I) Complexes 132–134 Obtained from Saturated Bisimidazolidinium Salts

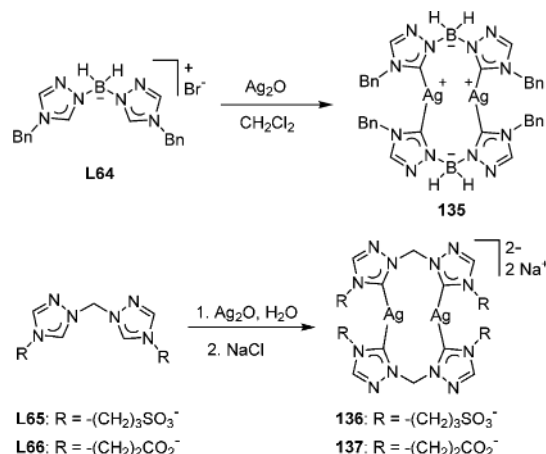


comparison to the isostructural derivatives with unsaturated NHC donors (Schemes 1–4) is found in the chemical shift of the resonance for the C<sub>NHC</sub> carbon atoms in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. These are found downfield at approximately δ 203 ppm for **132** and **133**, while the metric parameters of **132** and **133** strongly resemble those recorded for the dinuclear complexes

with unsaturated NHC donors. Complex **134** obtained from proligand **L63** proved unstable, and no analytical data have been reported.<sup>156</sup>

A number of dinuclear metallamacrocycles derived from bis(1,2,4-triazolium) salts have been prepared. The neutral complex **135** was obtained by metalation of the monoanionic proligand **L64** (Scheme 32, top).<sup>157</sup> Water-soluble dianionic

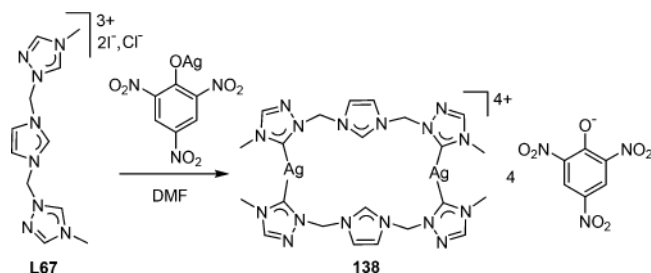
Scheme 32. Synthesis Silver(I) Complexes from Bis(1,2,4-triazolium) Salts



complexes **136** and **137** were prepared from the zwitterionic neutral proligands **L65** and **L66** (Scheme 32, bottom).<sup>94</sup> Related mononuclear water-soluble Ag-NHC complexes have also been described.<sup>158</sup>

An interesting metalation reaction of the bis(1,2,4-triazolium) salt **L67** has been reported. Instead of using Ag<sub>2</sub>O as a silver source, proligand **L67** was treated with silver picrate in dimethylformamide at room temperature to afford disilver(I) compound **138** in 35% yield (Scheme 33).<sup>159</sup> Interestingly, the

Scheme 33. Synthesis of Dinuclear Silver(I) Complex 138<sup>a</sup>



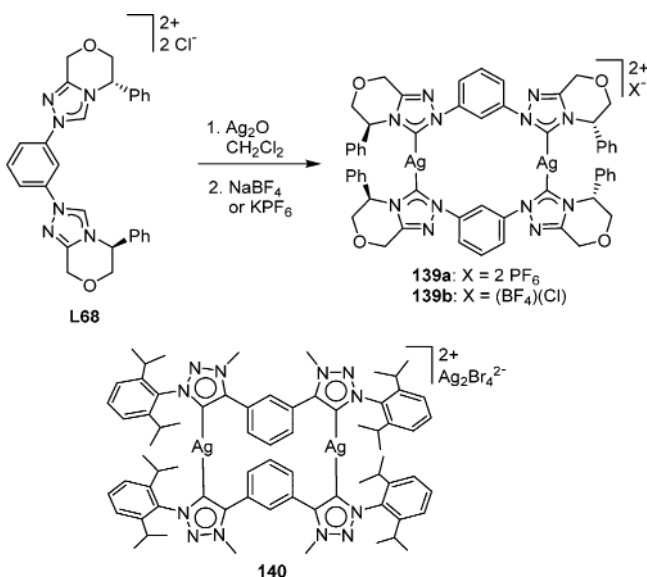
<sup>a</sup>Adapted with permission from ref 159. Copyright 2010 Springer Nature.

C5 atoms of the 1,2,4-triazolium groups were deprotonated in the reaction while the central imidazolium groups did not react, showing a resonance at δ 10.25 ppm for the C2–H protons in the <sup>1</sup>H NMR spectrum. In addition, the existence of weak  $\pi\cdots\pi$  interactions between the triazolin-5-ylidene units and the picrate anions, as well as between the picrate anions, was observed.

The chiral bisbicyclic bis(1,2,4-triazolium) salt **L68** has been employed for the preparation of chiral disilver metallamacrocycles **139a,b** (Scheme 34, top).<sup>160,161</sup> In addition, even a mesoionic carbene (MIC) dicarbene precursor has been prepared and utilized for the synthesis of metallamacrocycle **140** (Scheme 34, bottom).<sup>162</sup> MIC ligands are normally strong



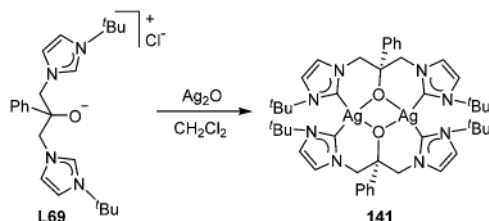
**Scheme 34. Synthesis of Dinuclear Silver(I) Complexes 139a,b and Drawing of MIC Complex 140**



donors, and their properties have been explored by various groups.<sup>30</sup> The air stable disilver(I) complex **140** featured an Ag<sub>2</sub>Br<sub>4</sub><sup>2-</sup> counterion. The characteristic resonance for the C<sub>MIC</sub> carbon atom was observed at  $\delta$  172.44 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The Ag–C<sub>MIC</sub> bond distances and C<sub>MIC</sub>–Ag–C<sub>MIC</sub> bond angles do not differ significantly from the values recorded for dinuclear metallamacrocycles obtained from bis-NHC ligands described previously.

Finally, a zwitterionic bisimidazolium salt **L69** has been prepared and employed as proligand for the synthesis of the neutral disilver(I) complex **141** (Scheme 35).<sup>163</sup> Reaction of

**Scheme 35. Synthesis of the Neutral Dinuclear Silver(I) Complex 141**

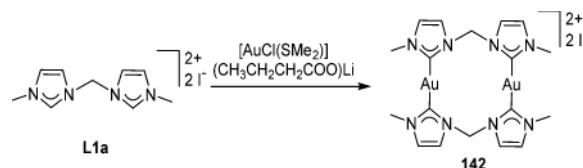


**L69** with Ag<sub>2</sub>O in dichloromethane in the presence of 4 Å molecular sieves yielded the neutral complex **141**. The C<sub>NHC</sub> resonance for this compound was recorded in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at  $\delta$  180.5 ppm and thus falls in the region where the resonances for the C<sub>NHC</sub> carbon atom of cationic metallamacrocycles are normally observed. Complex **141** was shown to be moderately sensitive toward air and light.

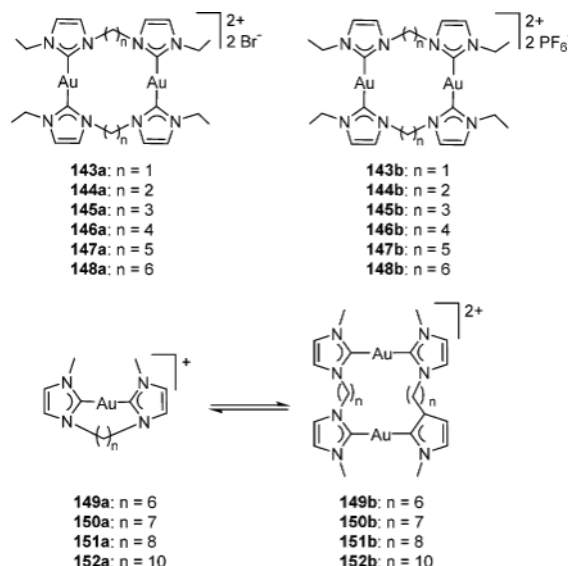
**2.1.2. Dinuclear Gold(I) Assemblies.** The coordination chemistry of gold(I) strongly resembles that of silver(I). Consequently, most bis-NHC gold complexes feature a linearly coordinated gold(I) atom. The M–C<sub>NHC</sub> bond distances are also very similar for silver(I) and gold(I) complexes. Two general strategies have been developed for the preparation of gold-NHC complexes. These are (i) the in situ metalation of the NHCs obtained by deprotonation of azolium salts and (ii) the transmetalation of the NHC ligand from silver(I) to gold(I).

The in situ metalation strategy is exemplified in Scheme 36. The digold complex **142** was prepared by the addition of the base to a mixture of **L1a** and [AuCl(SMe<sub>2</sub>)].<sup>164</sup>

**Scheme 36. Synthesis of Dinuclear Gold(I) Complex 142**



Subsequently, complexes **143–148** were prepared by the same methodology but using NaOAc as a base (Figure 11).<sup>165</sup>

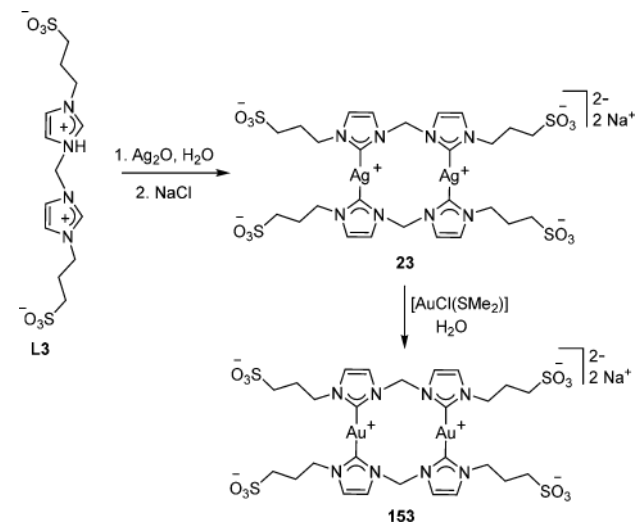


**Figure 11. Dinuclear gold(I) complexes 143–148 and equilibrium between mononuclear complexes and metallamacrocycles.**

Structure analyses for these complexes revealed Au–C<sub>NHC</sub> bond lengths of 2.00–2.06 Å and close to linear C<sub>NHC</sub>–Au–C<sub>NHC</sub> bond angles which became more linear with increasing length of the bridging alkyl chain. Complex **142** exhibited a folded conformation in the solid state, which was preserved in solution as indicated by doublet signals for the methylene protons (exo- and endo-) in the room-temperature <sup>1</sup>H NMR spectrum.<sup>164</sup> Similarly, inequivalent proton environments for the methylene protons (exo- and endo-configuration) in solution at room temperature were observed for **143a** and **143b** with interconversion at higher temperature.<sup>165</sup> Most of the digold metallamacrocycles feature C<sub>NHC</sub>–Au–C<sub>NHC</sub> bonds oriented in a parallel fashion. Exceptions to this are the ethylene-bridged complexes **144a,b**, wherein a backfolded conformation was observed which allowed formation of a short intramolecular Au...Au interactions (**144a**: 3.399 Å; **144b**: 3.233 Å).<sup>165</sup> The complexes with elongated alkyl chains between the NHC donors (**149–152**), which were prepared by transmetalation from the silver analogs (*vide infra*, Figure 11),<sup>93</sup> exist in an equilibrium between the mononuclear and dinuclear species.

Alternatively, gold(I) complexes are accessible by transmetalation of the NHC ligand from silver(I) to gold(I). This strategy is illustrated in Scheme 37. The sulfonate-functionalized zwitterionic bis-NHC precursor **L3** was metalated by Ag<sub>2</sub>O to give complex **23** (Scheme 5), which was not isolated but directly

Scheme 37. Synthesis of Complex 153 by Transmetalation



reacted with  $[\text{AuCl}(\text{SMe}_2)]$  to give the dianionic digold(I) complex 153.<sup>166</sup> Complex 153 was characterized by ESI-MS spectrometry, elemental analysis, and NMR spectroscopy. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed the resonance for the  $\text{C}_{\text{NHC}}$  atoms at  $\delta$  184.28 ppm. Complex 153 was also examined with respect to targeting selected proteins.

As stated before, most of the known gold(I) NHC complexes are prepared by the in situ metalation strategy or by transmetalation of NHCs ligand from silver to gold. The transmetalation strategy does not require the isolation of the silver NHC complex. The metric parameters of related silver(I) and gold(I) NHC complexes do not differ significantly, while the  $\text{C}_{\text{NHC}}$  resonances for the gold(I) complexes are normally observed about 5–10 ppm downfield shifted relative to the resonance of the silver(I) complexes.

Given the structural similarities of silver and gold NHC complexes, together with the facile synthesis of gold-NHC complexes by transmetalation, it is unsurprising that the gold analogs of most of the dinuclear silver assemblies described in the preceding section have been prepared as shown in Figure 12.

The dinuclear complex bearing two carboxylate-functionalized bis-NHC ligands 154 was prepared by transmetalation from the disilver(I) complex 24 (Scheme 5)<sup>94</sup> in deoxygenated water using  $[\text{AuCl}(\text{SMe}_2)]$  as a gold source.<sup>95</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum displayed the resonance for the  $\text{C}_{\text{NHC}}$  carbon atoms at  $\delta$  183.5 ppm, slightly downfield from the  $\text{C}_{\text{NHC}}$  resonances of the parent disilver(I) complex. The rigidity of the complex leads to the existence of diastereotopic methylene protons on the bridge between the NHC donors. The coordination environment of the gold atoms, including the  $\text{C}_{\text{NHC}}-\text{Au}-\text{C}_{\text{NHC}}$  angles,  $\text{Au}-\text{C}_{\text{NHC}}$  bond lengths, and the  $\text{Au}\cdots\text{Au}$  separation, is comparable to that observed for the analogs 142–143,<sup>164,165</sup> as determined by  $^1\text{H}$  NMR spectroscopy and X-ray diffraction studies.

Phenylacetamide- or benzylacetamide-functionalized bisimidazolium salts were used for the preparation of digold(I) complexes 155–156 by in situ metalation using  $[\text{AuCl}(\text{SMe}_2)]$  as a gold source and  $\text{NaOAc}$  as a base.<sup>167</sup> The propylene linked bis-NHC ligands are flexible enough to allow for a parallel orientation of the two  $\text{C}_{\text{NHC}}-\text{Au}-\text{C}_{\text{NHC}}$  axes and  $\text{Au}\cdots\text{Au}$  contacts of 3.0782(5) and 3.0779(9) Å for 155a and 156, respectively. Hydrogen bonds were found between the halogen

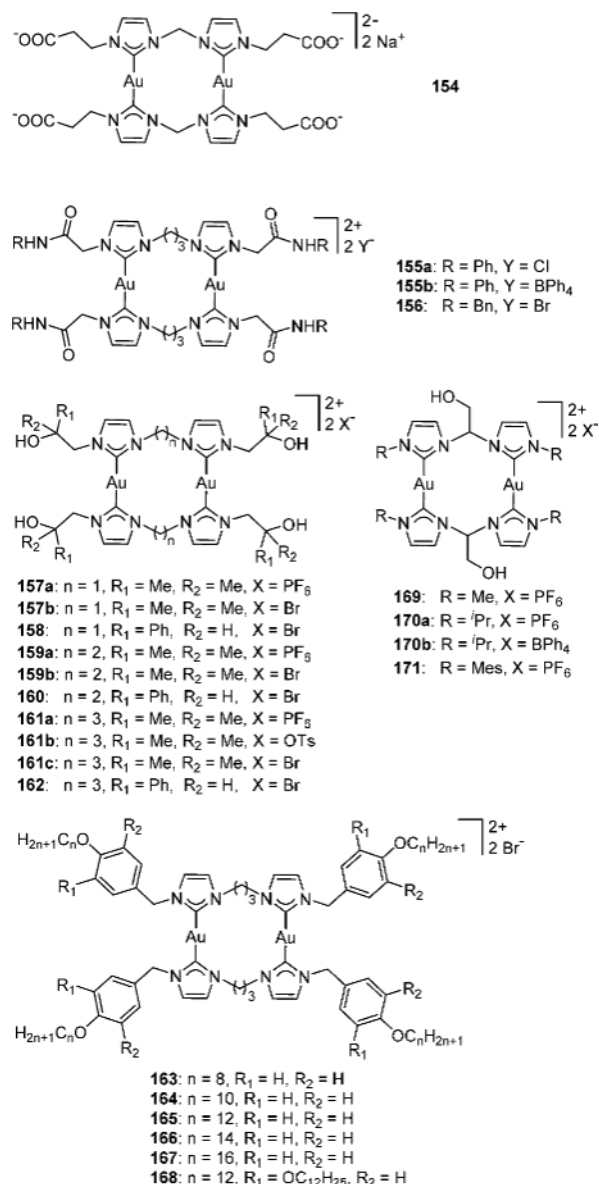


Figure 12. Dinuclear gold(I) metallacycles 154–171.

anions and the N–H groups of the wingtips, leading to the formation of a cage around the two gold atoms. The strength of the  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bonds was estimated via DFT calculations. As a control experiment,  $\text{BPh}_4^-$  was employed as a counterion in compound 155b. No hydrogen bonds between the cation and anion formed and consequently no “cage effect” was observed, leading to an  $\text{Au}\cdots\text{Au}$  separation of 6.280 Å, which is in line with DFT calculations. Apparently, the hydrogen bonds and the resulting “cage effect” enable the formation of short  $\text{Au}\cdots\text{Au}$  contacts in 155a and 156.

In addition, a series of alcohol-functionalized bisimidazolium salts has been used for the preparation of the dinuclear gold(I) metallacycles 157–162 by in situ metalation (Figure 12).<sup>95,98,168</sup> Alternatively, complexes 159b,<sup>95</sup> 161a, and 161b<sup>98</sup> have also been obtained by transmetalation from the appropriate silver(I) complexes (Scheme 6). Some of the gold complexes bearing alcohol-functionalized bis-NHC ligands have been tested regarding their antiplasmodial activity against the chloroquine-resistant *Plasmodium falciparum* strain FcM29-Cameroon.<sup>169</sup>

In the search for novel liquid crystals, digold(I) complexes bearing propylene-linked bis-NHC ligands featuring benzylic wingtips with long alkyl chains **163–168** were prepared by in situ metalation (Figure 12).<sup>170</sup> The  $\text{BF}_4^-$  and  $\text{PF}_6^-$  salts of **163–168** were prepared by anion metathesis. All prolignands and complexes are stable to 200 °C. While some of the prolignands behave as thermotropic liquid crystals in the temperature range of 100–200 °C, only the gold metallacycles with eight aliphatic chains (**168**,  $\text{BF}_4^-$  and  $\text{PF}_6^-$  salts) show mesomorphism.

Complex **169** was obtained by in situ metalation of the bisimidazolium salt **L7**<sup>99,171</sup> (Scheme 7) using  $[\text{AuCl}(\text{SMe}_2)]$  and  $\text{NaOAc}$ .<sup>99</sup> Later, compounds **170–171** bearing isopropyl and mesityl wingtips were prepared by transmetalation,<sup>100</sup> as was complex **169**.<sup>99</sup> Compared to the analogous silver(I) complexes (Scheme 7), the gold complexes are less fluxional, owing to the stronger  $\text{Au}-\text{C}_{\text{NHC}}$  bonds.<sup>100</sup> The distribution of *syn/anti* isomers in solution was investigated by variable-temperature NMR spectroscopy. X-ray diffraction studies revealed the *syn*-configuration for **169** and **170** and the *anti*-configuration for **171** in the solid state. Compound **169** exhibited moderate cytotoxicity against liver cancer cells but was nontoxic to lung cancer cells.<sup>100</sup>

Complex **172** (Figure 13) was prepared by transmetalation of the NHC ligand from the disilver complex **30** (Scheme 8) to

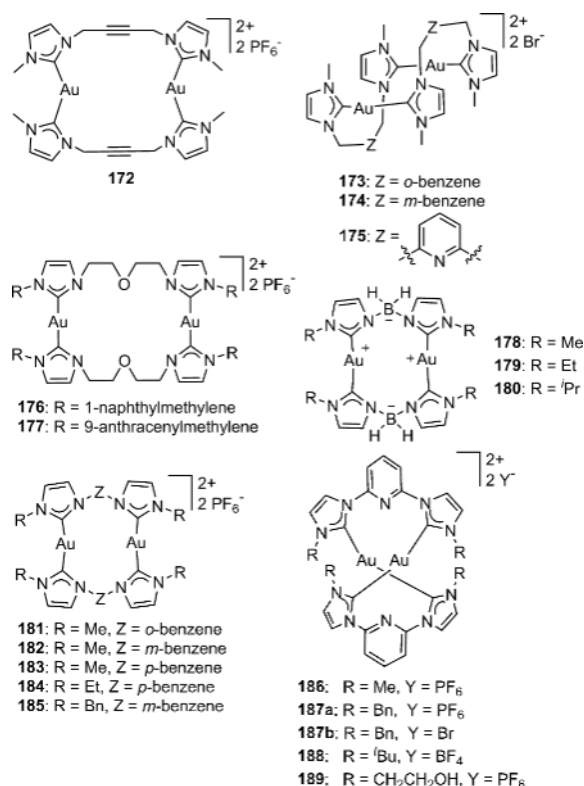


Figure 13. Dinuclear gold(I) metallacycles **172–189**.

$[\text{AuCl}(\text{SEt}_2)]$ .<sup>102</sup> Formation of **172** was initially confirmed by the 2.6 ppm downfield-shifted resonance for the  $\text{C}_{\text{NHC}}$  carbon atom relative to the disilver(I) complex. An X-ray structure analysis revealed that the disilver(I) complex **30** and **172** are isostructural.

In situ metalation of xylylene-bridged bisimidazolium salts with  $[\text{AuCl}(\text{SMe}_2)]$  yielded the digold(I) complexes **173–174** (Figure 13).<sup>164</sup> X-ray diffraction studies revealed a centrosymmetric structure for **174**. The *m*-xylylene bridges are fluxional in

solution and only one singlet at  $\delta$  5.29 ppm was observed in the  $^1\text{H}$  NMR spectrum, indicative of rapid interconversion of two benzylic proton positions (exo and endo). The digold(I) complexes **173** and **174** exhibited potential as antimitochondrial antitumor agents.<sup>172</sup> Compound **175**, with a similar coordination geometry (endo-conformation) to its analog **174**, was also synthesized by in situ metalation (Figure 13).<sup>164</sup> The fluxional behavior of the bridge in solution was comparable to that of the analog **174**, as was its bioactivity with respect to the rate and concentration of entering mitochondria.<sup>172</sup>

Digold(I) complexes **176–177** bearing ether-linked bis-NHC ligands were prepared in high yields by transmetalation using  $[\text{AuCl}(\text{SMe}_2)]$  as a gold source (Figure 13).<sup>111</sup> As was observed with the related disilver(I) complex **44** (Scheme 10), the two  $\text{C}_{\text{NHC}}-\text{Au}-\text{C}_{\text{NHC}}$  axes in **176** were twisted with respect to each other.

Three air-stable digold(I) complexes bearing bis-NHC ligands with dihydridoborate bridges **178–180** were obtained by deprotonation of the respective zwitterionic bisimidazolium salts with  $^t\text{BuLi}$  in THF at  $-78$  °C followed by reaction with  $[\text{AuCl}(\text{PPh}_3)]$  (Figure 13).<sup>173</sup> The X-ray structure analysis of **179** revealed that the 12-membered metallacycle adopts a twisted boat-like conformation with formation of weak intramolecular  $\text{Au}\cdots\text{Au}$  contacts [3.3610(7) Å].

The *o*-, *m*-, and *p*-benzene-bridged bis(imidazolin-2-ylidenes) were transferred from the disilver complexes **67–69** (Scheme 16) to give the gold(I) complexes **181–183** (Figure 13) as was confirmed by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy.<sup>122</sup> An X-ray diffraction analysis of **181** revealed a boat-type (“*syn*”) conformation with two mutually perpendicular mirror planes of symmetry. An  $\text{Au}\cdots\text{Au}$  separation of 3.656(2) Å was found.<sup>122</sup> Contrary to this situation, the digold(I) complex bearing the bis-NHC ligand with a *meta*-benzene spacer (**182**) features an *anti*-conformation of the benzene groups and a long  $\text{Au}\cdots\text{Au}$  separation of 7.140(2) Å. Complex **182** was also prepared by in situ metalation of prolignand **L23** (Scheme 16) with  $[\text{AuCl}(\text{THT})]$  in the presence of the base  $\text{NaOAc}$ .<sup>122</sup> While compound **183** was not structurally characterized, the analog bearing *N*-ethyl-wingtips (**184**) was.<sup>121</sup> Structural analysis revealed a long intramolecular  $\text{Au}\cdots\text{Au}$  separation of 7.213 Å. Finally, complex **185**, with a *meta*-benzene-bridged bis-NHC ligand and *N*-benzyl wingtips, was synthesized by the in situ metalation protocol. The metric parameters for **185** compare well to those of **182**, yet with a slightly shorter  $\text{Au}\cdots\text{Au}$  separation of 6.9842(3) Å.<sup>174</sup>

Similarly to the *m*-benzene bridged bis-NHC ligands, some *meta*-pyridine-linked bisimidazolium prolignands featuring different wingtips were used for the preparation of the dinuclear complexes **186–189**.<sup>98,125,174</sup> These metallacycles can adopt pseudoplanar (open) conformations with an essentially parallel orientation of the  $\text{C}_{\text{NHC}}-\text{Au}-\text{C}_{\text{NHC}}$  axes, similar to the complexes of *m*-benzene-bridged bis-NHC ligands **182** and **185**, or a twisted conformation with essentially orthogonal  $\text{C}_{\text{NHC}}-\text{Au}-\text{C}_{\text{NHC}}$  axes. The latter type of conformation allows the formation of short  $\text{Au}\cdots\text{Au}$  contacts.<sup>174</sup> The open conformation was observed for **186** and **187a** with  $\text{PF}_6^-$  anions, leading to intramolecular  $\text{Au}\cdots\text{Au}$  separations of 6.799(2) Å and 6.895(10) Å, respectively.<sup>174</sup> Exchange of the  $\text{PF}_6^-$  counteranions for  $\text{Br}^-$  in **187b** leads to the twisted conformation with an intramolecular  $\text{Au}\cdots\text{Au}$  distance of 3.225(7) Å.<sup>174</sup> The twisted conformation was also found for **188** and **189** with intramolecular  $\text{Au}\cdots\text{Au}$  distances of 3.2563(5) Å<sup>125</sup> and 3.2971(4)



Å,<sup>98</sup> respectively. The luminescence of **187b** and **189** was attributed to these Au...Au contacts.

Compounds **190–191**, bearing bis-NHC ligands with *meta*-pyrazine spacers, were prepared by in situ metalation of [AuCl(THT)] with the appropriate bisimidazolium salt and sodium acetate as base (Figure 14).<sup>174</sup> In the solid state, the two

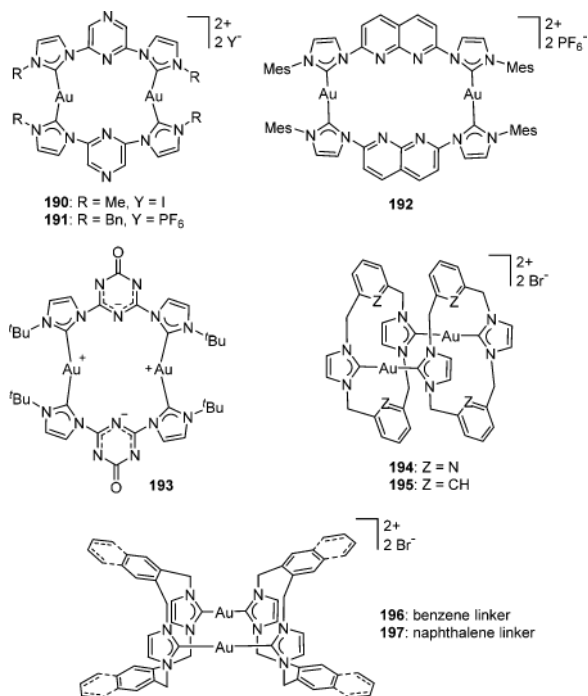


Figure 14. Dinuclear gold(I) metallacycles **190–197**.

bis-NHC ligands of **191** coordinate in a double-helical fashion with a intramolecular Au...Au separation of 3.414(1) Å. The C<sub>NHC</sub>–Au–C<sub>NHC</sub> angles deviate significantly from linearity, and the formation of short Au...N<sub>pyrazine</sub> contacts was also observed.

The dinuclear gold(I) metallacycle **192** (Figure 14) was obtained by transmetalation of the bis-NHC ligand with a naphthyridine linker from trisilver(I) complex **78** (Scheme 20) to [AuCl(SMe<sub>2</sub>)] in anhydrous CH<sub>2</sub>Cl<sub>2</sub>.<sup>175</sup> In contrast to the trisilver complex **78**, featuring C<sub>NHC</sub> and N coordination, only the C<sub>NHC</sub> atoms are coordinated to gold(I) in **192**. The complex is stable in air and wet solvents and even tolerates dissolution in CF<sub>3</sub>COOH/CDCl<sub>3</sub> at 50 °C over an extended period, which the authors took as an indication for the superb stability of the Au–C<sub>NHC</sub> bonds. While **192** shows no activity toward alkyne hydration or polymerization, it is active in the hydrolysis of 2,2,5-trimethyl-1,3-dioxane-5-methanol in aqueous medium.

The neutral digold(I) complex **193** (Figure 14) has been prepared by transmetalation of the anionic *meta*-triazinone-linked bis-NHC ligand from the dinuclear silver(I) complex **85** to [AuCl(THT)] (Scheme 21).<sup>176</sup> The complex features a helical conformation and a <sup>13</sup>C{<sup>1</sup>H} NMR C<sub>NHC</sub> resonance at δ 181.94 ppm. The authors attributed the emissive properties of **193** to its short intramolecular Au...Au contacts of 3.2797(9) Å.

