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Review

Organometallic mechanically interlocked molecules featuring N-heterocyclic carbene ligands: Recent advances in synthesis and applications

Yi Li, Ye Lu*, Shi-Ping Yang

The Education Ministry Key Lab of Resource Chemistry, Shanghai Frontiers Science Center of Biomimetic Catalysis, College of Chemistry and Materials Science, Shanghai Normal University, No. 100 Guiling Road, Shanghai, 200234, PR China

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ABSTRACT

Coordination-directed synthesis has emerged as an effective and versatile approach for constructing mechanically interlocked molecules (MIMs). This field has long been dominated by Werner-type complexes featuring oxygen and/or nitrogen donors, whereas assemblies incorporating N-heterocyclic carbene (NHC) donors remain underexplored. This review provides a comprehensive overview of the rapidly developing field of MIMs constructed from poly-NHC-based building blocks. By highlighting representative recent examples, this review focuses on the pivotal role of NHC ligands and the robustness of metal-C_{NHC} bond in the construction of metallosupramolecular interlocked structures. In addition, it summarizes contemporary strategies for achieving efficient assembly, analyzes defining structural attributes of the resulting architectures, and outlines current challenges and emerging opportunities for future developments in NHC-based MIMs.

1. Introduction

Since the conception of chemical topology, the study of mechanically interlocked molecules (MIMs) has grown from an academic curiosity into a flourishing field of synthetic chemistry [1,2]. Among various strategies developed, coordination-directed synthesis has emerged as a highly effective and versatile methodology for the construction of these architectures [3–6]. Initially, metal ions were employed as templates to orchestrate the assembly of molecular components [7,8]. In a seminal contribution, Sauvage and co-workers pioneered a metal-templated approach for the synthesis of [2]catenane [9–11]. This strategy leverages metal ions to guide chelating ligands into an entwined, pre-organized intermediate, which is then topologically locked by a final ring-closing reaction [12]. This approach not only provided a practical, high-yield route to catenanes but also demonstrated the feasibility of constructing more complex, higher-order entangled topologies [13–17]. In an alternative strategy, metal ions are incorporated directly into the structural backbones of the interlocked components [18]. The key advantages of this strategy lie in the reversibility of coordination bonds and the influence of weak noncovalent interactions, which facilitate spontaneous error correction under thermodynamic control [19,20]. This self-correction mechanism often results in high yields and the formation of products with greater topological complexity [21,22]. The continued development of these synthetic approaches has enabled the construction of a diverse array of intricate metallosupramolecular systems, including molecular links (catenanes) [23–29], rotaxanes [30], and knots [31–33]. Numerous excellent reviews have also been published, providing further insight into various areas of interlocked architecture chemistry [34–39]. Notably, this field is dominated by Werner-type coordination complexes featuring oxygen and/or nitrogen donors, such as carboxylic acid donors and pyridyl-functionalized organic linkers, whereas assemblies bearing carbon-donor ligands remain rare [22].

Over the past two decades, polydentate ligands featuring C-donor atoms, particularly poly-N-heterocyclic carbenes (poly-NHCs), have become powerful building blocks for a rapidly expanding library of metallosupramolecular architectures with diverse and well-defined topologies [40–44]. Owing to the strong σ-donating character of N-heterocyclic carbene (NHC) ligands, the coordination bonds they form with transition metals are substantially more robust than those involving conventional Werner-type ligands [45–48]. This enhanced stability, coupled with their well-defined structural features, has rendered these

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* Corresponding author. College of Chemistry and Materials Science, Shanghai Normal University, No. 100 Guiling Road, Shanghai, 200234, PR China.
E-mail address: yelu@shnu.edu.cn (Y. Lu).

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M−C_{NHC} based assemblies highly valuable for applications in catalysis [49–52], luminescence [53–56] and host-guest chemistry [57–60]. The significant progress in this field has been documented in some excellent reviews [61,62], with a recent account from Han and co-workers, highlighting their extensive work on the synthesis of such assemblies [63].

Building upon this established methodology, the use of NHC ligands for MIM synthesis has very recently become a prominent research hotspot, bridging the fields of poly-NHC-based metallosupramolecular chemistry and the broader domain of MIMs [64]. The incorporation of M−C_{NHC} bonds into these systems not only retains the convenience of coordination-driven self-assembly but also enhances the stability of the coordination bond and resulting in interlocked architectures [65,66]. Furthermore, the strategic placement of various substituents on the poly-NHC ligands is crucial for the successful formation of these interlocked structures. These substituents fulfill several distinct roles: i) N-alkyl groups provide essential steric protection for the reactive carbene center, ensuring the formation of stable M−C_{NHC} bonds [67]. ii) Bulky groups on the ligand backbone, such as those on adjacent aromatic rings, can act as steric barriers that direct the assembly towards an interlocked topology and prevent disassembly [68,69]. iii) these groups introduce solvophobic interactions to the systems, which help guide self-assembly in polar solvents and enhance the stability of the final architecture [70,71]. The unique combination of these features has spurred significant progress in a short period.

In this review, we provide a comprehensive overview of the synthetic strategies for constructing MIMs from poly-NHC-based building blocks. It highlights the pivotal role of NHC ligands and the robust M−C_{NHC} bonds in the construction of metallosupramolecular interlocked structures. Beyond synthesis, the characterization and potential applications of representative examples will also be detailed. The main body of this manuscript is organized into three sections according to the metal ions employed: (i) MIMs based on Ag(I)/Au(I)−NHC complexes, (ii) MIMs based on Ni(II)−NHC complexes, (iii) MIMs based on Ir(I)−NHC complexes. Through this structured presentation, we hope to provide a valuable reference for researchers and stimulate new thinking in this rapidly evolving field.

