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# Prototypes of molecular gears with an organometallic piano-stool architecture

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**Abstract** In the field of Molecular Machines, molecular gears have mainly been synthesized to be studied in solution. Then, the cogwheel subunits are restricted to be only arranged in an intramolecular manner. In the last years, the possibility to arrange a train of gears at the single molecular level and observe the propagation of a rotation motion from one molecule to its neighbor using Scanning Tunneling Microscopy (STM) opened new perspectives with the opportunity to have intermolecular arrangements on surfaces. In this chapter, we describe the research background of single molecular gears and our strategy using organometallic piano-stool complexes to anchor such gears on surfaces. Our molecules incorporate two subunits linked together through a ruthenium center acting as a ball bearing. The lower part is the anchoring tripodal ligand and the upper part the cogwheel. Various functionalities have been explored to behave as teeth, ranging from mono-dimensional phenyl rings to bi-dimensional porphyrin fragments.

**Keywords** Molecular machines - Molecular gear - Ruthenium complexes - Single molecule - Porphyrins - STM

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# 1. Introduction

## *1.1 Molecular Machines*

A revolution in the way chemists consider molecular systems and their associated motions took place over the last decades with the rise of a new field dedicated to Molecular Machines. Macromolecular biological systems acting as machines have been long optimized by Nature and are key elements to many functions in living organisms. However, in artificial molecular systems, the design and synthesis of molecular machines for which motion and function can be controlled remains a highly challenging task. In this context, Jean-Pierre Sauvage, Sir Fraser Stoddart and Ben Feringa were awarded the 2016 Nobel Prize of Chemistry for their seminal and fundamental contributions to this field [1-3].

A large variety of artificial molecular machines and motors have been developed in a monumentalization approach, starting with small molecular building blocks and building step by step a complexified architecture until the molecule becomes a machine. In particular, daily life macroscopic objects have been miniaturized according to a technomimetic approach [4] leading to nanometer scale syringes [5], wheels [6-9], wheelbarrows [10-12], vehicles [13-17], scissors [18], elevators [19], gyroscopes [20], motors [21-32] among others.

In spite of the tremendous developments witnessed in this field, applications of ultimately miniaturized machines in the macroscopic world are still rare. One of the strategies to exploit such nanoscale units is to deposit them on surface and use them as self-assembled monolayers or single molecules thanks to the amazing capabilities offered by Scanning Tunneling Microscopy (STM). Beyond the high-resolution imaging possibilities, the use of the STM tip can allow to induce and control precise molecular motions from the single molecular scale [33] to the switch of large domains [34].

In this context, one fascinating target is a train of molecular gears rotating synchronously on a surface to be able to transfer energy at the nanoscale from a molecule to another one over long distances.

## *1.2 Gears in the Insects' World*

The oldest known machine involving gearing mechanisms is the Antikythera machine, built around 200 BC. However, in contradiction with the common idea that gears are a human invention, micrometric gears were recently discovered in the nymphs of the planthopper *Issus coleoptratus* [35]. Indeed, the exoskeleton of their hind legs incorporates a curved strip with up to 12 micrometric gear teeth, as observed by Scanning Electron Microscopy (Figure 1). Both legs are thus mechanically coupled through this gearing mechanism, leading to a synchronized motion from the preparation to the propulsion of the jump, that can reach 2 m. Interestingly, it must be noted that the dissymmetric character of the teeth allows only one direction of powered rotation.

According to this recent discovery, synthesis of molecular gears can be defined not only as technomimetic [4] but also as biomimetic [36].

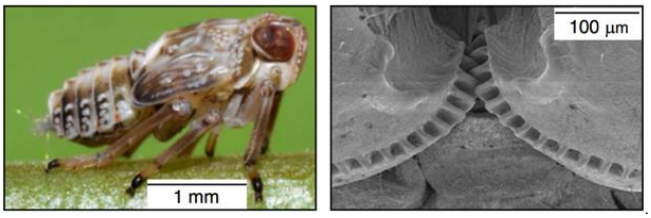



**Figure 1. Side view of a planthopper *Issus coleoptratus* nymph (left) and Scanning Electron Microscopy image of meshed micrometric gears located on the hind legs (right). From Ref. 35. Adapted with permission from AAAS.**

# 2 Molecular Gears from Solution to Surface

## *2.1 Gears in Solution: Drawbacks and Limitations*

The first examples of synthetic molecular gears appeared forty years ago as intramolecular systems involving two intertwined subunits undergoing correlated motion in solution. The two pioneers in this field, H. Iwamura [37] and K. Mislow [38], first reported compounds exhibiting bevel-gear mechanisms, with two triptycene moieties linked by a very short spacer such as a methylene group in the case of Mislow (Figure 2, left) or an oxygen atom in the case of Iwamura (Figure 2, center). The first molecular spur gears with two triptycene units having parallel axes of rotation (Figure 2, right) were designed and synthesized in 2012 by J. Siegel, a former PhD student of K. Mislow, with a particular attention paid to the inter-axle distance as key parameter in molecular gearing mechanisms [39].