Digold(I) complexes of cyclophane-type bis-NHC ligands **194–197** (Figure 14) have been prepared by in situ metalation of bisimidazolium salts using lithium butyrate as base.<sup>164</sup> Structure analyses revealed that the four benzene (or pyridine) linkers can be tilted toward or away from each other. The complexes featured short Au...Au separations and retained their rigidity in solution as demonstrated by <sup>1</sup>H NMR spectroscopy.

In search for gold-NHC complexes with red-shifted emission bands to be employed for fluorescence microscopy, complex **198**, bearing an unsymmetrical bridged bis-NHC ligand, was prepared by in situ metalation (Figure 15).<sup>177</sup> Owing to its lower

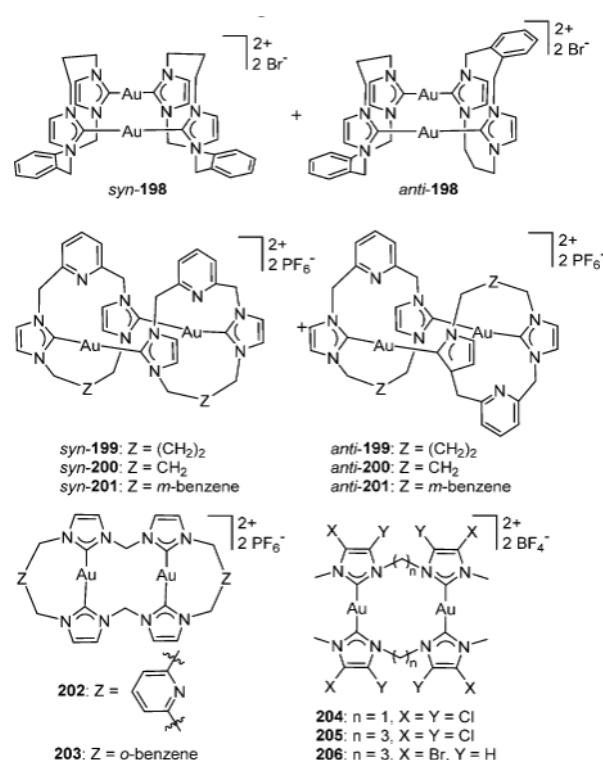


Figure 15. Dinuclear gold(I) metallacycles **198–206**.

solubility in water, *anti*-**198** could be separated from *syn*-**198** by fractional crystallization. The NMR spectra of both isomers feature an identical number of resonances as would be expected from inversion-symmetric (*anti*-**198**) or C<sub>2</sub>-symmetric (*syn*-**198**) complex cations. Both complex cations are rigid in solution as reflected by NMR spectroscopy. The luminescence properties and antimicrobial activity of *syn*-**198** were investigated.<sup>177</sup>

Additional digold(I) complexes **199–201**, bearing unsymmetrical bridged cyclic tetrakis-NHC ligands, were prepared by in situ metalation followed by anion metathesis (Figure 15).<sup>134</sup> The *syn*- and *anti*-isomer of each complex cation were identified by a combination of homo- and heteronuclear 2D NMR spectra, and the relative amounts in the isomer mixture were determined by <sup>1</sup>H NMR spectroscopy. The *syn*/*anti* ratios were found to be 2:1, 2:1, and 3:8 for complexes **199**, **200**, and **201**, respectively. The dynamic behavior of pure samples of the *anti*-isomers of **199–201** were investigated in solution by <sup>1</sup>H NMR spectroscopy where they showed only a single set of resonances, indicating the presence of high interconversion barriers (no or slow equilibria) between the two isomers. The authors ascribed this behavior to the greater strength of the Au–C<sub>NHC</sub> bond relative to that of the Ag–C<sub>NHC</sub> bond in the related disilver complexes (Figure 8). For the silver complexes, fast equilibration was established when a pure *anti*-isomer (*anti*-**94**) was dissolved.

As displayed in Figure 15, lutidine and *o*-phenylene-bridged cyclic tetrakis-NHC ligands have been used for the preparation of digold(I) complexes **202** and **203** by transmetalation from the disilver(I) precursor (Scheme 23).<sup>136,137</sup> The monogold



complexes, featuring a gold atom binding to diagonally disposed NHC donors, were also prepared.

The digold metallamacrocycles bearing 4,5-dichloro-substituted bis(imidazolin-2-ylidene) ligands **204**–**205** (Figure 15) were obtained by transmetalation from the related disilver(I) complexes (Scheme 25),<sup>139</sup> while the preparation of a digold(I) complex bearing a 4,5-dicyanide substituted bis-NHC ligand was attempted but ultimately unsuccessful. The complex with the bromo-functionalized bis-NHC ligand **206** was prepared analogously.<sup>156</sup> The chloro-substitution of the ligand backbone did not change the chemical shifts of the  $C_{NHC}$  resonances, which appeared at  $\delta = 184.1$  and  $182.5$  ppm for **204** and **205**, respectively, in the  $^{13}C$  NMR spectra. The metric parameters found in complex **205** strongly resemble those observed for related metallamacrocycles bearing propylene-linked bis-(imidazolin-2-ylidene) ligands.<sup>98,165,167,168</sup>

Even 1,2,3-triazole-substituted bis-NHC ligands were used for the preparation of digold(I) metallamacrocycles **207**–**208** by in situ metalation of  $[AuCl(SMe_2)]$  (Figure 16).<sup>140</sup> Both complexes showed an enhanced in vitro antiproliferative activity when compared to the complexes bearing nonfunctionalized bis-NHC ligands.

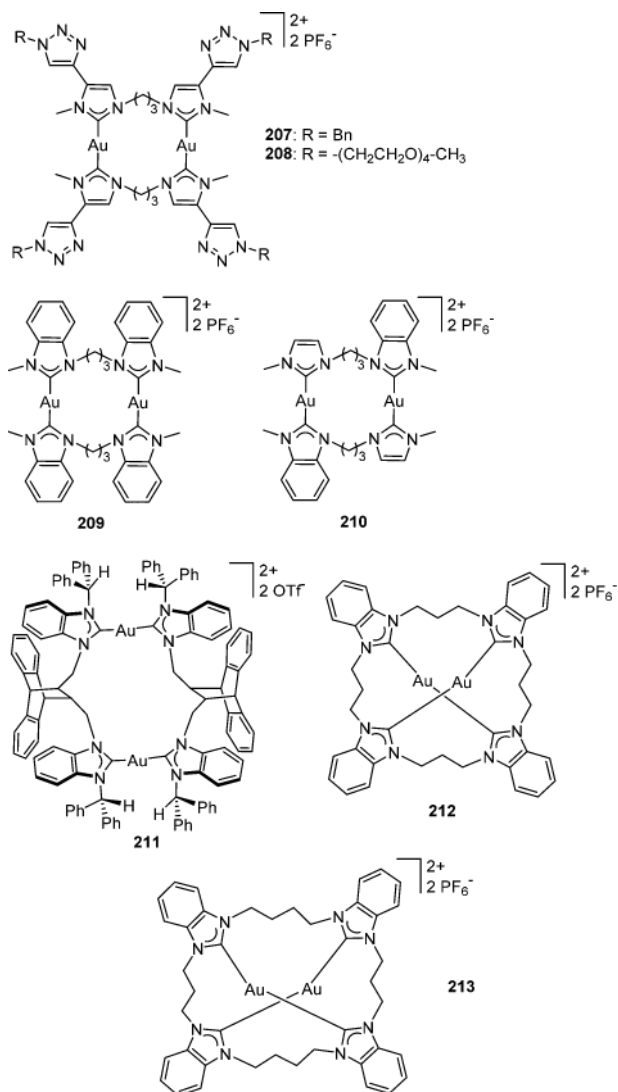


Figure 16. Dinuclear gold(I) complexes **207**–**213**.

A number of propylene-linked bisbenzimidazolium or mixed benzimidazolium-imidazolium salts underwent standard metalation with  $[AuCl(SMe_2)]$  in the presence of NaOAc to give the digold metallacycles **209** and **210** (Figure 16).<sup>156</sup> Digold(I) complex **209** featured a  $C_{NHC}$  resonance  $\delta = 190.9$  ppm in its  $^{13}C\{^1H\}$  NMR spectrum, slightly downfield from the resonances observed for the imidazolin-2-ylidene complexes. The mixed benzimidazolin-2-ylidene-imidazolin-2-ylidene bis-NHC ligand gave rise to two isomeric dinuclear gold(I) complexes (anti and syn) in a 4:1 ratio, and only the main anti-isomer is shown in Figure 16. As expected, two different  $C_{NHC}$  resonances were found in the  $^{13}C\{^1H\}$  NMR spectrum of *anti*-**210** for the benzimidazolin-2-ylidene at  $\delta = 190.8$  ppm and for the imidazolin-2-ylidene at  $\delta = 183.7$ . Closely related chemical shifts were found for the minor *syn*-isomer of **210**. A variable-temperature NMR experiment demonstrated that the major isomer *anti*-**210** slowly and irreversibly converts into the initially minor *syn*-isomer in  $d_6$ -DMSO at elevated temperatures ( $100$ – $150$  °C).

Racemic or enantiopure benzimidazolium proligands have been used for the preparation of enantiopure and racemic digold(I) complexes **211**( $\pm$ ), **211**(+), and **211**(–) (Figure 16).<sup>178</sup> These complexes were prepared by reaction of AuCl with the  $KN(Si(CH_3)_3)_2$ -deprotonated proligands in THF at  $-35$  °C. Racemic **211**( $\pm$ ) was characterized by various NMR techniques and X-ray diffraction. The racemate is cytotoxic against healthy and cancerous cell-lines, with no specificity.

Macrocyclic tetrakis-NHC ligands were used for the preparation of digold(I) complexes **212**–**213**. The compounds were prepared by transmetalation from the corresponding disilver(I) compounds.<sup>150</sup> Monometallic complexes were also obtained. The difference in emissive properties of **213** and **212** was tentatively ascribed to the differences in the Au...Au separation in the two complex cations.<sup>150</sup>

Kunz and co-workers described the digold(I) complexes **214** and **215**, which were prepared from the disilver derivatives **130** and **131** (Scheme 30) by standard transmetalation with  $[AuCl(SMe_2)]$  (Figure 17).<sup>153,154</sup> The characteristic  $^{13}C$

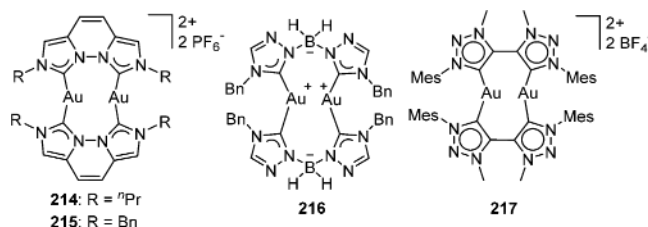


Figure 17. Dinuclear gold(I) complexes **214**–**217**.

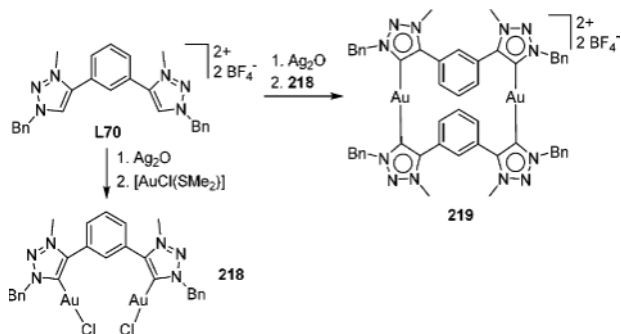
NMR resonance for the  $C_{NHC}$  carbon atoms was shifted slightly downfield in comparison to the disilver(I) analogues **130**–**131**. A molecular structure analysis with crystals of **215** showed the complex cation to possess a crystallographic 2-fold axis. Since the linker between the two NHC donors forces these to approach each other, a very short Au...Au separation of  $2.779$  Å was found.

Digold(I) complexes bearing two bis-1,2,4-triazolyldiene ligands **216**<sup>157</sup> or two bis-MIC ligands **217**<sup>179</sup> have also been described (Figure 17).

The preparation of the digold(I) complex bearing two *meta*-benzene-linked bistriazolyldiene ligands **219** was achieved in two steps. First proligand **L70** was metalated with silver(I), and

the bistriazolylidene ligand was then transmetalated to gold(I) to give the acyclic complex **218**. A second equivalent of proligand **L70** was then metalated with silver(I), and the bistriazolylidene from this complex was then transferred to **218** to give metallacycle **219** (Scheme 38).<sup>180</sup>

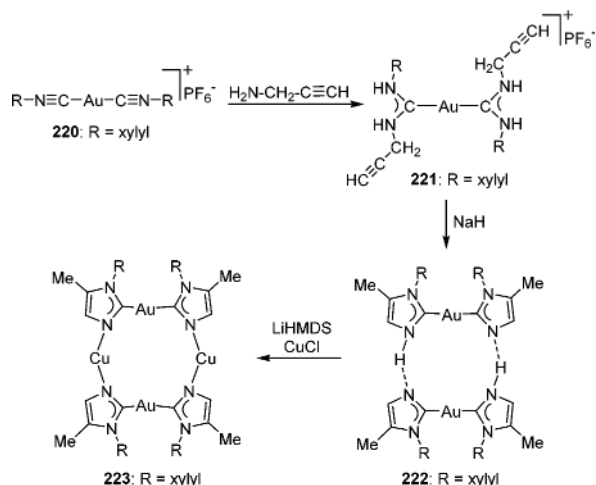
**Scheme 38.** Synthesis of Dinuclear Gold(I) Complex **219** via the Intermediate **218**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 180. Copyright 2011 Royal Society of Chemistry.

An interesting example of an Au/Cu assembly is depicted in Scheme 39.<sup>181</sup> The bisisocyanide complex **220** is attacked at the

**Scheme 39.** Synthesis of Neutral Heterobimetallic Gold(I)/Copper(I) Complex **223**<sup>a</sup>

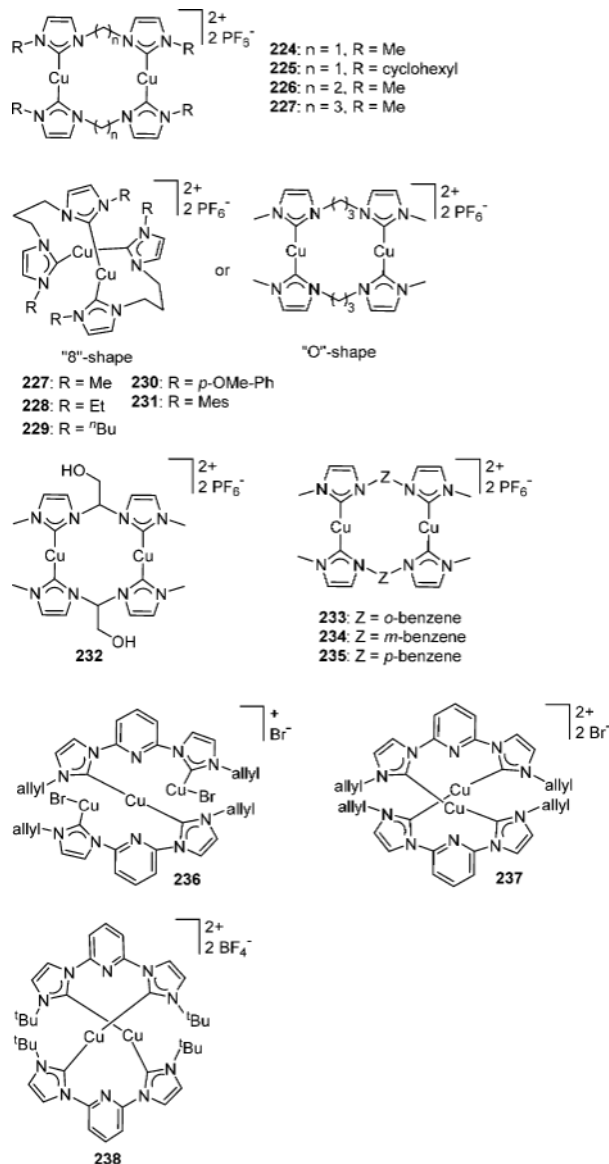


<sup>a</sup>Adapted with permission from ref 181. Copyright 2016 Wiley-VCH.

isocyanide carbon atom by propargylamine to give **221** bearing two acyclic diaminocarbene ligands. Deprotonation of the xylyl-substituted amine by NaH leads to intramolecular cyclization and formation of the neutral complex **222** containing two N-protonated NHC ligands and two C-metalated azolylato ligands.

N—H...N hydrogen bonds link the two complex moieties. Removal of the remaining N—H protons with LiHMDS in the presence of CuCl gave the heterobimetallic complex **223** featuring C- and N-metalated azolylato (anionic NHC) ligands. The intramolecular Au...Au and Cu...Cu separations were determined to be 4.152 and 5.072 Å, respectively. Complex **223** further aggregates via intermolecular Cu...Cu interactions of 2.590–2.621 Å. During the synthesis of **223**, a cluster of 20 Cu and 8 Au ions maintaining the Au(I)/bisimidazolate scaffold was obtained as a side product.

**2.1.3. Dinuclear Copper(I) Assemblies.** The coordination chemistry of copper(I)-NHC complexes (linear C<sub>NHC</sub>—Cu—C<sub>NHC</sub> bonds) resembles that of the silver(I) and gold(I) analogs. In addition, many copper(I)-NHC complexes have been prepared by transmetalation of NHC ligands from silver(I) to copper(I). Therefore, only copper(I)-NHC complexes featuring copper in a coordination number higher than two will be discussed in detail in this section. All other known copper(I)-NHC dinuclear assemblies are depicted in Figures 18 and 19.



**Figure 18.** Dinuclear copper(I) complexes **224**–**238**.

Dicopper(I) metallacycles **224**–**227** have been obtained by transmetalation of the bis-NHC ligand from the corresponding disilver compounds to CuI.<sup>81,182</sup> The catalytic performance of the dinuclear complexes has been evaluated in a range of transformations (nitrene transfer reactions, tosylamidation of C—H bonds).<sup>81</sup>

The influence of the wingtips in complexes bearing propylene-bridged bis-NHC ligands **227**–**231** [obtained by transmetalation from the silver(I) complexes] was studied.<sup>183</sup> The crystallographically characterized complexes **227**, **228**, and **230**

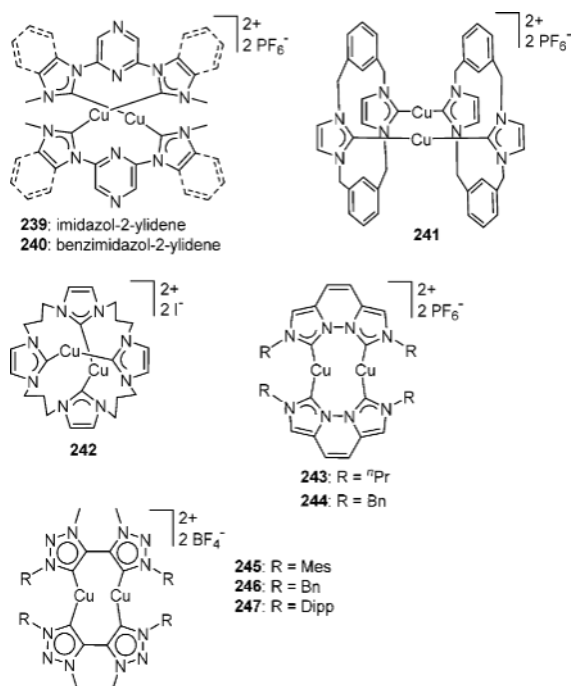


Figure 19. Dinuclear copper(I) complexes 239–247.

assume a double-helical “figure-eight” geometry. This arrangement led to intramolecular Cu⋯Cu interactions of 2.67–2.69 Å for **227** and **228** and a slightly larger Cu⋯Cu separation for **230**. In contrast, the 16-membered metallacycles formed an “O”-shaped geometry in complex **231**, featuring a much larger Cu⋯Cu separation (6.163–6.655 Å). The emissive properties of the complexes were correlated to their geometrical features (e.g., Cu⋯Cu separation), and the findings were further supported by DFT calculations. In addition, it was found that *p*-methoxyphenyl and mesityl wingtips efficiently enhanced the stability of **230** and **231** against chemical degradation.

The dinuclear copper(I) complex bearing hydroxymethyl-functionalized bis-NHC ligands **232** was obtained by transmetalation from the silver(I) derivative, and it was found to be isostructural with its silver(I) analog **27** (Scheme 7).<sup>99</sup>

The dicopper(I) assemblies **233**–**235**, featuring aromatic linkers between the NHC donors, were obtained by the standard transmetalation protocol by adding CuI to the disilver(I) precursors **67**–**69**.<sup>122</sup> Complex **233** required storage under strictly anaerobic conditions and underwent decomposition reactions such as solvolysis when exposed to air.

A stable dicopper(I) complex with a helical conformation (**237**) was serendipitously obtained by recrystallization of the tricopper(I) complex **236** in the presence of air and moisture.<sup>184</sup> The latter was prepared by in situ metalation of the corresponding bisimidazolium bromide using CuBr as a metal source. The related helical dicopper(I) complex **238** was obtained by transmetalation from the disilver(I) precursor **73** to [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub>.<sup>125</sup> The C<sub>NHC</sub>–Cu–C<sub>NHC</sub> angles deviated ca. 17° from linearity and an intramolecular Cu⋯Cu separation of 2.9431(8) Å was determined crystallographically.

Cuprous complex **239** was prepared by transmetalation from the corresponding in situ generated disilver(I) complex using CuI as copper(I) source.<sup>185</sup> Weak Cu⋯N<sub>pyrazine</sub> interactions (2.533–2.706 Å) and an intramolecular Cu⋯Cu separation of 2.974 Å were found by an X-ray diffraction study. The benzimidazolin-2-ylidene analog **240** was also prepared. Both

complexes **239** and **240** were used as catalysts for the hydrosilylation of acetophenone with triethylsilane.<sup>185</sup>

A continuous flow reactor was used for the synthesis of **241** from a cyclic bisimidazolium salt.<sup>186</sup> When the diimidazolium salt was reduced at the cathode, a sacrificial copper anode underwent oxidation with release of Cu<sup>+</sup> ions into the reaction medium. Dicopper(I) complex **241** was generated in 95% yield when the reaction medium was recirculated through the flow cell for 300 min.

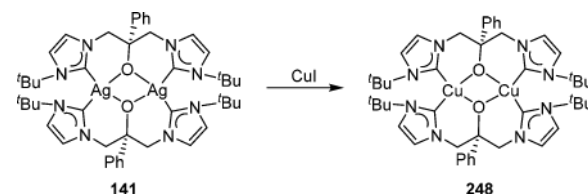
Similarly to the disilver(I) complex **98** (Scheme 24), dicopper(I) complex **242** was prepared in 53% yield from the cyclic tetrakisimidazolium salt **L44** and Cu<sub>2</sub>O in the presence of Na<sub>2</sub>OAc as a base (Figure 19).<sup>138</sup> Analogous to the Ag⋯Ag interaction in **98**, complex **242** exhibited an intramolecular Cu⋯Cu distance of 2.553(2) Å as revealed by an X-ray diffraction study.

Dicopper(I) complexes **243**–**244** were prepared by metalation of the appropriate bisimidazolium salt with Cu<sub>2</sub>O<sup>153,154</sup> or by transmetalation from the appropriate disilver complexes **130** and **131**.

Dinuclear copper(I) complexes were also prepared with bis-MIC ligands by initial metalation of the appropriate prolignands with Ag<sub>2</sub>O followed by transmetalation using CuI as copper source (Figure 19).<sup>187</sup> Complexes **245**–**247** were applied as precatalysts in the “click” reaction between phenyl azide and phenyl acetylene.

The neutral dinuclear dicopper assembly **248**, featuring two square-planar coordinated copper(I) ions, was obtained from the zwitterionic bisimidazolium salt **L69** as prolignand via the dinuclear silver(I) complex **141** (Scheme 35) followed by transmetalation with CuI (Scheme 40).<sup>163</sup> The C<sub>NHC</sub> resonance was observed at δ 177 ppm, slightly upfield from the equivalent resonance of **141** (δ 180.5 ppm). The Cu⋯Cu separation was found to be 3.1122(9) Å.

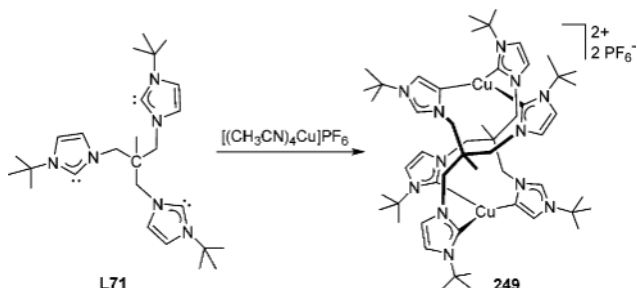
#### Scheme 40. Synthesis of Dicopper(I) Complex 248



An interesting dinuclear copper(I)-NHC complex was described by Meyer and co-workers, who obtained **249** from the reaction of the tripodal tris-NHC ligand **L71** with [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) (Scheme 41).<sup>188</sup> An X-ray diffraction study confirmed the coordination of two regular NHC donors, one from each of the two ligands, in addition to one abnormal NHC donor. This led to a trigonal-planar coordination environment for the copper(I) ions (average C–Cu–C angle of 119.73°) with Cu⋯Cu separations of about 5.2 Å. The two different types of carbon donors were identified by their resonances in a <sup>13</sup>C{<sup>1</sup>H} spectrum at δ 188.9 and 188.7 ppm (regular NHCs) and δ 168.7 ppm (abnormal NHC; the C2–H resonance for the abnormal NHC was found in the <sup>1</sup>H NMR spectrum at δ 8.41 ppm).

**2.1.4. Dinuclear Nickel(II) Assemblies.** Contrary to the previously discussed dinuclear assemblies based on silver(I), gold(I) and, in part, copper(I), dinuclear assemblies featuring transition metals such as nickel(II), palladium(II), platinum(II), or iridium(I) generally contain tetracoordinate square-planar



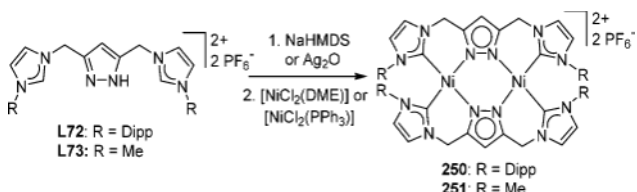
Scheme 41. Synthesis of Dinuclear Copper(I) Complex 249<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 188. Copyright 2003 American Chemical Society.

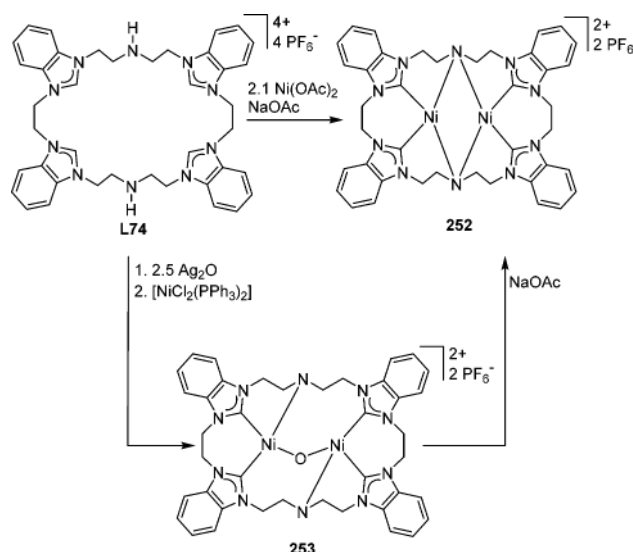
metal centers. Naturally, this situation influences the geometry of the resulting assemblies.

Two equivalents of the pyrazole-linked bisimidazolium salts L72–L73 provide, after imidazolium and pyrazole deprotonation, eight donor sites for binding of two nickel(II) ions to give compounds 250–251 (Scheme 42).<sup>189,190</sup> While compound 250 was obtained by in situ metalation<sup>189</sup> of [NiCl<sub>2</sub>(DME)], 251 was prepared by ligand transfer from an in situ generated dinuclear silver complex.<sup>190</sup>

Scheme 42. Synthesis of Dinuclear Nickel(II) Complexes 250 and 251



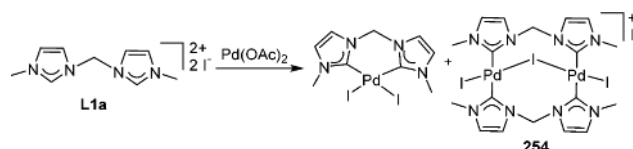
The nickel(II) complexes feature resonances in their <sup>13</sup>C{<sup>1</sup>H} NMR spectra at  $\delta$  153.2 (250) and 152.3 ppm (251) for the C<sub>NHC</sub> carbon atoms. Nonequivalent proton signals for the bridging methylene groups and the methyl groups of the Dipp substituents in the <sup>1</sup>H NMR spectrum indicated a nonplanar geometry of 250 in solution. An X-ray diffraction study revealed a distorted square-planar coordination geometry for the nickel atoms and intramolecular Ni...Ni separations of 3.712 and 3.873 Å in complexes 250 and 251, respectively. The catalytic activity of 251 in the Suzuki-Miyaura and Kumada-Corriu coupling reactions was investigated.<sup>190</sup> Scheme 43 displays dinickel(II) complex 252 obtained from cyclic tetrakisbenzimidazolium salt L74 (featuring two secondary amine linkers) by in situ metalation with Ni(OAc)<sub>2</sub>/NaOAc.<sup>151a</sup> Structural characterization revealed that each nickel ion is coordinated by two carbene donors and two bridging amide groups. The coordination geometry of the nickel(II) ions is only slightly distorted from perfect square-planar with a short intramolecular Ni...Ni separation of 2.8549(6) Å. Interestingly, dinickel(II) complex 253 with a bridging oxo group was obtained when the tetrakis-NHC ligand from the disilver complex 128 (Scheme 29) was transmetalated to [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. The presence of the  $\mu$ -O-bridge was ascribed to trace amounts of water in the reaction medium, even when dry solvents were employed. In the solid-state structure, one Ni–N bond in 252 is substituted for one Ni–O bond in 253, leading to an increase of the intramolecular Ni...Ni separation to 3.329(6) Å. Treatment of

Scheme 43. Synthesis of Dinuclear Nickel(II) Complexes 252 and 253<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 151a. Copyright 2017 American Chemical Society.

