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Review

The chemistry of 1,2,3,4,5-pentaphenylcyclopentadienyl hydrotris(indazolyl)borate ruthenium(II) complexes, building blocks for the construction of potential organometallic molecular motors

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Contents

Abstract

In recent years, we have developed a strategy to build electrically addressed molecular motors. The architecture of such compounds is centered around half-sandwich complexes of the family of pentaphenylcyclopentadienyl hydrotris(pyrazolyl)borate ruthenium(II). In this review article, we focus on the synthesis of various pentaphenylcyclopentadienyl ligands and on the peculiar reactivity of such hindered ligands in their coordination to a ruthenium(II) center. Finally, we report on the synthesis of the latest generation of fully equipped potential molecular motors. They bear ferrocene terminal electroactive groups linked to the central pentaphenylcyclopentadienyl ligand either by conjugated or insulating spacers, and are also functionalized to be anchored on various metallic or insulating surfaces in view of near-field microscopy experiments.

Keywords: Molecular motor; Half-sandwich complexes; Pentaphenylcyclopentadienyl ligand; Tris(indazolyl)borate ligand; Ruthenium; Platinum; Ferrocene

1. Introduction

Recent advances in the imaging and manipulation of single molecules [1] has stimulated much interest in the synthesis of molecules exhibiting unique electronic properties but also peculiar mechanical properties. This has stimulated the design and synthesis of a variety of compounds that resemble macroscopic machinery, for instance nanowheels [2], nanocars [3], wheelbarrows [4], nanogears [5], or more generally molecular machines [6]. The design and chemical synthesis of artificial molecular machines is currently an important challenge of nanosciences. A molecular-level machine can be defined as an assembly of molecular components designed to perform a controlled function in response to a stimulus. Among these machines, a motor is a machine, which consumes energy to do work repetitively and progressively on a system via a controlled movement [7a]. Molecular rotary motors represent a very particular challenge, especially the control of the directionality of a repetitive 360° rotary motion. Most of the reported molecular motors [7] have been designed to work in solution. On the contrary, our design is based on the use of a single molecule individually addressed after its deposition between

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two nanoelectrodes separated by a few nanometers (i.e. a nanojunction).

The family of potential molecular motors we present here is composed of two parts: a stator grafted on a solid surface to stay still, and a rotor which should be able to rotate under the influence of a suitably oriented electrical field. The two parts must be rigid in order to have only one significant degree of internal rotation. We have recently presented the concept of an electrically fuelled single-molecular rotary motor based on an organometallic center built around a half-sandwich complexes of the pentaphenylcyclopentadienyl hydrotris(pyrazolyl) borate ruthenium(II) family [8]. This organometallic center is neutral and exhibits a piano stool geometry which allows a free rotation of the cyclopentadienyl ligand (Cp) with respect to the tris(pyrazolyl) ligand (Tp). Moreover, pentaphenylcyclopentadienyl ligands have already been used as rotors in various systems [9] and can be easily substituted by electroactive groups. Their chemistry is very particular since these propeller-type ligands are capable of conferring novel steric and electronic properties to metal centers [10]. Unique properties arise from the steric hindrance provided by the five phenyl substituents, such as steric protection of the organometallic center or influence on the electron releasing ability of the complex. However, the coordination chemistry of such ligands therefore can be very adventurous and surprising. For instance, coordination of the peripheric phenyl rings can occur in place of the central cyclopentadienyl ring [11].

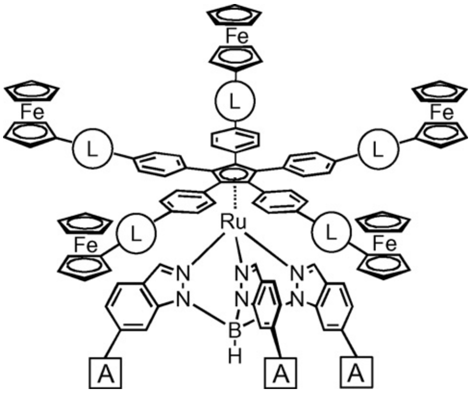


Fig. 1. Potential molecular motors based on a pentaphenylcyclopentadienyl tris(indazolyl)borate ruthenium complex. A symbolizes the different anchoring groups and L the different linkers.

The tris(pyrazolyl)borate ligands, also known as scorpionate ligands, were discovered by Trofimenko in the late 60s [12] and used increasingly since in bio-inorganic, organometallic and coordination chemistry [13]. For these ligands, the steric and electronic environment surrounding the metal center can be easily tuned by the modification of the functional groups connected to the pyrazolyl moiety. However its analogue hydrotris(indazolyl)borate (Tp^{4Bo}) [14], synthesized in 1995 and little studied since, bears some advantages over tris(pyrazolyl)borate and can play the role of the stator in our family of molecular motors. The rigidity of its indazolyl fragments, combined with its tripodal shape, should make it a good candidate for the surface deposition of metal complexes onto surfaces. By withdrawing the metal away from the surface, we can minimize interferences caused by metal–surface interactions, which is particularly important for near-field microscopy experiments. Substituting the indazole rings at the 6-position by anchoring groups will allow the grafting of the complex on the surface of study.