2. MIMs based on Ag(I)/Au(I)−NHC complexes

Ag(I)−NHC complexes are widely employed in coordination-driven self-assembly, owing to their facile synthesis and notable tolerance to air and moisture [72]. A key factor driving this application is the linear, two-coordinate preference of Ag(I) and Au(I), which is crucial for forming cyclic and chain-like structures from di-NHC ligands. These same features have also made them attractive precursors for constructing NHC-based MIMs. The Ag–C_{NHC} bond can dissociate and recover under thermodynamic control. This reversibility enables thermodynamic error correction during the self-assembly process, thereby driving the high-yield formation of the desired interlocked structures [73,74]. Beyond this utility in self-assembly, Ag(I) assemblies are good starting materials for transmetalation reactions of NHC ligands, which can be performed under rather mild conditions [75–77].

Ag_2O is an excellent Ag(I) source for the high-yield, one-pot synthesis of Ag(I)–NHC complexes. This *in situ* approach simplifies the procedure by avoiding the pre-synthesis of unstable free carbenes, with water as the sole, non-interfering byproduct. Subsequent transmetalation to the corresponding Au(I) complexes is achieved using [AuCl(THT)]. As the tetrahydrothiophene (THT) departs as a neutral ligand, this step cleanly affords the gold complex without introducing extraneous ions or causing side reactions.

In 2021, Han et al. reported a series of triply interlocked organometallic cages assembled from tris-NHC ligands and Ag(I)/Au(I) ions (Fig. 1) [64]. Three tris-NHC ligands with different substituent groups, designated **NL-A** (NL = NHC ligand, A = 1–3), were constructed from a central triazine unit and three imidazo[1,5-a]pyridine moieties. This structural motif was chosen to optimize π-stacking distances while minimizing steric hindrance. Driven by these favorable preorganized interactions, the triply interlocked cages **A-Ag^{I}** (A = 1–3) were formed via the Ag_2O route in high yields (80–92%), which were confirmed by NMR, ESI-MS and single-crystal X-ray crystallography. The structure is stabilized by significant π···π interactions, evidenced by four triazine rings stacked at short interplanar distances of 3.2–3.4 Å (Fig. 1). Notably, the corresponding triply interlocked cages **A-Au^{I}** (A = 1–3) could be subsequently obtained via transmetalation by stirring an

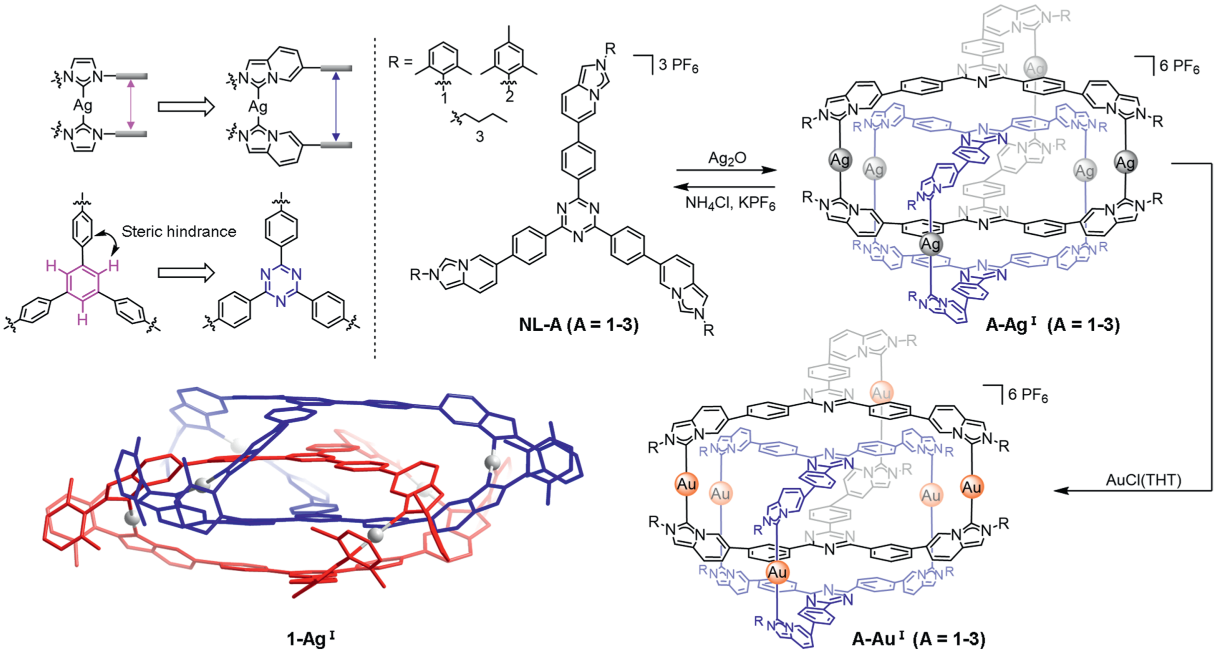

Fig. 1. Synthesis of Ag(I)−NHC-based triply interlocked organometallic cages **A-Ag^{I}** (A = 1–3).

acetonitrile solution of the Ag(I)-based analogues with six equivalents of [AuCl(THT)]. Both the Ag(I)- and Au(I)-based triply interlocked cages displayed considerable stability in solution; they did not decompose in solvents such as DMSO and nitromethane, nor did the addition of aromatic guests induce their dissociation. However, the Ag^I systems selectively disassembled upon addition of chloride salts due to the precipitation of AgCl.

This self-assembly strategy was further extended to construct an organometallic Ag(I)/Au(I)−NHC [2]catenanes from a pyrene-bridged di-NHC ligand (**NL-4**), which was designed to promote strong π···π stacking interactions (Fig. 2) [71]. The reaction of ligand **NL-4** with Ag_2O in acetonitrile led to the [2]catenane **4-Ag^I** in quantitative yield. The [2]catenane structure was unequivocally established by NMR, ESI-MS, and single-crystal X-ray crystallography. The crystallographic analysis revealed favorable stacking of all four pyrene units at intermolecular distances of 3.5–3.6 Å, providing direct evidence for the guiding role of π···π interactions. The self-assembly process demonstrated a pronounced sensitivity to both solvent polarity and concentration, governed by solvophobic effects. In acetonitrile, strong π-π interactions among the four pyrene rings effectively drove the formation of [2]catenane **4-Ag^I** in excellent yield. However, changing the reaction solvent to dimethylformamide (DMF) led to the isolation of the corresponding metallacycle **5-Ag^I** as the sole product. Similarly, dilution of the acetonitrile solution also induced the transformation of [2]catenane **4-Ag^I** into the metallacycle **5-Ag^I**. Thus, the formation of interlocked structure can be attributed to the combined effect of the strong π-π interaction driving force from the pyrene groups and the auxiliary stabilization from solvophobic effect. In contrast to its Ag(I) analog, the gold [2]catenane **4-Au^I**, generated via transmetalation, is highly stable. It does not readily decompose upon dilution or in DMF, unlike **4-Ag^I**, which possesses reversible Ag–C_{NHC} bonds. Interestingly, when the transmetalation reaction is performed in DMF, both silver [2]catenane **4-Ag^I** and metallacycle compound **5-Ag^I** converge to form the gold metallacycle compound **5-Au^I** as the sole product.