253 with NaOAc in DMSO yields 252 with the loss of one water molecule.

**2.1.5. Dinuclear Palladium(II) Assemblies.** Similarly to the situation in nickel(II) assemblies, palladium(II) usually adopts a square-planar coordination geometry in its polynuclear assemblies. The methylene-bridged bisimidazolium salt L1a, for example, reacts with Pd(OAc)<sub>2</sub> to give a mixture of the mononuclear chelate complex and 33% of the dinuclear metallacycle 254 (Scheme 44).<sup>191</sup> The observation of non-equivalent resonances for the protons of the bridging methylene group in the <sup>1</sup>H NMR spectrum were used to confirm and quantify the formation of 254.

Scheme 44. Synthesis of Metallacycle 254<sup>a</sup>

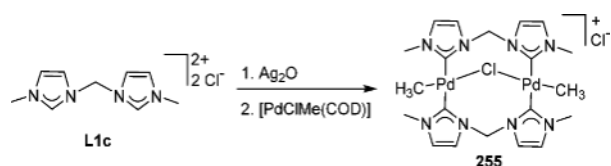
<sup>a</sup>Adapted with permission from ref 191. Copyright 2006 Elsevier.

An X-ray diffraction analysis revealed that the two palladium ions in 254 are organized in an A-frame structure with one bridging iodide [Pd–I bond length 2.6244(9) Å] and two capping iodides [Pd–I bond length 2.5692(10) Å]. The planes of the NHC donors are oriented perpendicular to the A-frame plane.

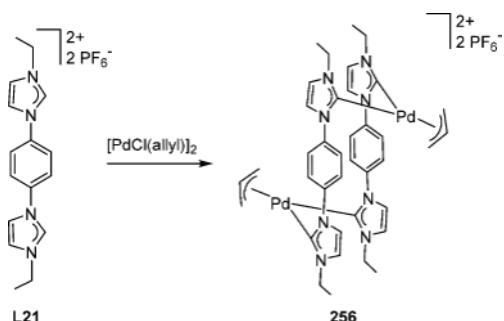
A related A-frame arrangement featuring a  $\mu$ -chloro bridge and two terminal methyl groups was found in complex 255 (Scheme 45).<sup>192</sup> Complex 255 was obtained by transmetalation of the dicarbene ligand from silver(I) to [PdClMe(COD)]. An X-ray diffraction analysis showed that the two palladium ions were nearly linearly coordinated by the bridging chloride and the methyl groups. Complex 255 was employed as catalyst in a C–H activation reaction of methane (TON = 22).

The *p*-benzene bridged bisimidazolium salt L21 (Scheme 15) was used for the preparation of the dinuclear palladium(II)



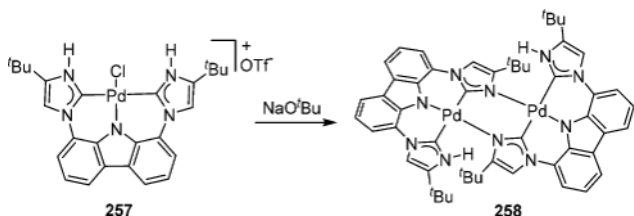
Scheme 45. Synthesis of Dinuclear Palladium(II) Complex **255**<sup>a</sup><sup>a</sup>Adapted with permission from ref 192. Copyright 2015 Elsevier.

metallacycle **256** by in situ metalation of  $[\text{PdCl}(\text{allyl})]_2$  in the presence of the base  $\text{Cs}_2\text{CO}_3$  (Scheme 46).<sup>193</sup> In contrast to the

Scheme 46. Synthesis of Palladium(II) Metallacycle **256**<sup>a</sup><sup>a</sup>Adapted with permission from ref 193. Copyright 2013 American Chemical Society.

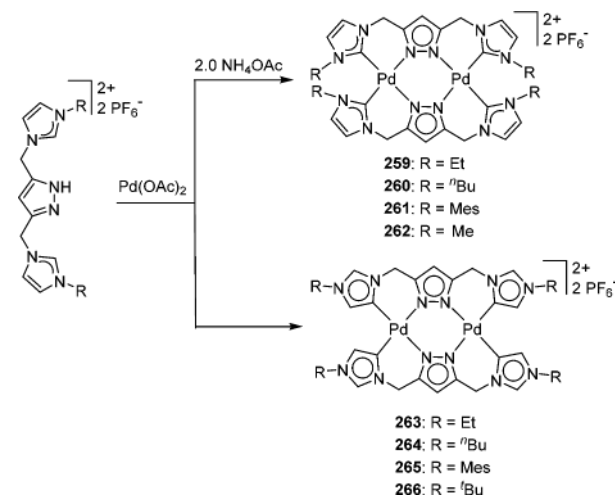
metallacycle obtained from **L21** and  $\text{Ag}_2\text{O}$ , where the metal atoms are located inside the macrocycle, the two  $\{\text{Pd}(\text{allyl})\}$  moieties are located on opposite sides of the plane made up by the four NHC donors, apparently to accommodate the allyl substituents. This allows for the formation of  $\pi\cdots\pi$  interactions between the bridging benzene linkers.

An interesting dinuclear assembly was obtained by the reaction of mononuclear complex **257** with  $\text{NaO}^t\text{Bu}$  to give complex **258** via deprotonation of the protic NHC ligands (Scheme 47).<sup>194</sup> The N–H signal of complex **257** emerged at ca.

Scheme 47. Deprotonation-Induced Assembly of **258** from **257**

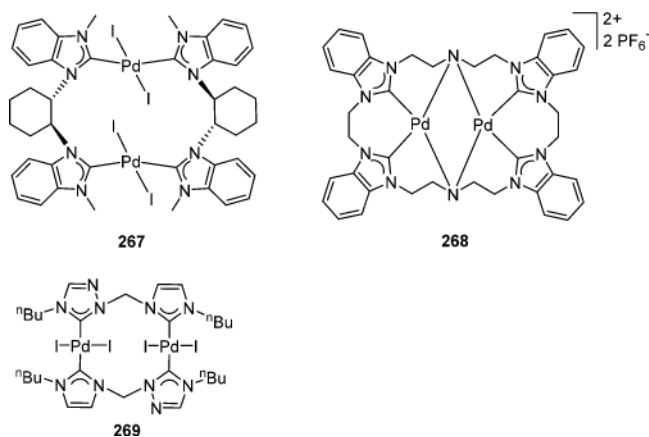
$\delta$  11 ppm in the  $^1\text{H}$  NMR spectrum. This resonance shifted upfield to  $\delta$  = 8.03 ppm (for the remaining two N–H protons) upon formation of **258**. This upfield shift was ascribed to shielding of the N–H protons by an imidazole ring.

A series of pyrazole-bridged bisimidazolium salts similar to **L72**–**L73**, but featuring various wingtip substituents, were used for the preparation the dinuclear metallacycles **259**–**266** by in situ metalation with  $\text{Pd}(\text{OAc})_2$  as palladium source (Scheme 48).<sup>195</sup> In the presence of 2 equiv (or more) of  $\text{NH}_4\text{OAc}$ , the tetrakis-NHC dipalladium(II) complexes **259**–**262** were obtained in moderate yields. These complexes were identified by the resonances for the  $\text{C}_{\text{NHC}}$  carbon atoms observed in the

Scheme 48. Synthesis of Assemblies **259**–**266**<sup>a</sup><sup>a</sup>Adapted with permission from ref 195. Copyright 2014 American Chemical Society.

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra at  $\delta$  154.5–161.8 ppm. In the absence of  $\text{NH}_4\text{OAc}$ , dipalladium(II) complexes **263**–**266** bearing C4/5-bound (abnormal) NHCs were obtained in yields of 42–62%. These complexes feature the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic resonance for the C4/C5 carbon atoms at ca.  $\delta$  139 ppm. X-ray diffraction studies with crystals of **260**, **261**, and **266** confirmed the different binding modes of the carbon donors.

A *trans*-cyclohexane-1,2-bisimidazolium iodide was used for the preparation of **267** by in situ metalation of  $\text{Pd}(\text{OAc})_2$  (Figure 20).<sup>196</sup> Complex **267** exhibited moderate activity in catalytic Suzuki–Miyaura and Heck cross-coupling reactions.

Figure 20. Dinuclear palladium(II) complexes **267**–**269**.

Dipalladium complex **268** is a homologue of nickel(II) complex **252** (Scheme 43) and was prepared analogously to **252** from proligand **L74** and  $\text{Pd}(\text{OAc})_2$ .<sup>151a</sup> Under the reaction conditions used, no analog of  $\mu$ -O-bridged nickel(II) complex **253** was observed.

Finally, palladium(II) metallacycle **269**, bearing an unsymmetrical imidazolylidene/triazolylidene ligand, was prepared from a methylene-bridged 1,2,4-triazolium/imidazolium iodide bis-NHC ligand precursor and  $\text{Pd}(\text{OAc})_2$  (Figure 20).<sup>197</sup> Two  $\text{C}_{\text{NHC}}$  resonances were recorded in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at  $\delta$  171.9 ppm (triazolin-5-ylidene) and at  $\delta$  165.8 ppm

(imidazolin-2-ylidene). An X-ray diffraction analysis showed a nearly perfect square-planar coordination environment for the palladium atoms with two trans-iodo and two trans- $C_{NHC}$  (triazolin-5-ylidene and imidazolin-2-ylidene) donors. The  $Pd-C_{triazolyldiene}$  bond distance was found to be 2.041(7) Å and is slightly longer than the  $Pd-C_{imidazolyldiene}$  bond distance of 2.013(7) Å.

**2.1.6. Dinuclear Platinum(II) Assemblies.** Similar to its palladium analog 258, platinum complex 271 (Figure 21) was

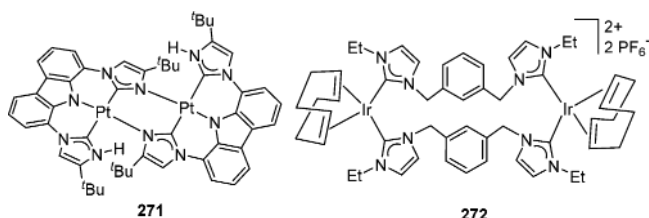


Figure 21. Platinum and iridium complexes 271–272.

prepared by deprotonation of the mononuclear platinum precursor 270 bearing a protic NHC ligand (similar to palladium complex 257, Scheme 47).<sup>194</sup> The coordination environment around the platinum atoms strongly resembles that of the palladium atoms in 258, as reflected by different NMR techniques and an X-ray diffraction study.

**2.1.7. Dinuclear Iridium(I) Assemblies.** A 20-membered air-stable diiridium(I) metallacycle featuring a “figure-eight” geometry (272) was prepared from the *meta*-xylylene-bridged bisimidazolium salt,  $[Ir(\mu-Cl)(COD)]_2$ , and  $CS_2CO_3$  (Figure 21).<sup>198</sup> The complex was identified by the  $C_{NHC}$  resonance at  $\delta$  177.5 ppm in its  $^{13}C\{^1H\}$  NMR spectrum and by X-ray diffraction showing  $C_{NHC}-Ir-C_{NHC}$  angles of 95.6(2) and 98.1(2)°.

**2.1.8. Dinuclear Mercury(II) Assemblies.** The coordination chemistry of mercury(II) with NHC donors often resembles that of silver(I) and gold(I) (i.e., dicoordinate metal ions with linear  $C_{NHC}-M-C_{NHC}$  bonds). Therefore, only mercury(II) complexes featuring mercury in a coordination a number higher than two will be discussed in detail in this section. All other dinuclear mercury(II)-NHC assemblies are depicted in Figure 22.

The dimercury metallamacrocycle 273 was obtained from the propylene bridged bisimidazolium salt by in situ metalation using  $Hg(OAc)_2$ . It is assumed to have a molecular structure similar to its silver(I) analog 9 (Figure 4), but its molecular structure has not been reported.<sup>199</sup>

The air-stable dimercury(II) complex 274,<sup>114</sup> featuring an anthracene spacer between the NHC donors, has a structure very similar to its disilver(I) analogue 48 (Figure 6). As was observed for the disilver complex, the two anthracene rings in 274 were found to be oriented in a parallel fashion forming  $\pi-\pi$  stacking interactions. The two  $-(CH_2)_2-$  linkers, however, were arranged in a *cis*-configuration with respect to the anthracene plane, thereby slightly differing from the structure of 48 (*trans* configuration).

Two dimercury(II) complexes with half-calix[4]arene spacers 275 and 276 were prepared by in situ metalation in dilute solution.<sup>200</sup> In the solid state, interactions between the mercuric ions and the methoxy oxygen atoms as well as with the wingtip naphthalene rings were observed by X-ray diffraction studies.

The dimercury(II) complexes 277 and 278 (Figure 22) possess a helical conformation.<sup>199,201</sup> A pathway for the stepwise

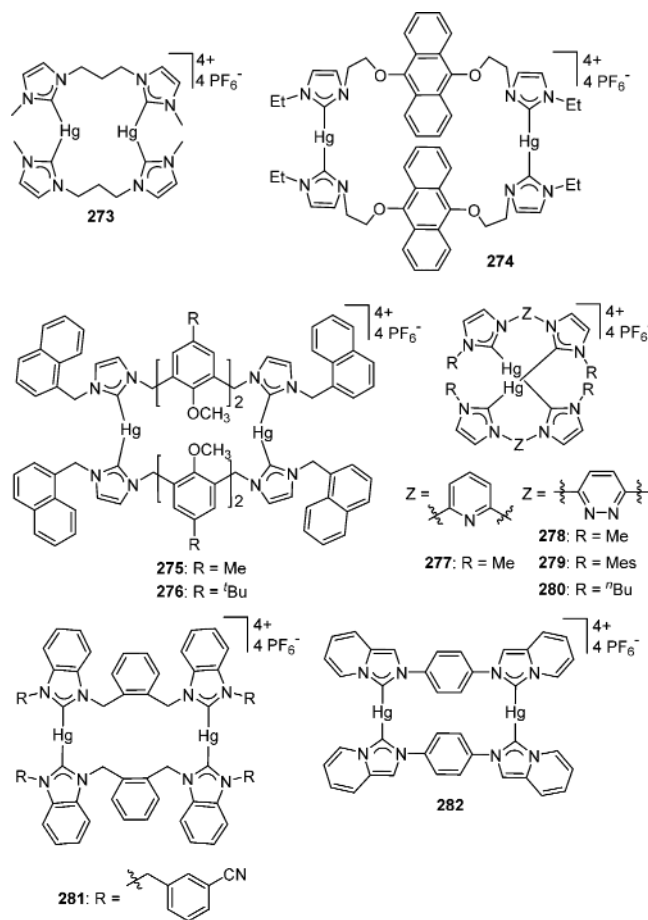


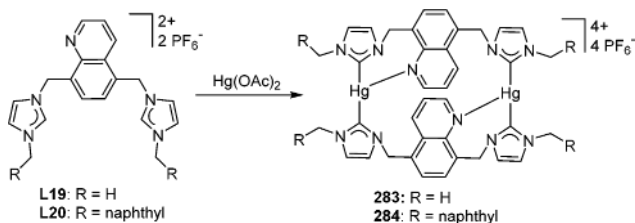
Figure 22. Dinuclear mercury(II) complexes 273–282.

formation of these complexes was proposed by monitoring intermediates in the reaction medium via  $^1H$  NMR spectroscopy. The  $C_{NHC}-Hg-C_{NHC}$  axes deviate by about 10° and 8° from linearity in complexes 277 and 278, respectively. In the solid state, weak interactions between the  $Hg^{2+}$  ions and  $PF_6^-$  counterions were found. Subsequently, complexes 279 and 280 were also prepared by in situ metalation of bisimidazolium proligands with  $Hg(OAc)_2$ .<sup>202</sup> The molecular structure of 279 compares well with that of 278.

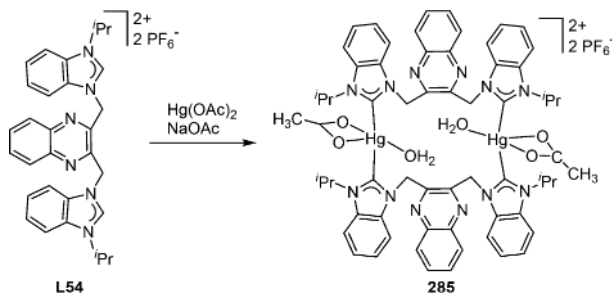
The dinuclear mercury(II) complex 281 bearing an *o*-benzene linked bisbenzimidazolin-2-ylidene ligand has been prepared by initial metalation of the proligand with  $Ag_2O$  followed by transmetalation to mercury.<sup>203</sup> Dimercury(II) complex 282 was obtained from proligand L58 (Scheme 30) by in situ metalation with  $Hg(OAc)_2$ .<sup>152</sup> An X-ray diffraction study revealed a helical conformation with a  $Hg\cdots Hg$  separation of 6.898 Å.

The quinoline-bridged proligands L19 and L20 were used for the preparation of dimercury(II) complexes 283–284 by in situ metalation (Scheme 49).<sup>120</sup> Magnetically inequivalent  $C_{NHC}$  atoms were observed in the  $^{13}C\{^1H\}$  NMR spectrum due to coordination of the nitrogen atom of the quinoline spacer. This situation was confirmed by an X-ray diffraction analysis with crystals of 283 ( $Hg-N$  distance of 2.779 Å) which also revealed  $\pi\cdots\pi$  stacking of the quinoline rings with face-to-face distances of 3.288 Å. Contrary to this situation, the silver(I) complexes of proligands L19 and L20 featured linearly coordinated silver atoms (Scheme 14).<sup>120</sup>

Finally, the *o*-quinoxaline-bridged proligand L54 (Scheme 28) was employed for the direct synthesis of dimercury(II)

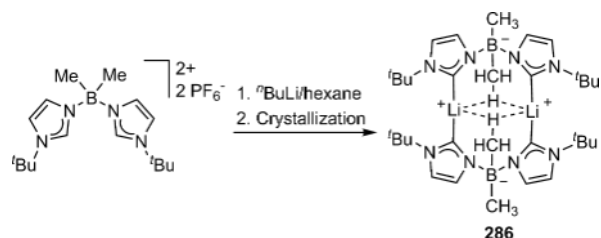
Scheme 49. Synthesis of Mercury(II) Complexes 283–284<sup>a</sup><sup>a</sup>Adapted with permission from ref 120. Copyright 2013 Wiley-VCH.

complex 285 (Scheme 50).<sup>149</sup> The 18-membered metallacycle 285 possessed an inversion center as reflected by X-ray

Scheme 50. Synthesis of Dimercury(II) Complex 285<sup>a</sup><sup>a</sup>Adapted with permission from ref 149. Copyright 2013 American Chemical Society.

diffraction analysis. The mercury atoms are pentacoordinate, with two NHC donors, a bidentate acetate anion, and a water molecule. The  $C_{\text{NHC}}\text{--Hg--}C_{\text{NHC}}$  angle of  $161.4(1)^\circ$  deviates significantly from linearity due to the coordination of additional donors.

**2.1.9. Dinuclear Poly-NHC Lithium(I) Assemblies.** Even the simple deprotonation of a bisimidazolium precursor can lead to a metallacycle, as demonstrated with dilithium tetrakis-NHC assembly 286 in Scheme 51.<sup>204</sup> The  $C_{\text{NHC}}$  resonance of 286

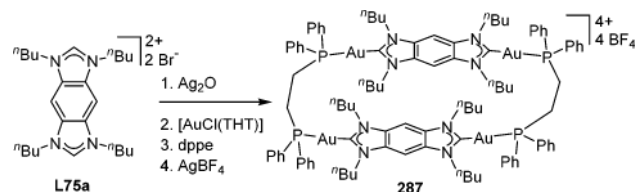
Scheme 51. Synthesis of Neutral Dilithium(I) Complex 286<sup>a</sup><sup>a</sup>Adapted with permission from ref 204. Copyright 2009 American Chemical Society.

appeared at  $\delta$  198.8 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum and thus falls close to the chemical shift range normally observed for free imidazolin-2-ylidenes.<sup>18,19</sup> The protons of the  $\text{BMe}_2$  spacer led to a broad singlet signal at  $\delta$  0.18 ppm in the  $^1\text{H}$  NMR spectrum of the complex. An X-ray molecular structure analysis revealed  $C_{\text{NHC}}\text{--Li--}C_{\text{NHC}}$  angles of  $160.0(3)$  and  $168.2(3)^\circ$ . In each  $\text{BMe}_2$  spacer, one proton of the *endo* methyl group interacted with a lithium ion in a bridging fashion with  $\text{Li}\cdots\text{H}$  contacts of  $2.12(2)$  Å. In addition, a dilithium complex bearing two BH-bridged tris(imidazolin-2-ylidene) ligands<sup>205</sup> and a

lithiated,  $\text{BH}_2$ -bridged bisimidazol-2-ylidene ligand have also been described.<sup>206</sup>

## 2.2. Tetranuclear Two-Dimensional Assemblies

**2.2.1. Tetranuclear Gold(I) Assemblies.** Similarly to the multitude of tetranuclear two-dimensional molecular squares and rectangles obtained from four bidentate Werner-type ligands and transition metals,<sup>1,3,8,12</sup> rigid bidentate bis-NHC ligands can also be used for the construction of such assemblies. One of the first examples for this approach is depicted in Scheme 52. The bisbenzimidazolium salt L75a reacts with  $\text{Ag}_2\text{O}$  to give

Scheme 52. Synthesis of the Tetranuclear Rectangle 287<sup>a</sup><sup>a</sup>Adapted with permission from ref 207. Copyright 2009 Royal Society of Chemistry.

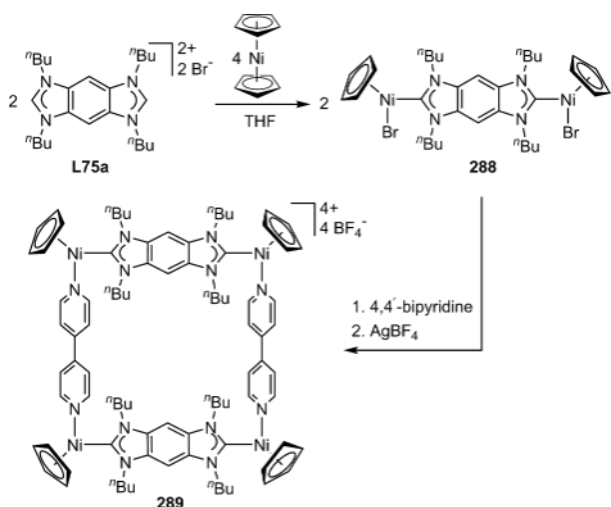
the linear disilver(I) complex and transmetalation yields the dinuclear gold(I) chloride complex.<sup>207</sup> Two equiv of the digold(I) complex were subsequently reacted with dppe (dppe = 1,2-bis(diphenylphosphino)ethane) in the presence  $\text{AgBF}_4$  to afford the tetragold(I) molecular rectangle 287.<sup>207</sup>

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 287 displayed the  $C_{\text{NHC}}$  resonance at  $\delta$  197.6 ppm as a doublet of doublets due to coupling to the phosphorus nuclei with coupling constants of  $^2J(^{13}\text{C}, ^{31}\text{P}) = 124.5$  Hz and  $^5J(^{13}\text{C}, ^{31}\text{P}) = 1.6$  Hz. A symmetrical structure was concluded from the observation of a single resonance at  $\delta$  36.14 ppm in the  $^{31}\text{P}$  NMR spectrum. A single-crystal X-ray diffraction study revealed two coplanar bis(NHC) ligands separated by 3.3 Å. The dppe-linked gold atoms were separated 3.3108(2) Å, and close to linear  $C_{\text{NHC}}\text{--Au--P}$  angles of  $170.08(10)$  and  $170.28(10)^\circ$  were found.

**2.2.2. Tetranuclear Nickel(II) Assemblies.** A related example for a molecular rectangle featuring two bis-NHC and two bidentate Werner-type ligands, which was also the first example for a molecular rectangle featuring linear bis-NHC ligands, is the tetranuclear nickel(II) rectangle 289 (Scheme 53).<sup>208,209</sup> This molecular rectangle was prepared in two steps. First the dinuclear nickel complex 288 was prepared by in situ metalation of the bisbenzimidazolium salt L75a with nickelocene. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 288 displayed the typical resonance for an  $C_{\text{NHC}}$  donor coordinated to nickel(II)  $\delta$  178.2 ppm. The rotation about the  $\text{Ni--}C_{\text{NHC}}$  bonds is restricted as indicated by two resonances for the  $\text{N--CH}_2$  units at  $\delta$  5.81 and  $\delta$  4.52 ppm. Such a restriction is essential to arrange the two  $\text{Ni--Br}$  bonds parallel and in one direction for the subsequent formation of the molecular rectangle. The preorganization of the  $\text{Ni--Br}$  bonds enables the formation of the rectangle and prevents the formation side products obtained by oligomerization.

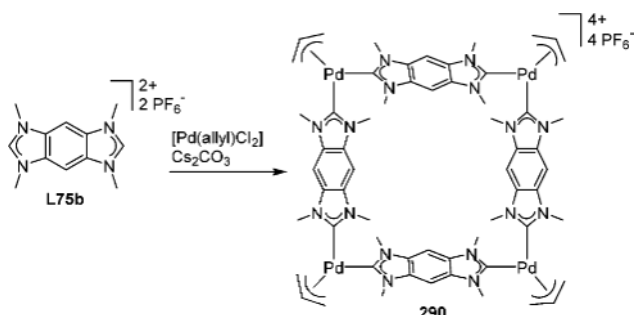
Subsequently, two equiv of 288 were reacted with 2 equiv of 4,4'-bipyridine in the presence of  $\text{AgBF}_4$  to give rectangle 289. The rectangular shape of assembly 289 was established by an X-ray diffraction study revealing  $C_{\text{NHC}}\text{--Ni--N}$  angles of  $94.6(3)$ – $95.4(3)^\circ$  and  $\text{Ni}\cdots\text{Ni}$  separations of  $10.910(2)$  Å and  $10.380(2)$  Å.



Scheme 53. Synthesis of Tetranuclear Nickel(II) Molecular Rectangle 289<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 209. Copyright 2009 Royal Society of Chemistry.

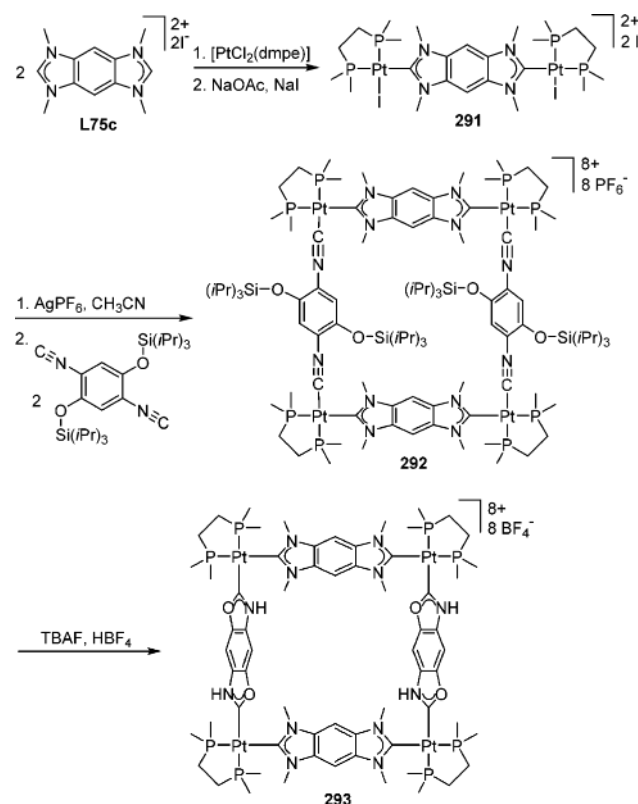
**2.2.3. Tetranuclear Palladium(II) Assemblies.** In search for additional metal complex fragments providing two cis-oriented coordination sites for the construction of molecular rectangles and squares, the {Pd(allyl)} complex fragment was studied next as a vertex for such assemblies. In situ metalation of proligand L75b with [Pd(allyl)Cl<sub>2</sub>] yielded the molecular square 290 in 54% yield in a one-step procedure (Scheme 54).<sup>210</sup> While HR-ESI mass spectrometry showed the formation

Scheme 54. Synthesis of Tetrapalladium(II) Molecular Square 290<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 210. Copyright 2017 Wiley-VCH.

of 290 and the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum exhibited the expected C<sub>NHC</sub> resonance for an NHC-palladium complex at δ 193.0 ppm, no suitable crystals for the determination of the molecular structure could be obtained.

**2.2.4. Tetranuclear Platinum(II) Assemblies.** Tetraplatinum rectangle 293 was prepared in a stepwise procedure (Scheme 55).<sup>211</sup> First, proligand L75c was metalated with [PtCl<sub>2</sub>(dmpe)] to afford the dinuclear platinum(II) complex 291, presumably in the syn-conformation. After anion exchange using AgPF<sub>6</sub> in acetonitrile, 291 was reacted with two equiv of β,β'-bis(triisopropylsiloxy)phenyl-1,4-diisocyanide to give the molecular rectangle 292 as an intermediate. Cleavage of the O–Si bonds in 292 led to an intramolecular nucleophilic attack of the liberated hydroxyl groups at the isocyanide carbon atoms and formation of 293.