In this review article, we will develop, first, the principle of an electrically addressed molecular motor. Secondly, we will focus on the synthesis of pentaphenylcyclopentadienyl ligands substituted in the para positions by bromine or alkyne groups and on the peculiar coordination behaviour of such hindered ligands towards a ruthenium(II) center. Finally, we will report on the synthesis of potential molecular motors, bearing ferrocene terminal electroactive groups linked to the central Cp by either conjugated or insulating spacers and functional-

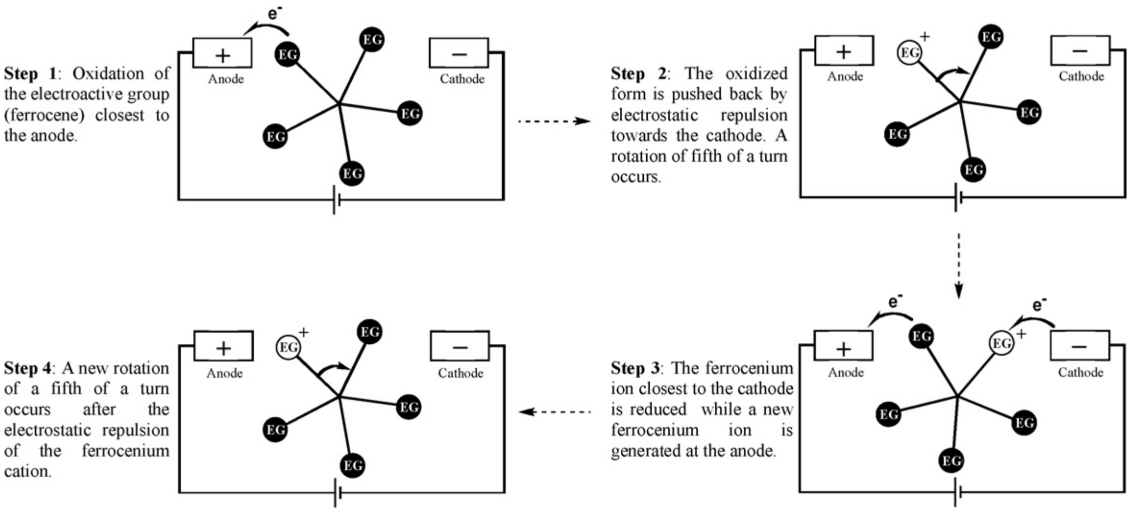


Fig. 2. Schematic representation of a molecule placed between the two electrodes of a nanojunction (EG stands for electroactive group). The transfer of electrons from the cathode to the anode through successive oxidation and reduction processes is expected to result in the clockwise rotation of the entire upper part of the molecule. In this figure is represented a fifth of a turn corresponding to the movement induced by the transfer of one electron.

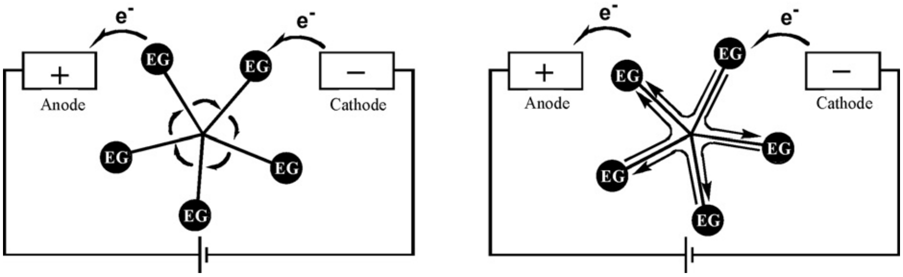


Fig. 3. On the left is shown the wanted phenomenon corresponding to the electron transport by a rotation of the rotor. On the right is represented the mechanism to minimize which is the intramolecular electron transfer without rotation of the rotor.

ized to be anchored on various metallic or insulating surfaces (Fig. 1).

2. Principle of the molecular motor

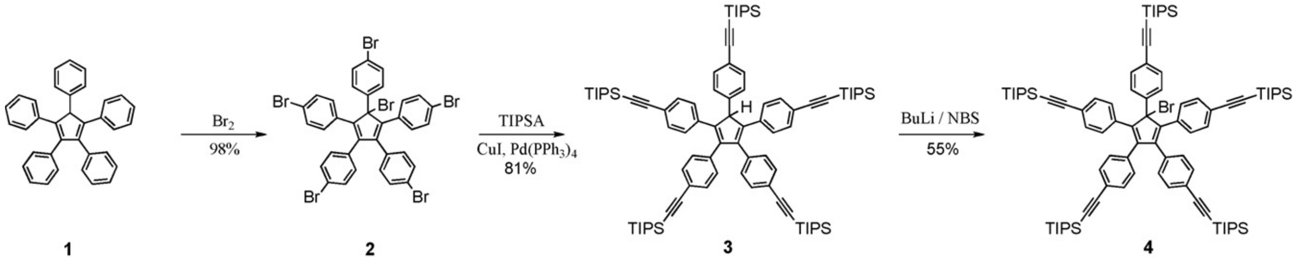
Our target molecules have been designed to be individually addressed after their deposition between two nanoelectrodes located a few nanometers apart (i.e. a nanojunction). The source of energy will be electric and the target molecule is supposed to convert an electric current into a directionally controlled rotary motion.