When the pyrene bridges were replaced with fluorenone groups (in the di-NHC ligand **NL-5**), a similar Ag(I)−NHC [2]catenane, **6-Ag^I** was formed (Fig. 3) [78]. Compared to the previous pyrene-based [2]catenane **4-Ag^I**, **6-Ag^I** exhibited better stability in acetonitrile solution, with its interlocked structure proving resistant to dilution. However, the less polar solvent DMF could still induce the transformation of [2]catenane **6-Ag^I** into the corresponding metallamacrocycle **7-Ag^I**. This observation again highlights that π-π stacking interactions and solvent polarity serve as key parameters for controlling the stability and reversible interconversion of these assembled structures. Interestingly, the dibenzo [b,d]thiophene-bridged ligand **NL-6** exclusively yielded the dinuclear metallamacrocycle **8-Ag^I** under the same conditions, attributed to putative intramolecular S···S interactions.

The utility of such NHC-metal assemblies has also been extended to the formation of soft materials. Han and co-workers prepared a Au(I)−NHC cage bearing multiple dibenzo-24-crown-8 units [79]. They reported that upon addition of a bisammonium salt as a cross-linker, the mixture formed a gel, presumably through host-guest interactions between the crown ether and ammonium moieties.

In 2021, Peris et al. reported a novel MIM called "clippane," formed by self-aggregation of two metallotweezers composed of Au(I)−NHC arms and a pyridine-centered pentacyclic linker (Fig. 4) [68]. The metallotweezers were synthesized by reacting pyrene-imidazolylidene Au(I)–NHC complexes (**9** or **10-Au^I**) with the bis-alkynyl pyridine-centere pentacyclic spacer **L-1** (L = ligand) in methanol. The only difference between **9** and **10-Au^I** is the substituent group: **10-Au^I** has two *tert*-butyl groups on the pyrene group, whereas **9-Au^I** does not. The reaction yielded metallotweezers **11** and **12-Au^I**, which dimerized via self-aggregation to give **13** and **14-Au^I**. The significant steric bulk of *tert*-butyl groups rendered the dimerized metallotweezer **14-Au^I** mechanically interlocked.

Consequently, the monomeric **12-Au^I** and dimerized **14-Au^I** could be separated by column chromatography and obtained in their pure forms. In contrast, **11-Au^I** and **13-A^I** gave an inseparable mixture because these two species are in equilibrium. Single-crystal X-ray diffraction confirmed the mechanically interlocked nature of **14-Au^I**, showing that the *tert*-butyl groups acted as steric barriers preventing dissociation (Fig. 4). This study demonstrates a clear strategy for converting a reversible supramolecular assembly into a stable, MIM through the introduction of bulky substituents. The resulting "clippane" thus represents a novel addition to the family of MIMs.

The principle of steric barriers was further applied to the preparation of suitanes (Fig. 5) [69]. In 2023, the same research group reported a pseudo-suitane, **G-1@16-Au^I**, where a guest molecule is physically locked within a metallobox. The host, **16-Au^I**, is a tetra-Au(I) metallobox constructed from bis-Au(I)-NHC precursor **15-Au^I** and carbazolyl-bis-alkynyl linker **L-2**. The guest, **G-1**, is a pyrene molecule functionalized with four long, flexible octynyl "limbs". This host-guest complex was formed in a one-pot reaction, where the precursor **15-Au^I** and linker **L-2** self-assembled around guest **G-1** as a template. Single-crystal X-ray diffraction analysis revealed that the pyrene core of the guest is perfectly sandwiched between the two pyrene platforms of

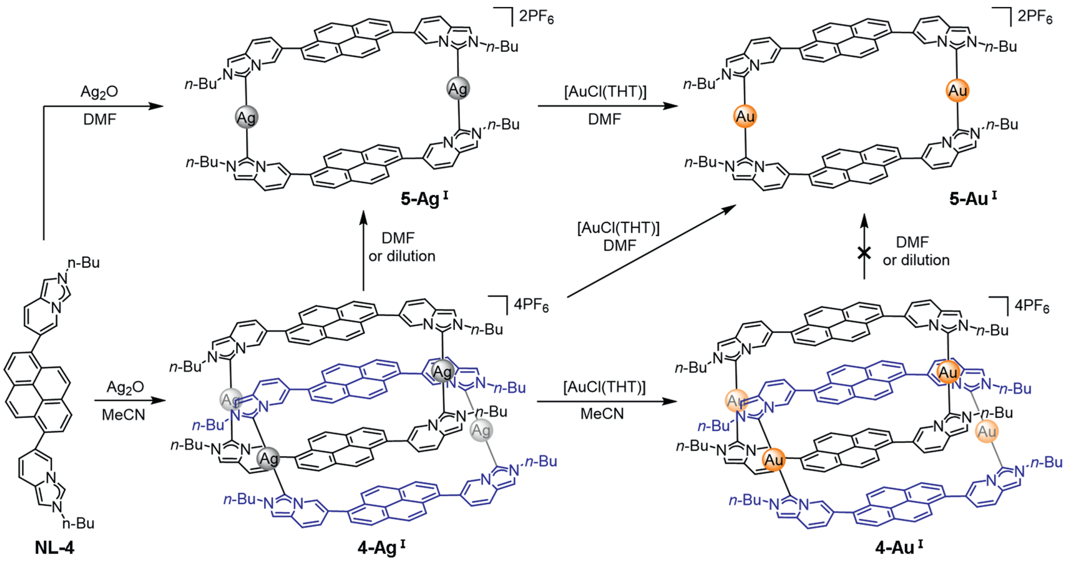

Fig. 2. Synthesis of Ag(I)/Au(I)–NHC-based [2]catenanes **4, 5-Ag^I** and **4, 5-Au^I**. Reprinted with permission from Ref. [71]. Copyright 2023, Wiley-VCH.