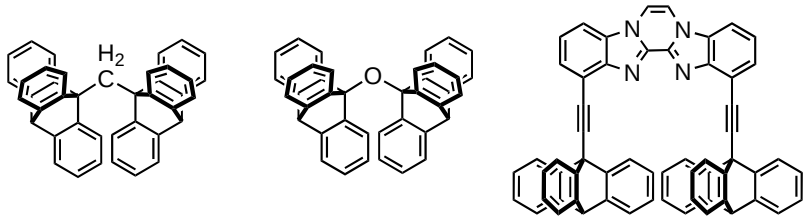



**Figure 2. Molecular gears proposed by K. Mislow [38] (left), H. Iwamura [37] (center) and J. Siegel [39] (right), all are based on triptycene cogwheels.**

In the last years, M. Shionoya reported a new series of molecular gears which can be controlled at will by an external stimulus. These complexes are based on platinum(II) with two azaphosphatriptycene ligands acting as cogwheels. Under thermal or photo-activation, *cis-trans* isomerization of the complex leads very elegantly to the engagement or disengagement of the cogwheels (Figure 3) [40].

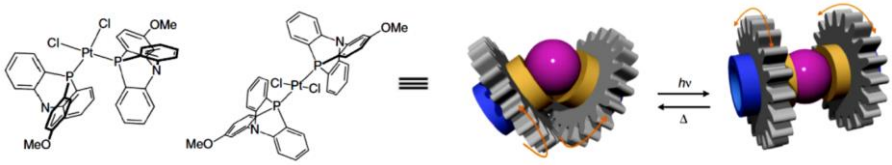



**Figure 3. Chemical structure (left) and schematic representation (right) of the engaged and disengaged molecular gears proposed by Shionoya et al. (adapted from Ref. 40).**

A vast majority of the studies on correlated motion, such as the ones presented above, have been performed in solution, at the intramolecular level. The observed behavior is thus the average behavior of an assembly of molecules and not of a single molecule. Moreover, the lack of orientation in solution prevents transfer of motions (i.e. energy) over long distances, which is a limitation for applications. As an alternative, intermolecular gearing becomes possible on a supporting surface, which enables to maintain the distance between cogwheels and the relative orientation of the axles.

## *2.2 Gears on Surface: Single Molecules and Atomic Resolution*

Intermolecular gearing on a surface was evidenced for the first time in 2007 by Moresco et al. in a rack and pinion device made of penta(*p-tert*-butylphenyl)-(*p-tert*-butylpyrimido)benzene molecules on a Cu(111) substrate (Figure

4) [41]. Indeed, STM lateral manipulation of one single molecule along the edge of the close-packed island obtained after on-surface deposition resulted in a rotary motion of this per-arylated benzene pinion, as a consequence of the teeth intertwining. This rotation was demonstrated by comparing successive STM images and following the trajectory of the chemically-tagged pyrimidine tooth.

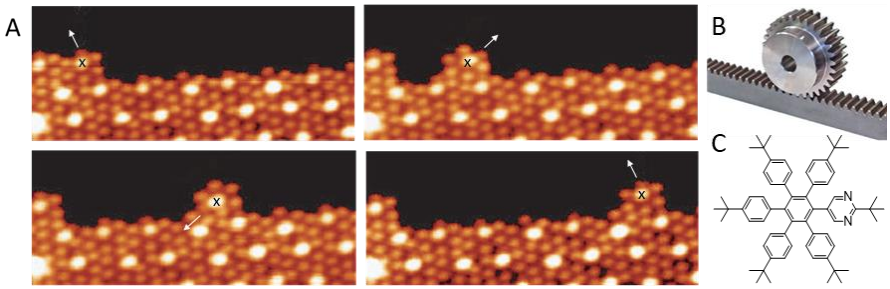



**Figure 4. STM images (A) showing the displacement of a pinion (single molecule) along a rack (self-assembled monolayer of the same molecule) on Cu(111). The white arrow gives the orientation of the molecule according to the pyrimidine tagged tooth. A macroscopic rack and pinion (B) and the chemical structure of the molecule (C). From Ref. 41, adapted with permission from Springer Nature.**

The same gear prototype was further investigated on Au(111) as a single molecule. When mounted on an atomic defect, the controlled and stepwise rotation of this per-arylated benzene molecule was successfully achieved [42], thus opening the way for intermolecular gearing on surface at the single molecular scale.