The concept of our electron-fuelled molecular rotary motor is shown in Fig. 2. The electroactive group (EG) closest to the anode would be oxidized (oxidized form EG^+, in white) and pushed back by electrostatic repulsion as previously shown for a 60-fullerene between two electrodes [15]. This motion would correspond to the start of the rotation. As a result, the oxidized electroactive group would approach the cathode and subsequently be reduced. At the same time, a second electroactive group would come close to the anode and would allow a second cycle to occur. A complete 360° turn would be achieved after five cycles, corresponding to the transport of five electrons from the cathode to the anode. This would correspond to the conversion of an electron flow into a movement of rotation, i.e. a redox-triggered molecular rotary motor. In order for the rotation to be directional, the molecule should be placed in a dissymmetrical environment. This could be achieved either by its disposition in the nanojunction, or by a secondary electric field perpendicular to the nanojunction.

In this design, the rotation has to compete with the undesired intramolecular electron transfer between the electroactive groups (Fig. 3, right). The rotation, a fifth of a turn in the case of a C_5-symmetric rotor, has to be as fast as possible to minimize the competing intramolecular electron transfer between two electroactive units, otherwise the electrons could travel through the carbon skeleton without rotation of the whole rotor. Since a conjugated skeleton can clearly not separate electronically the electroactive groups, we incorporated an organometallic insulating spacer to disrupt the electronic communication between the ferrocene group. Therefore the charge localization on one single oxidized ferrocenyl unit, which should be the site of the oxidoreduction cycles in the desired process, should be favoured.

3. Synthesis of the pentaphenylcyclopentadiene building blocks

The pentaphenylcyclopentadienyl anion is an attractive ligand, as its precursors are readily synthesized in large quantities and are air stable. The $C_5Ph_5^-$ ligand appears to be more electron withdrawing than cyclopentadienyl and pentamethylcyclopentadienyl anions and its large volume is reported to confer enhanced kinetic stability to organometallic derivatives [16]. The synthesis of the pentaphenylcyclopentadienyl ligands used in this study is outlined in Scheme 1. The commercially available 1,2,3,4,5-pentaphenylcyclopentadiene (**1**) was brominated in para position in neat bromine to give **2** in a 98% yield [17]. A Sonogashira coupling between **2** and an excess of tri(isopropyl)silylacetylene (TIPSA) gave the product of quintuple coupling **3** with a remarkable 81% isolated yield [18]. The bromine linked to the Cp ring is substituted by a hydrogen atom and no coupling reaction in this position was observed. The hydrogen atom can be substituted back by bromine by reacting **3** with *n*-butyllithium to form the corresponding cyclopentadienide anion, which is subsequently quenched with *N*-bromo succinimide (NBS). After



Scheme 1. Synthesis of the pentaphenylcyclopentadienyl ligands.

purification by column chromatography, the TIPS-protected penta(4-ethynylphenyl)cyclopentadiene (**4**) was obtained in a 55% yield [16]. This new synthon is a versatile precursor, very well suited to give access to a large variety of heteropolynuclear complexes due to its polytopicity. Indeed, its coordination can take place step by step, binding the Cp ring first and then the five alkyne functions or in the opposite way, depending on the types of metals.

This family of substituted pentaphenylcyclopentadienyl ligands derived from compound **4** was coordinated step by step, binding the Cp first to form the half-sandwich ruthenium complexes which make the core of our molecular motor.

4. Coordination of the pentaphenylcyclopentadiene ligands

Two routes have been described in the literature to synthesize half-sandwich RuCpTp and RuCp*Tp complexes. The most general one has been described by Mann et al. [19] using the η^5-cyclopentadienyltris(acetonitrile)ruthenium(II) complex where the labile acetonitrile ligands can be easily substituted by a Tp ligand. A second route has been described by Singleton [20] using as intermediate the chloro η^5-cyclopentadienyl η^4-cycloocta-1,5-diene ruthenium(II) complex.

In the route described by Mann, the key cyclopentadienyltris(acetonitrile) ruthenium complex can be obtained by a photolabilization of η^5-cyclopentadienyl η^6-arene ruthenium(II) complex precursors in acetonitrile. These arene ruthenium complexes can be synthesized from various precursors depending on the source of ruthenium (Fig. 4). The complex $RuCp(C_6H_6)^+$ can be obtained by the reaction between the oligomer $[Ru(C_6H_6)Cl_2]_n$ and thallium cyclopentadienyl [21]. For $RuCp_2$, the exchange of a Cp ligand by an arene has been shown by Vol'kenau et al. [22]. A ruthenium complex with the pentamethylcyclopentadienyl (Cp*) ligand can be obtained following the methodology of Kudinov by reacting Cp*H with ruthenium(III) chloride in benzene [23]. The ruthenium carbonyl cluster can also be used as a source of ruthenium as shown by Mann et al. [24].

We have tried to adapt the procedures [23,25,26] used to coordinate cyclopentadiene or pentamethylcyclopentadiene to a ruthenium atom to the functionalized pentaphenylcyclopentadienyl ligands **1** and **3**. Different strategies depending on the source of ruthenium were considered. Ruthenium chloride is known to react with pentamethylcyclopentadiene (Cp*H) in ethanol to form the $[Cp^*RuCl_2]_n$ oligomer which can be reduced in the presence of an arene to yield the $[Cp^*Ru(arene)]^+$ complex [23,25]. However, by heating at reflux **1** in ethanol with benzene no reaction was observed (Fig. 5). This lack of reactivity may be due to the lack of solubility of the ligand **1**. The same reaction with **3**, which is more soluble due to the triisopropylsilyl groups, did not yield a better result even by adding zinc powder as a reducing agent [26]. These two ligands seem to be too hindered to form an oligomer with ruthenium(III) chloride.