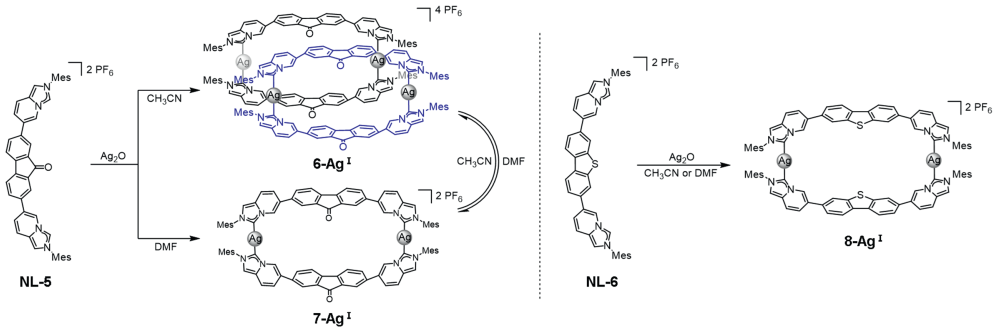

Fig. 3. Synthesis of Ag(I)–NHC-based [2]catenane **6-Ag^I** and metallamacrocycle **7, 8-Ag^I**.

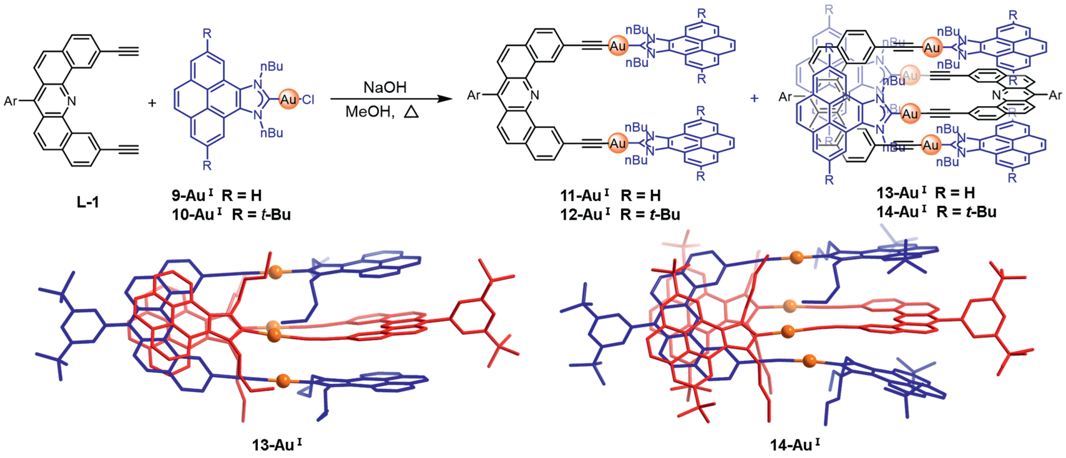

Fig. 4. Synthesis of Au(I)–NHC-based clippane **14-Au^I**.

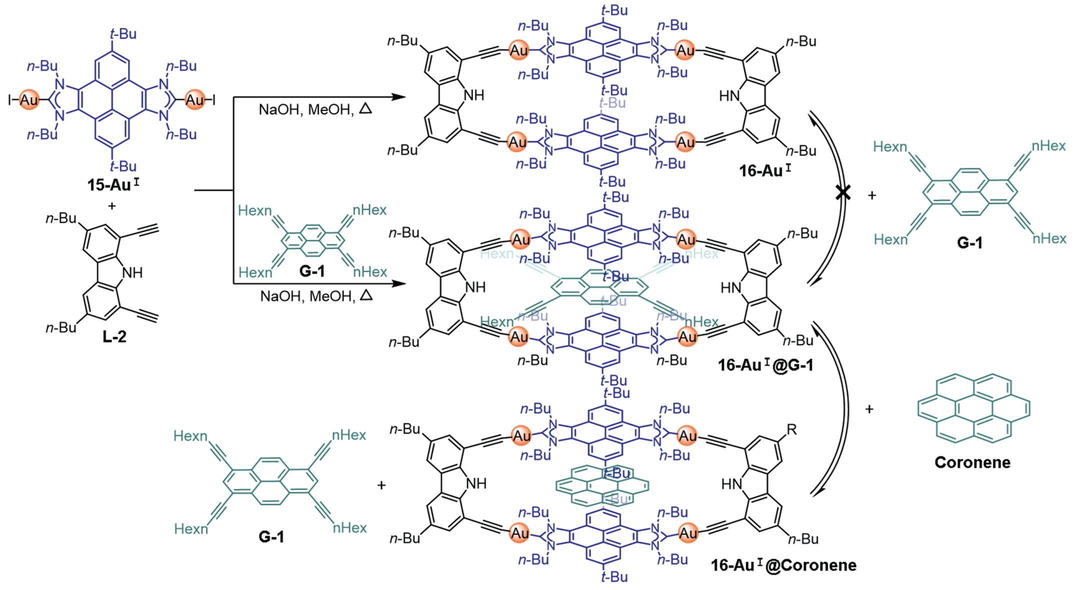

Fig. 5. Synthesis of Au(I)–NHC-based pseudo-suitane **G-1@16-Au^I**.

the host, with its four long limbs protruding from the cage's open portals, physically locking it in place. The pseudo-suitane **G-1@16-Au^I** is stable for extended periods at room temperature and can withstand heating at 80 °C for hours without releasing the guest. Furthermore, a control experiment confirmed that the interlocked state is kinetically trapped; when the pre-formed empty host **16-Au^I** was mixed with the free guest **G-1** and heated, no encapsulation occurred.

