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Synthesis of a photoswitchable azobenzene-functionalized tris(indazol-1-yl) borate ligand and its ruthenium(II) cyclopentadienide complex☆

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ABSTRACT

In this paper, the design and synthesis of a new indazole bearing a photoisomerizable fragment at its 4-position are presented as well as the photoisomerization studies on both the indazole precursor and the final ruthenium model complex. It was obtained after five steps, the last one being the cleavage of the indazole protecting group. Reaction of 1 equiv of this functionalized indazole with 2 equiv of plain indazole and dibromophenylborane gave access to a mixture of four tripodal ligands of the tris(indazolyl)borate family. In a last step, complexation of this mixture with $[RuCp(CH_3CN)_3]PF_6$ yielded the corresponding ruthenium complexes from which the target ruthenium complex coordinated to a dissymmetric azobenzene-functionalized tripodal ligand was successfully isolated. Photoisomerization occured reversibly upon irradiation with UV light at 365 nm.

1. Introduction

In the past 10 years, chemists have been able to build more and more complex molecular architectures following a bottom-up strategy.[1] This approach consists to synthesize molecules and to use them as elementary building blocks to construct multifunctional nanomachines.[2] Among others, biomimetic or technomimetic[3] nanomachines like molecular gears,[4] molecular muscles,[5] nanowheels,[6] nanovehicles,[7] wheelbarrows,[8] molecular rotors,[9] motors[10] and turnstiles[11] are the archetypes of such as molecular machinery. They provide a basis for the future design of bottom-up nanoscale systems and materials to perform tasks as varied as nanoscale manipulation, information storage, molecular electronics and mechanics. Study of the features of such molecules could be achieved with the help of sophisticated tools such as close field microscopies (STM and NC-AFM), which are able to image and manipulate single molecular objects on atomically-controlled surfaces.[12] In this perspective, a family of molecular motors was designed and developed in the group to study the possibility to control and exploit a controlled rotation on a surface.[13] These molecules belong to a family of half-sandwich ruthenium complexes, in which the metallic atom acts as a joint between a penta(ethynyl ferrocenyl)phenylcyclopentadienyl rotor and a hydrotris (indazol-1-yl) borate stator (Fig. 1). Our current goal is to integrate an additional functionality in the molecule by introducing an isomerizable fragment in the backbone of the tripodal ligand. With this aim in view, a dissymmetric tripodal ligand was designed and synthesized, one indazole being functionalized by an azobenzene fragment.

Since the discovery of the tris(pyrazolyl)borate ligand in the late 60s by Trofimenko,[14] several structural modifications have been developed to such tripodal ligands by adjustment of the pyrazole or the indazole rings.[15] Electronic properties and steric hindrance could be easily modified through the modulation of the azole building blocks. In our family of molecular motors, a series of tris(indazolyl)borate ligands bearing functional groups at the 6-position of each indazole was recently described.[16] Ester functions were introduced to anchor the molecule by chemisorption to an oxide surface, while functionalization by thioethers is expected to allow covalent attachment of the ruthenium complexes on metallic surfaces. Moreover, such molecular motors were designed in order to be placed between two electrodes of a nanojunction. These molecules have ferrocenyl electroactive groups connected to a central cyclopentadiene (Cp) ring. Each of them will be the siege of successive oxidoreduction processes inducing the rotation of the upper part (the Cp ligand) compared to the lower part (the tripodal ligand). In this paper we present the integration of a photoswitchable azobenzene fragment aimed at acting as a light-driven brake to control the rotor's speed of rotation.

☆ In memory of Christiane O. Dietrich-Buchecker (1942–2008).

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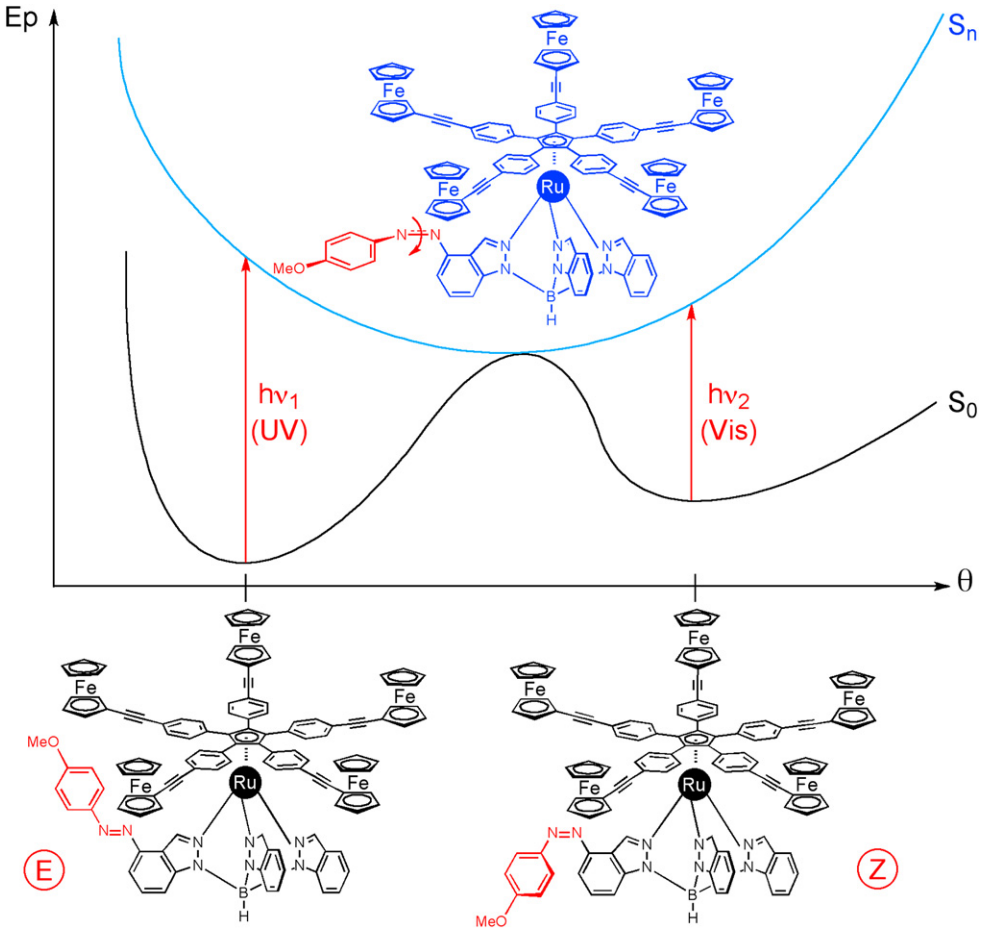