A procedure using the $[Ru(p\text{-cymene})Cl_2]_2$ dimer as a ruthenium source for coordinating a substituted Cp ligand has also been described [27]. *n*-Butyllithium was added to a solution of **1** in THF at −78 °C to generate the pentaphenylcyclopentadienide anion, which was subsequently reacted with $[Ru(p\text{-cymene})Cl_2]_2$ at room temperature. After solvent evaporation and anion metathesis with NH_4PF_6, a green precipitate was obtained in low yield. However, instead of the expected complex, a ruthenium complex with an additional chloride was obtained, as indicated by mass spectrometry.

The reactivity of the substituted pentaphenylcyclopentadienyl ligand seems to be very different from the one of cyclopentadiene and pentamethylcyclopentadiene, probably due to a strong difference in the steric hindrance at the level of the Cp ring.

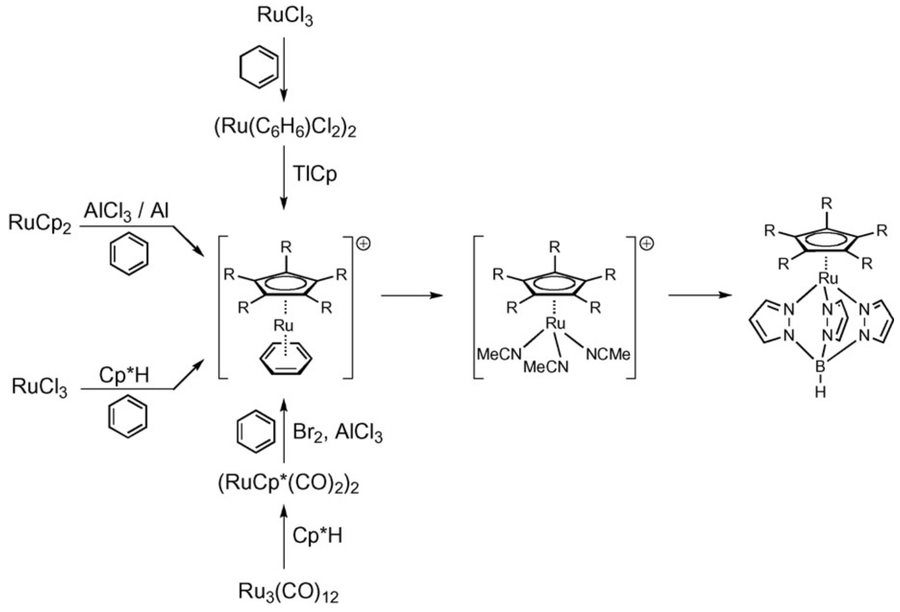


Fig. 4. Various synthetic routes for the synthesis of $[RuCp(arene)]^+$ complexes.

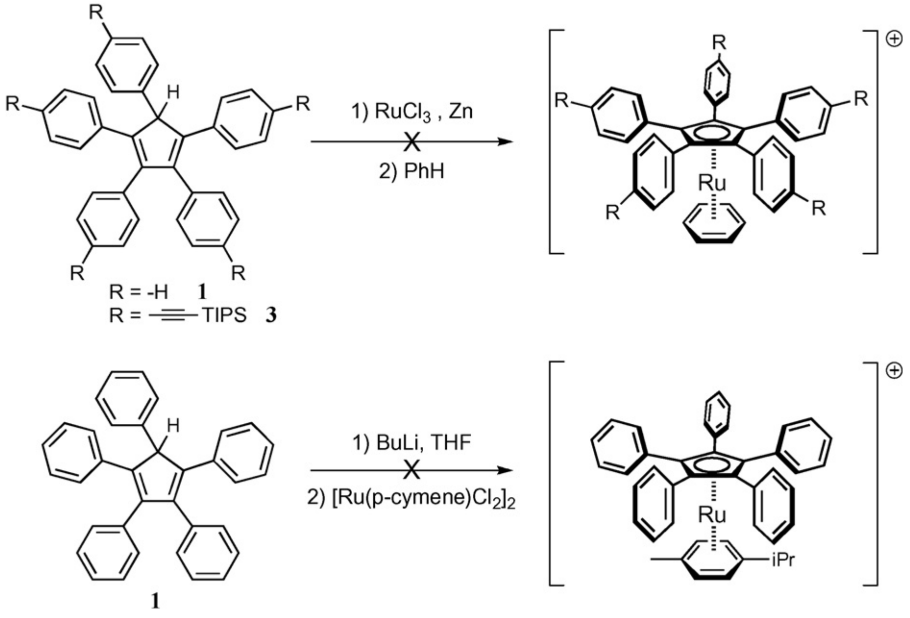
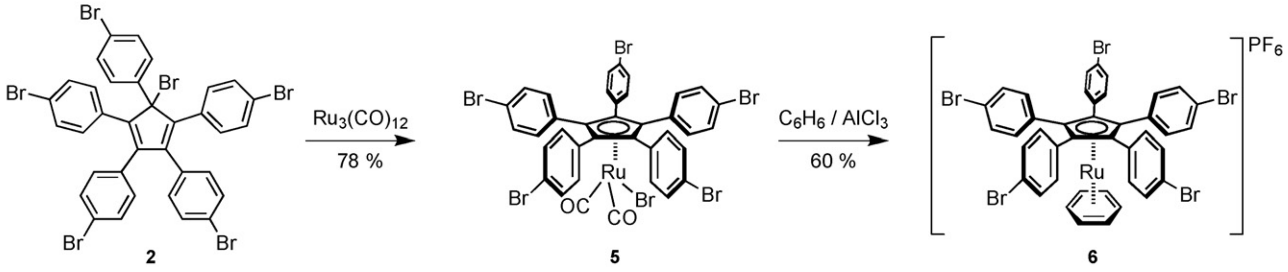