Remarkably, this robust physical lock could be opened through the addition of coronene, which triggered the release of tetra-substituted pyrene guest **G-1**. This release process is not a simple displacement reaction but rather requires the cooperative action of two coronene molecules. These two coronene molecules position themselves at the two entrances of the metallobox, forming a "narrow corridor" that exerts pressure on the flexible limbs of the trapped guest. This external compression forces the guest's limbs into a slender, "folded" conformation, reducing its effective size. Once compressed, the guest can slide smoothly out of the cavity. This hetero-guest assisted unlocking, or "shoehorning", is a fundamentally new concept, demonstrating that a mechanical bond can be cleverly circumvented by using anexternal molecular tool to manipulate the guest's conformation.

Altmann and Pöthig reported a reactive organometallic [2]rotaxane capable of a reversible, pH-triggered structural transformation into a purely organic [3]rotaxane (Fig. 6) [80]. The parent [2]rotaxane, **17-Ag$^{\text{I}}$**, comprising a dodecyl axle threaded through an octanuclear Ag (I)–NHC pillarplex host, could be converted to its Au(I) analogue via transmetalation. Upon treatment with acid, the Ag(I) host of **17-Ag$^{\text{I}}$** decomposed, yet the two resulting metal-free macrocycles remained kinetically trapped on the axle, converting the assembly into a purely organic [3]rotaxane **18**. This transformation was fully reversible by adding a base, establishing the system as a pH-dependent molecular switch.

Significantly, this mechanical entanglement led to a dramatic enhancement in chemical stability. The interlocked host proved to be over 1000 times more resistant to acid decomposition than the free pillarplex. The authors termed the phenomenon as "rotaxand effect".

Building upon their investigation of pillarplex-based rotaxanes, the Pöthig group reported a subsequent study focusing on the influence of the mechanical bond on the reactivity of the axle's stoppers (Fig. 7) [81]. They synthesized a [2]rotaxane **19-Ag$^{\text{I}}$** composed of the same Ag(I)–NHC pillarplex host but with an axle capped by base-labile 2,7-di-tert-butyl-9-fluorenylmethoxycarbonyl (Fmoc*) groups. Contrary to the common expectation that a macrocycle sterically hinders adjacent functional groups, they observed that the pillarplex macrocycle significantly accelerated the base-induced deprotection of the Fmoc* stopper, resulting in a 36-fold rate enhancement compared to a non-interlocked control compound. This was quantified through kinetic studies, which determined a second-order rate constant of 20.5 M^{-1} h^{-1} [CI$_{95}$%: 16.9, 24.1] for the rotaxane system, while the non-interlocked control exhibited only 0.56 M^{-1} h^{-1} [CI$_{95}$%: 0.27, 0.85]. This rate promotion was attributed to a conformational preorganization of the stopper by the macrocycle. As evidenced by NMR, X-ray, and DFT studies, specific and directional CH-π and hydrogen bonding interactions orient the stopper in a way that exposes its reactive site, rather than shielding it. To describe this phenomenon, the authors introduced the term "mechanosteric effect", defining it as the modulation-either promotion (positive) or inhibition (negative) of functional group reactivity imposed by the mechanical bond.

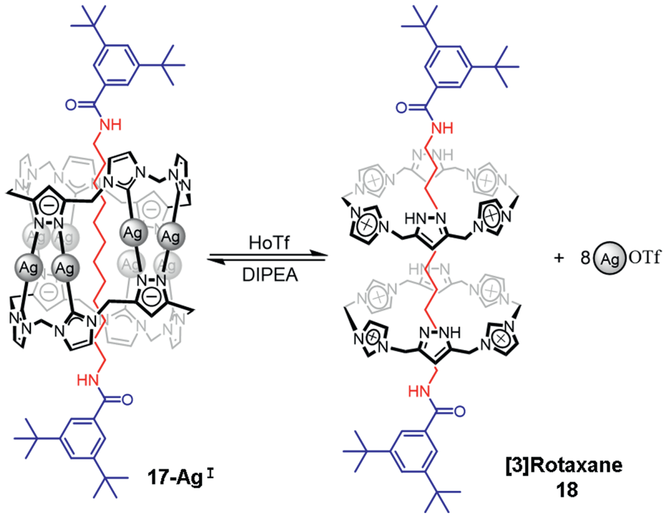

Fig. 6. Reversible transformation between Au(I)–NHC-based [2]rotaxane **17-Ag$^{\text{I}}$** and organic [3]rotaxane **18**.

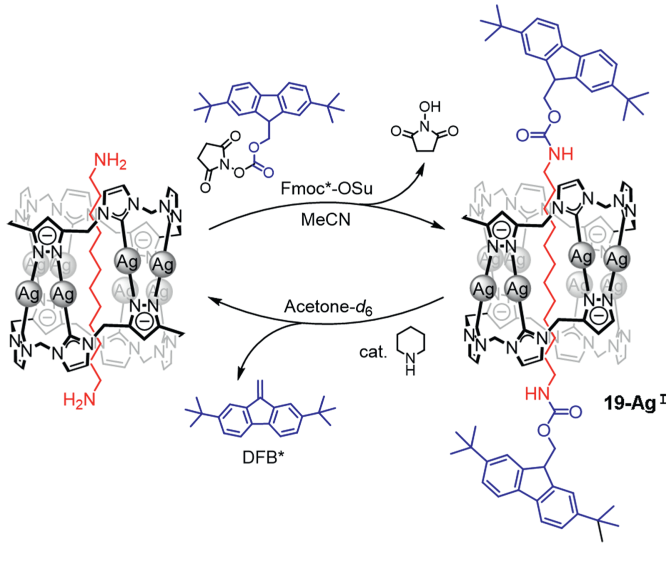

Fig. 7. Stoppering with Fmoc* N-hydroxysuccinimide (Fmoc*-OSu) and piperidine-induced Fmoc* deprotection trigger rotaxane disassembly.