Unfortunately, when a second molecule was added in close vicinity to form a train of two gears, no correlated motion could be observed due to diffusion of the cogwheels. This underlines the prime importance of rotation axles to anchor cogwheels on surface at optimized intermolecular distances, as a prerequisite to favor transmission of rotary motion over diffusion.

A promising strategy to build intermolecular gearing systems consists in mounting molecular cogwheels on top of single atoms deposited on surface. This has been recently demonstrated by Joachim et al., who successfully mounted by STM lateral manipulation the per-arylated benzene cogwheel depicted in Figure 4 on top of a Cu single atom on a Pb(111) surface. In the presence of this centered rotational axle, controlled rotation of single cogwheels and correlated motion within a train of two gears was achieved [43].

## *2.3 Our Strategy*

As an alternative, we envisioned to pre-assemble the cogwheel on top of a single atom axle in the frame of a coordination complex, synthesized in solution and subsequently deposited on surface. The architecture of our previously-reported ruthenium-based motor [29] appeared particularly promising, since it has been shown that such structures can be displaced and arranged in a very precise assembly through STM lateral manipulation at 77 K, while diffusion is frozen at 5 K. This would thus enable the specific arrangement of trains of organometallic gears with finely tuned intermolecular distances at 77 K and would prevent gears disengagement due to diffusion by lowering the temperature to 5 K. Indeed, at that temperature, the motion of such ruthenium complexes is efficiently restricted by the strong interaction between the surface and the tripodal scorpionate ligand [44], which not only prevents translation but also gives a very efficient control on the geometry of the whole architecture thanks to the presence of three anchoring points.

This rigid tripodal ligand also holds a second key function as it supports the ruthenium ion, acting as single atom axle for the star-shaped cogwheel. The structure of the cogwheel should be as rigid as possible with few degrees of freedom in order to obtain a maximum control over the mechanically-driven motion. Indeed, in these experiments, the STM tip will be used as a source of mechanical energy to induce the rotary motion of the first cogwheel, that will be mechanically transmitted to the next one if gearing mechanism is effective (Figure 5). The propagation of rotary motion within the train of gears will then be evidenced by comparing the STM images of the initial and final states. As we will see later, it will be helpful to have one of the teeth chemically or sterically tagged.

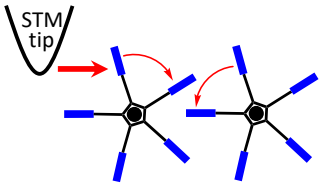



**Figure 5. Expected transmission of rotation from one molecule to its neighbor using a STM tip as source of mechanical energy.**

In this chapter we will focus on the design and molecular synthesis of cogwheel prototypes to build a train of gears based on star-shaped organometallic ruthenium complexes.

## 3 Molecular Gears Based on Organometallic Ruthenium Complexes

### *3.1 Design*

As mentioned above, our design for molecular gears including a rotational axle is based on the previously-reported ruthenium-based motor [29] shown Figure 6 (left). The lower part of gears is a tripodal thioether-functionalized hydrotris(indazolyl)borate ligand to anchor molecules on metallic surfaces, but also to alleviate the ruthenium rotational axle and thus the upper cogwheel. A pentaphenylcyclopentadienyl moiety is used in this case as a central platform to modularly attach various peripheral groups acting as teeth. We explored two types of architectures, which are schematically presented in Figure 6 (center and right): the first architecture integrates five mono-dimensional arms and the second one five bi-dimensional paddles.

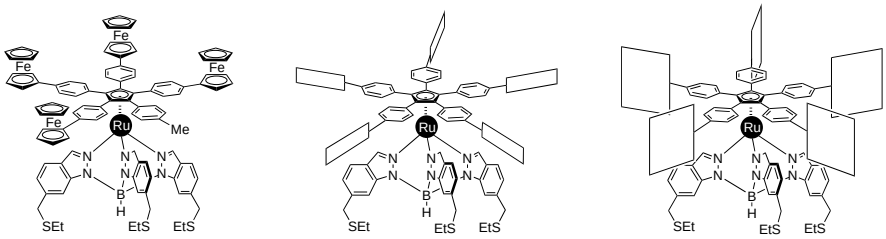



**Figure 6. Structure of the parent compound, a molecular motor [29] (left), and of the cogwheels with five mono-dimensional arms (center) and with five bi-dimensional paddles (right).**