Figure 1. Simplified isomerization mechanism of the target cyclopentadienyl ruthenium(II) complex. In the *Z* conformation, rotation of the Cp ring would be blocked due to the insertion of the azobenzene between two arms of the rotor. Irradiation of the diazobenzene fragment and isomerization to the *E* conformation releases the brake and allows rotation.

Azobenzenes are well-known to photoisomerize reversibly from the *Z* to the *E* conformation, both isomerization processes occurring under irradiation at different wavelengths. Isomerization from the *E* to the *Z* form occurs under UV irradiation, whereas the reverse transformation follows irradiation in the visible range. Besides, the $Z \rightarrow E$ conversion is also thermally triggered. The most likely mechanism for this isomerization is presented in Figure 1.[17] This diagram illustrates the bistability of the azobenzene fragment. Nevertheless, both isomers always coexist due to the photostationary equilibrium, the minor one being present in a non-negligible ratio. Isomerization from one conformation to the other by light excitation occurs via a $\pi_{N=N} \rightarrow \pi_{N^{*}=N}$ transition through an excited state S_N. Relaxation follows a non-radiative pathway due to several intersystem crossings[18] and isomerization occurs via rotation around the N–N bond.

According to the geometry of the N=N bond and the steric hindrance it induces, control of the rotation in the target molecular motor is expected to occur as shown in Figure 1. For that purpose an azobenzene fragment was introduced in the design. In this paper, the synthesis and characterization of a dissymmetrized tris(indazolyl) borate ligand bearing an azobenzene substituent and its cyclopentadienyl ruthenium(II) complex is described, as well as the photoisomerization studies on the azobenzene-functionalized indazole and on the model ruthenium complex.

Moreover, a tripodal ligand with one functionalized indazole is also of special interest for subsequent studies on surfaces since it presents the advantage to integrate a tag. One indazole ring being different from the two unfunctionalized indazoles, it enables to establish if the stator is properly (i.e., covalently) fixed on the surface.[19]

2. Results and discussion

2.1. Molecular modelling

Once the functional brake fragment had been chosen, the question of the best position to incorporate it in the design was addressed by molecular modelling. Theoretical calculations on the *Z* and *E* isomers substituted at the 4- and 5-position of the indazole showed that in only the *E* isomer substituted at the 4-position, the rotation is effectively blocked by an efficient steric hindrance (Fig. 2 top left) since the diazobenzene fragment fits between two phenylethynylferrocenyl substituents of the pentaphenylcyclopentadienyl ligand. On the contrary, the rotor appears to be free to rotate in the *Z* conformation, this geometry being reached after UV irradiation (Fig. 2, top). The calculations also showed (Fig. 2 bottom left) that the functionalization at the 5-position is inefficient with respect to locking the rotation, the steric hindrance between the azobenzene fragments and the pentaphenylcyclopentadiene fragments being totally supressed.