The Chiu group demonstrated its application in synthesizing Pd(II)–NHC [2]rotaxane by transmetalation from Ag(I)–NHC intermediates (Fig. 8) [82]. Starting with a Ag(I)–NHC [2]rotaxane **20-Ag$^{\text{I}}$**, a subsequent reaction with palladium(II) chloride yielded three distinct chiral and achiral [2]rotaxanes, **21-Pd$^{\text{II}}$**, **22-Pd$^{\text{II}}$** and **23-Pd$^{\text{II}}$**. **21-Pd$^{\text{II}}$** exhibits C_2-symmetrical chirality originating from a distorted square-planar geometry at the Pd(II) center, where the interlocked architecture stabilizes the otherwise labile stereogenic nitrogen atoms of the macrocycle. **22-Pd$^{\text{II}}$** displays planar chirality, which arises from the metal coordination inducing directionality in both the macrocycle and the axle, leading to an asymmetric arrangement. **23-Pd$^{\text{II}}$** itself is achiral.

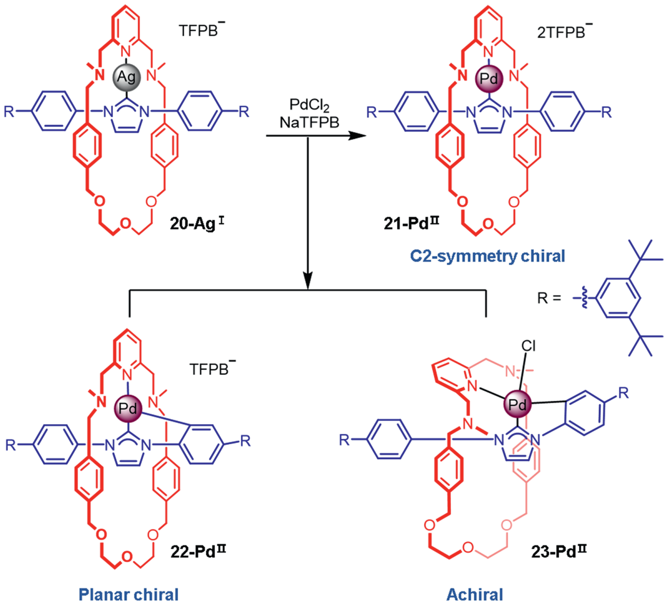

Fig. 8. Synthesis of Pd(II)–NHC-based [2]rotaxanes.

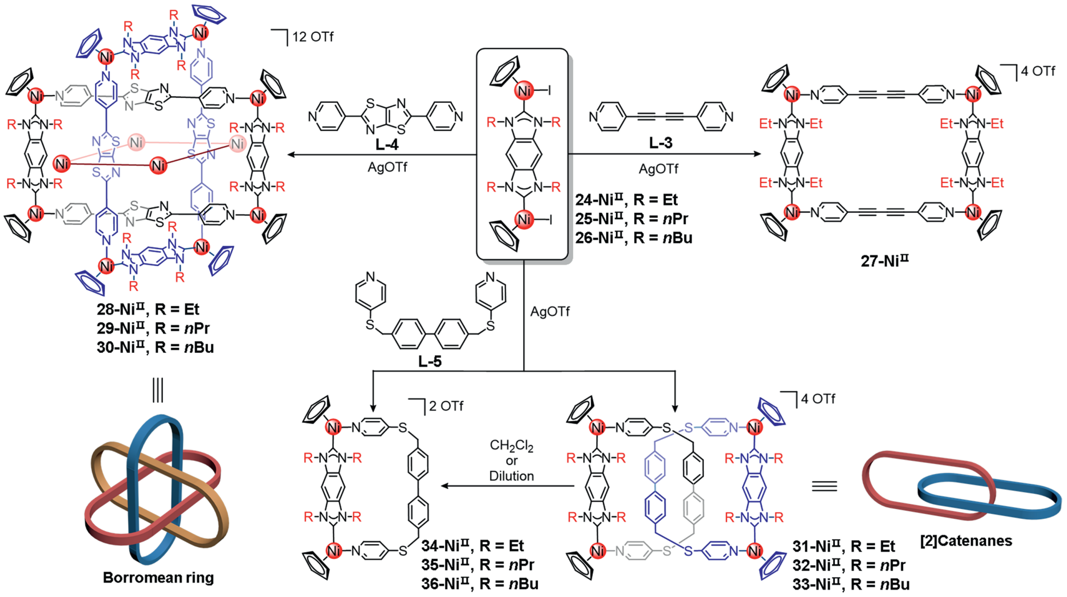

Fig. 9. Synthesis of Ni(II)–NHC-based Borromean rings and [2]catenanes. Reprinted with permission from Ref. [70]. Copyright 2023, Wiley-VCH.

3. MIMs based on Ni(II)—NHC complexes

Ni(II)–NHC complexes serve as another important class of building blocks for constructing organometallic MIMs. The square planar geometry of Ni(II) provides a powerful platform for constructing such architectures. Specifically, when a cyclopentadienyl (Cp) ligand occupies two coordination sites of the Ni(II) center, a rigid 90° angle is established between the two remaining sites. This well-defined geometry is ideal for incorporating two distinct and orthogonal ligands—for example, an NHC and a pyridyl-based ligand. This strategy enables the formation of molecular rectangles where ligand placement is exclusive. Furthermore, these molecular rectangles can serve as supramolecular synthons that self-assemble into complex interlocked structures through various non-covalent interactions. A common route uses nickelocene (Cp_2Ni) as the nickel source and proceeds without additional base. Additionally, the Cp groups generated as byproducts are readily volatile and can be easily removed, thereby circumventing the formation of substantial quantities of inorganic salt byproducts [83].