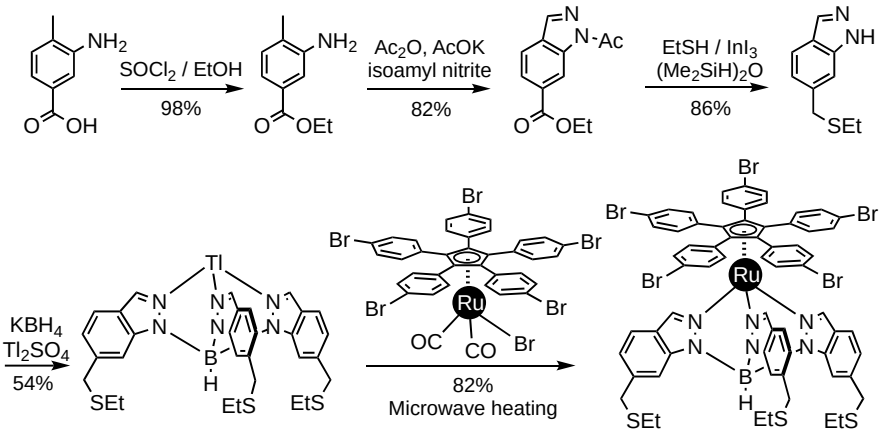
### *3.2 Efficient Synthesis of the Ruthenium Complex Precursor*

From a synthetic point of view, both architectures of molecular gears featuring five identical mono- or bi-dimensional teeth stem from the same precursor via five-fold cross-coupling reactions. The key intermediate in this

strategy is thus a ruthenium(II) complex bearing the tripodal scorpionate ligand on one side and a penta(*p*-bromophenyl)cyclopentadienyl ligand on the other side (Scheme 1). Owing to the importance of this building block for the synthesis of ruthenium-based rotary molecular machines, its synthesis was recently optimized [45]. It is now prepared in a reproducible manner in 5 steps and 31% overall yield on the longest linear sequence, compared to 8 steps formerly with a maximum yield of 4%.

3-Amino-4-methylbenzoic acid was first protected as an ethyl ester under standard conditions, and the o-toluidine moiety was next converted into an indazole scaffold using the modified one-pot Jacobson procedure with isoamylnitrite as nitrosating agent. Step economy was achieved at that stage in this optimized route thanks to a highly efficient one-pot "*N*-deprotection / ester reductive sulfidation" sequence mediated by indium(III), allowing the direct conversion of *N*-acetyl indazolyl ester into the corresponding *N*-deprotected indazolyl thioether in a single step (instead of three). The reaction proceeds in the presence of indium(III) iodide as Lewis acid, an excess of 1,1,3,3-tetramethyldisiloxane as reducing agent and ethanethiol as nucleophile. Importantly, this one-pot sequence not only shortens the synthetic route towards the key ruthenium complex but also avoids the troublesome isolation of intermediates.

The next major improvement in the synthetic sequence relies on the replacement of potassium by thallium during the formation of the tripodal ligand. Indeed, the thallium salt of the tris(indazolyl)borate ligand was obtained via a thermally-controlled reaction of indazolyl thioether with potassium borohydride in the presence of thallium sulfate, leading to a highly pure crystalline product. Finally, the ruthenium(II) key precursor resulted from a ligand exchange on the bromidodicarbonyl-1,2,3,4,5-penta(*p*-bromophenyl)cyclopentadienyl ruthenium(II) complex, with a positive effect of microwave irradiation on this reaction.




**Scheme 1: Optimized synthetic route yielding the ruthenium key precursor coordinated to the tripodal ligand (lower side) and a pentabrominated functionalized cyclopentadiene (upper side).**

## *3.3 Molecular Gears Based on Cogwheels with mono-Dimensional Arms*

With an optimized and shortened access to this ruthenium complex precursor, the synthesis of molecular gear prototypes has been pursued and cogwheels with mono-dimensional teeth were first targeted. In this family, the cyclopentadienyl ring is thus surrounded with five 4,4'-biphenyl moieties, each carrying one or two methyl or *tert*-butyl substituents on the outer positions (Figure 7). The synthesis of these three prototypes relies on a five-fold Suzuki-Miyaura cross-coupling reaction of the penta(*p*-bromophenyl)cyclopentadienyl ruthenium(II) key precursor in the presence of an excess of the appropriate boronic acid derivative [46]. Using $Pd(OAc)_2$ / SPhos as catalytic system and potassium phosphate as base in anhydrous toluene, the penta-substituted gear prototypes were obtained in 52 to 82% yield. These optimized conditions thus allow an efficiency as high as 88 to 96% for each single C-C bond formation. Full characterization of each complex confirmed the $C_5$-symmetric character of the upper cogwheel.