Fig. 5. Attempts of direct coordination of ligands **1** and **3**.



Scheme 2. Efficient coordination of pentaphenylcyclopentadiene to ruthenium.

The only methodology described in the literature for the coordination of a pentaphenylcyclopentadienyl ligand is the one described by Manners [28]. 1-Bromo-1,2,3,4,5-penta(phenyl)cyclopentadiene gives an oxidative addition on the $Ru_3(CO)_{12}$ cluster to yield bromo η^5-1,2,3,4,5-penta(phenyl)cyclopentadienyl dicarbonyl ruthenium(II). The brominated ligand **2** was refluxed in toluene with ruthenium carbonyl to yield, after purification by column chromatography, to the ruthenium complex **5** (Scheme 2). This complex was characterized by ^{1}H NMR which shows only one AA'BB' system for the aromatic protons. Moreover the IR spectra showed two characteristic vibration bands of the carbonyl ligands at 2003 and 2048 cm^{-1} comparable to the ones in $[RuCpBr(CO)_2]$ [28]. The substitution of the carbonyl and bromine ligand by benzene has been described for the bromo η^5-1,2,3,4,5-penta(phenyl)cyclopentadienyl dicarbonyl iron(II) [29].

The same procedure was followed for **5**, which was refluxed in benzene with $AlCl_3$ during 6 days. After an anion exchange by hexafluorophosphate, the benzene ruthenium complex **6** was isolated after recrystallization in a 60% yield. The simplicity of the NMR spectra showed the free rotation of the two ligands coordinated to the ruthenium.

In this family of complexes, the arene ligand can be photolabilized under UV irradiation. If the reaction is performed in acetonitrile the arene is substituted by three acetonitrile ligands

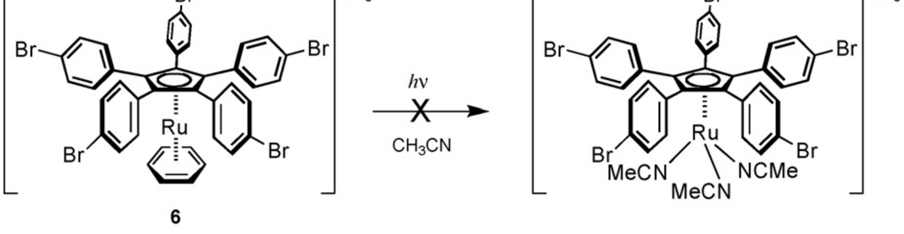
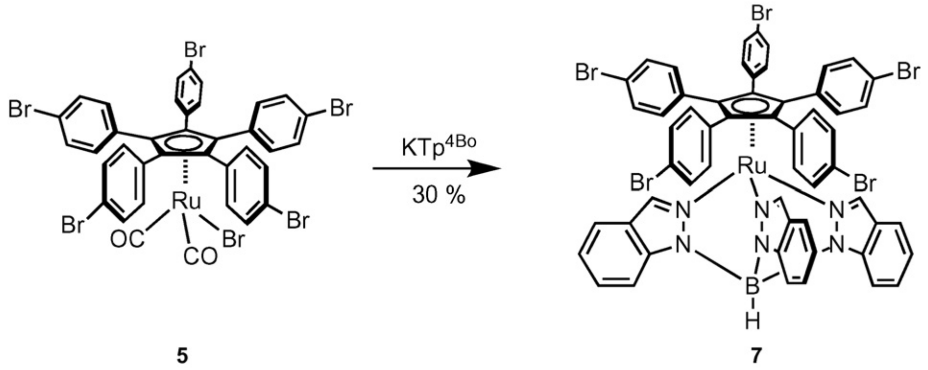


Fig. 6. Attempt of photolabilization of brominated ruthenium arene complexes.



Scheme 3. Synthesis of the key ruthenium complex **7**.

[19]. However when the complex **6** was irradiated in acetonitrile, only decomposition products were observed, probably produced by the cleavage of the carbon–bromine bond during the irradiation process (Fig. 6). Therefore, we adopted an alternative synthetic strategy to reach our goal.