Hahn et al. provide a systematic demonstration that solvophobic effects can be harnessed to control the self-assembly and stability of complex organometallic MIMs (Fig. 9) [70]. The authors first reacted a dinuclear Ni(II)–NHC-based precursor **24-Ni^{II}** bearing ethyl substituents with a linear linker 4,4′-bipyridylacetylene (**L-3**), which yielded a discrete tetranuclear molecular rectangle **27-Ni^{II}**. Building on this, another bipyridyl ligand featuring a thiazolo-thiazole core (**L-4**) was used to replace **L-3** for introducing π-π stacking interactions. The self-assembly of dinuclear precursor **24-Ni^{II}** with bipyridyl ligand **L-4** led to the formation of organometallic Borromean rings **28-Ni^{II}**, confirmed by single-crystal X-ray diffraction. By synthesizing additonal Ni(II)–NHC-based precursors with progressively longer N-alkyl chains, *n*-propyl-based **25-Ni^{II}** and *n*-butyl-based **26-Ni^{II}**, the researchers observed that the stability of the Borromean rings **28-Ni^{II}**, **29-Ni^{II}**, **30-Ni^{II}** was significantly enhanced with chain length.

To further probe and quantify this solvophobic influence, they replaced the rigid linker **L-4** with a more flexible bipyridyl ligand (**L-5**), which led to the formation of [2]catenanes, **31-Ni^{II}**, **32-Ni^{II}** and **33-Ni^{II}**, corresponding to the ethyl, *n*-propyl and *n*-butyl substituents, respectively. These [2]catenanes were not stable in solution but existed as a dynamic equilibrium between the interlocked [2]catenanes and their corresponding monomeric metallamacrocycles, **34-Ni^{II}**, **35-Ni^{II}** and **36-Ni^{II}**. Detailed NMR analysis showed that the equilibrium could be shifted to favor the [2]catenane by increasing the length of N-alkyl

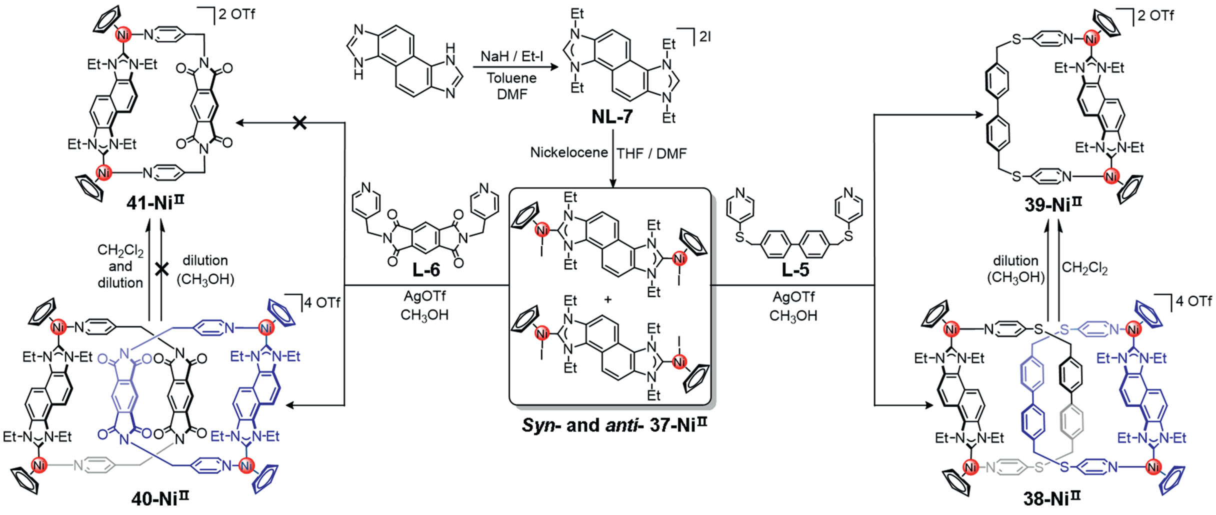

Fig. 10. Synthesis of Ni(II)—NHC-based stable [2]catenane. Reprinted with permission from Ref. [71]. Copyright 2023, Wiley-VCH.

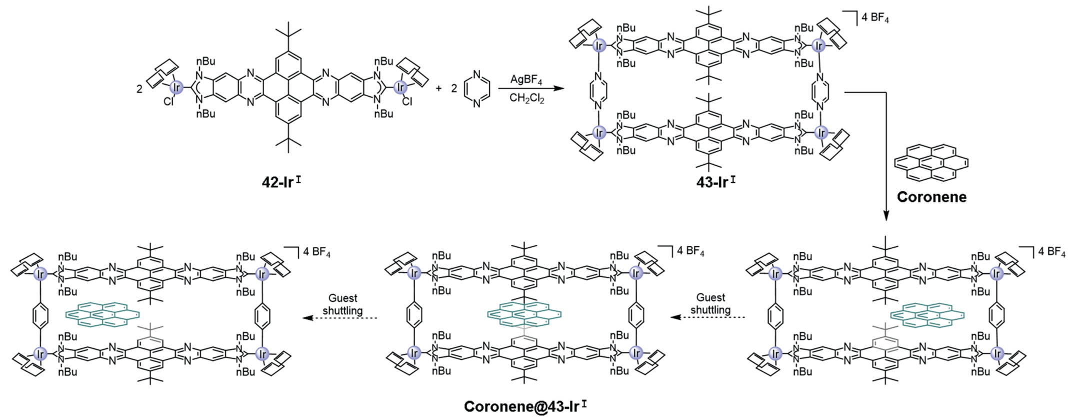

Fig. 11. Guest-shuttling in Ir(I)−NHC-based metallobox.

substituents. This effect, which strengthens the intramolecular association of the nonpolar chains within the interlocked structure, was further amplified by increasing the solution concentration or using more polar solvents.

Continuing their investigation into the driving forces of MIM self-assembly, the Hahn group reported the synthesis of [2]catenanes using a dinuclear nickel(II) naphthobiscarbene precursor **37-Ni^{II}** as a core building block. Reaction of **37-Ni^{II}** with a flexible bipyridyl ligand (**L-5**) produced an equilibrium mixture of [2]catenane **38-Ni^{II}** and the corresponding monomeric metallamacrocycle **39-Ni^{II}**. Characterization indicated that significant π-π stacking interactions were absent in the interlocked structure, so formation of the catenane was attributed mainly to solvophobic effects.