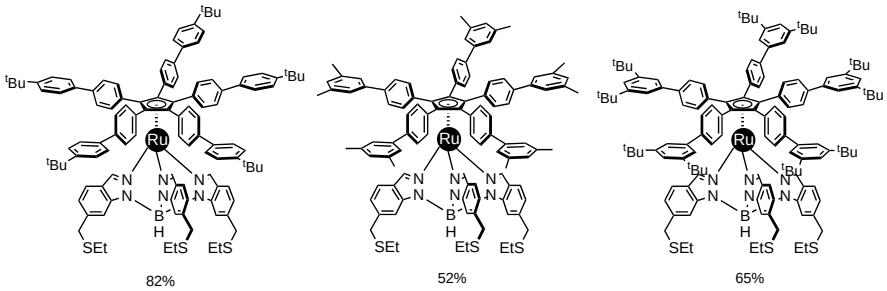



**Figure 7. Chemical structure of the three gear prototypes with mono-dimensional arms and respective yields of the quintuple cross-coupling reaction to form them.**

According to preliminary studies, such gear prototypes seem to be ineffective in propagating rotary motion to their neighbors. Theoretical calculations performed on intricated gears revealed that upon rotation of the first cogwheel, a vertical deformation of the teeth can occur, thus preventing the transfer of rotation to the next molecule.

To shut down this deformation pathway, the design of gear prototypes was adapted with 2D-paddles (Figure 6, right) instead of 1D-teeth (Figure 6, center). The very large steric hindrance of the groups surrounding the cyclopentadienyl core in this second generation of cogwheels is expected to prevent gear slippage. Indeed, according to the size and rigidity of these paddles, it seems impossible to rotate the first gear without rotating its neighbor provided the intermolecular distance is appropriate, and mechanical transmission of motion should thus be favored with this new design.

## *3.4 Molecular Gears Based on Cogwheels with bi-Dimensional Paddles*

Three different chemical fragments exhibiting flat structures and large areas were selected as bi-dimensional paddles for this second generation of cogwheels. Four gear prototypes incorporating carbazoles, BODIPYs and porphyrins as paddles and exhibiting increasing diameters up to 5.2 nm were thus synthesized [46]. Their chemical structures are shown in Figure 8, and one can notice that bulky alkyl groups have systematically been added to paddles to increase the solubility during the synthesis and above all, to avoid π-stacking between neighboring molecules on surface, as this could hamper the gears motion.

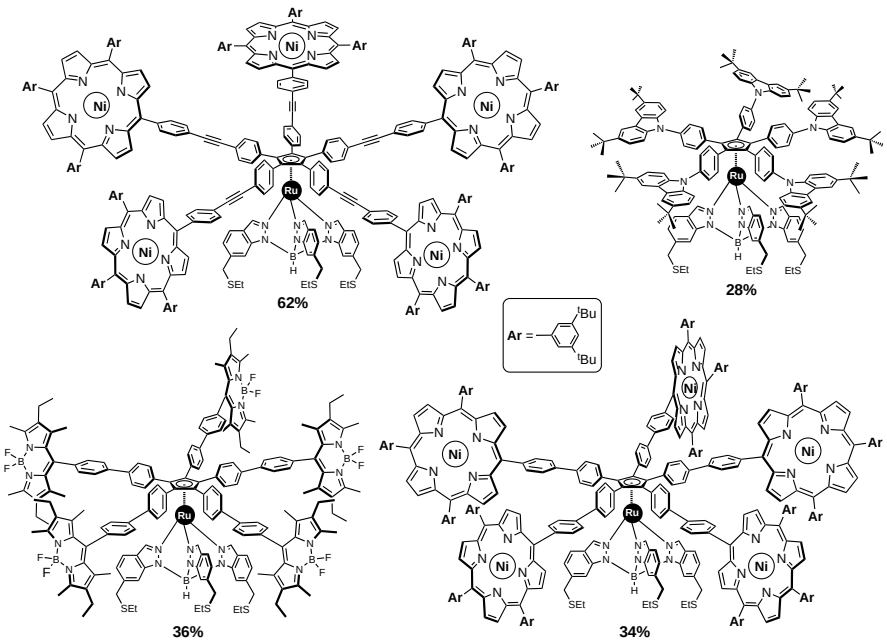


**Figure 8. Chemical structure of the four gears with bi-dimensional paddles and respective yields of the quintuple cross-coupling reaction to form them.**