Scheme 55. Synthesis of Tetranuclear Molecular Rectangle 293 via Rectangle 292<sup>a</sup>

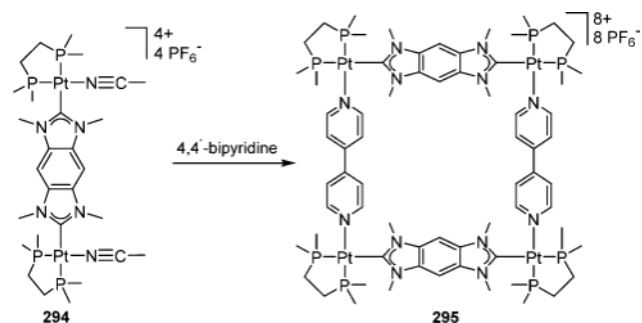
<sup>a</sup>Adapted with permission from ref 211. Copyright 2012 Wiley-VCH.

Molecular rectangle 293 features two different bridging bis-NHC ligands obtained by in situ metalation of L75c (NR,NR-NHCs) and by cyclization of the β,β'-functionalized diisocyanide (NH,O-NHCs). The different bridging ligands give rise to two different resonances for the phosphorus atoms located in trans-positions to the two different NHC donors. The <sup>31</sup>P{<sup>1</sup>H} spectrum exhibited one resonance at δ 30.6 ppm [<sup>1</sup>J(<sup>31</sup>P, <sup>195</sup>Pt) = 2140 Hz, <sup>2</sup>J(<sup>31</sup>P, <sup>31</sup>P) = 7.5 Hz], while the other one appeared at δ 28.3 ppm [<sup>1</sup>J(<sup>31</sup>P, <sup>195</sup>Pt) = 2175 Hz, <sup>2</sup>J(<sup>31</sup>P, <sup>31</sup>P) = 7.5 Hz]. An X-ray diffraction analysis showed Pt–C<sub>NHC</sub> bond distances of comparable lengths of 2.042(7)–2.053(8) Å for the NR,NR-NHC donors and 2.011(7)–2.021(7) Å for the NH,O-NHC donors. The platinum ions were separated by 10.534 Å by the bis(NH,O-NHC) ligands and by 10.671 Å by the bridging bis(NR,NR-NHC) ligand, making 293 in spite of the different bridging ligands almost a regular molecular square.

It was subsequently found that the conformation of the dinuclear complexes of type 291 plays a crucial role for the subsequent formation of the tetranuclear assemblies.<sup>212</sup> If the two M–X bonds in the dinuclear complexes of type 291 (Scheme 55) are not oriented in syn-fashion (i.e., in the same direction) or cannot rearrange to the syn-geometry, oligomeric instead of macrocyclic structures are obtained in the next reaction steps. With this in mind, molecular rectangle 295 was constructed using the dinuclear platinum complex 294 and 4,4'-bipyridine as components (Scheme 56).<sup>212</sup> While the conformation of 294 (syn- or anti-orientation of the Pt–NCCH<sub>3</sub>) bonds could not be determined, the complex either existed in the syn-conformation or rotation about the Pt–C<sub>NHC</sub> bonds gave access to this rotamer. Therefore, contrary to the reaction of a dinuclear complex bearing sterically more



**Scheme 56. Synthesis of Tetranuclear Platinum(II) Molecular Rectangle 295<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 212. Copyright 2013 Royal Society of Chemistry.

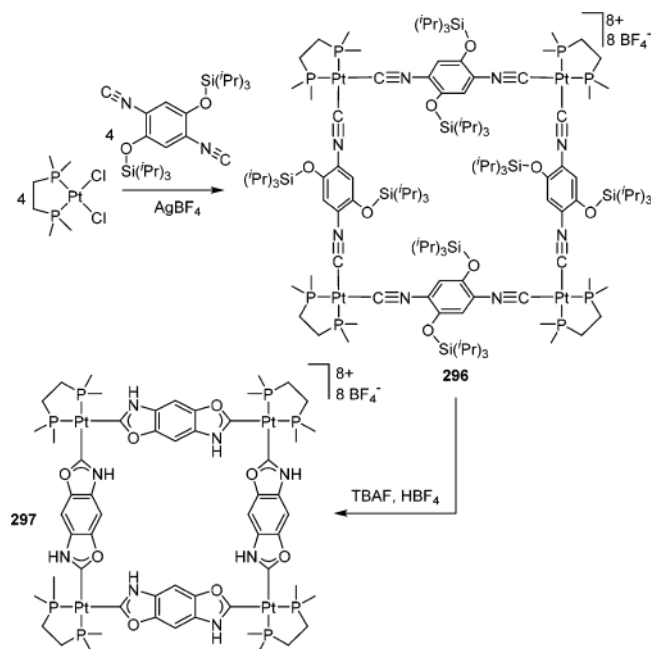
demanding substituents at the bis-NHC nitrogen atoms, complex **294** reacted with 4,4'-bipyridine to give the molecular rectangle **295** in 79% yield. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed the resonance for the  $\text{C}_{\text{NHC}}$  carbon atoms at  $\delta$  180.9 ppm as a doublet of doublets [ $^2J(^{13}\text{C}, ^{31}\text{P}_{\text{trans}}) = 122.3$  Hz,  $^2J(^{13}\text{C}, ^{31}\text{P}_{\text{cis}}) = 9.6$  Hz]. The  $^{31}\text{P}$  spectrum featured the expected two resonances for the chemically inequivalent phosphorus atoms at  $\delta$  34.0 ppm [ $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2282$  Hz,  $^2J(^{31}\text{P}, ^{31}\text{P}) = 4.2$  Hz] assigned to the phosphorus atom trans to the carbene donor and at  $\delta = 19.7$  ppm as a doublet of doublets [ $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2988$  Hz,  $^2J(^{31}\text{P}, ^{31}\text{P}) = 4.2$  Hz] assigned to the phosphorus atom in the trans-position to the amine donor.

Molecular squares can also be synthesized using exclusively the cyclization of  $\beta, \beta'$ -functionalized 1,4-phenyl isocyanides. The reaction of 4 equiv of  $\beta, \beta'$ -bis(triisopropylsiloxy)phenyl-1,4-diisocyanide with  $[\text{PtCl}_2(\text{dmpe})]$  afforded the diisocyanide-bridged relatively unstable complex **296**. This complex was not isolated but directly treated with TBAF/HBF<sub>4</sub> to give the molecular square **297** held together by four bis(NH,O-NHC) ligands (Scheme 57).<sup>212</sup> Coordination of the bridging diisocyanide ligands in **296** was confirmed by the resonance  $\delta$  138.3 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, which falls in the typical range for platinum-isocyanide complexes. Complex **297** was characterized by HR-MS spectrometry. In addition, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum featured only one resonance at  $\delta$  28.8 ppm [ $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2194$  Hz], reflecting the highly symmetric nature of the compound. Unfortunately, no further structural characterization proved possible.

**2.2.5. Tetranuclear Iridium(I/III) Assemblies.** The unambiguous characterization of a molecular square featuring four bridging, linear bis-NHC ligands and was finally possible with assembly **300**. This compound was prepared in a stepwise manner similar to the procedure applied for the synthesis of **297**. First, the dinuclear bisisocyanide-bridged complex **298** was prepared from  $\beta, \beta'$ -bis(triisopropylsiloxy)phenyl-1,4-diisocyanide and  $[\text{Ir}(\text{Cp}^*)\text{Cl}_2]_2$  in an almost quantitative yield (Scheme 58).<sup>213</sup> The complex was identified by the resonance for the isocyanide carbon atoms recorded in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at  $\delta$  136.0 ppm, significantly upfield shifted from the equivalent resonance for the free diisocyanide ( $\delta$  169.8 ppm) and by the shift of the  $\text{C}\equiv\text{N}$  stretching frequency from  $\nu = 2130$   $\text{cm}^{-1}$  in the free diisocyanide to  $\nu = 2152$   $\text{cm}^{-1}$  in **298**.

Abstraction of the chloro ligands from **298** by  $\text{AgBF}_4$  in the presence of 2 equiv of diisocyanide resulted in the formation of complex **299**. Subsequent cleavage of the eight O–SiR<sub>3</sub> bonds with  $\text{HCl}/i\text{PrOH}$  resulted in an intramolecular nucleophilic

**Scheme 57. Synthesis of Tetranuclear Platinum(II) Molecular Squares 296 and Square 297<sup>a</sup>**

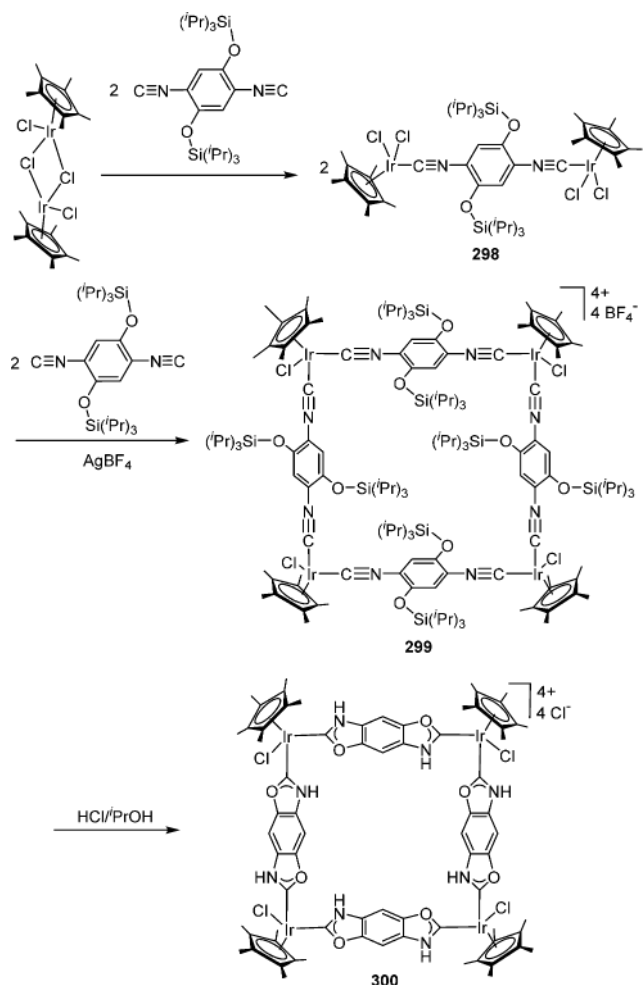


<sup>a</sup>Adapted with permission from ref 212. Copyright 2013 Royal Society of Chemistry.

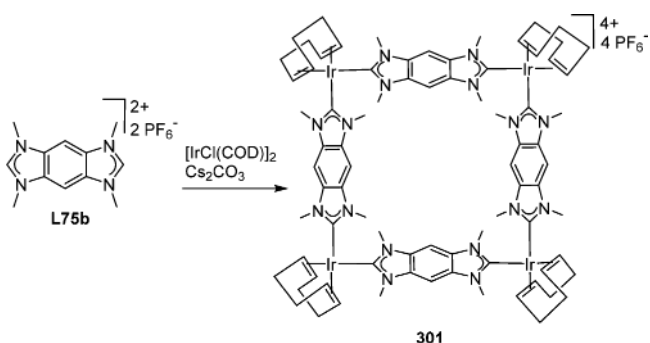
attack of the liberated hydroxyl groups at the isocyanide carbon atoms yielding the molecular square **300**. Multiple spectroscopic techniques and an X-ray diffraction study confirmed the formation of the molecular square. The tetracation of **300** resides on a crystallographic 4-fold axis with  $\text{C}_{\text{NHC}}\text{—Ir—C}_{\text{NHC}}$  bond angles of  $85.7(4)^\circ$ , Ir– $\text{C}_{\text{NHC}}$  bond lengths of  $2.001(10)$ – $2.013(11)$  Å, and an Ir···Ir separation of  $10.5000(9)$  Å.

Similarly to the direct reaction of proligand **L75b** with  $[\text{Pd}(\text{allyl})\text{Cl}_2]$  (Scheme 54), the  $\{\text{Ir}(\text{COD})\}$  complex fragment was tested as a vertex for the direct synthesis of molecular squares from benzobiscarbene precursors. The reaction of proligand **L75b** with  $[\text{IrCl}(\text{COD})]_2$  in the presence of  $\text{Cs}_2\text{CO}_3$  yielded the molecular square **301** in a one-step procedure (Scheme 59).<sup>210</sup> The absence of a C2–H proton resonance in the  $^1\text{H}$  NMR spectrum and the presence of a resonance for the  $\text{C}_{\text{NHC}}$  carbon atom in the  $^{13}\text{C}\{^1\text{H}\}$  spectrum at  $\delta$  189.1 ppm indicated the formation of the poly-NHC assembly. Formation of **301** was confirmed by an X-ray diffraction analysis. The complex cation resides on a crystallographic inversion and features unspectacular metric parameters. The bridging bis-NHC ligands assume pairwise a slightly concave or convex conformation, leading to a slightly unsymmetrical structure with Ir···Ir separations of  $10.6204(6)$  and  $10.6510(6)$  Å. The facile preparation of **301** in a one-step synthesis highlights the utility of this protocol.

**2.2.6. Tetranuclear Ruthenium(II) Assemblies.** Only one two-dimensional, tetranuclear ruthenium assembly has been described so far. The trimethyltriazolium salt **L76** is (after double deprotonation) capable of acting as a bridge between two metal centers. Deprotonation of **L76** with KHMDS and subsequent treatment with  $[\text{RuCl}_2(p\text{-cymene})]_2$  yielded a dinuclear ruthenium complex. However, reaction of **L76** with  $\text{AgOAc}$  followed by treatment with  $[\text{RuCl}_2(p\text{-cymene})]_2$  gave the tetranuclear assembly **302** in 57% yield (Scheme 60).<sup>214</sup> The presence of the silver ions in the latter reaction apparently

Scheme 58. Synthesis of Tetranuclear Iridium(III) Molecular Square 300<sup>a</sup>

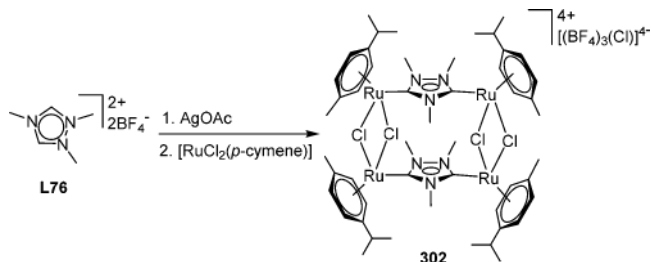
<sup>a</sup>Adapted with permission from ref 213. Copyright 2011 American Chemical Society.

Scheme 59. Synthesis of Molecular Square 301<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 210. Copyright 2017 Wiley-VCH.

facilitate the removal of two chloro ligands from the ruthenium atoms, thereby enabling the formation of the tetranuclear assembly.

The <sup>13</sup>C NMR spectrum of **302** displayed the resonance for the metalated C<sub>NHC</sub> atoms in the expected range at δ 185.5 ppm. Firm evidence for the formation of the tetranuclear complex were provided by ESI-MS spectrometry and an X-ray diffraction study. The two [RuCl(*p*-cymene)]<sub>2</sub> motifs are connected by two

Scheme 60. Synthesis of Ruthenium(II) Complex 302<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 214. Copyright 2007 American Chemical Society.

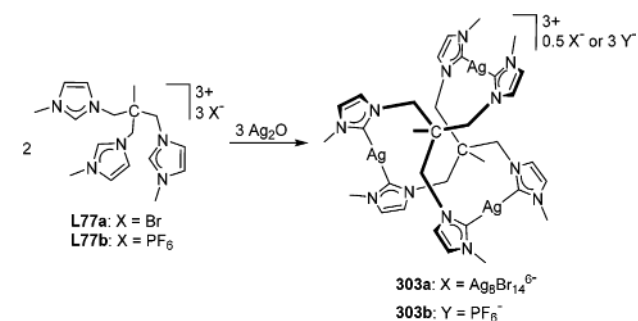
bidentate triazolyldene units. The average Ru–C<sub>NHC</sub> bond length was determined to be 2.065 Å, and the slight variations observed for this parameter were attributed to different orientations of the *N*-methyl groups. The Cl–Ru–C<sub>NHC</sub> angles were close to 90°, thus affording an orthogonal cavity. Subsequently, complex **302** was employed as a catalyst in the β-alkylation of secondary alcohols with primary alcohols.

### 3. THREE-DIMENSIONAL MOLECULAR CAGES

In addition to two-dimensional metallacycles, molecular rectangles and squares, three-dimensional metallacages have also been obtained from poly-NHC ligands using the previously described synthetic strategies (in situ metalation or/and transmetalation). Suitable poly-NHC precursors are nonlinear tris-, tetrakis-, or hexakisimidazolium salts as well as trisbenzimidazolium salts or tris(1,2,3-triazolium) salts. Details about the synthesis and properties of such cage-like assemblies are presented in this section.

#### 3.1. Trinuclear Three-Dimensional Structures

**3.1.1. Trinuclear 3D Silver(I) Assemblies.** Among the first cage-like trisilver assemblies prepared from poly-NHC ligands were compounds **303a,b** obtained by in situ metalation of the tripodal trisimidazolium salts **L77a,b** (Scheme 61).<sup>215,216</sup> The

Scheme 61. Synthesis of Silver(I) Cages 303a,b<sup>a</sup>

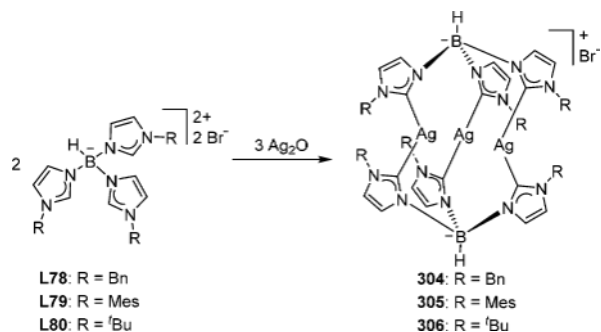
<sup>a</sup>Adapted with permission from ref 215. Copyright 2003 American Chemical Society.

molecular structure determination with **303a** showed two complex cations bridged by an [Ag<sub>8</sub>Br<sub>14</sub>]<sup>6-</sup> anion via Ag...Br interactions. The intramolecular Ag...Ag distances ranged from 2.9300(14) to 3.1369(14) Å. The complex anion in compound **303b** exhibits D<sub>3</sub> symmetry in the solid state. Approximately linear C<sub>NHC</sub>–Ag–C<sub>NHC</sub> axes [178.56(13)°] and Ag–C<sub>NHC</sub> bond distance in the expected range of 2.082(2) Å were found.

Later scorpionate-type tris-NHC precursors **L78–L80** were used for the preparation of a series of trisilver(I) hexacarbene

cages **304–306** by in situ metalation in moderate yields (Scheme 62).<sup>217</sup> While no structural information on these compounds is available, they were studied by NMR spectroscopy and ESI mass spectrometry.

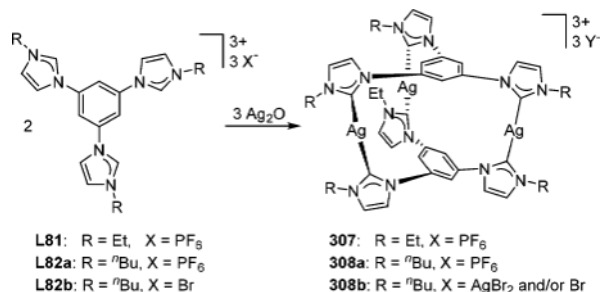
**Scheme 62. Synthesis of Silver(I) Cages 304–306<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 217. Copyright 2008 Elsevier.

In order to increase the size of the cavity in trisilver(I) hexacarbene cages, 1,3,5-benzene-bridged trisimidazolium salts **L81–L82b** were prepared and directly metalated with Ag<sub>2</sub>O to give the cylinder-like trinuclear hexacarbene assemblies **307** and **308** in good yields (Scheme 63).<sup>218,219</sup> These

**Scheme 63. Synthesis of Cylinder-Type Trinuclear Silver(I) Complexes<sup>a</sup>**



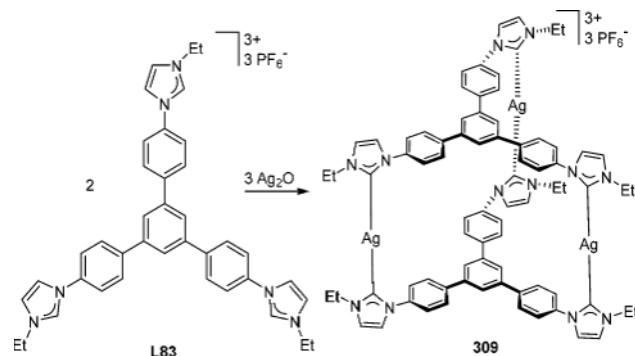
<sup>a</sup>Adapted with permission from ref 219. Copyright 2011 American Chemical Society.

complexes were characterized by NMR spectroscopy and ESI mass spectrometry, and the molecular structure of **308a** was determined by X-ray diffraction. The <sup>13</sup>C NMR spectra displayed characteristic C<sub>NHC</sub> resonances at about δ 181 ppm.

The X-ray diffraction analysis with crystals of **308a** revealed three silver atoms sandwiched in between two tris-NHC ligands. The silver atoms formed a distorted triangle with Ag...Ag separations ranging from 6.0091(3) to 6.1069(4) Å. The observed metrical parameters fall in the expected range for silver-bis-NHC complexes. To form the assembly, the NHC donors rotate clockwise by about 45° out of the plane of the central benzene ring. This causes the C<sub>NHC</sub>–Ag–C<sub>NHC</sub> axes not to be oriented perpendicular to the central benzene ring, and this in turn leads to a decrease of the separation between the central benzene rings. The stability of the compounds was found to depend strongly on the counterion. Complex **308b**, prepared from the trisimidazolium bromide **L82b** and Ag<sub>2</sub>O in methanol, was found to be extremely sensitive toward light, while the complexes containing the hexafluorophosphate anions are much more stable.

A further expansion of the size of the backbone in disklike trisimidazolium salts led to the preparation of proligand **L83**. Similarly to its smaller analogs, it can be metalated with Ag<sub>2</sub>O to give the cylinder-like structure **309** in 77% yield (Scheme 64).<sup>220</sup> Formation of **309** was confirmed by NMR spectroscopy and HR-ESI mass spectrometry.

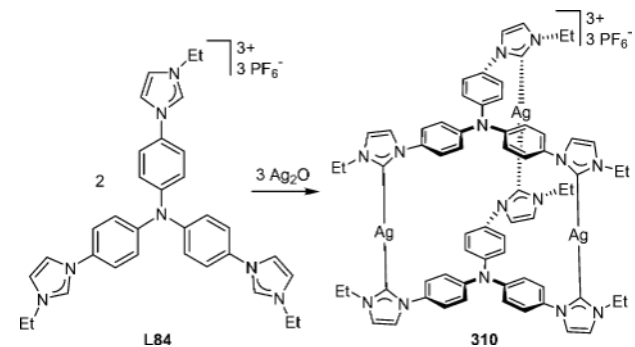
**Scheme 64. Synthesis of Cylindrical Trinuclear Silver(I) Complex 309<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 220. Copyright 2014 American Chemical Society.

Noncarbon atoms can be employed as the central backbone building block for disklike trisimidazolium salts as demonstrated with proligand **L84**. In situ metalation of **L84** with Ag<sub>2</sub>O yielded the cylinder-line assembly **310** (Scheme 65).<sup>221</sup> The molecular

**Scheme 65. Synthesis of Trinuclear Assembly 310<sup>a</sup>**

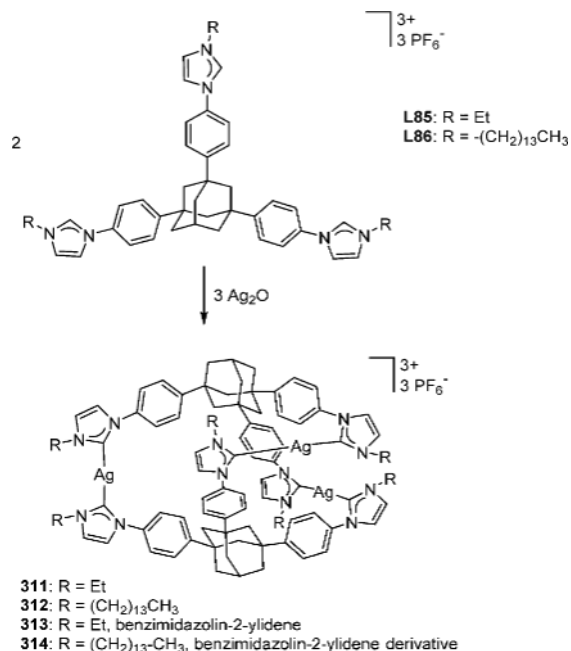


<sup>a</sup>Adapted with permission from ref 221. Copyright 2017 Wiley-VCH.

structure of compounds **310'** (featuring two tris-NHC ligands with N-*n*-butyl wingtips instead of N-ethyl wingtips) has been determined by X-ray diffraction analysis.<sup>221</sup>

While trisimidazolium salts with an essentially planar backbone have been employed successfully for the preparation of cylinder-like trinuclear hexacarbene assemblies, even nonplanar derivatives such as the adamantyl-bridged proligands **L85** and **L86** are suitable starting materials for such assemblies. Both proligands react with Ag<sub>2</sub>O to give the three-dimensional cage-like complexes **311** and **312** (Scheme 66).<sup>222,223</sup> The molecular structure of **311** was initially determined in solution by NMR spectroscopy and high-resolution cold-spray ionization mass spectrometry (CSI-MS). An X-ray diffraction study showed subsequently that the trisilver hexacarbene complex cation features only a small internal cavity with nonbonding distances between the silver atoms ranging from 12.53 to 13.36 Å. All other metric parameters were nonspectacular.

Scheme 66. Synthesis of Silver(I) Complexes 311–314



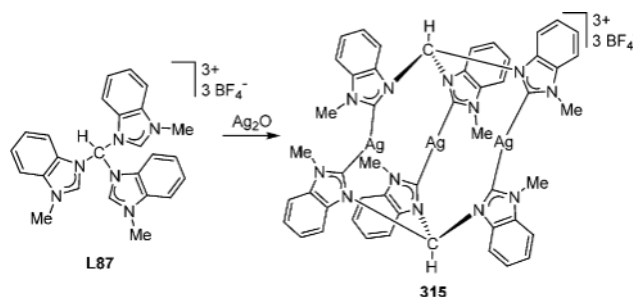
Following the same *in situ* metalation protocol, the complex **312** bearing long alkyl N-wingtips was prepared.<sup>223</sup> In addition to characterization by NMR spectroscopy and CSI-MS spectrometry, its morphology was characterized by SEM. Compound **312** was found to self-assemble into hollow spherical aggregates with a diameter of ca. 110 nm in polar organic solutions.

The benzimidazolin-2-ylidene analogs of **311** and **312** bearing the same N-wingtips have also been prepared. Complexes **313** and **314** were synthesized as described for **311** and **312** (Scheme 66).<sup>222,223</sup> The introduction of the larger benzimidazolin-2-ylidenes does not alter the structural parameters significantly, and the molecular structures of **311** and **313** are thus very similar. Again, the complex with the long N-alkyl wingtips **314** aggregated into a vesicular structure with a diameter of ca. 220 nm as reflected by SEM, TEM, and DLS. The thickness of the vesicular wall (13–20 nm) was estimated by TEM.

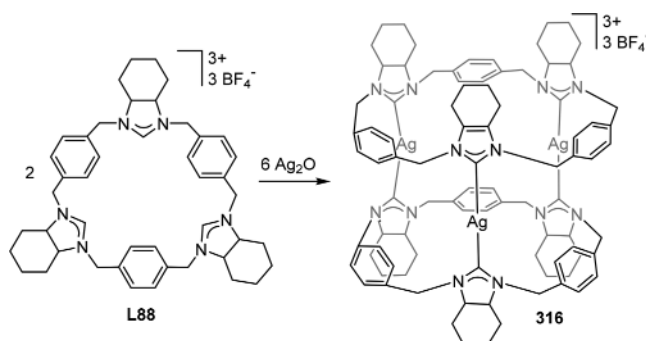
The trisbenzimidazolium salt **L87** resembles the imidazolium derivatives **L77a,b** but features apart from the benzimidazolium groups also a central C–H building block (instead of a C–CH<sub>2</sub> unit in **L77a,b**, Scheme 61). These changes led to significant differences in the stability of the resulting trisilver assemblies. Reaction of **L87** with Ag<sub>2</sub>O very likely yields the trinuclear silver(I) complex **315**, but its instability in solution prevented a detailed characterization (Scheme 67).<sup>217</sup>

An interesting example for a cylinder-like assembly obtained from a chiral macrocyclic trisimidazolidinium salt **L88** and Ag<sub>2</sub>O is depicted in (Scheme 68).<sup>224</sup> The cyclic (saturated) trisimidazolidinium salt was prepared from chiral *R,R*-1,2-diaminohexane. <sup>1</sup>H NMR spectroscopy and an X-ray diffraction study confirmed the presence of only one configuration of the three imidazolidinium groups.

An X-ray diffraction analysis of the trinuclear assembly **316** revealed the formation of a chiral trisilver(I) cationic cage in which all of the asymmetric carbon atoms are presented in a homochiral fashion. The complex cation is highly symmetrical, residing on a 3-fold crystallographic axis where the silver atoms form a triangular plane with an Ag...Ag separation of 8.26 Å. The

Scheme 67. Synthesis and Proposed Molecular Structure of Trisilver Cage 315<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 217. Copyright 2008 Elsevier.