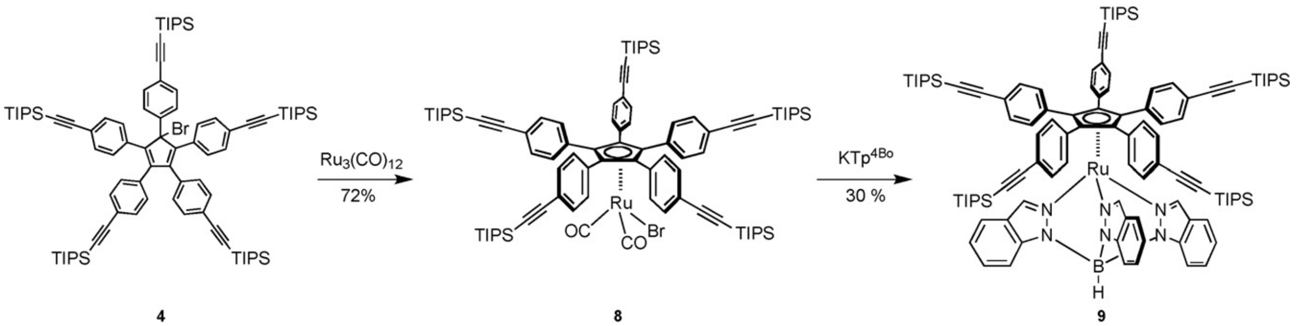
The direct substitution of the carbonyl and bromine ligands by a Cp ligand has been described for bromo 1,2,3,4,5-penta(phenyl)cyclopentadienyl dicarbonyl iron(II) [29,30]. The bromine is substituted by η^1-cyclopentadiene, then a thermal decarbonylation yields the pentaphenylferrocene. Similarly, the synthesis of complex **7** was realized by a direct substitution of the carbonyl and bromine ligands of **5** by the scorpionate ligand hydrotris(indazolyl)borate [31] (Scheme 3).

Coordination of the scorpionate ligand was achieved by a one-pot substitution of the bromide ligand and CO displacement by heating **5** with 2 equiv. of potassium hydrotris(indazolyl)borate for 24 h in freshly distilled THF under argon. After purification by column chromatography, **7** was obtained with a 30% yield. Reaction time, temperature and solvent have been varied, but none of these changes resulted in an improved yield. Nevertheless, the coordination of the tripodal ligand is the result of two steps and the presence of various ligands (Tp^{4Bo}, Cp, CO, Br) in the reaction mixture may allow numerous side reactions. The use of two equivalents of hydrotris(indazolyl)borate seems to be necessary, given that the yield drops to 16% if only one equivalent is used. The use of microwave irradiation reduces the reaction time to 5 min with a similar yield of 25%. Trimethylamine-*N*-oxide has been widely used in the literature to remove carbonyl ligands by oxidizing them to CO_2 [28,32]. However, in our case, the use of trimethylamine-*N*-oxide did not improve the reaction yield.

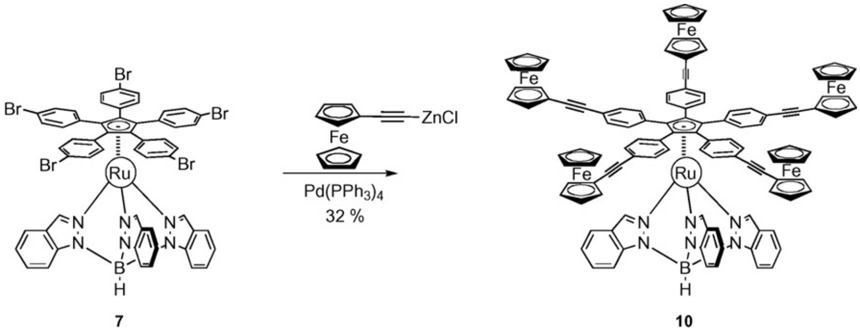
In summary, the key half-sandwich ruthenium complex **7** was obtained in three steps from pentaphenylcyclopentadiene with an overall yield of 23%. The same procedure can be used to coordinate the alkyne-substituted pentaphenylcyclopentadiene ligand **4** (Scheme 4). Ruthenium was coordinated to **4** by an oxidative addition on $Ru_3(CO)_{12}$, giving complex **8** in 72% yield after chromatography. Reacting **8** with potassium tris(indazolyl)borate (KTp^{4Bo}) yielded complex **9**, together with another unidentified complex of similar polarity that was hardly separable by chromatography. An analytically pure sample of **9** could be obtained in 30% yield after a second chromatographic purification, although the yield of the reaction was clearly higher.

5. Synthesis of a family of potential molecular motors

The synthesized ruthenium complexes **7** and **9** are the cores of our molecular motors. The presence of the five aryl bromide groups of on complex **7** allows the direct connection of the ferrocene electroactive groups, leading to complex **10** after a quintuple coupling reaction provided by a Pd-catalyzed C–C coupling reaction. All attempts performed under Sonogashira conditions with various catalysts and phosphines, and even the very bulky and electron-rich tris(tert-butyl)phosphine, resulted in no reaction. This may be due to the high electron density of the bromide derivative, which is covalently linked to a formally anionic entity (Cp). The electron-rich character of the C–Br bond



Scheme 4. Synthesis of the key ruthenium complex **9**.