The four gear prototypes bearing 2D-paddles were prepared via a five-fold cross-coupling reactions applied to the appropriate brominated or iodinated penta(*p*-halogenophenyl)cyclopentadienyl ruthenium(II) key precursor. By way of example, a five-fold copper-catalyzed *N*-arylation reaction in the presence of 3,6-di-*tert*-butyl-*9H*-carbazole afforded the pentacarbazole gear (Scheme 8, top right). Starting from penta(*p*-bromophenyl)cyclopentadienyl ruthenium(II) precursor, the target compound was obtained in 19% yield under optimized conditions involving copper iodide and (±)-*trans*-cyclohexane-1,2-diamine as catalytic system in combination with potassium phosphate as base in refluxing 1,4-dioxane. Interestingly, when the same reaction conditions were applied to the more reactive iodinated precursor (same ruthenium complex with 5 iodine atoms instead of five bromines), the yield could be increased to 28%, corresponding to 78% per C-N coupling.

BODIPY fragments were next selected to vary the nature of the paddles and enlarge the cogwheel diameter. The standard Suzuki-Miyaura conditions used previously for the preparation of gears with 1D-arms failed to efficiently deliver the desired penta-substituted product, leading to mixture of compounds resulting from one to five C-C couplings. After optimization, it appeared that higher coupling efficiency could be reached in a ternary solvent system combining toluene, ethanol and water (2:2:1), and the penta-BODIPY gear prototype was obtained in 36% yield.

Finally, the largest paddle scaffold relied on a nickel porphyrin macrocycle featuring 3,5-di-*tert*-butylphenyl groups on three *meso* positions to enhance stability as well as solubility and limit π-stacking. Metallation of the porphyrin moieties with nickel(II) was meant to prevent any undesired metallation on surface during STM studies, owing to the robustness of nickel porphyrins.

As a strategy to modulate the diameter of the cogwheel, it was envisioned to vary the length of the spacer between the cyclopentadienyl and tetrapyrrole cores. Starting from penta(*p*-halogenophenyl)cyclopentadienyl ruthenium(II) key precursor, a Suzuki-Miyaura coupling would deliver a biphenyl spacer whereas a Sonogashira reaction would provide a longer phenylethynylphenyl linker. The required $A_3B$-type porphyrin precursors incorporating a phenylboronic ester moiety or a phenylethynyl group on the distinct meso position were synthesized under statistical conditions according to Lindsey's method [47].

The pentabrominated key precursor and its porphyrinic boronic acid pinacol ester coupling partner were submitted to Suzuki-Miyaura reaction conditions in the presence of $Pd(dppf)Cl_2$ as catalyst and cesium carbonate as base at 100 °C in a DMF/water system (99:1). The desired gear carrying five porphyrin paddles and 4,4'-biphenyl spacers was obtained in 34% yield.

Extension of the cogwheel diameter was next attempted by reacting the pentaiodinated precursor with the alkynylporphyrin under milder conditions involving $Pd(PPh_3)_2Cl_2$ and CuI as catalysts in triethylamine at 45 °C. The pentaporphyrin gear resulting from a five-fold Sonogashira reaction and exhibiting a diameter over 5 nm was obtained in 62% yield.

All these gear prototypes were fully characterized by standard techniques involving mass spectrometry and NMR spectroscopy. The latter unambiguously showed that free rotation of the upper platform is maintained at room temperature, even in the most sterically hindered architectures.

In view of on-surface studies, it was anticipated that a dissymmetry element in the cogwheels, acting as a tag, would be desirable to monitor by STM possible gearing effect. The design and synthesis of ruthenium complexes carrying a dissymmetrized cogwheel was thus tackled.

## *3.5 Dissymmetrized Cogwheels*

### *3.5.1 How Can we Probe the Rotation using STM?*

In the absence of time-resolution in STM imaging, molecular motion is probed by comparing images taken before and after the rotation event. When deposited on surface, the gear prototypes synthesized above will appear as pseudo $C_5$-symmetric objects, in line with the cogwheel structures. Tracking and quantifying motion might thus be challenging. The presence of a tag, *i.e.* a chemical or steric variation lowering the object symmetry, appears highly desirable for in-depth mechanical studies at the molecular scale. As depicted on Figure 9, dissymmetrized cogwheels incorporating one distinct arm (in red) would allow for a straightforward differentiation between the initial configuration and the final state, resulting from disrotatory motion of neighboring molecules.