2.2. Retrosynthetic analysis

Two retrosynthetic approaches were considered for the synthesis of an indazole bearing an azobenzene substituent (Scheme 1). The first one envisages to form the diazo bridge first and the

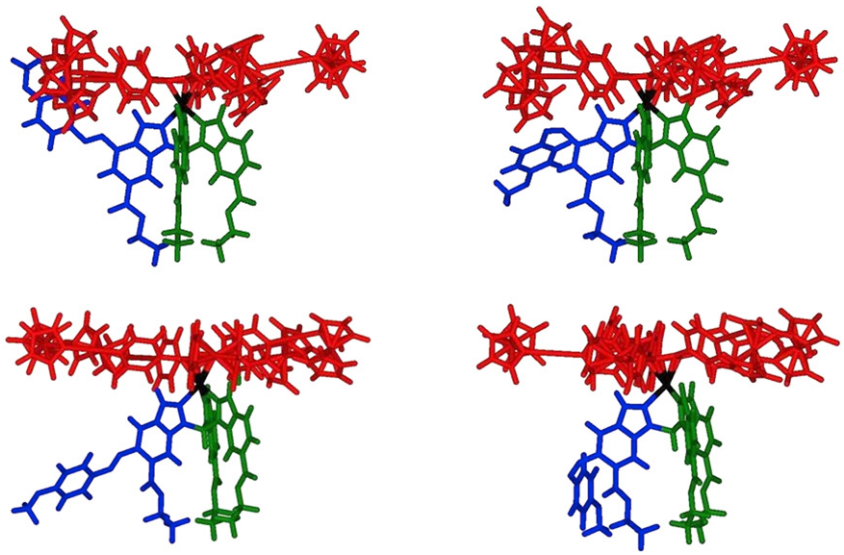
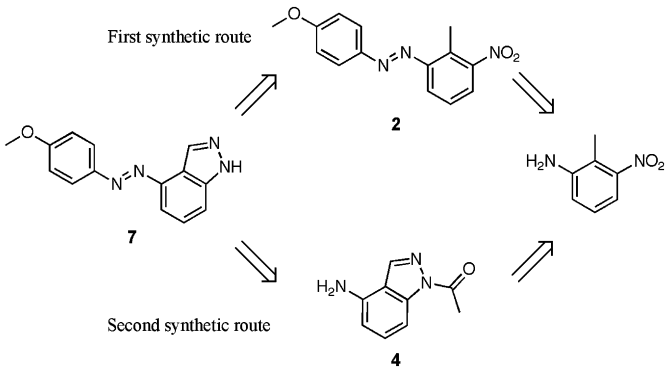


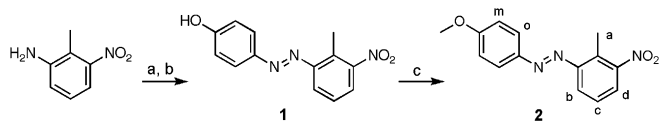
Figure 2. Top: azobenzene fragment connected to the 4-position of the indazole ring (left the *E* isomer, right the *Z* isomer). Bottom: azobenzene fragment connected to the 5-position of the indazole ring (left the *E* isomer, right the *Z* isomer). Clearly, the *E* azobenzene fragment connected at the 4-position (top left) is the most suitable isomer to lock the rotation. Whereas in the 5-position, the photoisomerizable group does not have sufficient interaction with the rotor (upper ligand in red).

indazole ring subsequently. The second one proceeds in the reverse order. Purification is expected to be facilitated in the first case because pyrazole and indazole derivatives show strong H-bonding interactions with silica gel, which usually renders their chromatographic separation tedious.



Scheme 1. Retrosynthetic analysis for the formation of the diazobenzene-functionalized indazole. The first synthetic route introduces the diazo bridge at the beginning of the strategy whereas the second one creates the indazole ring first.

As shown in Scheme 2, compound **2** was obtained in two steps. Among all the possible ways to create the diazo bridge, a phenolic coupling under basic conditions between 1-methyl-2-nitroaniline and phenol was selected.[20]

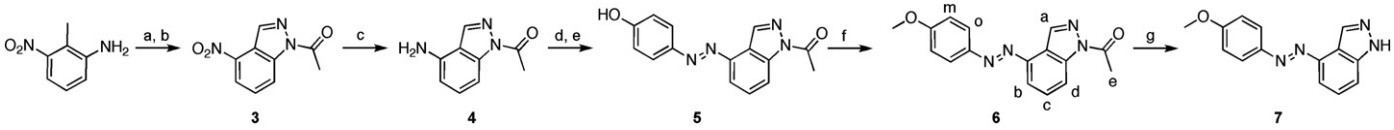


Scheme 2. First synthetic route for the formation of the functionalized indazole. a) $NaNO_2$, HCl, H_2O/acetone (1/1), 15 min, 0 °C; b) PhOH, NaOH, Na_2CO_3, 2 h, 0 °C, 59%; c) MeI, K_2CO_3, toluene, 3 h, 65 °C, 53%.

First, conversion of the amino functional group to the corresponding diazonium salt was achieved, followed by an electrophilic substitution with phenolate. After acidic work-up, the phenol was methylated via a nucleophilic substitution using methyliodide under basic conditions. This protection was performed to avoid unwanted reactions of the phenolic protons during the subsequent steps of the synthesis, such as O-coordination to the boron atom during the tripode formation step but also the tautomeric equilibrium between the phenol and the quinone–hydrazone form.[21] An overall yield of 31% was obtained for these two steps. Reduction of the nitro functional group to amino failed using various conditions such as classical hydrogenation catalyzed with Pd/C, tin chloride in stoichiometric amount or tin(0) in acidic conditions.[22] Many side reactions involving the diazo bridge could explain this result since reduction of the diazo group to form hydrazine derivatives has been observed, but one could also imagine a reduction to an oxime or Mills' reaction.[23]