Scheme 68. Synthesis of the Chiral Trinuclear Silver(I) Complex 316<sup>a</sup>

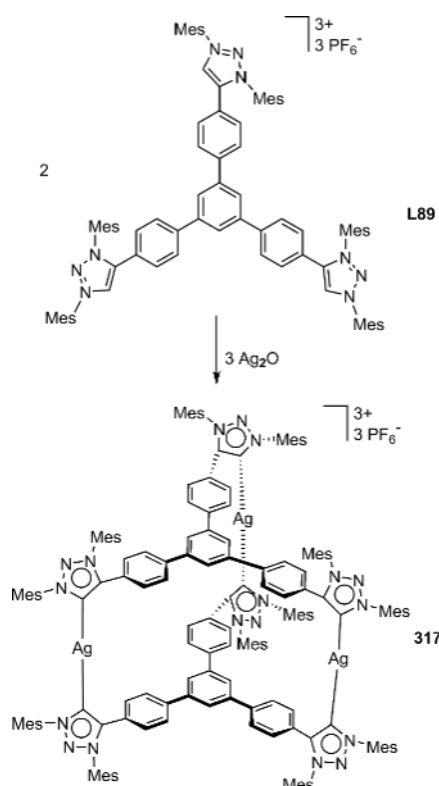
<sup>a</sup>Adapted with permission from ref 224. Copyright 2010 Royal Society of Chemistry.

complex cation features an internal cavity with a diameter of about 1 nm. It could encapsulate a BF<sub>4</sub><sup>−</sup> anion with formation of Ag...F interactions. Furthermore, complex **316** showed a size-selective enantioselective catalytic performance for the cyanosilylation of Schiff-base substrates.

Finally, a first example for a homoleptic tris-MIC derived cylinder-like trisilver assembly has been described (Scheme 69).<sup>225</sup> Compared to classical NHC donors, MIC ligands are assumed to have stronger electron donor properties and have thus attracted significant attention. Incorporation of MIC donors into metallocsupramolecular assemblies could thus lead to particularly stable derivatives. The reaction of proligand **L89** with 1.5 equiv of Ag<sub>2</sub>O afforded the trisilver assembly **317** in a moderate yield of 42% yield. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **317** showed the C<sub>MIC</sub> resonance at δ 169.7 ppm as a doublet of doublets [<sup>1</sup>J(<sup>13</sup>C, <sup>109</sup>Ag) = 190.5 Hz, <sup>1</sup>J(C, <sup>107</sup>Ag) = 165.0 Hz]. As expected for silver(I)-MIC complexes, this resonance is shifted upfield relative to the equivalent resonance of silver(I)-NHC complexes. The metric parameters of **317**, however, do not differ significantly from those observed for the Ag(NHC)<sub>2</sub> complexes discussed previously in this section.

**3.1.2. Trinuclear 3D Gold(I) Assemblies.** As already mentioned during the discussion of dinuclear metallocycles featuring two silver (section 2.1.1) or two gold atoms (section 2.2.1), the coordination chemistry of silver(I) and gold(I) are very similar. In addition, most gold(I) NHC complexes are obtained from the silver(I) derivatives by transmetalation with overall retention of the molecular structure. This is particularly true for the trigold(I) complexes discussed in this section, which were all obtained by transmetalation from the corresponding



Scheme 69. Synthesis the Trinuclear Silver(I)-MIC Assembly 317<sup>a</sup>

<sup>a</sup>Adapted with permission from ref 225. Copyright 2015 Royal Society of Chemistry.

trisilver(I) derivatives. Therefore, the molecular structures of the trigold(I) cage compounds are summarized in Figure 23, and only selected features of their synthesis and geometrical properties will be discussed subsequently.

The tris-NHC ligand from the first trinuclear silver(I) cylinder (303b in Scheme 61) was easily transmetalated to give the trigold(I) compound 318 with retention of the 3D metallosupramolecular structure using  $[\text{AuCl}(\text{SMe}_2)]$  as a gold source (Figure 23).<sup>216</sup> The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of a gold complex 318 show only slight variations when compared to the data obtained for the trisilver analog 303b. Comparable metric parameters of the two assemblies obtained by X-ray diffraction also do not differ significantly.

Transmetalation of the tris-NHC ligands from the trisilver complexes 304–306 (Scheme 62) to  $[\text{AuCl}(\text{SMe}_2)]$  yielded the trigold complexes 319–321 (Figure 23), presumably also with retention of the molecular structure although no structural data were provided.<sup>217</sup> By addition of 3 equiv of  $[\text{AuCl}(\text{SMe}_2)]$  to the trinuclear silver(I) complexes 307 and 308a, the trigold(I) complexes 322 and 323 were obtained in good yields.<sup>218,219</sup> Even an increase of the size of the backbone from benzene to triphenylbenzene did not hamper the transmetalation as demonstrated with complex 324 which was obtained from its trisilver analog 309 (Scheme 64) and  $[\text{AuCl}(\text{SMe}_2)]$  in 70% yield.<sup>220</sup> An X-ray diffraction study of 324 revealed that the enlarged backbone allows the central benzene rings to orient in a parallel fashion and to approach each other with the centroid-to-centroid separation measuring 3.644 Å. This was taken as an indication for the existence of  $\pi\cdots\pi$  interactions between these rings. A rather large Au $\cdots$ Au separation of about 1.4 nm was also

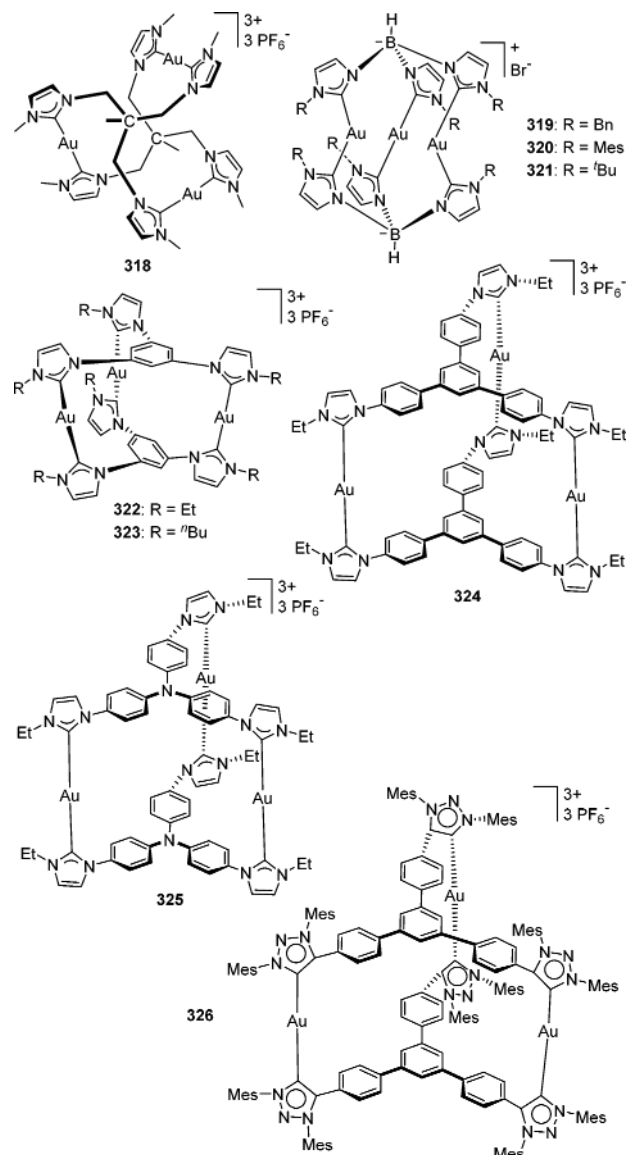


Figure 23. Trinuclear cylinder-like gold(I) assemblies.

observed in 324. Assuming a pseudotriangular-prismatic structure for 324, the internal volume of the cavity was estimated to be 360 Å<sup>3</sup>, which is about four times larger than that of 323.

Trigold(I) cage compound 325, featuring a smaller triphenylamine backbone, was also prepared by transmetalation from the corresponding trisilver complex 310.<sup>221</sup> Finally, even the transmetalation of this tris-MIC ligand from trisilver(I) complex 317 to  $[\text{AuCl}(\text{SMe}_2)]$  with formation of 326 proved possible in 63% yield (Figure 23).<sup>225</sup>

**3.1.3. Trinuclear 3D Copper(I) Assemblies.** Similarly to the gold(I) complexes, most copper(I) complexes resemble their silver(I) analogs and are normally synthesized from these by transmetalation. Therefore, tricopper(I) cylinder-like compounds are only briefly discussed here. The known complexes are depicted in Figure 24.

The tricopper complex 327 was obtained by transmetalation of the tris-NHC ligand from assembly 303b to CuBr. Alternatively, compound 327 was prepared in a yield of 27% from the in situ generated tris-NHC ligand, obtained by deprotonation of proligand L77a (Scheme 61), and CuOTf.<sup>216</sup>

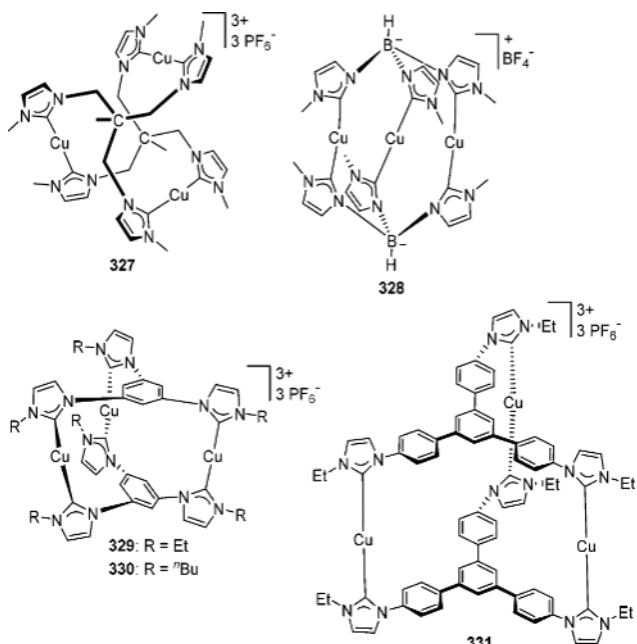


Figure 24. Trinuclear cylinder-like copper(I) complexes.

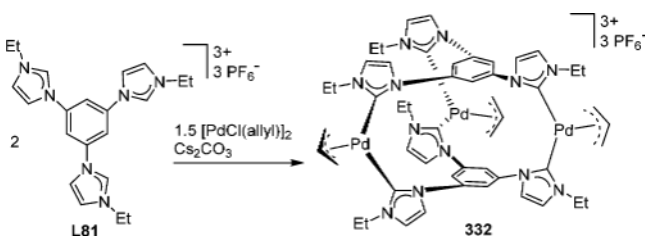
Its diagnostic  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic resonances were similar to those of its silver(I) and gold(I) analogs.

Tricopper complex **328** was prepared by deprotonation of the appropriate trisimidazolium salt with  $n\text{BuLi}$  followed by reaction with  $[\text{CuBr}(\text{PPh}_3)_3]$ .<sup>226</sup> The compound was characterized by NMR spectroscopy and ESI-MS spectrometry. No structural data are available, but the +1 oxidation state of the copper atom was established by XPS spectroscopy. The activity of **328** in catalytic Ullmann-type arylation reactions was subsequently investigated.

Cylinder-type tricopper(I) complexes **329** and **330** were prepared by transfermetalation of the tris-NHC ligands from silver(I) compounds **307** and **308a** (Scheme 63) to  $\text{CuBr}$ .<sup>219</sup> Their spectroscopic and structural data resemble those of the silver(I) and gold(I) analogs. The same transmetalation methodology was used for the synthesis of **331** from **309**, except that  $\text{CuI}$  was used as a copper source.<sup>220</sup>

**3.1.4. Trinuclear 3D Palladium(II) Assemblies.** Cylinder-like trinuclear assemblies have also been obtained from square-planar palladium(II) compounds and trisimidazolium salts. As shown in Scheme 70,  $[\text{PdCl}(\text{allyl})_2]$  reacts with proligand **L81** in the presence of  $\text{Cs}_2\text{CO}_3$  to give the trinuclear assembly **332**.<sup>227</sup> An X-ray diffraction study revealed each  $\{\text{Pd}(\text{allyl})\}$  fragment is coordinated by two NHC donors arranged in cis-positions

Scheme 70. Synthesis of Trinuclear Palladium(II) Assembly **332**.<sup>a</sup>

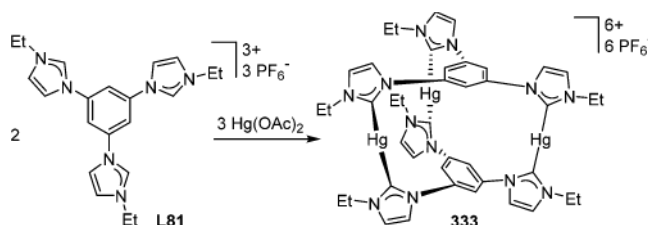


<sup>a</sup>Adapted with permission from ref 227. Copyright 2013 Royal Society of Chemistry.

[range of  $\text{C}_{\text{NHC}}\text{--Pd--C}_{\text{NHC}}$  angles  $91.2(4)\text{--}95.5(4)^\circ$ ]. This arrangement forces the two parallel-oriented central benzene rings into close proximity (centroid-to-centroid distance  $3.717\text{ \AA}$ ), indicating the presence of  $\pi\cdots\pi$  interactions between these rings. The  $\text{Pd}\cdots\text{Pd}$  separations increased accordingly and in comparison to silver(I) and gold(I) assemblies obtained from **L81** to values of  $6.9156(10)\text{--}7.2267(9)\text{ \AA}$ .

**3.1.5. Trinuclear 3D Mercury(II) Assemblies.** Finally, a cylinder-like trinuclear mercury(II) assembly **333** was prepared by the direct reaction of the proligand **L81** with  $\text{Hg}(\text{OAc})_2$  (Scheme 71).<sup>121</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum displayed a  $\text{C}_{\text{NHC}}$

Scheme 71. Synthesis of Cylindrical Mercury(II) Assembly **333**.<sup>a</sup>



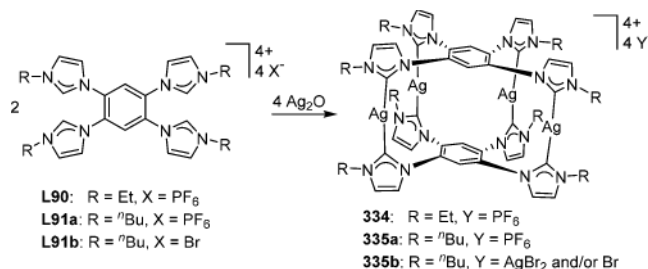
<sup>a</sup>Adapted with permission from ref 121. Copyright 2011 American Chemical Society.

resonance in the expected range at  $\delta\ 174.3\text{ ppm}$ . Comparable metric parameters for **333** strongly resemble those of the related silver(I) (**307**) and gold(I) (**322**) assemblies. As noted previously for related compounds, the  $\text{C}_{\text{NHC}}\text{--Hg--C}_{\text{NHC}}$  axes are not oriented perpendicular to the central benzene ring which decreased the distance between the centroids of the benzene rings to  $4.978\text{ \AA}$ , a value slightly larger than observed for the related silver(I) and gold(I) compounds.

### 3.2. Tetranuclear Three-Dimensional Structures

**3.2.1. Tetranuclear 3D Silver(I) Assemblies.** Apart from the trinuclear 3D assemblies, a series of tetranuclear three-dimensional metal-polycarbene structures have been described. The simplest of these were obtained from the 1,2,4,5-benzene bridged tetrakisimidazolium salts **L90** and **L91**. A straightforward approach uses these tetrakisimidazolium salts in the direct reaction with  $\text{Ag}_2\text{O}$  to give the tetrasilver octacarbene assemblies **334** and **335a,b** (Scheme 72).<sup>218,219</sup> Multinuclear NMR spectroscopy and ESI-MS spectrometry were used to characterize the compounds featuring the expected resonances for the  $\text{C}_{\text{NHC}}$  carbon atoms in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. The molecular structure of **335a** was determined by X-ray diffraction

Scheme 72. Synthesis of Cylindrical Tetranuclear Silver(I) Assemblies.<sup>a</sup>

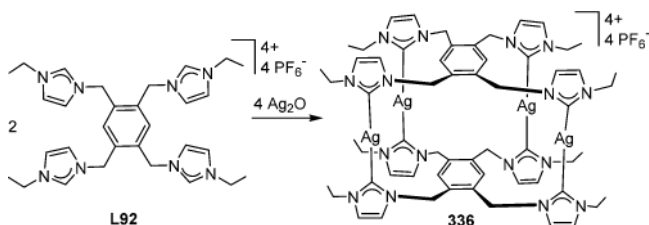


<sup>a</sup>Adapted with permission from ref 219. Copyright 2011 American Chemical Society.

showing four silver atoms sandwiched in between two tetrakis-NHC ligands. As was observed for the trinuclear assemblies, the planes of the NHC donors are rotated relative to the central benzene plane, and the  $C_{NHC}-Ag-C_{NHC}$  axes are also not arranged perpendicular to the central benzene rings. The four metal atoms formed a planar rectangle with  $Ag\cdots Ag$  separations of about 3.4 and 5.9 Å.

The type and size of the NHC N-wingtips proved important in the synthesis of tetranuclear assemblies from tetrakis-NHC ligands. The reaction of  $Ag_2O$  with proligand **L92** bearing ethyl wingtips afforded the tetranuclear molecular box **336** in a yield of 68% (Scheme 73).<sup>228</sup> Smaller (methyl) or larger (benzyl) N-

**Scheme 73. Synthesis of a Tetranuclear Molecular Box<sup>a</sup>**

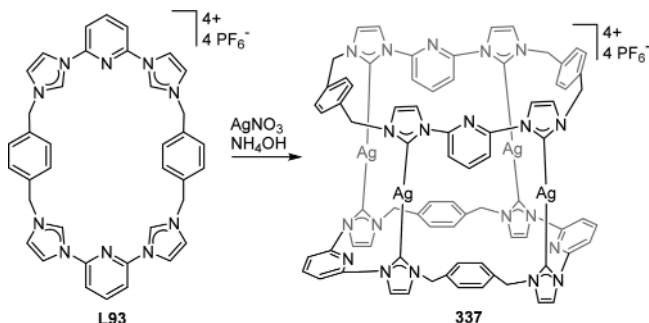


<sup>a</sup>Adapted with permission from ref 228. Copyright 2013 American Chemical Society.

wingtips, however, led to the formation of dinuclear complexes where two NHC donors in 1,3- or 2,5-positions at a central benzene ring coordinated to one silver(I) ion. This is apparently enabled by the methylene spacers between the central benzene ring and the NHC donors. No such behavior has been observed with tetrakis-NHCs obtained from proligands such as **L90** or **L91**. An X-ray diffraction analysis of **336** showed the NHC donors oriented orthogonally to the central benzene rings they were attached to. The centroid...centroid distance between the benzene rings was determined to be 4.923 Å. The exact reason for the formation of different assemblies by using very similar ligands remains unclear.

Tetranuclear molecular cylinders or boxes have also been obtained from cyclic tetrakisimidazolium salts. Complex **337**, for example, was obtained in 60% yield from the reaction of cyclic tetrakisimidazolium salt **L93** and  $AgNO_3$  in the presence of  $NH_4OH$  as a base (Scheme 74).<sup>133</sup> NMR spectroscopy indicated a highly symmetrical compound since only one set of signals was detected. This observation was subsequently confirmed by an X-ray diffraction study. Two macrocyclic

**Scheme 74. Synthesis of the Cylindrical Tetranuclear Silver(I) Assembly 337<sup>a</sup>**

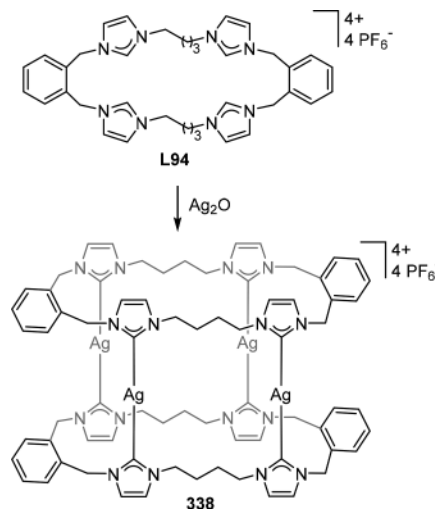


<sup>a</sup>Adapted with permission from ref 133. Copyright 2010 Wiley-VCH.

tetrakis-NHC ligands and four bridging silver ions are combined into a molecular cylinder of high symmetry.

A reduction of the size of one of the linkers between the NHC donors is also possible and was achieved with the macrocyclic tetrakisimidazolium salt **L94**. The flexible linked proligand **L94** reacts with 2.5 equiv  $Ag_2O$  providing the tetranuclear tetrasilver(I) box **338** in 83% yield (Scheme 75).<sup>229</sup>

**Scheme 75. Synthesis of Tetranuclear Silver Box 338<sup>a</sup>**

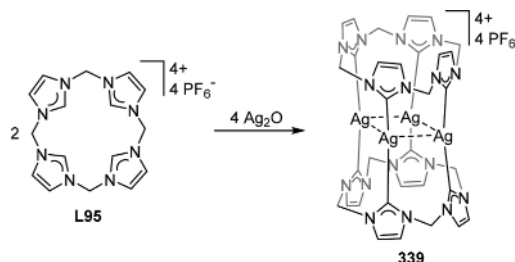


<sup>a</sup>Adapted with permission from ref 229. Copyright 2015 Royal Society of Chemistry.

The eight chemically equivalent  $C_{NHC}$  carbon atoms gave rise to a resonance at  $\delta$  180.6 ppm with the characteristic coupling to the silver isotopes [ $^1J(^{13}C, ^{109}Ag) = 207$  Hz and  $^1J(^{13}C, ^{107}Ag) = 178$  Hz]. An X-ray diffraction analysis confirmed the cylindrical structure of **338**. Note that proligand **L94** cannot accommodate two linearly coordinated silver atoms inside the macrocycle as the distance between two NHC donors located opposite to each other is too small. This situation changes if the bridging *o*-benzene groups is substituted for a 2,6-pyridine or *m*-benzene unit (addition of one atom to the linker), which allowed the formation of the dinuclear complexes of types **96** and **97** (Scheme 23).

A further reduction of the lengths of the spacers between the imidazolium groups in macrocyclic tetrakisimidazolium proligands led to the preparation of **L95**. This proligand reacts with  $Ag_2O$  to give the tetranuclear assembly **339** (Scheme 76).<sup>230</sup> Next to the spectroscopic characterization, an X-ray diffraction analysis revealed the formation of a tetranuclear rhombus of four silver(I) atoms sandwiched in between two tetrakis-NHC

**Scheme 76. Synthesis of Tetranuclear Complex 339<sup>a</sup>**

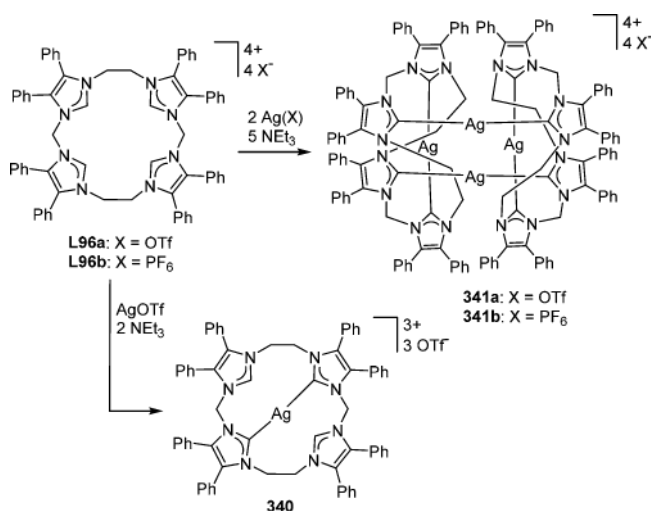


<sup>a</sup>Adapted with permission from ref 230. Copyright 2016 Wiley-VCH.

ligands. The  $C_{NHC}-Ag-C_{NHC}$  angles deviate from linearity (average  $166^\circ$ ), most likely due to strain caused by the short linkers between the NHC donors. On the other hand, the short linkers force the silver atoms in close proximity with  $Ag\cdots Ag$  distances of  $3.1749(3)-3.2366(3)$  Å. Interestingly, the reaction of proligand **L95** with group 10 metal complexes  $[MCl_2(PPh_3)_2]$  ( $M = Ni, Pd,$  and  $Pt$ ) led to mononuclear saddle-shaped complexes as these metals can accommodate two NHC donors in cis-positions. The metal ions in **339** form a planar  $Ag_4$  square. It should be noted that a related  $Ag_4$  square was observed when proligand **L73** (Scheme 42) was reacted with  $Ag_2O$ .<sup>231</sup>

Yet another approach to the construction of poly-NHC-based box-type assemblies starts with the macrocyclic tetrakisimidazolium salts **L96a,b** which reacted with two equiv of silver salts in the presence of five equiv of  $NEt_3$  to give the tetrasilver complexes **341a,b** (Scheme 77).<sup>232</sup>

**Scheme 77. Synthesis of Tetrasilver(I) Molecular Boxes **341a,b** and of Monomeric Silver Complex **340**<sup>a</sup>**

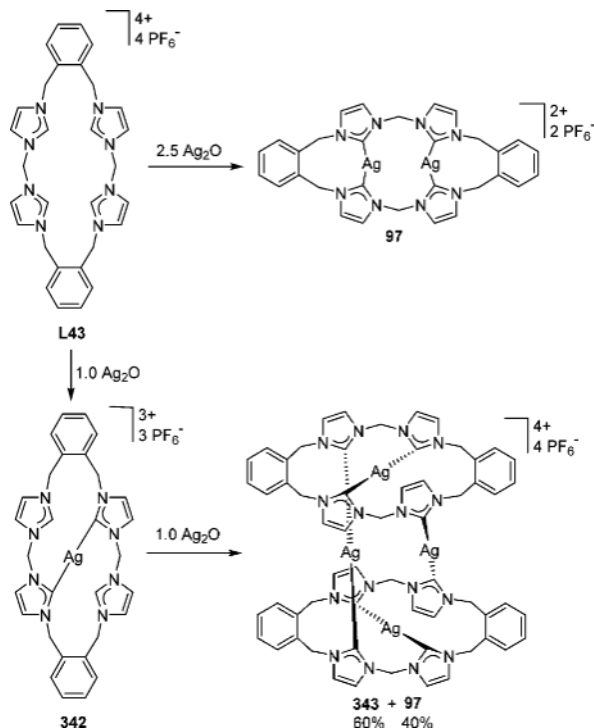


<sup>a</sup>Adapted with permission from ref 232. Copyright 2012 Royal Society of Chemistry.

Two  $C_{NHC}$  carbon resonances for the chemically inequivalent NHC donors were recorded at  $\delta$  183.18 [ $^1J(^{13}C, ^{109}Ag) = 200$  Hz and  $^1J(^{13}C, ^{107}Ag) = 168$  Hz] and  $\delta$  176.96 ppm [ $^1J(^{13}C, ^{109}Ag) = 218$  Hz and  $^1J(^{13}C, ^{107}Ag) = 190$  Hz] in the  $^{13}C\{^1H\}$  NMR spectrum of complex **341a** with similar values observed for **341b**. An X-ray diffraction study with **341b** showed that one silver atom binds to two NHC donors from each tetrakis-NHC ligand, while the other two act as bridges between two ligands. Interestingly, the  $Ag-C_{NHC}$  bond distances within one ligand [ $2.143(3)-2.144(3)$  Å] are longer than those for the silver atoms in bridging positions [ $2.077(3)-2.092(3)$  Å]. It should be noted that the reaction of **L96a** with 1 equiv of  $AgOTf$  and 2 equiv of  $NEt_3$  under the same reaction conditions yielded the monosilver complex **340** in 80% yield.

The stepwise formation of a tetranuclear silver(I) octacarbene assembly **343** is displayed in Scheme 78.<sup>137</sup> As mentioned before (see Scheme 23), proligand **L43** cannot accommodate two linearly coordinated silver(I) in a strain-free fashion to give **97**, and therefore, diagonal coordination of only one silver atoms is preferred. This monosilver complex **342** has been isolated and reacted with additional  $Ag_2O$  to give the tetranuclear complex

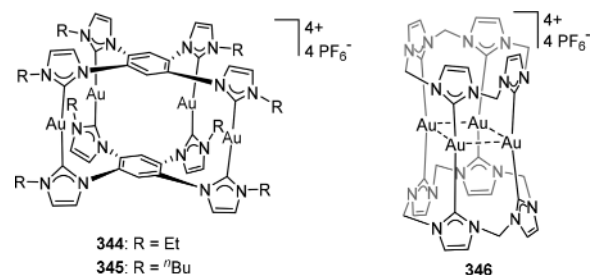
**Scheme 78. Stepwise Formation of Tetranuclear Silver(I) Complex **343**<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 137. Copyright 2013 Royal Society of Chemistry.

**343** as the major reaction product next to the dinuclear complex **97**. Assembly **343** is composed of two monometalated metalloligands obtained by double deprotonation of the remaining imidazolium groups in **342**. The metalation of **342** with additional transition metals to give heterobimetallic complexes has recently also been demonstrated.<sup>151b</sup>

**3.2.2. Tetranuclear 3D Gold(I) Assemblies.** The gold(I) analogs of selected tetranuclear assemblies discussed in the previous section have been prepared by ligand transmetalation. The gold(I) complexes obtained are essentially isostructural to their silver analogs. They will not be discussed in detail here and are depicted in Figure 25.