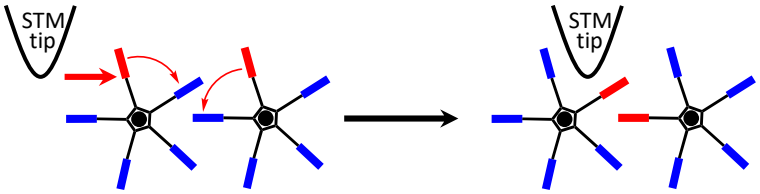


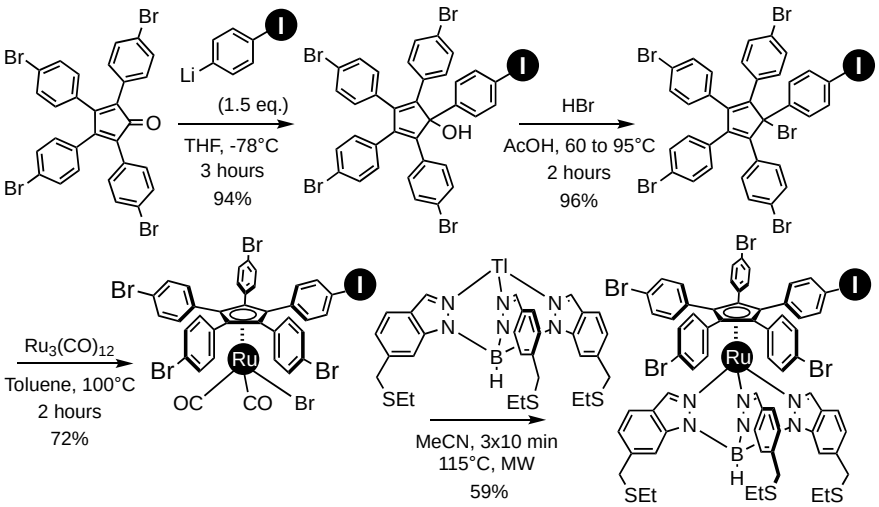

**Figure 9. Principle of the motion transmission through a molecular gear train actuated by a STM tip. Initial configuration (left) and final configuration (right) after a fifth of a turn (72°). The first gear rotates clockwise pushed by the STM tip and induces the counterclockwise rotation of the next molecule.**

It was thus envisioned to synthesize a family of star-shaped ruthenium complexes incorporating one tagged porphyrinic paddle. To this aim, the possibility to tune the length of the spacer between cyclopentadienyl and porphyrinic cores was exploited to incorporate one longer arm in the cogwheel structure. A single Sonogashira coupling on one halogenophenyl position of the ruthenium(II) key precursor would generate the longer phenylethynylphenyl spacer and subsequent four-fold Suzuki-Miyaura cross-couplings on the remaining positions would lead to the four shorter 4,4'-biphenyl linkers.

In view of the functionalization of one single arm via Sonogashira coupling, it is important to note that the five halogenated positions in the key building block are equivalent and thus react independently when submitted to statistical reactions conditions, leading to mixture of mono- and polysubstituted products. To overcome this issue, a chemoselective single Sonogashira reaction relying on the higher reactivity of aryl iodides compared to aryl bromides was targeted, and the corresponding penta(*p*-halogenophenyl)cyclopentadienyl ruthenium(II) precursor carrying one iodine and four bromine atoms was prepared [48].

### *3.5.2 Synthesis of a Dissymmetric Ruthenium Precursor*

The dissymmetric ruthenium key precursor bearing one pre-activated position in view of a chemoselective single cross-coupling was obtained in four steps from tetra(*p*-bromophenyl)cyclopentadienone (Scheme 2). Introduction of the iodinated arm was performed by 1,2-addition of 4-iodophenyllithium to give the corresponding cyclopentadienol in 94% yield. Bromination using a mixture of hydrobromic and acetic acids almost quantitatively afforded bromocyclopentadiene as a mixture of three regioisomers. Subsequent reaction with ruthenium(0) cluster $Ru_3(CO)_{12}$ led to a selective insertion into the central C-Br bond to yield a single ruthenium(II) complex carrying the dissymmetrized penta(*p*-halogenophenyl)cyclopentadienyl ligand. Finally, ligand exchange in the presence of the thallium salt of thioether-functionalized tripod afforded the desired dissymmetric precursor in 38% overall yield.