2.3. Synthesis of the azobenzene-functionalized indazole

The second synthetic route shown in Scheme 3 yielded the desired indazole **7**. The synthesis of the indazole functionalized with an azobenzene fragment was achieved in five steps. The indazole ring was formed in a first step according to Jacobson's procedure.[24] 1-Methyl-2-nitro-aniline was reacted with acetic anhydride and potassium acetate followed by isoamylnitrite, yielding the desired protected indazole (**3**). It is interesting to note that cleavage of the *N*-acetyl protecting group by hydrochloric acid was not performed as it is usually done. This presents the advantages to mask the nucleophilicity of the indazole fragment for further steps and to ease the purification by column chromatography by avoiding the presence of a free NH group, which would strongly interact with the stationary phase. *N*-Acetyl-4-nitro-indazole (**3**) was obtained in 60% yield. A catalytic hydrogenation was then performed under a hydrogen atmosphere using Pd/C as catalyst, which gave access to **4** with a 82% yield. The next step involved the formation of the azobenzene bridge. Compound **4** was first reacted with sodium nitrite and hydrochloric acid to give the corresponding diazonium salt. Subsequently, an aqueous solution of phenolate was added to yield the diazobenzene-functionalized indazole (**5**) with a satisfying 78% yield. As previously described (vide supra), the phenol function was methylated to avoid any possible side-reaction of the phenolic proton. The methylated derivative **6** was thus obtained in 74% yield. The last step consisted in the selective cleavage of the *N*-acetyl protective group of the indazole ring performed quantitatively by action of a 0.01 M of sodium

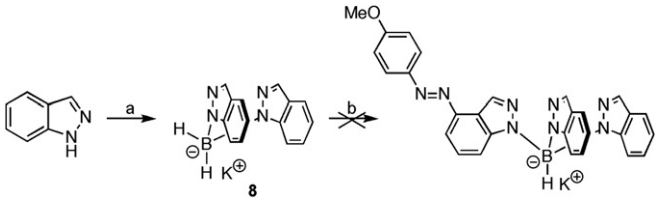


Scheme 3. Synthesis of 4-(diazenyl(4-methoxyphenyl))indazole (**7**). a) AcOK, Ac_2O, toluene, 15 min, 25 °C; b) isoamylnitrite, toluene, reflux, overnight, 60%; c) H_2, Pd 10%/C, THF, 12 h, 25 °C, 82%; d) $NaNO_2$, HCl, H_2O/acetone (1/1), 15 min, 0 °C; e) PhOH, NaOH, Na_2CO_3, 2 h, 0 °C, 78%; f) MeI, K_2CO_3, THF, overnight, 65 °C, 74%; g) MeONa, MeOH, 20 min, 25 °C, 98%.

methoxide solution.[25] In summary, the synthesis of the indazole integrating an azobenzene function (**7**) was realized in five steps with a global yield of 28%.

2.4. Synthesis of the tripodal ligand: first attempt

The synthesis of the target tripodal ligand was first attempted following the method developed by Trofimenko for tris(pyrazolyl)borates. This strategy is based on the thermal control of the number of coordinated pyrazoles on the boron centre: coordination of two pyrazoles requires heating with KBH_4 at 120 °C without any solvent. A temperature of 180 °C allows the coordination of a third pyrazole and finally a fourth pyrazole at a temperature above 220 °C. However following the procedure described in the literature for the synthesis of dihydrobis(pyrazolyl) borate, formation of dihydrobis (indazolyl)borate (**8**) could not be achieved.[26] In the indazole series, the optimized preparation of potassium dihydrobis(indazolyl)borate involved heating 4 equiv of indazole with KBH_4 at 170 °C (Scheme 4) until the expected volume of dihydrogen had been evolved.



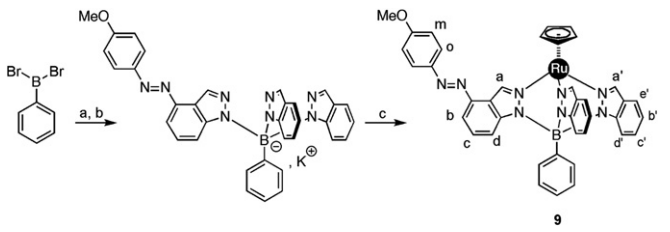
Scheme 4. Synthesis of potassium dihydrobis(indazolyl)borate and attempt of formation of the corresponding potassium hydro-4-((*p*-methoxyphenyl)diazenyl) indazolylbis(indazolyl)borate. a) 4 equiv Indazole, KBH_4, 170 °C, argon, 3 h; b) **7**, 180 °C, Ar, 3.5 h.

It is obvious to note that the temperature should be precisely monitored to avoid the formation of hydrotris(indazolyl)borate, which could be initiated at such temperature.

Since column chromatography is totally inefficient for such compounds due to the strong and similar interactions of the different borate ligands with the stationary phase (silica or alumina), the desired compound was purified by sublimation and then trituration in hot toluene. This work-up protocol allowed isolation of potassium dihydrobis(indazolyl) borate **8**, as confirmed by ^{1}H NMR analysis. The synthesis of the dissymmetric tripodal ligand was attempted by mixing **7** and **8** (1/1) in a mortar and heating this homogeneous powder at 180 °C during 3.5 h under an argon atmosphere. The medium turned black and an evolution of gas was observed but the desired compound was not present in the mixture.