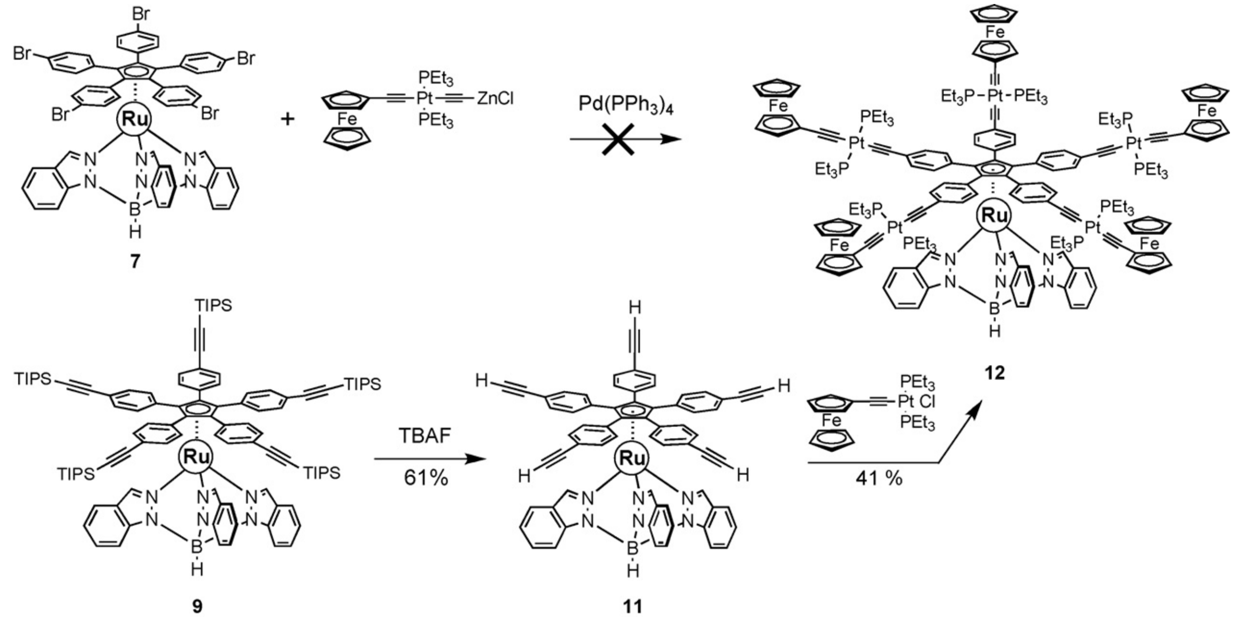


Scheme 5. Synthetic scheme of the molecular motor **10**. The lower ligand is the stator and the upper ligand is the rotor with five ferrocene-terminated arms. The ruthenium plays the role of joint between the two ligands.

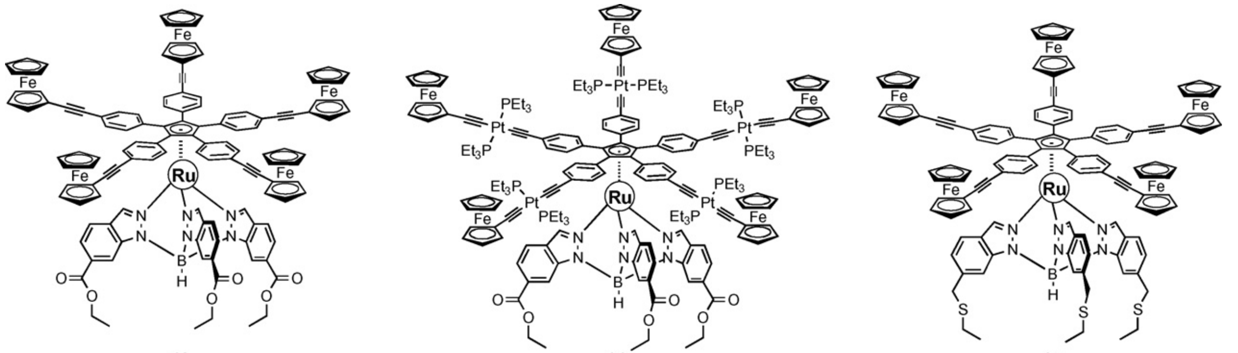
precludes oxidative addition on the palladium catalyst. However, the five electroactive groups could be simultaneously covalently attached to the rotor by a quintuple coupling of ethynylferrocene with **7** under Negishi conditions (Scheme 5) [8a]. The specificity of this protocol resides in the use of a freshly prepared alkynyl zinc chloride solution instead of an alkynyl cuprate generated in situ. **7** was reacted with two times 20 equiv. of freshly prepared [(ferrocenyl)ethynyl]zinc chloride in the presence of $Pd(PPh_3)_4$ in refluxing THF. **10** was isolated by column chromatography in 32% yield, which corresponds to a yield of 80% per coupling. ^{1}H NMR spectroscopy clearly showed an AA’BB’ pattern for the phenyl groups attached to the central Cp ring and the signals of the ferrocene units integrated for 45 protons.