**Figure 25. Cylindrical tetranuclear gold(I) complexes.**

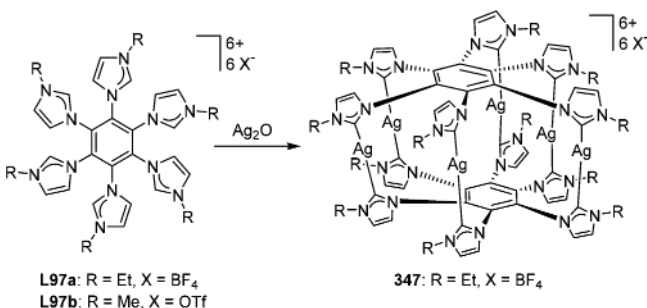
The tetranuclear cylinder-like tetragold(I) assemblies **344**–**345** were obtained by transmetalation from the silver complexes **334**–**335a** using  $[AuCl(SMe_2)]$  as gold(I) source.<sup>218,219</sup> The tetragold(I) analog of tetrasilver complex **339**, assembly **346** has also been prepared by ligand transmetalation to  $[AuCl(SMe_2)]$ .<sup>230</sup>



### 3.3. Hexanuclear Three-Dimensional Structures

**3.3.1. Hexanuclear 3D Silver(I) Assemblies.** Extending the number of imidazolium groups attached to a benzene backbone, the hexakisimidazolium salts **L97a,b** were prepared. Proligand **L97a** reacts with  $\text{Ag}_2\text{O}$  to give the hexasilver dodecacarbene assembly **347** (Scheme 79).<sup>233</sup> Confirmation

**Scheme 79. Synthesis Hexanuclear Dodecacarbene Silver(I) Assembly 347<sup>a</sup>**

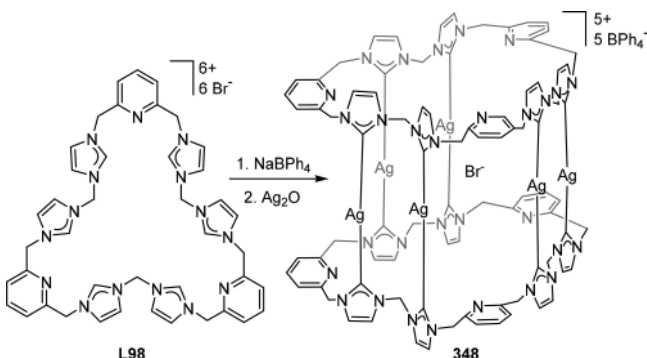


<sup>a</sup>Adapted with permission from ref 233. Copyright 2014 American Chemical Society.

of the molecular structure proposal for **347** was provided by an X-ray diffraction analysis showing the silver atoms coordinated in a nearly linear fashion with  $\text{C}_{\text{NHC}}\text{--Ag--C}_{\text{NHC}}$  angles of  $171.1(4)\text{--}173.4(6)^\circ$ .

The hexakisimidazolium salt **L98** was obtained as a side product in the synthesis of the cyclic tetrakisimidazolium salts **L42a,b**.<sup>136</sup> Cyclophane-like **L98** reacts, after incomplete anion-exchange with  $\text{NaBPh}_4$ , with  $\text{Ag}_2\text{O}$  to give the hexanuclear dodecacarbene assembly **348** (Scheme 80).<sup>136</sup> The X-ray

**Scheme 80. Synthesis of the Hexanuclear Cage 348<sup>a</sup>**

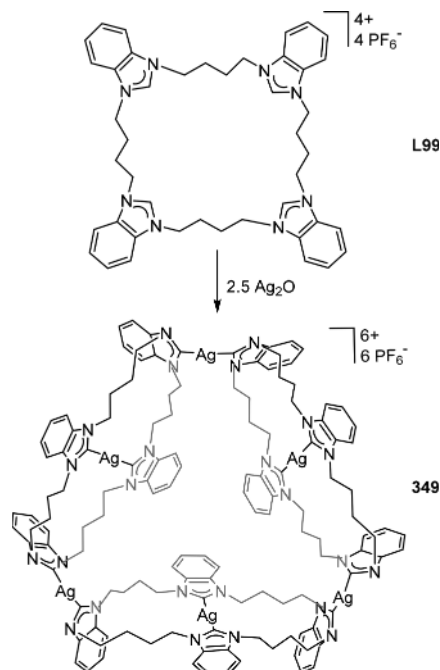


<sup>a</sup>Adapted with permission from ref 136. Copyright 2008 Wiley-VCH.

diffraction analysis revealed the presence of one bromide anion within the cylinder-like structure. Rather nonlinear  $\text{C}_{\text{NHC}}\text{--Ag--C}_{\text{NHC}}$  angles [range  $161.4(3)$  to  $165.3(3)^\circ$ ] angles were observed, while the  $\text{Ag--C}_{\text{NHC}}$  bond distances fell in the expected range. It was assumed that the bromide anion acts as a template in the self-assembly process.

Scheme 81 illustrates the synthesis of the propeller-like hexanuclear complex **349**.<sup>150</sup> This hexanuclear assembly was obtained from the reaction of the butylene-bridged tetrakisbenzimidazolium salt **L99** with  $\text{Ag}_2\text{O}$  in DMF in 48% yield (Scheme 81).<sup>150</sup> The molecular structure is best described as composed of three monometallate macrocycles where the silver atoms are coordinated in a diagonal fashion. Three of these monometallic

**Scheme 81. Synthesis of Silver(I) Assembly 349<sup>a</sup>**

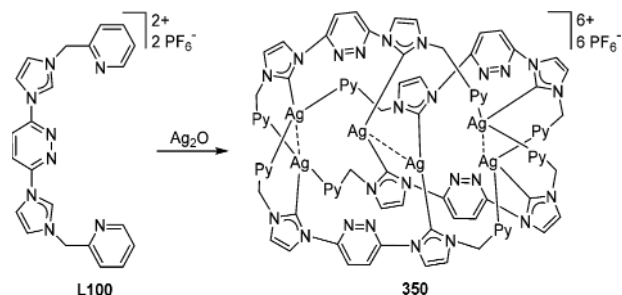


<sup>a</sup>Adapted with permission from ref 150. Copyright 2017 Royal Society of Chemistry.

complexes are then linked together by coordination of the remaining NHC donor functions to additional silver atoms. This building principle resembles the one found in **343** (Scheme 78) where the macrocycle is also monometallated followed by supramolecular assembly of the metalloligands with additional silver atoms. Assembly **349** possessed a hexagonal cavity which accepted a hexafluorophosphate anion as a guest.

Assembly **350** constitutes an example for a hexanuclear pseudo-cagelike structure (Scheme 82).<sup>234</sup> It is composed of

**Scheme 82. Synthesis of Hexanuclear Silver Complex 350<sup>a</sup>**

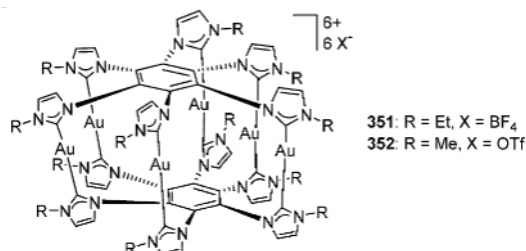


<sup>a</sup>Adapted with permission from ref 234. Copyright 2007 American Chemical Society.

four bis-NHC ligands obtained by deprotonation of prolignand **L100** and six silver atoms. Each bis-NHC ligand features two pyridyl-wingtips which participate in the coordination. When imidazolium salt **L100** was mixed with  $\text{Ag}_2\text{O}$  in  $\text{CH}_3\text{CN}$ , the exclusive formation of the hexasilver assembly **350** was observed. In this assembly, each ligand is linked to four different silver atoms acting as a tetradentate bridge, while the central pyridazine nitrogen atoms remain uncoordinated. Three short  $\text{Ag}\cdots\text{Ag}$  contacts of  $3.249(2)$ ,  $3.014(2)$ , and  $3.089(2)$  Å were found. Among these six silver atoms, two were coordinated by

two NHC donors, while the other four featured mixed NHC/pyridine coordination. Four additional pyridine donors interacted very weakly with the silver atoms.

**3.3.2. Hexanuclear 3D Gold(I) Assemblies.** Only one type of hexanuclear gold(I)-NHC assembly has been described so far. The hexanuclear complexes **351** and **352** were obtained by metalation of the hexakisimidazolium salts **L97a,b** with  $\text{Ag}_2\text{O}$  followed by transmetalation to  $[\text{AuCl}(\text{SMe}_2)]$  (Figure 26).<sup>233</sup>



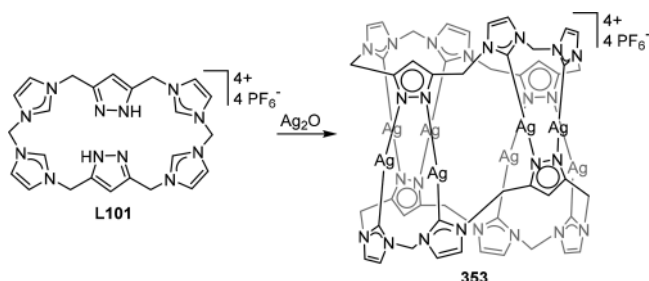
**Figure 26.** Cylindrical hexanuclear gold(I) assemblies. Adapted with permission from ref 233. Copyright 2014 American Chemical Society.

The complexes were characterized by NMR spectroscopy and ESI-MS spectrometry, confirming their composition. While no structural information on these complexes is available, it can be assumed that they are isostructural to their silver(I) analog **347**.

### 3.4. Octanuclear Three-Dimensional Silver(I) and Gold(I) Structures

Inspired by the tubular-shaped pillar[*n*]arenes and cucurbit[*n*]urils, a metallocavitand octasilver(I) complex bearing two calix[4]imidazolylidene[2]-dipyrazolato ligands was prepared (Scheme 83).<sup>235</sup> The reaction of proligand **L101** with an excess

**Scheme 83.** Synthesis of “Pillarplex” **353**<sup>a</sup>

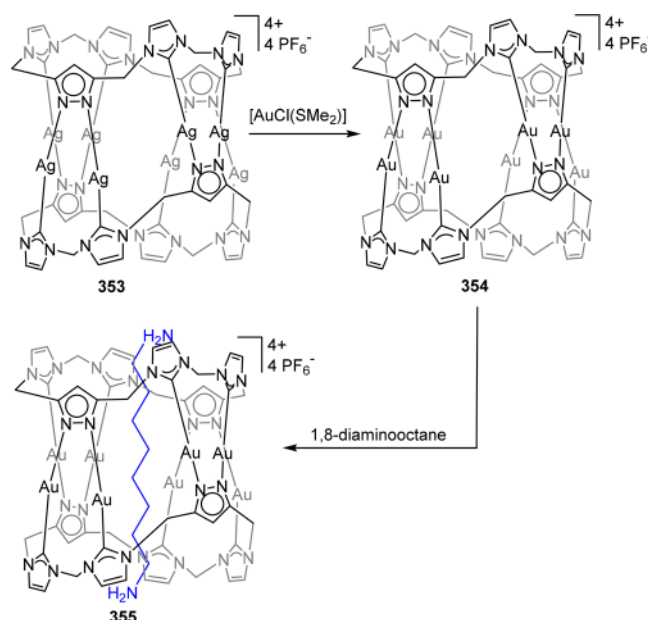


<sup>a</sup>Adapted with permission from ref 235. Copyright 2016 American Chemical Society.

of  $\text{Ag}_2\text{O}$  in acetonitrile resulted in the formation of assembly **353** in 79% yield. The octanuclear  $\text{Ag}_8\text{L}_2$ -type complex was found to have a highly symmetric geometry by spectroscopic analysis. Its composition was confirmed by elemental analysis and mass spectrometry.

Subsequently, the octadentate tetrakis-NHC ligand from **353** was transferred from silver(I) to gold(I), giving complex **354** (Scheme 84). The tubular structure of **354** (and **353**) was assumed to be of perfect size to host small linear molecules. An NMR titration of **354** with 1,8-diaminooctane as a model guest indicated indeed encapsulation of the diamine. Crystallization of **354** in the presence of 1,8-diaminooctane yielded **355** (Scheme 84) with an encapsulated 1,8-diaminooctane molecule which adopted the all-anti conformation to penetrate the cavity. Considering the structural resemblance of **353/354** to the well-established class of organic pillar[*n*]arenes regarding the cavity

**Scheme 84.** Synthesis of Assemblies **353** and **354** and of Host-Guest Assembly **355**



shape and size as well as the host–guest interaction properties, the authors selected the name “pillarplexes” for their complexes.

In a subsequent study, a rare example for an organometallic [2]rotaxane was prepared from “pillarplex” **353**, 1,2-diaminododecane and 3,5-di-*tert*-butylbenzoic anhydride (Scheme 85).<sup>236</sup> The [2]rotaxane **356** was obtained in nearly quantitative yield from these components and was completely characterized, including an X-ray diffraction study.

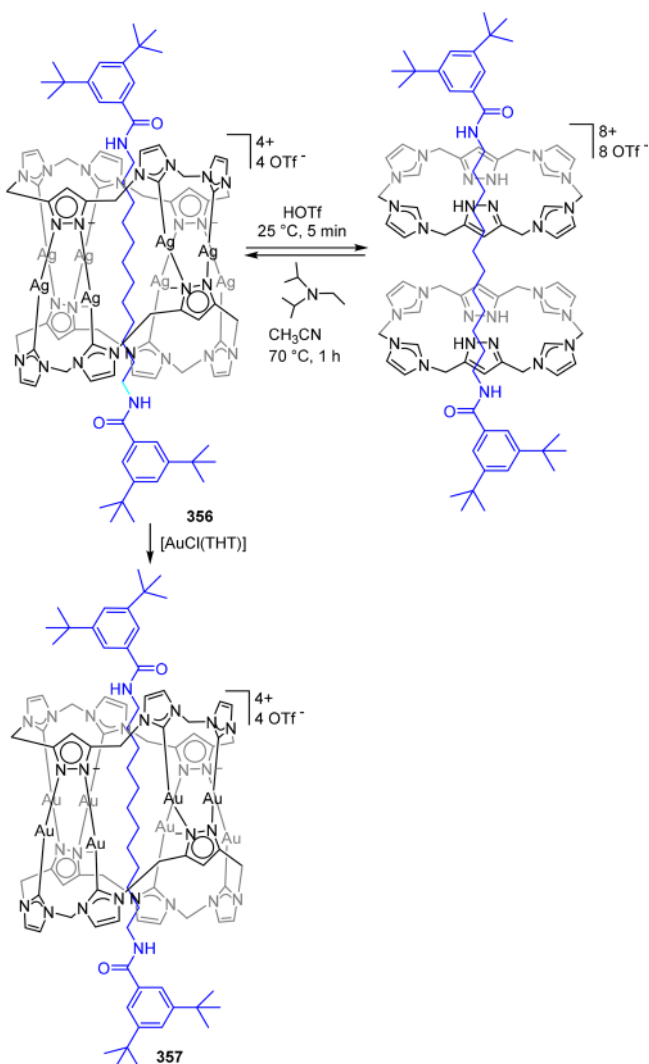
Interestingly, the ligands from [2]rotaxane **356** could be transferred to gold(I) using  $[\text{AuCl}(\text{THT})]$  as a source of gold to give [2]rotaxane **357** with retention of the structure and the guest (Scheme 85). Furthermore, addition of a small excess of the superacid  $\text{HOTf}$  to **356** causes a rapid and complete removal of all metal ions, leading to a new organic rotaxane without amide cleavage. Upon addition of a suitable base to the demetalated compound, the organometallic rotaxane **356** is regenerated. It is worth noting that rotaxane **356** constitutes the first example for an organometallic rotaxane that can be reversibly transformed into a purely organic rotaxane by changing of the pH value.

## 4. OTHER STRUCTURES

In this section, selected structures that can not be classified to any of the aforementioned types will be discussed.

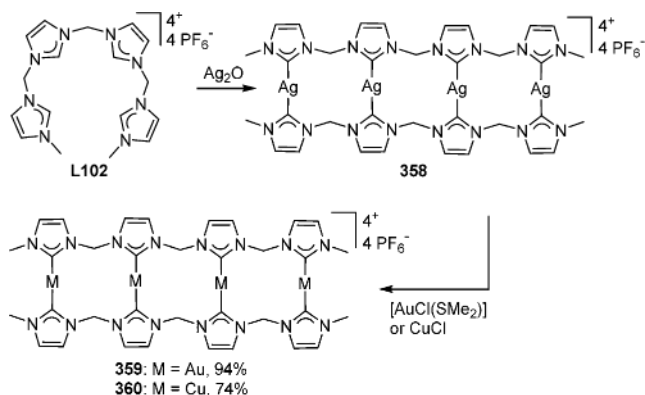
Reaction of the acyclic tetrakisimidazolium salt **L102** with an excess of  $\text{Ag}_2\text{O}$  afforded the tetrasilver(I) octakis-NHC complex **358** (Scheme 86).<sup>237</sup> In addition to characterization by ESI-MS spectrometry, elemental analysis, and NMR spectroscopy, an X-ray diffraction analysis revealed its double helical structure. Transmetalation with  $[\text{AuCl}(\text{SMe}_2)]$  as a gold source or  $\text{CuCl}$  as a copper source gave the tetranuclear structures **359** and **360** (Scheme 86).<sup>238</sup> No structural information on the gold(I) complex is available. An X-ray structural analysis of copper assembly **360** revealed that two acetonitrile molecules coordinate to two of the inner copper atoms with a concurrent reduction of the  $\text{C}_{\text{NHC}}\text{—Cu—C}_{\text{NHC}}$  angle to  $137.3(11)^\circ$  for the three coordinated copper atoms. The two outer copper atoms are dicoordinated in an almost linear fashion. Interestingly,

**Scheme 85.** Transmetalation of the Ligands from 356 to 357 and Reversible [2]Rotaxane Demetalation<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 236. Copyright 2017 Wiley-VCH.

**Scheme 86.** Synthesis of Tetranuclear Assemblies 358–360

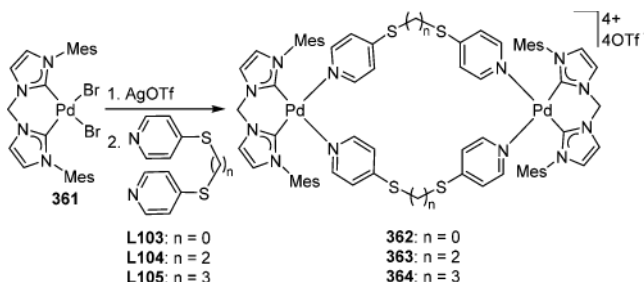


elongation of the bridging alkyl chains resulted in the formation of dinuclear silver(I), copper(I), and gold(I) complexes coordinated by only one tetrakis-NHC ligand.<sup>237,238</sup>

Three palladium metallamacrocycles **362**–**364** were obtained by self-assembly from bis-NHC chelated monopalladium complex **361** and bidentate ligands **L103**–**L105**, respectively

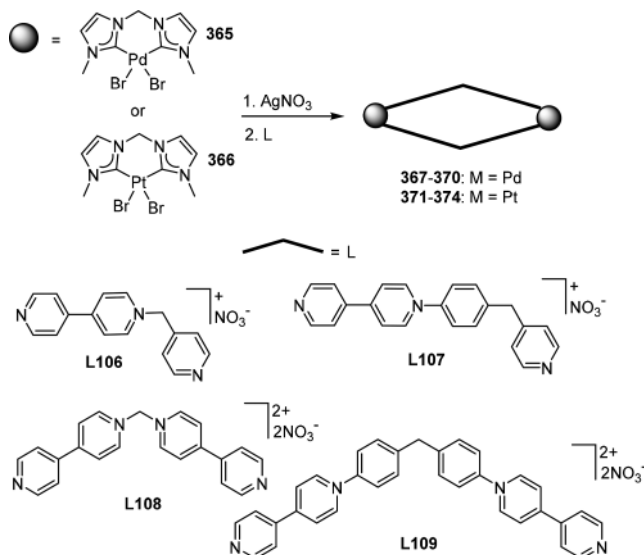
(Scheme 87).<sup>239</sup> Structural analyses were performed for assemblies **362** and **363**. Complex **362** exhibited a chairlike conformation, while **363** adopts a boatlike conformation in the solid state.

**Scheme 87.** Self-Assembly of Palladium(II) Complex 360 with Pyridine Type Ligands to give Complexes 362–364<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 239. Copyright 2010 American Chemical Society.

Self-assembly between bis-NHC palladium complex **365** or platinum complex **366** with *N*-monoalkyl-4,4'-bipyridinium or *N*-monoaryl-4,4'-bipyridinium salts was also studied (Figure 27).<sup>240</sup> The dipalladium metallacycles **367**–**370** were generated



**Figure 27.** Self-assemblies of metallacycles **367**–**374**. Adapted with permission from ref 240. Copyright 2017 Royal Society of Chemistry.

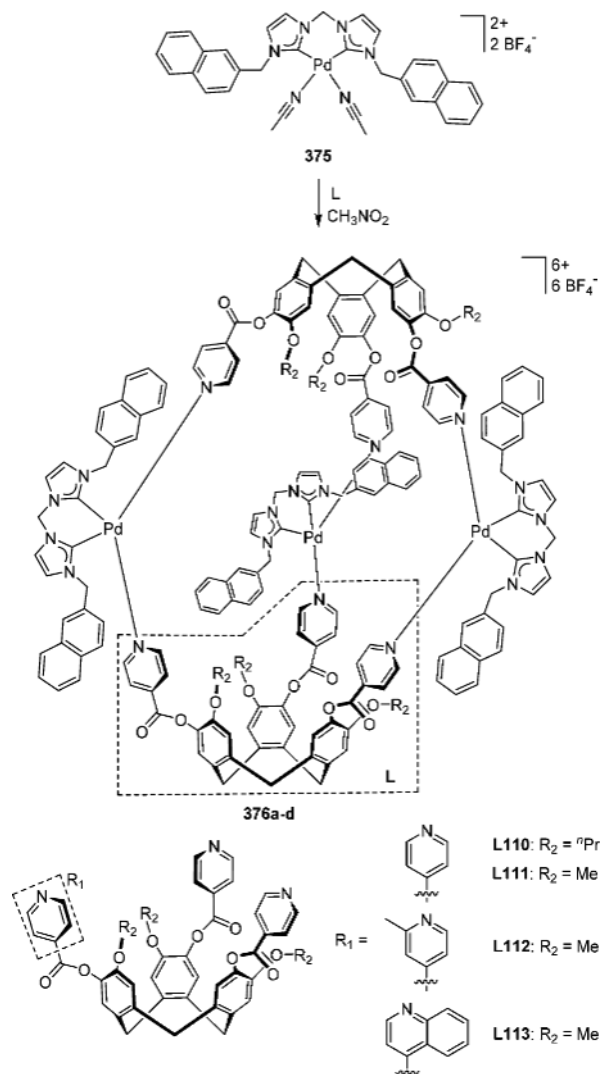
in water and further underwent structural characterization using one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy. Except for the absence of the  $C_{NHC}$  signal in complex **370**, the  $C_{NHC}$  resonances of dipalladium(II) complexes **367**–**369** (about  $\delta = 152$  ppm) shifted about 6 ppm downfield upon formation of the assemblies. A boat conformation was shown for **369** by X-ray crystallography, wherein the palladium coordination geometry deviated from square-planar. A volume of  $55.8 \text{ \AA}^2$  was estimated for the inner cavity of **369**. The potential of the complexes as metallacyclic receptors was also investigated.

Similarly to the palladium assemblies **367**–**370**, a platinum bis-NHC complex fragment was employed as a corner for the assembly of metallacycles **371**–**374** (Figure 27).<sup>240</sup> The chelating coordinated NHCs induced a sufficient trans-effect

at platinum to allow the formation of the self-assembled diplatinum metallacycles at room temperature. The conformation of **373** is similar to that of the palladium analogue **369**.

A series of metallo-cryptophane cages **376a–d** were assembled from cyclotrimeratrylene-type ligands **L110–L113** and bis-NHC palladium chelate complex **375** (Scheme 88).<sup>241</sup>

**Scheme 88.** Self-Assembly of Palladium Metallacycles **376a–d**<sup>a</sup>



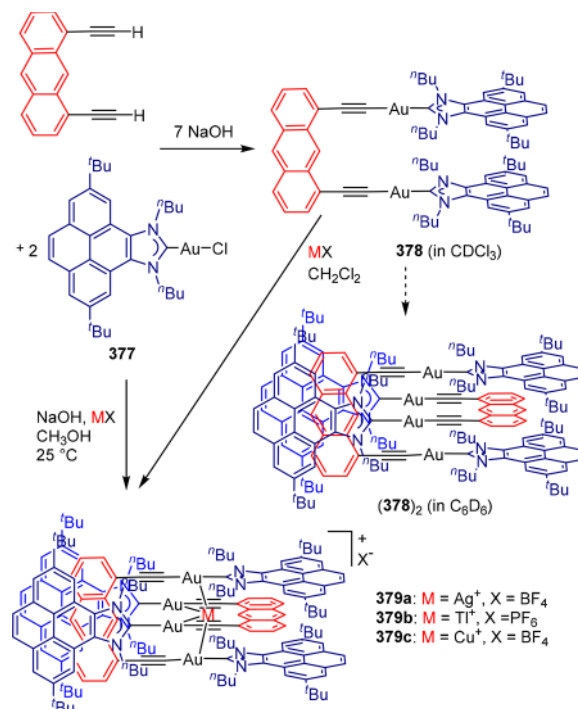
<sup>a</sup>Adapted with permission from ref 241. Copyright 2014 American Chemical Society.

The latter functioned as corners to connect two cyclotrimeratrylene-type ligands via palladium(II)-pyridine coordination. The resulting cages were characterized by FT-IR spectroscopy, HR-MS spectrometry, and NMR spectroscopy. In cage **376a**, the chemical shift recorded for the protons at the pyridyl group indicated a  $\pi \cdots \pi$  stacking interaction between the pyridyl groups and the naphthyl wingtips of the imidazolin-2-ylidene moieties. X-ray diffraction structural analyses showed the cages **376a–c** to be isostructural. The uptake of guest molecules by these cages was also investigated.

The molecular tweezer **378** was prepared from 1,8-diethynylantracene and the monogold(I) complex **377** (also bearing an extended  $\pi$ -system) in MeOH using an excess of

NaOH (Scheme 89).<sup>242a</sup> Tweezer **378** was characterized by NMR spectroscopy in  $\text{CDCl}_3$ , indicating the structure depicted

**Scheme 89.** Synthesis of Organogold Tweezers **378**/**(378)<sub>2</sub>** and Products of Encapsulation **379a–c**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 242. Copyright 2017 Wiley-VCH.

in Scheme 89.<sup>242</sup> A significant upfield shift of the resonances in the  $^1\text{H}$  NMR spectrum recorded in  $\text{C}_6\text{D}_6$  indicated the formation of a self-complementary duplex cleft **(378)<sub>2</sub>**, which was subsequently confirmed by TOF-MS spectrometry and X-ray diffraction analysis.

Treatment of compound **378** with  $\text{AgBF}_4$ ,  $\text{TlPF}_6$ , or  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$  yielded the inclusion complexes **379a–c**, respectively, in quantitative yield. Formation of **379a** and **379b** was confirmed by single-crystal X-ray diffraction studies, revealing a metal ion ( $\text{Ag}^+$  for **379a**,  $\text{Tl}^+$  for **379b**) inside the duplex molecule **(378)<sub>2</sub>**. Interestingly, the same type of inclusion complexes was obtained from the reaction of 1,8-diethynylantracene and gold(I)-NHC complex **377** in the presence of two equiv of NaOH and  $\text{AgBF}_4$  or  $\text{TlPF}_6$  in a one-pot reaction. Fluorescence spectroscopy titrations allowed one to determine the association constants of the inclusion duplex complexes to be  $2.7 \times 10^9$ ,  $4.2 \times 10^8$ , and  $7.9 \times 10^5 \text{ M}^{-2}$  for **379a**, **379b**, and **379c**, respectively. The tweezer complex **378** represents a new type of NHC-based molecular receptor for the encapsulation of metal cations in solution. Some related metal-NHC assemblies featuring an extended  $\pi$ -system and their application in the recognition and binding of organic substrates via  $\pi \cdots \pi$  interactions have also been described.<sup>242b–f</sup>

## 5. POST-ASSEMBLY MODIFICATION OF POLY-NHC METAL ASSEMBLIES

### 5.1. Oxidation Reactions

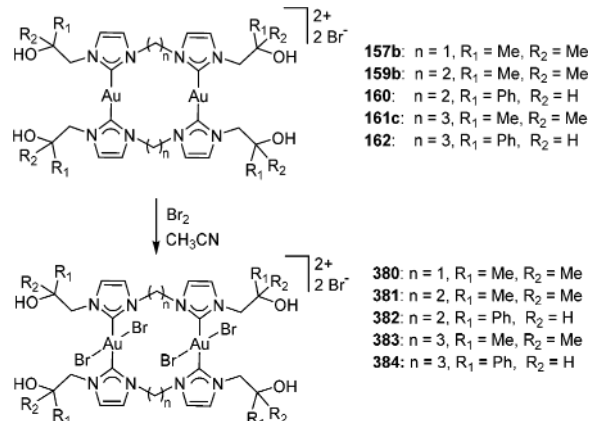
Parallel to the rapid development of gold(I)-NHC coordination chemistry, the chemistry of gold(III) complexes developed and various applications for such complexes have been described.



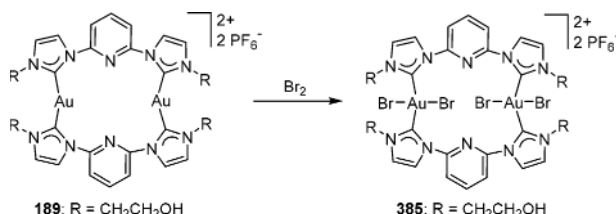
However, gold(III) complexes still form a minority among the gold-NHC complexes in general. Generally, gold(III)-NHC complexes can be obtained by the in situ metalation of NHCs using a gold(III) precursor, by transmetalation between a gold(I)-NHC complex and a gold(III) precursor, or by oxidative addition of halogens to gold(I) complexes. The latter protocol was found to be a simple and convenient reaction.<sup>243</sup>

A series of dinuclear gold(III) tetrakis-NHC complexes **380**–**385** were prepared by oxidation of the gold(I)-NHC complexes with elemental halogens [Schemes 90 and 91; for the synthesis

**Scheme 90. Synthesis of Digold(III) Complexes 380–384 by Oxidative Addition of Bromine**



**Scheme 91. Synthesis of Digold(III) Complex 385 by Oxidative Addition of Bromine<sup>a</sup>**

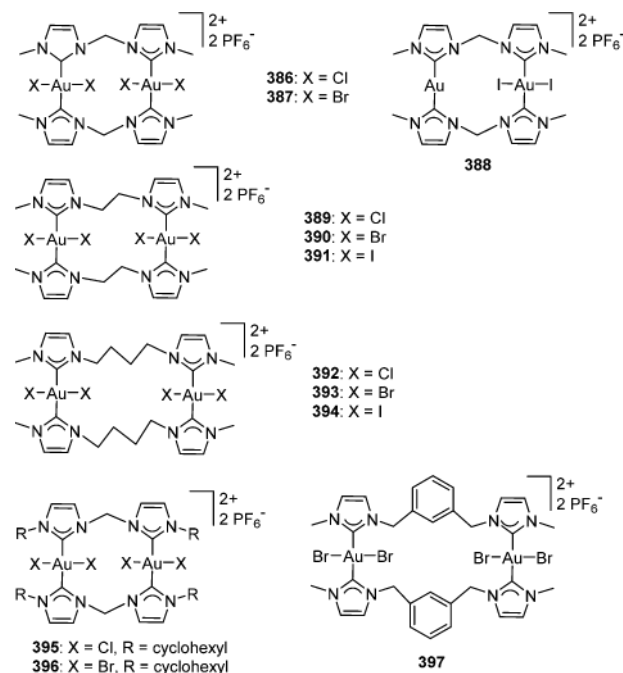


<sup>a</sup>Adapted with permission from ref 98. Copyright 2009 Royal Society of Chemistry.

of the parent gold(I) complexes see Figure 12].<sup>98,168</sup> The oxidative addition reactions were performed by reaction of the gold(I) complexes **157b**, **159b**, **160**, **161c**, **162**, and **189** with an excess of elemental bromine in acetonitrile at room temperature. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra confirm the formation of the gold(III) complexes by exhibiting upfield shifted  $C_{\text{NHC}}$  resonances in the range of  $\delta = 150.0$ – $153.2$  ppm.