2.5. Alternative synthesis of the tripodal ligand and its cyclopentadienyl ruthenium(II) complex

An alternative strategy presented in Scheme 5 was finally employed to synthesize the tripodal ligand. It was based on the statistical reaction of two different types of indazoles with phenyldibromoborane as boron precursor.[27] This compound was obtained by reaction of boron tribromide on trimethylsilylbenzene via an electrophilic substitution at the *ipso*-position. Then, 2 equiv of indazole were statistically reacted with



Scheme 5. One pot synthesis of potassium phenyl-(4-(*p*-methoxyphenyl) (diazenyl)indazolylbis(indazolyl)borate and formation of its cyclopentadienyl ruthenium(II) complex. a) **7** and indazole (1/2), benzene, NEt_3, 12 h, 25 °C; b) ^{t}BuOK, THF/benzene (1/1), 12 h, Ar, 60 °C; c) $[RuCp(NCCH_3)_3]PF_6$, MeCN, 12 h, Ar, reflux, 3%.

1 equiv of the azobenzene-functionalized indazole (**7**) in the presence of 2 equiv of triethylamine. It is important to note that a higher proportion of base led to an unidentified product. After filtration under argon, a solution of 1 equiv of potassium *tert*-butoxide was added to the medium. After evaporation of the solvents, the mixture of the corresponding tripodes was extracted with diethylether. Their presence was confirmed by mass spectrometry, which presented a clear spectrum with only four signals corresponding to the statistical mixture of the four possible tripodal ligands: phenyltris(indazolyl) borate, the desired phenyl-(4-(*p*-methoxyphenyl)(diazenyl)indazolyl)bis(indazolyl)borate, phenylbis((4-(*p*-methoxyphenyl)diazenyl) indazolyl)indazolylborate and phenyltris(4-(*p*-methoxy phenyl)diazenyl)indazolyl borate as potassium salts. At this stage, the relative ratio of the four tripodes could not be established by ^{1}H NMR due to the superimposition of broad multiplets, the molecules being highly dissymmetric. Moreover, no separation was possible through classical chromatographic techniques due to the anionic nature of the molecules.

Coordination to the ruthenium centre allowed to separate the desired coordinated tripodal ligand. After coordination, the complexes are neutral, which facilitates the chromatographic separation. Cyclopentadienyltris(acetonitrile)ruthenium(II) hexafluorophosphate was chosen as ruthenium precursor since it gave excellent results in this family of sterically hindered Cp ring in past studies.[28] After heating under reflux in acetonitrile, the medium turned dark green and after purification, the desired green complex was characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry and UV–vis spectroscopy. The absorption spectrum showed two major bands characteristic of the azobenzene fragment at 295 and 384 nm. In addition, the ruthenium-based transition is expected to be found around 390 nm as described in analogous complexes,[16] and is therefore most probably hidden beneath the 384 nm transition. This could be explained because the azobenzene fragment is a stronger chromophore than the metal-centred chromophore.

2.6. Photoisomerization studies

The isomerization reactions were achieved and monitored by UV–vis spectroscopy on the azobenzene-functionalized indazole and on the model ruthenium complex. The azobenzene moieties in both molecules undergo reversible photoisomerization upon irradiation with UV light at 365 nm ($E \rightarrow Z$). The photostationary state is obtained after 10 min for the free indazole **7** and after 15 min for the ruthenium complex **9**. Figure 3 shows the UV–vis spectral changes.

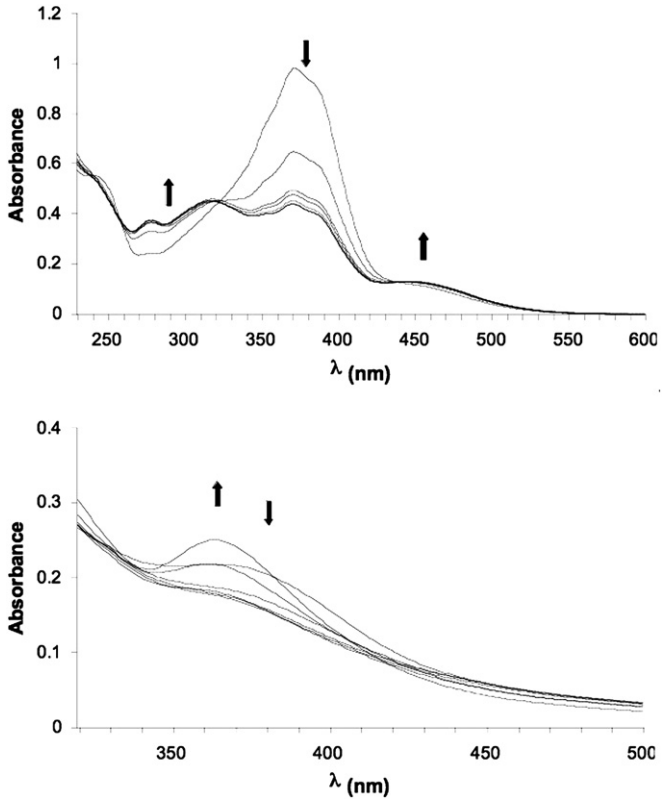


Figure 3. UV–vis spectral changes (upon irradiation with 365 nm light) of dichloromethane solutions in of **7** (top, 2×10^{-4} mol L^{-1} after 0, 15 s, 30 s, 1 min, 5 min and 10 min) and **9** (bottom, 4×10^{-4} mol L^{-1} after 0, 15 s, 30 s, 1 min, 5 min, 10 min and 15 min).