Once the active part of the molecular motor **10** was synthesized, all the requirements for such a molecule to operate as a molecular motor were checked. (i) The oxidation potential of the iron is lower (0.52 V/SCE) compared to the ruthenium center (0.82 V/SCE) which is compatible with our objective, in the sense that the ruthenium center will remain inert towards the redox cycles of the peripheral electroactive groups. (ii) Electrochemical processes are reversible, showing the robustness of the molecule towards oxidation. (iii) No intervalence band was observed by spectroelectrochemistry, showing that the electronic communication between two iron centers is very weak. Electronic communication is here an unwanted phenomenon since it would allow a charge transport by intramolecular electron hopping between different ferrocene centers, without real motion of the rotor. (iv) The rotation barrier of the rotor is very low. Magnetic equivalence of different nuclei, as observed in solution NMR studies, are a good probe for free rotation. This is a random process in which the rotor part of the molecule explores rapidly many conformations, with back and forth irregular motions. This is very different from the rotation occurring in a macroscopic mechanical motor. At the molecular scale, the inertial forces play a negligible role, and cannot sustain the directionality of the motion. A variable low temperature ^{1}H NMR study of **10** down to −90 °C did not give any information concerning the barrier of rotation which is therefore supposed to be lower than 10 kcal mol^{-1}. DFT calculations allowed us to evaluate this barrier to 4.5 kcal mol^{-1} [33].

The absence of intervalence transition in the complex does not guarantee that the rate of ferrocene–ferrocenium exchange will



Scheme 6. Synthesis of the molecular motor **12** fully equipped with insulated electroactive groups.



13 **14** **15**

Fig. 7. Three potential molecular motors with different functionalized tripodal stators. **13** and **14** are equipped with the ester functions to be deposited on alumina in between two electrodes of a nanojunction and **15** with the thioether groups to be anchored on metallic surfaces.

be sufficiently small for our purpose. Moreover, a conjugated skeleton can clearly not separate electronically the electroactive groups. Therefore, we also developed the synthesis of insulating spacers based on platinum acetylide fragments [18,34]. Such spacers are presumed to insulate the ferrocene groups by disrupting the electronic communication between them, possibly due to the σ character of the Pt–C bonds, which breaks the conjugation of the different submodules. Therefore the charge localization on one single oxidized ferrocenyl unit, which should be the site of the oxidoreduction cycles in the desired process, should be favoured. A theoretical approach combining geometry optimization by DFT and extended Hückel calculations on bis-ferrocenyl model compounds allowed to estimate the electronic communication parameter V_{ab} between ferrocene units, showing a fourfold attenuation in the presence of a *trans*-platinum spacer between the two iron centers [34].

Since the direct coupling between **7** and an ethynyl(ethynylferrocenyl)platinum complex under Negishi conditions failed, a second route using complex **9** was followed (Scheme 6). The alkyne functions carried by the ruthenium core were coupled to a chloro ethynylferrocenyl platinum complex [34]. The TIPS protecting groups of the ruthenium complex **9** were removed by overnight reaction with TBAF to yield the pentayne ruthenium precursor complex **11**. Its quintuple coupling with the chloro ethynylferrocenyl platinum complex gave the desired product **12** in 41% isolated yield. This star-shaped heterotrimetallic complex was fully characterized by multinuclear NMR spectroscopy, MALDI-TOF spectrometry and cyclic voltammetry. Oxidation of the five iron centers occurs simultaneously at a potential of 0.31 V/SCE, followed by oxidation of the ruthenium center at 0.60 V/SCE. These values are lower than the potentials measured in the non-insulated complex **10**, which presents an oxidation wave at 0.52 V/SCE, showing the electron-rich character of the diphosphinoplatinum fragments that are able to stabilize the Fe(III) oxidation state. The platinum centers were not oxidized within the potential window used (−1.8 to +1.5 V/SCE in dichloromethane). In addition, preparative electrolysis of **12** was performed on a platinum grid, first to oxidize the ferrocene sites, then to oxidize the ruthenium site. After back reduction, the starting material was recovered unchanged, showing the robustness of the molecule towards oxidation. Finally, after performing a partial oxidation of the ferrocene sites, no intervalence transition between Fe(II) and Fe(III) was observed, thus confirming the absence of measurable electronic communication between the electroactive ferrocene units.

6. Current directions

Recently we developed the synthesis of functionalized tris(indazolyl)borate ligands and synthesized the corresponding molecular motors. The functionalized borate ligands were designed to have three functional groups pointing on the opposite direction of the coordination site in order not to interfere sterically with it. Each of the three legs of the tripodal unit bears a functional group connected at the 6-position of indazole, which should be, on the basis of the X-ray structures obtained on the cyclopentadienyl model complexes [35], the optimal orientation for anchoring on a surface. The first one incorporates ester-functionalized indazoles to anchor complexes onto the oxide surface used as insulator in molecular scale non-contact atomic force microscope (NC-AFM) experiments. The second tripod bears thioether-functionalized indazoles to anchor complexes onto metal surfaces such as gold or copper in view of STM experiments. The coordination of both ligands was similar to the coordination of the unfunctionalized tripod and the redox potentials are still compatible with our project, the ruthenium center being oxidized at higher potentials than the ferrocene centers. The three ruthenium complexes synthesized with the ester or thioether-functionalized ligand is shown in Fig. 7.

7. Concluding remarks

Work is currently underway to anchor molecule **15** on a metallic surface. Using variable temperature STM should grant us to have access to the temperature threshold above which the rotor will rotate freely as well as to the rotation barrier. Work is also underway to anchor molecules **13** and **14** on an oxide surface in view of addressing them by the means of two metallic electrodes. The demonstration of a controlled rotary movement will then need further experimental developments by physical methods such as scanning probe microscopies or the analysis of the time dependence of the current in a two-electrode configuration.

Although some progress has been made, it is still a long way to practical applications.

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