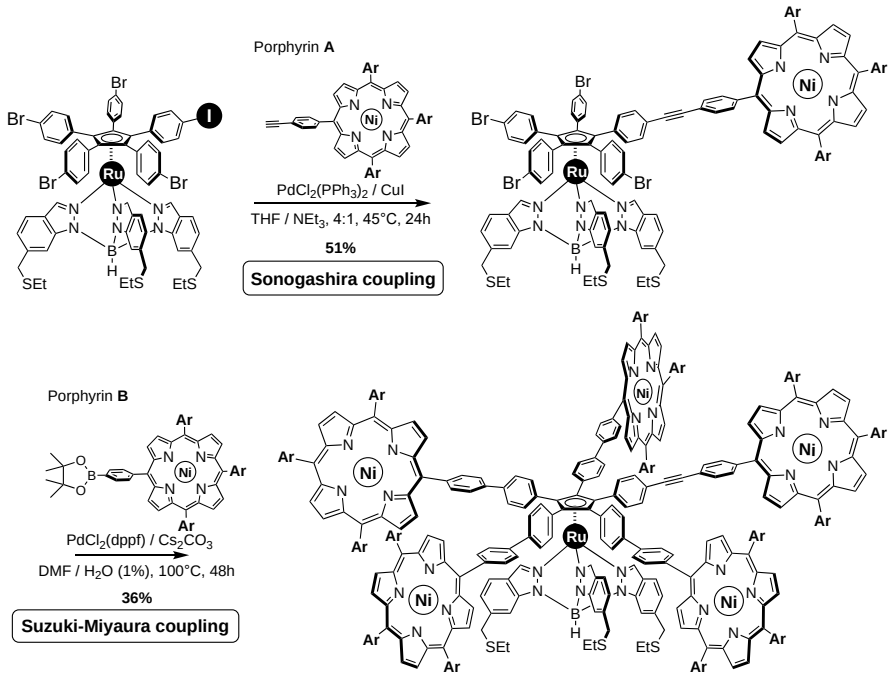

**Scheme 2. Synthesis of 1-(*p*-iodophenyl)-2,3,4,5-tetra(*p*-bromophenyl)cyclopentadienyl hydrotris(indazolyl)borate ruthenium(II).**

This dissymmetric penta(*p*-halogenophenyl)cyclopentadienyl ruthenium(II) key building block was then used for the selective synthesis of a gear prototype with a sterically-tagged cogwheel.

### *3.5.3 Synthesis of a Dissymmetric Pentaporphyrinic Cogwheel*

As shown on Scheme 3, the dissymmetrized key precursor was engaged in sequential cross-coupling reactions, to selectively install the longer tooth in a first step and subsequently insert the four remaining shorter teeth. It is important to note that the nickel porphyrin structure remains identical in the five paddles and dissymmetry only arises from the length of the linkers.

The Sonogashira coupling was carried out under mild conditions in the presence of the $A_3B$-type porphyrin **A** bearing a terminal alkyne to chemoselectively functionalize the iodinated position of the precursor. Using $PdCl_2(PPh_3)_2$ and CuI as catalysts in a mixture of tetrahydrofuran and triethylamine (4:1), the desired monoporphyrinic ruthenium complex was isolated in 51% yield after 24h at 45 °C. This monofunctionalized intermediate was next reacted with a large excess of $A_3B$-type porphyrin **B** bearing a boronic ester in the presence of cesium carbonate as base and $PdCl_2$(dppf) as catalyst. After 48h at 100 °C in a DMF/water (99:1) mixture, all the remaining *p*-bromophenylene groups were functionalized and the gear prototype carrying five identical porphyrin fragments but different spacers was obtained in 36% yield [48].




**Scheme 3. Synthetic route to the dissymmetrized gear prototype. One of the spacers between the cyclopentadienyl ligand and the porphyrins contains an additional ethynyl fragment. Ar = 3,5 di-*tert*-butylphenyl.**

This first example of a dissymmetric ruthenium-based molecular gear was thus obtained in two steps from 1-(*p*-iodophenyl)-2,3,4,5-tetra(*p*-bromophenyl)cyclopentadienyl hydrotris(indazolyl)borate ruthenium(II) *via* sequential chemoselective Sonogashira / four-fold Suzuki-Miyaura cross-couplings.

## 4 Conclusion and Perspectives

Alternative strategies are now developed to obtain dissymmetric gears with spacers of identical length, using various porphyrin structures. For that purpose, chemoselective conditions of Suzuki-Miyaura couplings must be identified to discriminate iodoaryl versus bromoaryl groups. Work is also underway to study such dissymmetric molecular gears on surface.

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