3. Conclusion

Synthesis of a new half-sandwich ruthenium complex equipped with an azobenzene-functionalized tripodal ligand to act as a brake for the full size Cp rotor (represented in Fig. 1) has been presented. The key intermediate was the azobenzene-functionalized indazole, which was prepared in five steps with easy and efficient chromatographic purification thanks to the introduction of a protecting group on the indazole ring. The tripodal ligand was obtained by a statistical reaction of phenyldibromoborane with 2 equiv of indazole and 1 equiv of 4-((*p*-methoxyphenyl)diazenyl)indazole. The model ruthenium complex bearing an azobenzene moiety in the 4-position of its indazole ligand undergoes UV-induced $E\rightarrow Z$ photoisomerization. Work is now underway to combine this brake-integrated tripodal ligand and the pentaferrocenyl substituted Cp ruthenium complex to obtain a fully equipped molecular motor able to switch from a stationary state to a rotary motion with light.

4. Experimental section

4.1. General

All commercially available chemicals were of reagent grade and were used without further purification. 1-Methyl-2-nitroaniline, isoamylnitrite, phenol and methyliodide were purchased from Aldrich. Cyclopentadienyl tris(acetonitrile)ruthenium(II) hexafluorophosphate was purchased from STREM chemicals. Indazole, boron tribromide (1 M in dichloromethane) and trimethylsilylbenzene were purchased from Acros. Diethylether and THF were dried over sodium with benzophenone and dichloromethane was dried over CaH_2. All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Flash column chromatography was carried out on silica gel 230–400 mesh from SDS. NMR spectra were recorded on Bruker Avance 300 or Avance 500 spectrometers and full assignments were made using COSY, ROESY, HMBC and HMQC methods. Chemical shifts are defined with respect to TMS=0 ppm for ^1H and ^{13}C NMR spectra and were measured relative to residual solvent peaks. The following abbreviations have been used to describe the signals: s for singlet; d for doublet; t for triplet; q for quadruplet; dd for doublet of doublet, dt for doublet of triplet, td for triplet of doublet, m: for multiplet. The numbering scheme used in this article is given in Scheme 2 (molecule **2**), Scheme 3 (molecule **6**) and Scheme 5 (molecule **9**). FAB and DCI mass spectrometry were performed using a Nermag R10-10. UV spectrum was performed with a Varian 5000 UV–vis–NIR spectrometer. All geometries were minimized with Cerius2 software[29] (version 4.2) using the Universal Force Field 1.02.

4.2. Photoisomerization studies

Photoirradiation experiments were performed on solutions of the sample dissolved in dichloromethane of 2×10^{-4} mol L^{-1} (for ligand **7**) and 4×10^{-4} mol L^{-1} (for complex **9**). The solutions were irradiated in a quartz cuvette with a 6 W 365 nm lamp (Vilber Lourmat VL-6.LC).

4.3. Synthesis

*4.3.1. 4-(2-(2-Methyl-3-nitrophenyl)diazenyl)phenol (**1**).* To a solution of 1-methyl-2-nitroaniline (1 g, 6.56 mmol, 1 equiv) in a water/acetone mixture (20 mL, 1/1), was added concentrated HCl (2 mL) at 0 °C. After 15 min., a solution of sodium nitrite (0.86 g, 12.5 mmol, 1.9 equiv) in water (20 mL) was added slowly. After stirring for 15 min, phenol (0.62 g, 6.56 mmol, 1 equiv), sodium hydroxide (0.40 g, 10 mmol, 1.5 equiv) and sodium carbonate (1 g, 9.43 mmol, 1.4 equiv) dissolved in water (20 mL) were added dropwise and the mixture was stirred at 0 °C for 2 h. After concentration of the filtrate, the crude product was purified on column chromatography (SiO_2, CH_2Cl_2). **1** was obtained as a yellow solid in 59% yield. MS (DCI/CH_4): 258.09 ($[M+H]^+$, calcd 258.08); ^1H NMR: (300 MHz, CD_2Cl_2) 7.92 (2H, m, H_o); 7.82–7.85 (2H, m, H_{b-d}); 7.42 (1H, t, J=9 Hz, H_c); 7.01 (2H, m, H_m); 5.50 (1H, s, OH); 2.85 (3H, s, H_a); ^{13}C NMR ($CDCl_3$) δ: 159.0; 151.8; 151.2; 147.2; 131.9; 126.5; 125.5; 125.3; 120.0; 115.95; 13.0.