To introduce and assess π-π stacking contributions, **L-5** was replaced with **L-6**, a ligand containing an electron-deficient pyromellitic diimide unit designed to interact with the electron-rich naphthyl unit of precursor **37-Ni^{II}**. The reaction of **37-Ni^{II}** with **L-6** afforded the stable [2] catenane **40-Ni^{II}** (Fig. 10) [71]. This [2]catenane exhibited enhanced stability and was immune to the dilution in methanol solutions. Only upon reducing the solvent polarity and concentration together was the [2]catenane **40-Ni^{II}** forced to transform into the corresponding monomeric metallamacrocycle **41-Ni^{II}**. This result demonstrated that the stability of the interlocked structure could be augmented by incorporating specific donor-acceptor π-π stacking interactions alongside the solvophobic effects. These findings are expected to guide the synthesis and design of novel supramolecular structures and materials [84–86].

4. MIMs based on Ir(I)−NHC complexes

Conventionally, molecular shuttles are defined by the rotaxane architecture, thus classifying them as a subset of MIMs in which motion is governed by a mechanical bond [87]. The concept can be extended and described as a system capable of controlled, reciprocating movement. The work reported by the Peris group is an excellent illustration of molecular shuttling based on a host-guest system [88]. Although a host-guest system is not a classic MIM, this work is included here because it demonstrates, using an Ir(I)–NHC moiety, that a key dynamic function of MIMs can be realized through a non-interlocked design.

A tetracationic metallorectangle **43-Ir^{I}** was assembled from the dinuclear Ir(I)–NHC precursor **42-Ir^{I}** and pyrazine as a linear pillar affording a rigid nanosized box ca. 2 nm in length (Fig. 11). Its host-guest properties were probed by ^{1}H NMR titrations with a panel of planar aromatic guests. Kinetic behavior depended strongly on guest size with pyrene, triphenylene, tetracene and perylene exhibiting fast exchange on the NMR timescale, whereas coronene, *N,N*′-dimethyl naphthalenetetracarboxy diimide (NTCDI) and 2,4,7-trinitro-9-fluorenone (TNFLU) displayed slow exchange. The slow-exchange regime implied confined dynamic motion, which was corroborated by variable-temperature ^{1}H NMR experiment. At ambient temperature, a single averaged set of host aromatic signals was observed. Upon cooling, these signals first broadened and then resolved into two distinct sets which evidenced two distinct chemical environments averaged by rapid translational motion at higher temperature.

To precisely identify the nature of this motion, the authors rigorously quantified its kinetics for the coronene guest. Through detailed ^{1}H NMR line-shape simulations and Eyring analysis, they determined the activation Gibbs energy ($\Delta G^{\ddagger}$) for the guest's movement between the two sides of the cavity to be 11.0 kcal/mol. Crucially, this value was compared against the energy barrier for a dissociative exchange pathway (i.e., the guest leaving and re-entering the host). The barrier for this external exchange was estimated to be significantly higher, with a lower limit of > 13.1 kcal/mol. This pronounced energy difference provided definitive evidence that the observed dynamics correspond to a purely intramolecular sliding of the guest along the cavity, rather than a process involving its egression into the bulk solution.

X-ray diffraction structures of the coronene, NTCDI and TNFLU complexes reveal one guest holds asymmetrically on one side of the cavity near a pyrazine pillar, consistent with the variable temperature ^{1}H NMR experiment. These observations show that the larger planar guests undergo one-dimensional site-to-site shuttling between two degenerate positions along the long axis of the metallobox, extending the molecular shuttle concept beyond mechanically interlocked rotaxanes to a non-interlocked host-guest system.

5. Conclusion

The field of MIMs constructed from poly-NHC building blocks has witnessed remarkable advancements, as highlighted in this review. By leveraging the robust M–C$_{\mathrm{NHC}}$ bonds, researchers have successfully synthesized a diverse array of interlocked architectures, including interlocked cages, [2]catenanes, rotaxanes, Borromean rings, and novel structures like clippanes and pseudo-suitanes. The strategic use of metal ions such as Ag(I), Au(I), Ni(II), Pd(II) and Ir(I) has enabled coordination-driven self-assembly, with key driving forces including π-π stacking, solvophobic effects, and steric barriers. These interactions not only facilitate high-yield formation but also enhance the stability of the resulting assemblies, allowing for applications in catalysis, host-guest chemistry, and even stimuli-responsive materials and molecular shuttles.

Looking ahead, this emerging field presents exciting challenges and opportunities, particularly in two key areas.

1. The synthesis of increasingly complex interlocked structures remains a challenge for synthetic chemists. In contrast to traditional Werner-type ligands, NHC ligands and their robust metal-carbon bonds offer a compelling combination of enhanced stability, strong σ-donation,

and reversibility under thermodynamic control. These properties could be harnessed to construct higher-order topologies, such as multi-interlocked systems or intricate knots. Exploring innovative strategies to utilize these advantages—perhaps through advanced ligand design or multi-metal coordination—represents a highly attractive research hotspot, pushing the boundaries of topological chemistry.

2. Equally important is the exploration of broader applications. While current work is predominantly focused on synthesis, the unique attributes of NHC-metal bonds provide a solid foundation for advanced functional materials. Their inherent robustness and tolerance to diverse environments are particularly promising for developing applications in areas such as luminescent materials for optoelectronics, magnetic systems for data storage, and biomaterials for drug delivery or sensing. To realize this potential, incorporating a wider range of metals, including Pt or Ir derivatives, and rare-earth elements, could introduce tunable properties like enhanced photophysical behavior or magnetic responsiveness, thereby bridging the gap between fundamental synthesis and practical utility.

In summary, poly-NHC-based MIMs offer a valuable platform for advancing interlocked molecular systems through organometallic chemistry. We believe this domain has a promising future, with the potential to contribute to ongoing developments in chemistry and related disciplines.

CRediT authorship contribution statement

Yi Li: Writing – original draft. **Ye Lu:** Writing – review & editing, Writing – original draft, Conceptualization. **Shi-Ping Yang:** Writing – review & editing.

Declaration of competing interest

The authors declare no competing interests.

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