Elemental analyses of complexes **380**–**385** suggested that each gold ion was bound to two bromo ligands. X-ray diffraction analyses confirmed this assumption and revealed in addition a square-planar coordination environment of gold(III) in complexes **380** and **384**.<sup>168</sup> Two bromo anions were coordinated in trans-geometry to the gold(III) atoms. The  $C_{\text{NHC}}\text{--Au--}C_{\text{NHC}}$  axes were oriented nearly parallel to each other and nearly perpendicular to the  $\text{Br--Au--Br}$  axes.

Using the oxidative addition protocol and elemental bromine, iodobenzene dichloride, or elemental iodine as oxidants, various oxidized digold(III)-NHC complexes **386**–**397** have been prepared (Figure 28).<sup>244,245</sup> Except for **388** with an gold(III)/gold(I) core, only gold(III)/gold(III) were obtained. However,



**Figure 28. Reaction products obtained by the oxidative addition of halogens to dinuclear gold(I) complexes.**

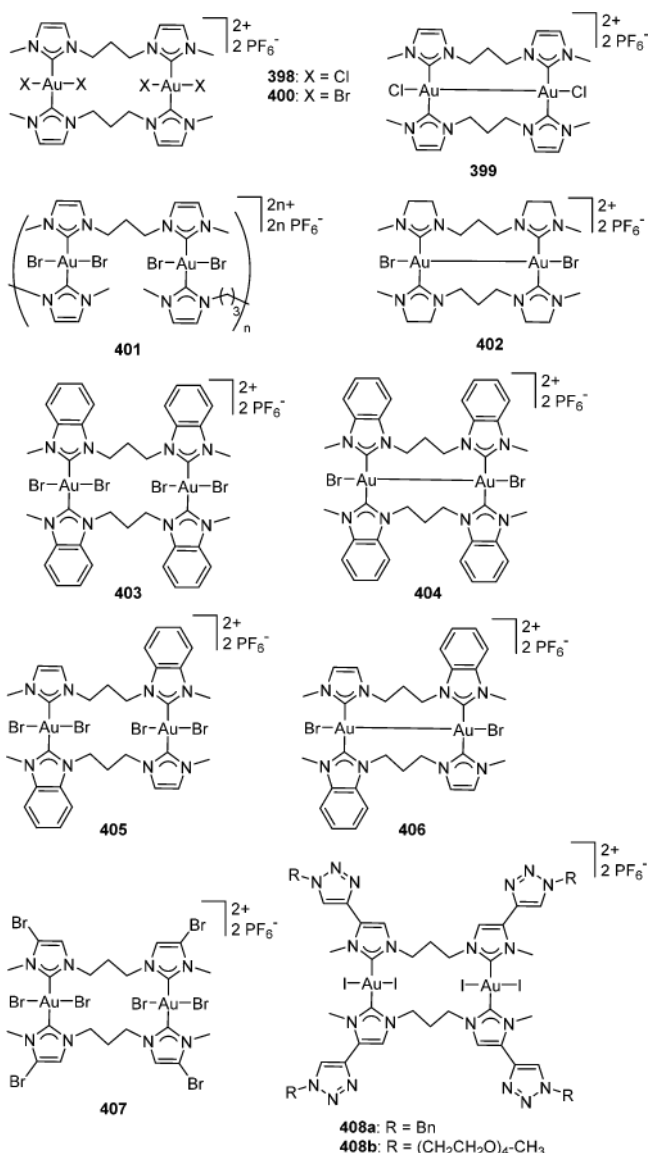
bromine reductive elimination can lead to the mixed valence gold(III)/gold(I) complexes. For complexes featuring a mixed valence gold(III)/gold(I) core, a linear coordination of the gold(I) ion and a square-planar coordination of the gold(III) ion was established by X-ray diffraction analyses.

The outcomes of the oxidative addition for complexes bearing propylene-linked bis-NHC ligands is often complicated, but a few common features could be identified for such cases. Chlorine oxidation resulted in the formation of a mixture of gold(III)/gold(III) (**398**) and gold(II)/gold(II) complexes (**399**) featuring a gold–gold bond (Figure 29).<sup>244</sup> The analogous bromine oxidation, however, led to the gold(III)/gold(III) complex **400** and a polymeric compound **401**.<sup>245</sup> The outcome of the bromine oxidation also varied, depending on the type of NHC ligand used (Figure 29).<sup>156</sup>

From the complex bearing saturated imidazolidin-2-ylidene ligands, a gold(II)/gold(II) complex **402** was obtained. However, a mixture of gold(III)/gold(III) and gold(II)/gold(II) complexes **403** and **404** was formed when gold was coordinated by benzimidazolin-2-ylidene donors. A similar tendency was observed for complexes **405** and **406**, bearing the heterodonor imidazolin-2-ylidene/benzimidazolin-2-ylidene ligands. In case the 5-position of the diaminoheterocycle is substituted with bromide, gold(III)/gold(III) complex **407** was obtained. Iodine oxidation of a complex bearing a triazole-substituted bis-NHC ligand gave the gold(III)/gold(III) complexes **408**.<sup>140</sup>

## 5.2. Photochemical [2 + 2] Cycloaddition Reactions

In general, photochemical [2 + 2] cycloaddition reactions between two olefins will occur when the olefins are arranged in an approximately parallel fashion and are separated by less than 4.2 Å.<sup>246–252</sup> For cases in which the structural requirements are met, a few examples of photochemical [2 + 2] cycloaddition reactions in discrete metallacycles have been described.<sup>253–256</sup> Photochemical [2 + 2] cycloaddition reactions have provided an



**Figure 29.** Products of the oxidative addition to digold(I) complexes bearing propylene linked bis-NHC ligands.

efficient route to postsynthetic modification of selected complexes in the solid state and in solution.<sup>257,258</sup>

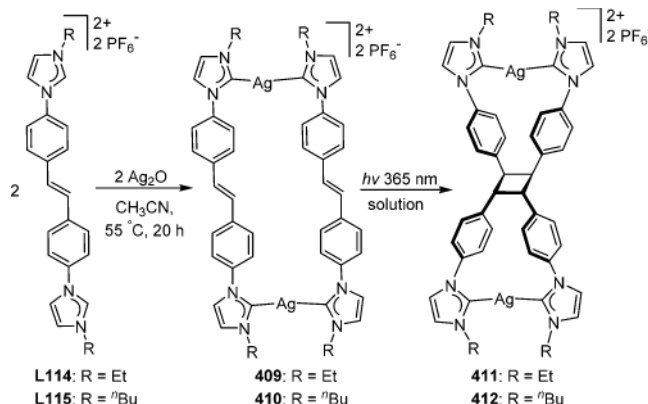
The photochemical [2 + 2] cycloadditions protocol can also be employed for properly substituted metal-NHC complexes, where NHC coordination generates the required geometric features for the cycloaddition to proceed. Selected examples for such postsynthetic modifications of poly-NHC complexes will be discussed in this section.

The application of the [2 + 2] cycloaddition reaction for the postsynthetic modification of poly-NHC-metal assemblies has only been developed recently.<sup>259</sup> As discussed in section 2.1, a useful consequence of the M–C<sub>NHC</sub> bonds in dinuclear molecular rectangles of type [M<sub>2</sub>(bis-NHC)<sub>2</sub>]<sup>2+</sup> [M = silver(I), gold(I)] is to bring the two bis-NHC ligands in close proximity. This provides the opportunity of postassembly modifications of olefin-bridged bis-NHC scaffolds by an intramolecular photochemical [2 + 2] cycloaddition reaction.

The first example for such a postsynthetic photochemical modification of a poly-NHC assembly utilized the dinuclear metallacycles **409** and **410** obtained from bisimidazolium

proligands **L114** and **L115** (Scheme 92).<sup>259</sup> Both metallacycles were characterized by multinuclear NMR spectroscopy and ESI

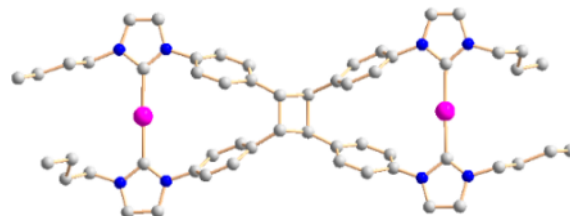
**Scheme 92.** Synthesis of Metallacycles **409** and **410** Followed by Photochemical [2 + 2] Cycloaddition<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 259. Copyright 2013 American Chemical Society.

or MALDI-TOF mass spectrometry. A clear and rapid conversion to the dinuclear *rcctt*-cyclobutane silver complexes **411** or **412** was observed when solutions of **409** or **410** were irradiated with UV light (Hg lamp, λ = 365 nm).

NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) confirmed that the conversion was complete after 2.5 h. In addition, formation of the cyclobutane ring was confirmed by an X-ray diffraction analysis with crystals of **412**, which revealed a four-membered ring featuring typical single bond C–C distances [1.551(3) and 1.583(4) Å] and C–C–C angles only slightly different from 90° (Figure 30).

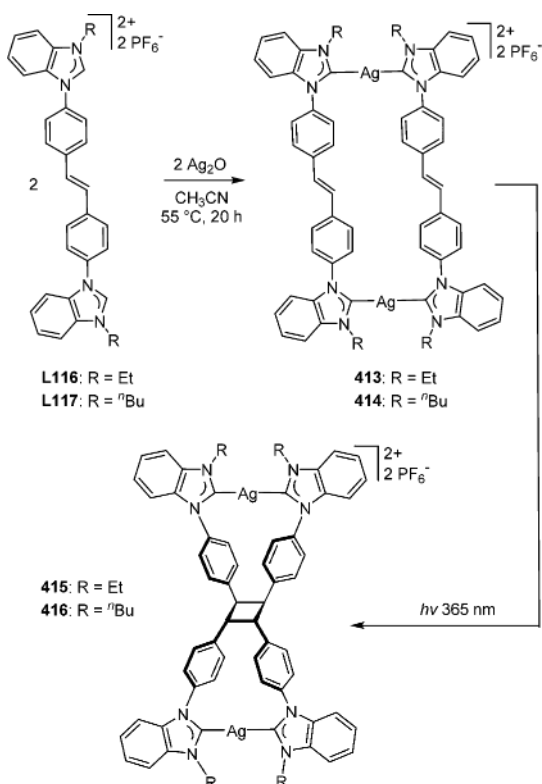


**Figure 30.** Molecular structure of tetrakis-NHC complex **412**. Color code: silver, pink; nitrogen, blue; carbon, gray. Adapted with permission from ref 259. Copyright 2013 American Chemical Society.

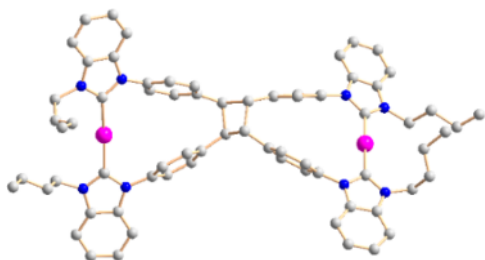
The same strategy can be applied to bisbenzimidazolium starting materials featuring an internal olefin group such as **L116** and **L117**, which cleanly react with Ag<sub>2</sub>O to give the metallacycles **413** and **414** (Scheme 93).<sup>260</sup> The subsequent photochemical [2 + 2] cycloadditions were carried out in degassed *d*<sub>6</sub>-DMSO in a Pyrex tube with UV light (Hg lamp, λ = 365 nm). In each case, the cycloaddition was complete after 30 min, resulting in the formation of the dinuclear silver complexes **415** and **416**, each bearing a tetracarbene-substituted *rcctt*-cyclobutane ligand. Progress of the reaction was monitored by the disappearance of the resonance for the olefin protons and the appearance of the resonance for the cyclobutane protons in the <sup>1</sup>H NMR spectrum.

An X-ray diffraction analysis of the dinuclear complex **416** confirmed the formation of the cyclobutane ring (Figure 31). The cyclobutane formation did not cause any additional strain as

**Scheme 93.** Synthesis of Dinuclear Complexes **415** and **416** by Intramolecular [2 + 2] Cycloaddition<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 260. Copyright 2015 American Chemical Society.



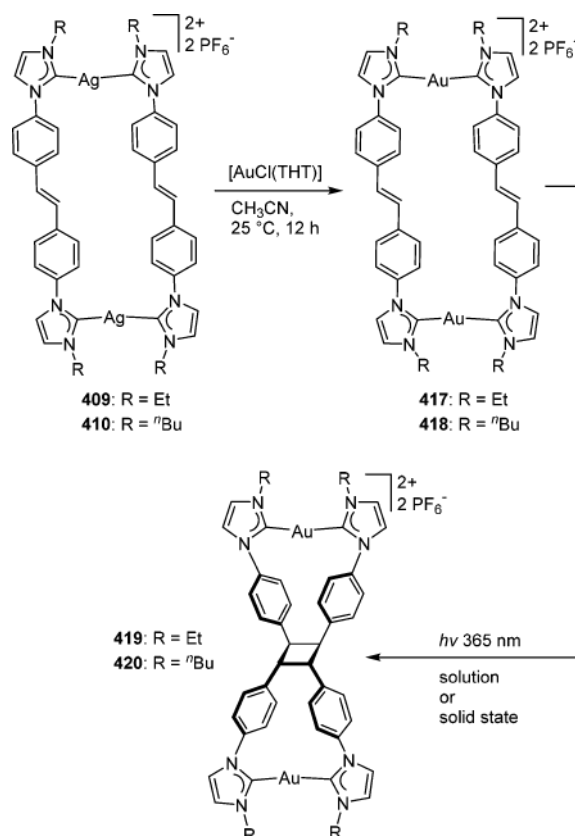
**Figure 31.** Molecular structure of tetrakis-NHC complex **416**. Color code: silver, pink; nitrogen, blue; carbon, gray. Adapted with permission from ref 260. Copyright 2015 American Chemical Society.

judged from the unspectacular M–C<sub>NHC</sub> bond distances [2.080(7) to 2.099(8) Å] and the nearly linear C<sub>NHC</sub>–M–C<sub>NHC</sub> angles [177.1(3) and 177.3(3)°] found for complex **416**.

As expected, the silver(I) complexes **409** and **410** (Scheme 92) as well as **413** and **414** (Scheme 93) are light sensitive and tend to decompose, thereby limiting their suitability for subsequent photochemical reactions. Therefore, the presumably more stable dinuclear gold(I) complexes **417** and **418** were prepared from **409** and **410** using the well-established transmetalation protocol (Scheme 94).<sup>259</sup>

The [2 + 2] cycloaddition with **417** and **418** was investigated both in solution and in the solid state.<sup>259</sup> Both complexes underwent rapid and nearly quantitative [2 + 2] cycloaddition upon irradiation (UV, λ = 365 nm) in CD<sub>3</sub>CN solution giving the dinuclear *rc*tt-cyclobutane gold(I) complexes **419** and **420**. Complexes **419** and **420** can also be obtained from the silver(I) analogs **411** and **412** by transmetalation.

**Scheme 94.** Synthesis of **417** and **418** by Transmetalation and Subsequent [2 + 2] Cycloaddition to give **419** and **420**<sup>a</sup>



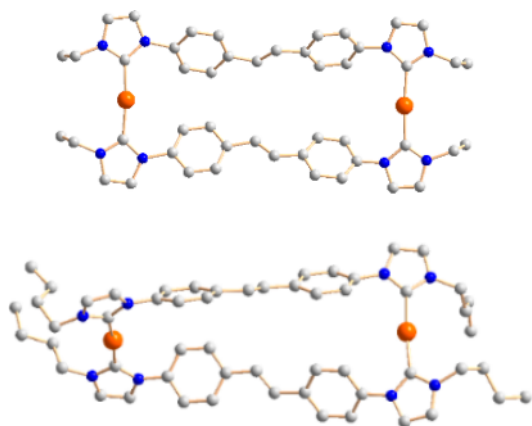
<sup>a</sup>Adapted with permission from ref 259. Copyright 2013 American Chemical Society.

The cycloaddition with gold(I) complexes **419** and **420** proceeded differently in the solid state. Irradiation of powdered solid metallacycle **417** for 12 h gave the *rc*tt-cyclobutane derivative **419** exclusively and with excellent conversion. Contrary to this, irradiation of powdered **418** yielded after 72 h only about 25% of **420** and 75% of unreacted **418** could be recovered. These results suggested that the structures and particularly the orientation of the olefin groups in these two complexes are different in the solid state. Indeed, X-ray diffraction analyses with **417** and **418** revealed that the olefin groups are arranged in a parallel fashion in **417** (enabling the [2 + 2] cycloaddition) but almost orthogonally in **418** (Figure 32), thus explaining the reactivity differences in the [2 + 2] cycloaddition reactions in the solid state.

One attractive feature of the postsynthetic transformation is the possibility to generate novel organic molecules not accessible by standard synthetic routes. A prerequisite for this approach is the possibility to revolve the metal ions after the postsynthetic modification. It was therefore attempted to liberate the tetrakis(benz)imidazolium salts from the cyclobutane-bridged tetracarbene complexes **411**, **412**, **415**, and **416**. The more stable gold(I) complexes (**419** and **420**), although better suited for the postsynthetic modifications, are less suitable for such an approach due to their enhanced stability.

Attempts to remove the metal ions from complexes **411**, **412**, **415**, and **416** by addition of ammonium chloride to solutions of the complexes resulted in the precipitation of silver chloride and

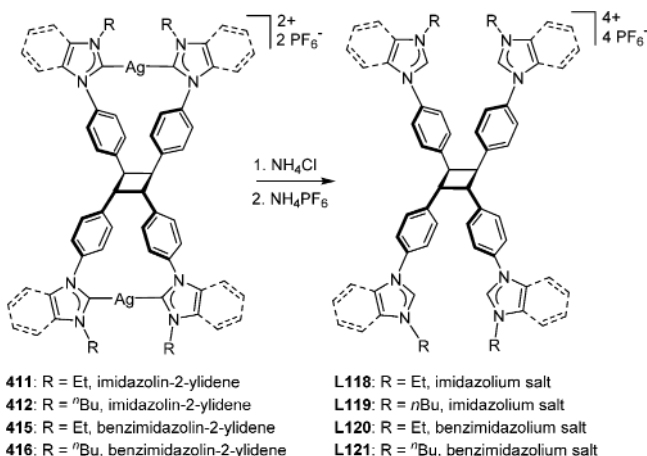




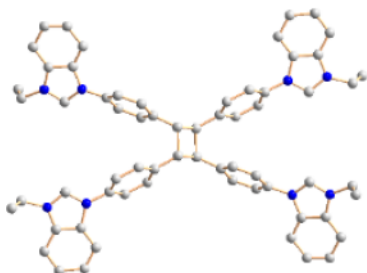
**Figure 32.** Molecular structures of **417** (top) and **418** (bottom). Color code: gold, orange; nitrogen, blue; carbon, gray. Adapted with permission from ref 259. Copyright 2013 American Chemical Society.

isolation the tetrakisimidazolium salts **L118–L119** and the tetrakisbenzimidazolium salts **L120–L121** (Scheme 95).<sup>259,260</sup>

**Scheme 95. Liberation of Tetrakisazolium Salts L118–L121 from Complexes 411, 412, 415, and 416**



The tetrakisazolium salts exhibited characteristic NMR spectra for symmetrical compounds. Apart from the unchanged resonances for the four cyclobutane protons, sharp resonances for the azolium C2–H protons were found in a 1:1 ratio to the cyclobutane protons. An X-ray crystal structure analysis of **L120** (Figure 33) confirmed the release of the tetrakisbenzimidazolium salt with retention of the cyclobutane ring.<sup>260</sup> The

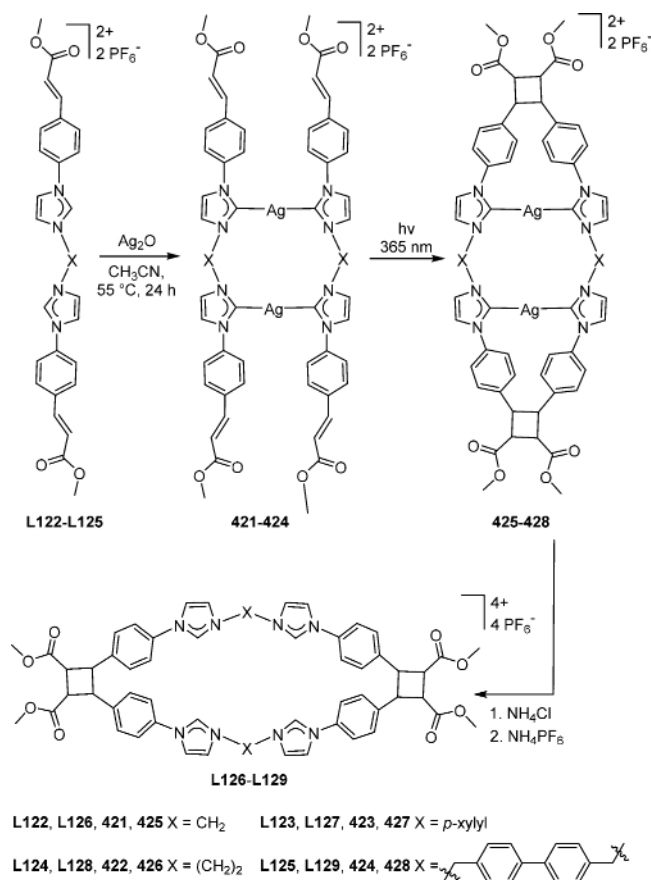


**Figure 33.** Molecular structure of **L120**. Color code: nitrogen, blue; carbon, gray. Adapted with permission from ref 260. Copyright 2015 American Chemical Society.

template/postsynthetic modification strategy outlined above proved also useful for the preparation of large polyazolium cages as potential binding sites for selected anions (*vide infra*).

Formation of cyclobutanes by [2 + 2] cycloaddition between coordinated olefin-functionalized NHC ligands can also be used for the preparation of polyimidazolium- cyclophanes.<sup>261</sup> This strategy involved three individual steps: first, two suitable ligands to yield the cyclophane have to be preorganized at one or more metal centers with the olefin groups arranged in a parallel fashion for subsequent formation of the cyclobutane link; second, photodimerization should give the metal-coordinated macrocycle; and third, the macrocycle must be liberated from the metal complex. This strategy is depicted in Scheme 96.<sup>261</sup>

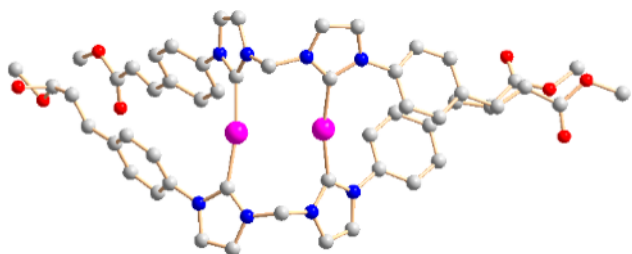
**Scheme 96. Synthesis of Dinuclear Metallacycles 421–424, Reaction Products of the [2 + 2] Cycloadditions 425–428, and Polyimidazolium Salts L126–L129<sup>a</sup>**



<sup>a</sup> Adapted with permission from ref 261. Copyright 2015 Wiley-VCH.

First the dinuclear silver metallacycles **421–424** were prepared in good yield by reacting the four bisimidazolium salts **L122–L125** with Ag<sub>2</sub>O in CH<sub>3</sub>CN. Complexes **421–424** were fully characterized by NMR spectroscopy, indicating formation of the dinuclear tetrakis-NHC metallacycles in all four cases.

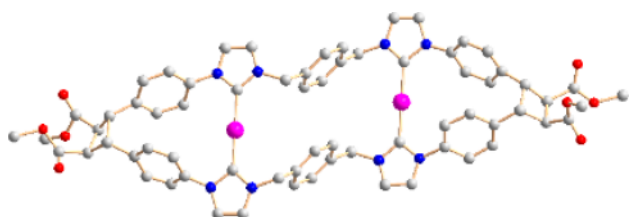
An X-ray structure analysis of **421** provided insight into the molecular parameters of this assembly (Figure 34). The two dicarbene ligands and the two silver atoms form a metallacycle with unspectacular Ag–C<sub>NHC</sub> and C<sub>NHC</sub>–Ag–C<sub>NHC</sub> bond parameters. The four terminal cinnamic ester groups are properly oriented (at least in the solid state) for a subsequent [2 + 2] cycloaddition to give two cyclobutane bridges between the two bis-NHC ligands. The distance between the midpoints



**Figure 34.** Molecular structure of silver(I) complex **421**. Color code: silver, pink; oxygen, red; nitrogen, blue; carbon, gray. Adapted with permission from ref 261. Copyright 2015 Wiley-VCH.

for each pair of cinnamic ester double bonds was determined to be approximately  $\sim 3.6$  Å. This distance is perfectly suitable for an intramolecular  $[2 + 2]$  cycloaddition reaction. It can be assumed that the molecular parameters of **422–424** are similar to those of **421**.

Irradiation of complexes **421–424** (UV,  $\lambda = 365$  nm) in  $\text{CD}_3\text{CN}$  or  $d_6$ -DMSO led to quantitative formation of the macrocyclic cycloaddition products **425–428**, as judged by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The photodimerization of the terminal cinnamic ester groups was found to be complete, and no signals for olefinic groups were observed after the photochemical reaction. Even at low concentration, the photochemical cyclodimerization of the cinnamic esters was efficient and gave nearly quantitative conversion. The photodimerization is highly selective, and no photoisomerization, deconjugation, or cross-cycloaddition reactions between adjacent molecules have been observed. The formation of the two cyclobutane rings on both sides of the complex was confirmed by the X-ray diffraction analysis of **427** (Figure 35).

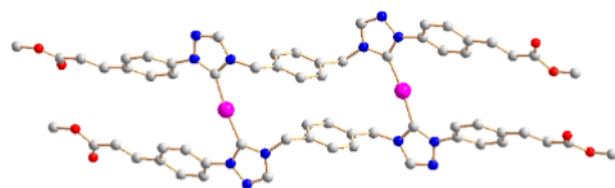


**Figure 35.** Molecular structure of **427**. Color code: silver, pink; oxygen, red; nitrogen, blue; carbon, gray. Adapted with permission from ref 261. Copyright 2015 Wiley-VCH.

Finally, the macrocyclic imidazolium-cyclophanes **L126–L129** of different sizes and shapes have been isolated in good yields after removal of silver ions from the silver-NHC complexes **425–428** (Scheme 96). Preliminary results indicate that these cyclophanes can be utilized for the size-selective detection/encapsulation of various small anions.

Following the same strategy, metallacycles bearing two bis-NHC ligands terminally substituted with cinnamic ester groups but derived from bis(1,2,4-triazolium) salts have been prepared. The molecular structure of one of these (**429**) is shown in Figure 36. Upon irradiation, metallacycles of type **429** also react via  $[2 + 2]$  cycloaddition of two adjacent cinnamic ester groups with formation of two cyclobutane rings. Removal of the metal ions to yield the macrocyclic tetrakis(1,2,4-triazolium) salts was also possible.<sup>262</sup>

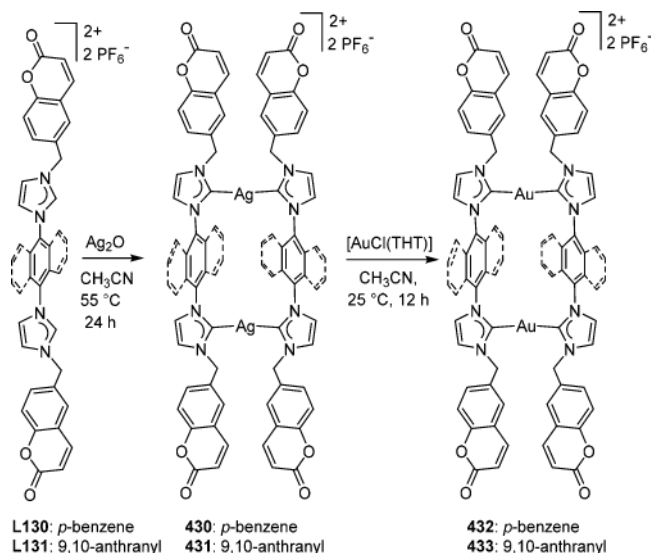
Modifying the linker bridging the NHC donors in bisimidazolium salts as well as changing of the terminal olefin groups for the cycloaddition proved easily possible. For example,



**Figure 36.** Molecular structure of metallacycle **429** obtained from cinnamic acid ester substituted bis(1,2,4-triazolium) salts. Color code: silver, pink; oxygen, red; nitrogen, blue; carbon, gray. Adapted with permission from ref 262. Copyright 2018 Royal Society of Chemistry.

bis-NHC proligands **L130** and **L131** featuring an aromatic linker and coumarin pendants were used to prepare the metallacycles **430** and **431** (Scheme 97).<sup>263</sup> The dinuclear silver(I) complexes react under transmetalation to give the gold(I) complexes **432** and **433**.