*4.3.2. 1-(p-Methoxyphenyl)-2-(2-methyl-3-nitrophenyl)diazene (**2**).* Dried potassium carbonate (8 g, 57.9 mmol, 30 equiv) and 4-(2-(2-methyl-3-nitrophenyl)diazenyl)phenol (**1**) (500 mg, 1.94 mmol, 1 equiv) were heated at 65 °C in DMF (25 mL). A solution of iodomethane (180 μL, 2.91 mmol, 1.5 equiv) in DMF (50 mL) was added dropwise. After 3 h at 65 °C, the red mixture was poured in ice and the salts were filtered. After evaporation of the solvent from the filtrate, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 3/7). Compound **2** was obtained as an orange solid in 53% yield. MS (DCI/NH_3): 272.4 ($[M+H]^+$, calcd 272.09); ^1H NMR: (300 MHz, CD_2Cl_2) δ 7.94 (2H, m, H_o); 7.87 (1H, m, H_{b-d}); 7.81 (1H, m, H_{b-d}); 7.38 (1H, dd, H_c); 7.01 (2H, m, H_m); 3.89 (3H, s, OCH_3); 2.84 (3H, s, H_a); ^{13}C NMR: (75 MHz, CD_2Cl_2) δ: 162.9; 151.8; 151.1; 147.1; 131.9; 126.6; 125.3; 119.9; 114.4; 55.7; 12.8.

*4.3.3. N-Acetyl-4-nitroindazole (**3**).* Acetic anhydride (6.9 mL, 70.8 mmol, 3.6 equiv) was added slowly to a solution of 1-methyl-2-nitroaniline (3 g, 19.7 mmol, 1 equiv) and potassium acetate (2.01 g, 21.7 mmol, 1.1 equiv) in toluene (60 mL) at room temperature. After 15 min of stirring, isoamylnitrite (5.52 mL, 41.4 mmol, 2.1 equiv) was added dropwise and the mixture was refluxed overnight. After evaporation of the solvent, the crude product was

purified by column chromatography (SiO_2, CH_2Cl_2/hexane 1/1). Compound **3** was obtained as a yellow solid in 60% yield. MS (DCI/NH_3): 205.1 ($[M]^+$, calcd 205.1); ^1H NMR: (300 MHz, $CDCl_3$) δ 8.86 (1H, m, H_b); 8.80 (1H, s, H_a); 8.29 (1H, m, H_d); 7.71 (1H, t, J=9 Hz, H_c); 2.85 (3H, s, H_e); ^{13}C NMR: (75 MHz, $CDCl_3$) δ: 220.5; 171.3; 138.2; 129.1; 122.2; 121.0; 23.2.

*4.3.4. N-Acetyl-4-aminoindazole (**4**).* Palladium on carbon (10%, 1.248 g, 1.17 mmol, 0.1 equiv) was added to a solution of *N*-acetyl-4-nitroindazole (**3**) (2.4 g, 11.7 mmol, 1 equiv) in distilled THF (250 mL) at room temperature. After stirring 12 h under a dihydrogen atmosphere, the mixture was filtered over Celite, evaporated and purified by column chromatography (SiO_2, CH_2Cl_2). Compound **4** was obtained as an orange solid in 82% yield. MS (DCI NH_3): 176.09 ($[M+H]^+$, 100%, calcd 176.08); ^1H NMR: (300 MHz, $CDCl_3$) δ 8.07 (1H, s, H_a); 7.81 (1H, m, H_d); 7.33 (1H, m, H_c); 6.56 (1H, m, H_b); 4.18 (2H, s, NH_2); 2.77 (3H, s, H_e); ^{13}C NMR ($CDCl_3$) δ: 171.0; 140.3; 139.9; 136.6; 131.0; 115.6 108.5; 105.6; 23.1.

*4.3.5. N-Acetyl-4-((p-hydroxyphenyl)diazenyl)indazole (**5**).* Concentrated HCl (2.2 mL) at 0 °C was added to a solution of *N*-acetyl-4-amino-indazole (**4**) (1.24 g, 7.08 mmol, 1 equiv) in a water/acetone mixture (60 mL, 1/1). A solution of sodium nitrite (0.79 g, 13.3 mmol, 1.6 equiv) in water (20 mL) was added slowly. After 15 min of stirring, phenol (0.67 g, 7.08 mmol, 1 equiv), sodium hydroxide (0.43 g, 10.75 mmol, 1.5 equiv) and sodium carbonate (1.07 g, 9.91 mmol, 1.4 equiv) dissolved in water (20 mL) were added dropwise. The mixture was then stirred at 0 °C for 2 h. After evaporation of the solvent, the product was extracted with dichloromethane and washed with a saturated NaCl solution. After concentration in vacuum, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt 99/1). Compound **5** was obtained as a yellow solid in 78% yield. MS (DCI/CH_4): 281.09 ($[M+H]^+$, 100%, calcd 281.28); ^1H NMR: (300 MHz, $CDCl_3$) δ 8.80 (1H, s, H_a); 8.56 (1H, m, H_d); 7.98 (2H, m, H_o); 7.94 (1H, m, H_b); 7.71 (1H, dd, H_c); 7.02 (2H, m, H_m); 5.23 (1H, s, OH); 2.84 (3H, s, H_e); ^{13}C NMR ($CDCl_3$) δ: 171.4; 158.9; 149.9; 147.4; 139.7; 129.8; 125.2; 123.3; 118.2; 117.4; 115.9; 26.9; 23.2.