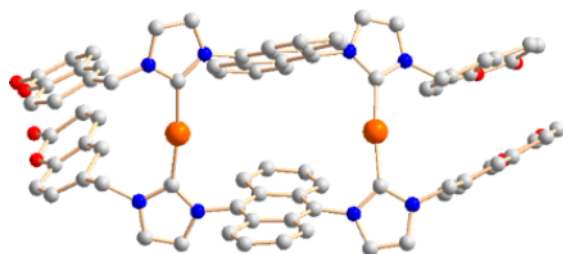
#### Scheme 97. Synthesis of Metallacycles **430** and **431** and Transmetalation to Gold(I) Metallacycles **432** and **433**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 263. Copyright 2015 Wiley-VCH.

An X-ray diffraction analysis of gold(I) complex **433** (Figure 37) showed a dinuclear rectangular cation with four coumarin pendants. The gold atoms were almost linearly coordinated [angles  $\text{C}_{\text{NHC}}\text{--Au--C}_{\text{NHC}}$   $172.8(4)\text{--}173.9(4)^\circ$ ].

Most importantly, the coumarin substituents are arranged in pairs (most likely involving  $\pi$ -stacking interactions) with distances of about 4.2 Å between the midpoints of the olefinic

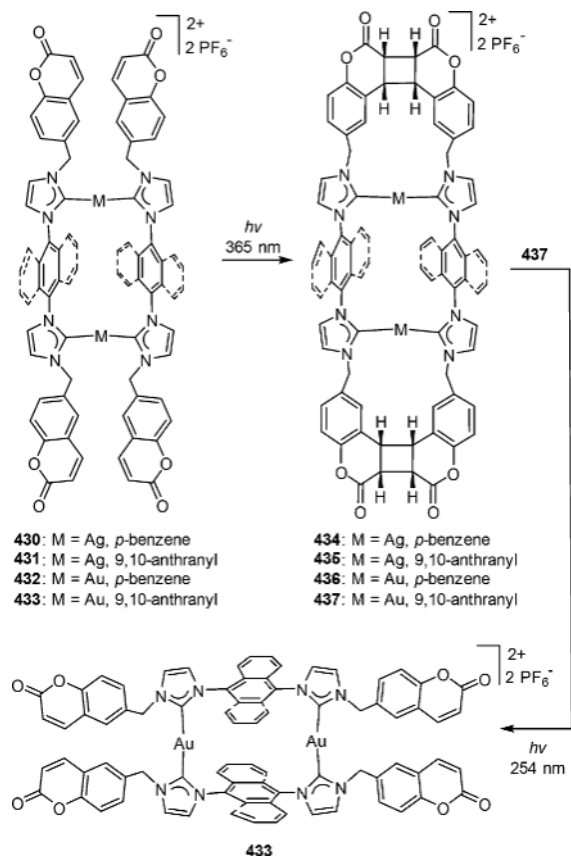


**Figure 37.** Molecular structure of dinuclear metallacycle **433**. Color code: gold, orange; oxygen, red; nitrogen, blue; carbon, gray. Adapted with permission from ref 263. Copyright 2015 Wiley-VCH.

C = C bonds. This arrangement will favor a subsequent syn-head-to-head [2 + 2] cycloaddition reaction.

In fact, exclusive formation of the syn-head-to-head cycloaddition products **434–437** was observed upon irradiation (UV,  $\lambda = 365$  nm) of the dinuclear metallacycles **430–433** in  $d_6$ -DMSO or  $CD_3CN$  as established by  $^1H$  NMR spectroscopy (Scheme 98). MALDI-TOF experiments confirmed that the

**Scheme 98.** Macrocycle Synthesis by [2 + 2] Cycloaddition at Complexes **430–433** to give **434–437** and Photocleavage of **437**<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 263. Copyright 2015 Wiley-VCH.

photodimerization proceeded in an intramolecular fashion, and any intermolecular photodimerization or photoisomerization of the anthracene bridges could be ruled out.

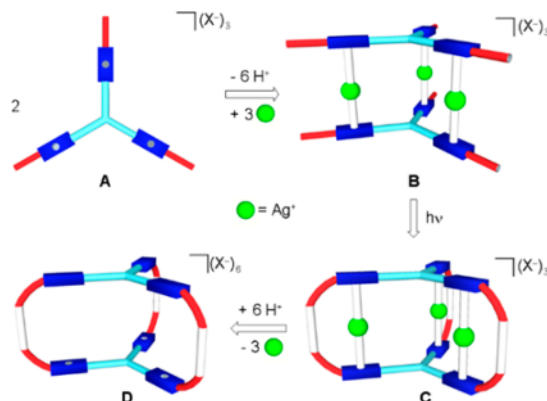
Noteworthy is the observation of a photocleavage reaction which occurred when a solution of **437** was irradiated at  $\lambda = 254$  nm. As a result, complex **433** was formed and identified by the reappearance of the absorption band at  $\lambda = 322$  nm in the UV-vis spectrum caused by the coumarin groups.

While the postsynthetic [2 + 2] cycloaddition to yield macrocycles is possible starting from dinuclear tetrakis-NHC complexes bearing bis-NHC ligands with coumarin pendants, the use of the coumarin groups may be suboptimal due to the instability of the photodimerization product at certain wavelengths. No photocleavage was observed with the cyclobutanes obtained from cinnamic acid ester groups (Scheme 96).

Most rewarding, the [2 + 2] cycloaddition strategy can also be used for the generation of three-dimensional polyimidazolium cage-compounds as a new class of cryptands for the recognition and binding of anions.<sup>264</sup> Such molecules are not easily accessible by conventional organic synthesis and have been

elusive until very recently. A synthetic strategy for the synthesis of hexakisimidazolium cage-compounds by a template-controlled approach is depicted in Scheme 99.

**Scheme 99.** Template-Controlled Polyimidazolium Cage-Closing Strategy<sup>a</sup>



<sup>a</sup>Adapted with permission from ref 264. Copyright 2018 Wiley-VCH.

The synthetic strategy depicted in Scheme 99 involves template metals [silver(I) or gold(I) in green] and trigonal trisimidazolium salts **A** functionalized with terminal olefin groups (red). Triple deprotonation of the trisimidazolium salts **A** and reaction of the resulting tris-NHC ligands with suitable template metals yields trinuclear cylinder-like hexakis-NHC complexes **B**, and various examples for such complexes have been described in this review (Schemes 63–65). Upon formation of the trisilver-hexakis-NHC assembly **B**, the six olefin pendants may arrange in three pairs, which by subsequent irradiation can react in a photochemical [2 + 2] cycloaddition reaction to give the closed-cage complex **C**. Removal of the template metals yields the organic 3D hexakisimidazolium closed-cage cation **D**.

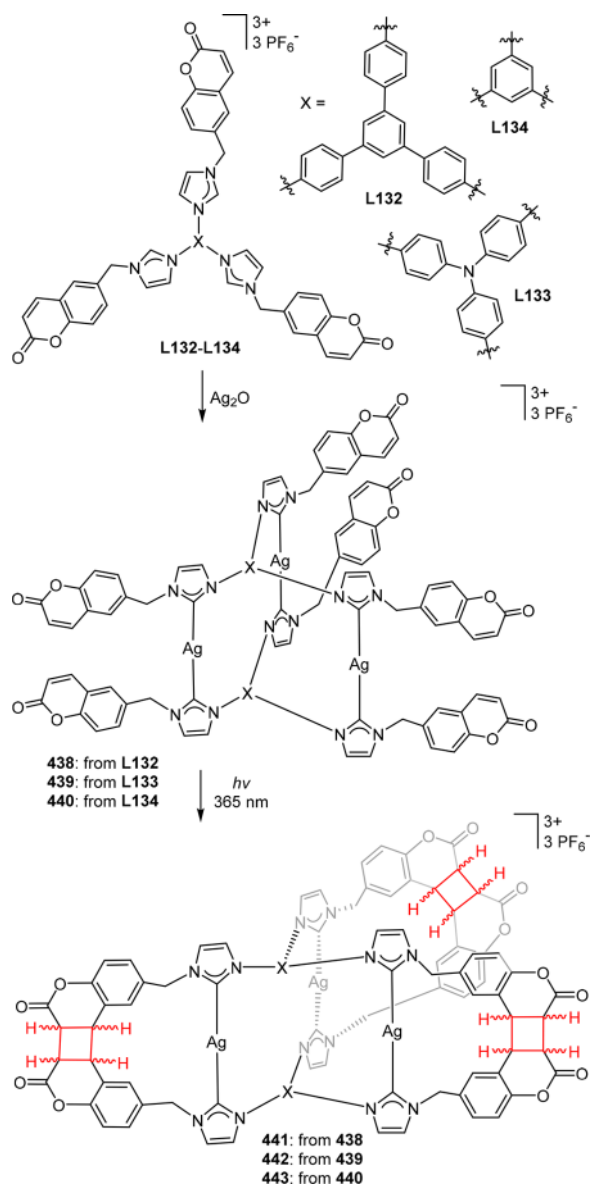
This strategy was initially pursued with the coumarin-functionalized trisimidazolium salts **L132–L134** (Scheme 100).<sup>264</sup> Indeed, the trinuclear hexakis-NHC complexes **438–440** were obtained in good yields from these proligands. The transmetalation to give the homotrinuclear gold(I) complexes (not depicted) was also performed. The trinuclear silver(I) and gold(I) complexes are soluble in polar organic solvents such as acetonitrile and DMSO.

The molecular structure of **439** was determined by X-ray diffraction. The complex cation consists of three silver(I) ions sandwiched in between two trigonal tris-NHC ligands (Figure 38). The coumarin rings are nearly perfectly oriented for a subsequent [2 + 2] cycloaddition.

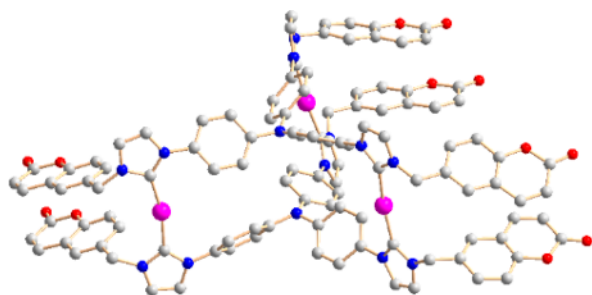
The triple [2 + 2] cycloaddition to form the closed-cage structure was investigated next. Upon irradiation (UV,  $\lambda = 365$  nm), complexes **438–440** react under triple [2 + 2] cycloaddition to give the silver(I) complexes **441–443** bearing a closed-cage hexakis-NHC ligand in nearly quantitative yield.

For example, upon irradiation of a  $CD_3CN$  solution of **439**, the disappearance of the two doublet resonances for the coumarin olefin protons was observed with the concurrent appearance of the typical multiplet resonance at  $\delta$  4.15 ppm for the cyclobutane protons of **442**. UV-vis spectroscopic data also confirm the absence of coumarin groups after irradiation. Cage-formation was also observed upon irradiation of the related gold(I) complexes. Unfortunately, all attempts to liberate the

**Scheme 100. Synthesis of Silver(I) Assemblies 438–440 and [2 + 2] Cycloaddition to Give Closed-Cages 441–443<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 264. Copyright 2018 Wiley-VCH.

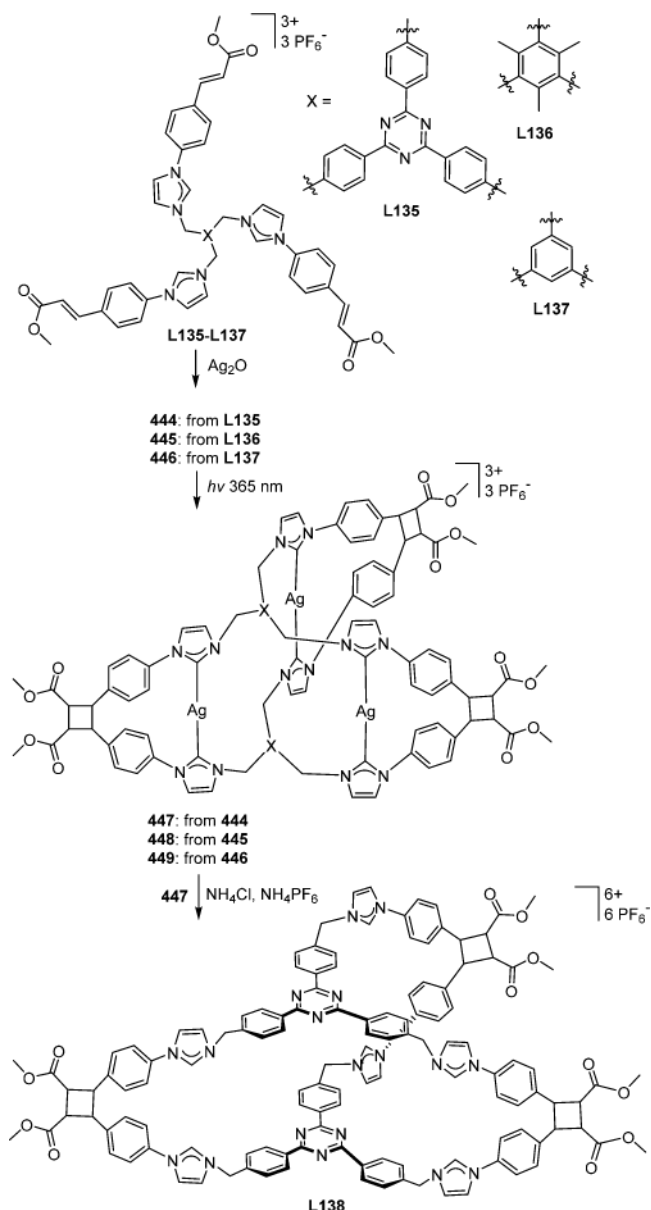


**Figure 38.** Molecular structure of the cylinder-like silver(I) hexakis-NHC assembly 439. Color code: silver, pink; oxygen, red; nitrogen, blue; carbon, gray. Adapted with permission from ref 264. Copyright 2018 Wiley-VCH.

hexakisimidazolium cages only gave product mixtures, most likely due to ring opening of the lactone.<sup>265</sup>

Successful isolation of a three-dimensional hexaimidazolium-cage has been achieved by the same strategy as outlined in Scheme 100 but by using cinnamic acid ester substituted trisimidazolium salts. The cinnamic acid methylester functionalized proligands L135–L137 were reacted with Ag<sub>2</sub>O to give the molecular cylinders 444–446 (Scheme 101). Subsequent

**Scheme 101. Synthesis of Silver Assemblies 444–446, [2 + 2] Cycloaddition to give Closed Cages Complexes 447–449 and Liberation of Hexakisimidazolium Cage–Compound L138<sup>a</sup>**



<sup>a</sup>Adapted with permission from ref 264. Copyright 2018 Wiley-VCH.

irradiation (UV,  $\lambda = 365$  nm) resulted in the cage complexes 447–449 in nearly quantitative yields. The conversion can be easily monitored by <sup>1</sup>H NMR spectroscopy. Addition of ammonium chloride to a solution of 447 followed by anion exchange with NH<sub>4</sub>PF<sub>6</sub> yielded the first example of a 3D hexakisimidazolium-cage compound L138 which was fully characterized by NMR spectroscopic (<sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H–<sup>1</sup>H COSY, HSQC, and HMBC) and ESI-MS measurements.



## 6. POTENTIAL APPLICATIONS OF POLY-NHC METAL ASSEMBLIES

### 6.1. Catalysis

A number of the poly-NHC metal assemblies described in the previous sections have been applied as catalysts for selected transformations. Dicopper(I) metallacycles **225**–**227**, for example, were employed as (pre)catalysts in nitrene and carbene transfer reactions.<sup>81</sup> The hydrosilylation of acetophenone using triethylsilane proceeded in the presence of dicopper(I) complexes **239**–**240**.<sup>185</sup> Apart from these more specific applications, typical copper-catalyzed “click” reactions between phenyl acetylene and phenyl azide were carried out using dicopper(I) complexes **245**–**246** as precatalysts.<sup>187</sup> Trinuclear cage **328** was used as catalyst in Ullman-type arylations between azoles (amides or phenols) and aryl halides.<sup>226</sup>

Dinickel(II) complex **251**<sup>190</sup> and dipalladium(II) complex **267**<sup>196</sup> were employed in the catalytic Suzuki-Miyaura coupling in addition to Kumada-Corriu coupling<sup>190</sup> and Heck cross-coupling reactions.<sup>196,197</sup> Strassner and co-workers used the  $\mu$ -chloro-bridged dipalladium(II) derivative **255** for C–H activation reactions in methane.<sup>192</sup> Later, Peris reported an interesting example of  $\beta$ -alkylation of secondary alcohols with primary alcohols using tetraruthenium rectangle **302** as a catalyst.<sup>214</sup> Various additional applications of polynuclear assemblies in catalysis have been mentioned in the previous sections.

The catalytic application of discrete poly-NHC metal assemblies generally benefit from the presence of multiple metal centers. Such applications, however, are at an early stage of development, and the effect of the multiple metal centers is not yet well understood.<sup>266</sup> Poly-NHCs and their polynuclear metal complexes and metallosupramolecular assemblies have received increasing attention recently. Examples of such applications can be found in organocatalysis,<sup>267</sup> organometallic catalysis,<sup>268</sup> chiral asymmetric catalysis,<sup>269</sup> and cooperative catalysis and activation.<sup>270</sup>

Toward the goals of sustainability and clean energy, the contribution of metal-NHC catalysts is noteworthy. Due to their good  $\sigma$ -donor properties and their ability to stabilize transition metals in high oxidation states, “normal” and “abnormal” NHC donors have been incorporated into carbene-based ruthenium or iridium complexes and these were applied in catalytic H<sub>2</sub>O oxidation processes.<sup>271</sup> One interesting example involves an iridium(I) complex bearing methylene-bridged bis-NHC (derived from proligand **L1**) and its use as a catalyst for water oxidation.<sup>90</sup> In addition to acting as catalysts in photosynthesis, poly-NHC metal complexes have found use as photosensitizers.<sup>66</sup>

One of most important concepts of modern synthesis is “green chemistry”, which aims to minimize hazardous substances, prevent pollution, and reduce the consumption of nonrenewable resources.<sup>272,273</sup> As the “greenest” and most abundant of all solvents, utilization of water as a reaction medium in chemical conversion is highly desirable when considering cost and environmental aspects.<sup>274</sup> In pioneering work carried out by Peris and co-workers, water-soluble bis-NHC chelated metal complexes were applied in the photodriven hydrogenation of CO<sub>2</sub>.<sup>275–277</sup> Various water-soluble NHC complexes have been reported, and examples of water-soluble polynuclear assemblies are **23**–**26**,<sup>94–98</sup> **136**–**137**,<sup>94</sup> **153**–**154**,<sup>94,95</sup> and **157**–**162**.<sup>95,98,168</sup> The design of multifunctional

poly-NHC-metal catalysts and their application in aqueous-phase reactions is an exciting challenge for the future.<sup>278,59</sup>

When considering the cost of homogeneous organometallic complexes, as well as the environmental issues related to their separation and recovery in industrial processes, the heterogenization of homogeneous NHC-metal catalysts is also of great interest.<sup>279,280</sup> Metal–organic frameworks (MOFs), with defined structures and isolated catalytic sites,<sup>281,282</sup> have been employed as carriers for the heterogenization of NHC-metal catalysts.<sup>283–297</sup> In addition, a number of examples of coordination polymers with pendant poly-NHC units have been described.<sup>298,299</sup>

Alternatively, poly-NHC ligands can directly function as bridging ligands to generate coordination polymers. In pioneering work, Bielawski and co-workers employed bidentate benzobis-NHC building blocks for the generation of such materials.<sup>300–303</sup> Inspired by these early studies, various bis-,<sup>304–309</sup> tris-,<sup>310,311</sup> and tetrakis-NHC building blocks were incorporated into coordination polymers.<sup>312</sup> Taking advantage of their hydrothermal stability and chemical robustness, porous organic poly-NHC- and poly azolium-polymers, as well as the metalated derivatives obtained therefrom, have been developed and applied in catalysis.<sup>313–324</sup> An efficient synthetic route to bifunctional polymeric heterometallic catalysts derived from mononuclear NHC building blocks has also been described.<sup>325</sup>

### 6.2. Pharmaceutical Applications

Utilization of poly-NHC organometallics as potential antibiotics and antitumoral drugs constitutes another promising application.<sup>326–332</sup> The long history of silver-based medicines and antibacterial agents encouraged the development of NHC-based silver(I) complexes and their application in biological activity studies.<sup>329,330</sup>

In medicinal chemistry, NHCs have mostly been utilized as carrier molecules for silver(I) and other transition metals. Specifically, silver(I)-NHCs have been investigated as potent antibacterial agents and chemotherapeutics. They have shown activity against a wide range of both Gram-positive and Gram-negative bacterial strains. In addition, selected silver(I)-NHC compounds exhibit remarkable efficacy as antitumor agents with comparable or better activity than classical chemotherapeutics such as cisplatin or 5-fluorouracil.

As indicated in the previous sections, selected disilver(I) complexes exhibited high cytotoxicity against human immortalized myelogenous leukemia cell lines K562, when compared to standard drug 5-fluorouracil (IC<sub>50</sub> = 35.9  $\mu$ M).<sup>85</sup> Other silver(I) assemblies proved active against the breast cancer cell line MCF-7.<sup>86,107</sup> Willans and co-workers found enhanced cytotoxicity of complexes **37** (IC<sub>50</sub> = 7.9  $\pm$  0.9  $\mu$ M), **38** (IC<sub>50</sub> = 5.4  $\pm$  0.4  $\mu$ M), and salt **34** with the Br<sup>−</sup> anion (IC<sub>50</sub> = 4.1  $\pm$  0.6  $\mu$ M) or the BF<sub>4</sub><sup>−</sup> anion (IC<sub>50</sub> = 4.6  $\pm$  0.3  $\mu$ M) toward colon adenocarcinoma cell line DLD1, which is comparable to that of the standard drug cisplatin (IC<sub>50</sub> = 2.4  $\pm$  1.0  $\mu$ M).<sup>107</sup> The antibiotic activity of disilver(I) complexes **32**,<sup>104</sup> **36**,<sup>104</sup> **39**–**41**,<sup>108</sup> **42**,<sup>109</sup> and **92** has also been evaluated.<sup>132</sup> It is worth noting that disilver(I) metallacycle **72** showed remarkable inhibition of HIV-1 via a presumed interaction with its envelope proteins.<sup>124</sup> In addition, the inhibitory effects of water-soluble digold(I) complex **153** on thioredoxin reductase TrxR and glutathione reductase GR were investigated.<sup>166</sup>

While silver(I)-NHC compounds have shown particular promise in medical applications, their clinical use has not yet

been achieved and thus constitutes another goal of contemporary research into these complexes.

### 6.3. Photophysical and Host–Guest Chemistry

In modern supramolecular chemistry, host–guest inclusion compounds represent one of the most important aspects. However, only very few examples of host–guest interactions involving poly-NHC-metal assemblies have been reported. Selected metallamacrocycles such as **47** have been shown to encapsulate *p*-phenylenediamine.<sup>113</sup> Calix[*n*]arene-type compounds **52**, **59**, and **60** are able to incorporate C<sub>60</sub> or C<sub>70</sub> into their cavity.<sup>116,117</sup> The tubular-shaped organometallic assembly **353** (“pillarplex”) constitutes another interesting example of a molecular host which can be transformed into a [2]rotaxane (**356**).<sup>235,236</sup>

The cage-like hexakisimidazolium salt **L138**<sup>264</sup> obtained from the cylinder-type trinuclear hexacarbene complex **447** by demetalation represents another example of the successful application of poly-NHC metal assemblies.<sup>264</sup> The metal-template-controlled synthesis giving **L138** is rather flexible and should allow the construction of additional polycationic cages with potential applications in anion recognition and binding.

An interesting example of an emissive compound has been described recently, based on a failed attempt to generate a tetranuclear poly-NHC assembly.<sup>333</sup> Tetraphenylethylene decorated with four imidazolium groups at the para-positions of the aromatic rings does not react with Ag<sub>2</sub>O to give the tetranuclear octacarbene assembly similar to **334–335** (Scheme 72), but instead the dinuclear complex where two NHC donors linked to different carbon atoms of the tetraphenylethylene coordinate to one silver atom. Transmetalation yields the dinuclear gold(I) complex. While the tetrakisimidazolium salt is nonemissive in solution, the tetraphenylethylene backbone becomes rigidified upon complex formation, leading to a highly emissive compound even in dilute solution. This rigidification by complex formation constitutes an interesting alternative to the known aggregation-induced emission (AIE), known for tetraphenylethylene derivatives.

## 7. SUMMARY AND OUTLOOK

Over the past 20 years, the preparation of poly-NHC ligands and their use for the preparation of polynuclear NHC-metal assemblies has received increasing attention. This development is reflected in this review, where various examples of poly-NHC-metal assemblies with well-defined shapes and geometries have been discussed. These include simple two-dimensional metal-lacyclic rectangles/squares and metalloprisms/cylinders.

Currently, the two major trends in poly-NHC-metal assemblies are (i) the use of such assemblies as hosts for selected substrates, polynuclear catalysts, and carriers for selected metal atoms for medical applications, and (ii) the construction of new discrete assemblies with well-defined structures by coordination-driven self-assembly. Both of these research areas are being actively investigated by various research groups.

The catalytic application of poly-NHC-metal assemblies is emerging as an important field of research. The presence of multiple metal centers in such assemblies may give rise to applications in cooperative catalysis in the future. Additional functional groups can also be installed.

The further extension of NHC-based organometallics to the field of antibiotics and anticancer drugs is another promising

area of future work. In addition to broadening the range of novel NHC compounds, it is essential to enhance their biospecific accumulation and ability to discriminate between specific cell lines. Their mechanisms of action need to be studied in greater detail to ensure safety for clinical applications. Effective chemotherapeutic agents may emerge from NHC-based organometallics in the future.

While preliminary investigations into the host–guest chemistry of poly-NHC-metal assemblies hint at their potential application in this area, most three-dimensional assemblies lack the required geometrical properties due to their small inner cavities. The design and construction of new poly-NHC-metal assemblies with nanosized internal cavities remains a challenge. Such assemblies might also contain chemically active sites, thus improving their usefulness as hosts for the encapsulation and chemical transformation of selected substrates.

The template-controlled generation of 2D macrocyclic and 3D cage-like polyimidazolium cations by [2 + 2] cycloaddition reactions constitutes a first step toward new hosts for the recognition and selective encapsulation of anions. The first examples of polyimidazolium compounds featuring large internal cavities have emerged<sup>264</sup> only recently and promise exciting developments in this area in the future.

Recent research has also shown that poly-NHC-metal assemblies, particularly those featuring labile C<sub>NHC</sub>–Ag bonds, are capable of self-assembly and self-sorting,<sup>72,221</sup> analogous to assemblies obtained from Werner-type ligands and metal ions.<sup>334</sup> This observation promises to lead to new poly-NHC-metal assemblies with differing sizes and shapes, which will find multiple applications in the future.

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### Notes

The authors declare no competing financial interest.

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Le Zhang was born in 1993 in Shaanxi province, China. In 2016, he received his B.S. degree from Yan'an University (China). Afterward, he joined the group of Prof. Ying-Feng Han at Northwest University in Xi'an (China), and he is pursuing a M.S. degree. His research interests are in the synthesis and postsynthetic modification of poly-NHC metal structures.

Yao-Yu Wang is the Shaanxi Three Qin Scholar Chair Professor at College of Chemistry and Materials Science, Northwest University (China). He was engaged in his postdoctoral work at Xi'an Institute of Optics and Precision Mechanics of CAS and worked as a senior visiting scholar at National Taiwan University. His research interests mainly focus on functional coordination chemistry, crystal engineering, and materials chemistry.

F. Ekkehardt Hahn was born in 1955 in Jena, Germany. He studied chemistry at the Technische Universität Berlin and the University of Oklahoma (M.S. 1982). He graduated with a Dr. rer. nat. degree from the Technische Universität Berlin in 1985. After a postdoctoral stay with Prof. Raymond at UC Berkeley (1985–1988), he completed the Habilitation in 1990 and became Associate Professor at the Freie Universität Berlin (1992–1998) before moving in 1998 to a position as Chair of Inorganic Chemistry at the University of Münster. His research is centered on the chemistry of N-heterocyclic carbenes and isocyanide ligands. He has been appointed Senior Editor of Chemistry Letters in 2014. Since 2004, he acts as Permanent Secretary of the International Conference of Organometallic Chemistry (ICOMC).

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## ABBREVIATIONS

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
Bn	benzyl
<sup>n</sup> Bu	butyl
<sup>t</sup> Bu	tert-butyl
COD	1,5-cyclooctadiene
COSY	correlation spectroscopy

Cp*	pentamethylcyclopentadiene
CSI-MS	cold-spray ionization mass spectrometry
CuAAC	copper(I)-catalyzed azide alkyne cycloaddition
DCM	dichloromethane
DFT	density functional theory
Dipp	2,6-diisopropyl phenyl
DLS	dynamic light scattering
DME	dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
ESI-MS	electrospray ionization-mass spectrometry
Et	ethyl
FAB-MS	fast atom bombardment-mass spectrometry
FT-ICR MS	Fourier transform-ion cyclotron resonance mass spectrometry
HMBC	heteronuclear multiple-bond correlation spectroscopy
HSQC	heteronuclear single-quantum correlation spectroscopy
Me	methyl
Mes	mesityl
MIC	mesoionic carbenes
MOF	metal-organic frameworks
MS	mass spectrometry
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
OTf	triflate
OTs	tosylate
PAM	postassembly modification
Ph	phenyl
<sup>i</sup> Pr	iso-propyl
<sup>n</sup> Pr	propyl
rt	room temperature
SEM	scanning electron microscopy
PSM	postsynthetic modification
TEM	transmission electron microscopy
THF	tetrahydrofuran
THT	tetrahydrothiophene
TOF-MS	time-of-flight mass spectrometry
TON	turnover number

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