*4.3.6. 1-Acetyl-4-((p-methoxyphenyl)diazenyl)indazole (**6**).* Dried potassium carbonate (23 g, 0.166 mol, 30 equiv) and *N*-acetyl-4-(diazenyl(4-hydroxyhenyl))indazole (**5**) (1.54 g, 5.50 mmol, 1 equiv) were heated at 65 °C in distilled THF (120 mL). A solution of iodomethane (1.0 mL, 16.5 mmol, 3 equiv) in distilled THF (80 mL) was added dropwise. After stirring overnight at 65 °C, the solvent was evaporated and the crude product purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 8/2). Compound **6** was obtained as an orange solid in 74% yield. MS (DCI /CH_4): 295.12 ($[M+H]^+$, 100%, calcd 295.31); ^1H NMR: (300 MHz, $CDCl_3$) δ 8.79 (1H, s, H_a); 8.54 (1H, m, H_d); 8.01 (2H, m, H_o); 7.94 (1H, m, H_b); 7.70 (1H, dd, H_c); 7.05 (2H, m, H_m); 3.82 (3H, s, OCH_3); 2.83 (3H, s, H_e); ^{13}C NMR: (75 MHz, $CDCl_3$) δ:171.4; 162.6; 147.2; 145.4; 140.2; 139.8; 129.8; 125.0; 123.2; 118.2; 117.4; 114.4; 55.6; 23.2.

*4.3.7. 4-((p-Methoxyphenyl)diazenyl)indazole (**7**).* To a solution of sodium (780 mg, 3.41 mmol, 1 equiv) dissolved in dried methanol (340 mL), 1-acetyl-4-(diazenyl(4-methoxyphenyl))indazole (**6**) was added (1 g, 3.41 mmol, 1 equiv). After 20 min of stirring at room temperature, the mixture was acidified to pH=1 by addition of aqueous HCl (5 M). After evaporation of the methanol, the aqueous layer was extracted with dichloromethane. The organic layers were washed with a saturated NaCl solution, dried over sodium sulfate and then evaporated. Compound **7** was obtained as an orange solid in 98% yield. MS (DCI /CH_4): 253.10 ($[M+H]^+$, 100%, calcd 253.10); ^1H NMR: (300 MHz, $CDCl_3$) δ: 8.83 (1H, s, H_a); 8.54 (1H, m, H_d); 8.03 (2H, m, H_o); 7.85 (1H, m, H_b); 7.60 (1H, m, H_c); 7.06 (2H, m, H_m); 3.92 (3H, s, OCH_3); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 162.3; 147.5; 146.1; 127.3; 124.8; 123.4; 114.4; 112.5; 55.7; λ_{max} (ε) (CH_2Cl_2).

*4.3.8. Dihydrobis(indazolyl)borate (**8**).* Indazole (2 g, 16.93 mmol, 4 equiv) and potassium borohydride (228 mg, 4.22 mmol, 1 equiv) were grinded in a mortar. The solid mixture was heated at 170 °C under an argon atmosphere until the expected volume of dihydrogen had been evolved, and the mixture was allowed to room temperature. After sublimation and trituration in hot toluene, the purified compound was stored in a dessicator. Compound **8** was obtained as a white solid in 47% yield. MS (DCI/CH_4): 247 ($[M-K]^-$, 100%, calcd 247); ^1H NMR: (300 MHz, $CDCl_3$) δ 7.33 (2H, dt, $H_{e'}$, J=8,5 Hz, J=0.9 Hz); 7.32 (2H, d, $H_{a'}$, J=0.9 Hz); 7.08 (2H, dt, $H_{d'}$, J=8 Hz, J=1.1 Hz); 6.61 (2H, td, $H_{b'}$, J=8.5 Hz, J=1.1 Hz); 6.38 (2H, td, $H_{c'}$, J=8.0 Hz, J=0.9 Hz); ^{13}C NMR: (75 MHz, $CDCl_3$) δ: 143.3; 132.8; 131.5; 121.5; 120.5; 120.0; 112.1.

Microanalysis calculated for $C_{14}H_{12}BN_4K$: C 58.76; H 4.23; N 19.58. Found: C 58.31; H 4.06; N 19.17.

*4.3.9. Phenyl-4-((p-methoxyphenyl)diazenyl)indazolylbis(indazolyl) borate cyclopentadienylruthenium (II) (**9**).* In a schlenk flask equipped with a Teflon stopper, a 1 M solution of boron tribromide in dichloromethane (39 μL, 0.39 mmol, 1 equiv) was added to trimethylsilylbenzene (68.5 μL, 0.39 mmol, 1 equiv). After 3 days at room temperature, solvent and bromotrimethylsilane were evaporated under vacuum. The freshly synthesized dibromophenylborane was dissolved in 3 mL of distilled benzene and a solution of triethylamine (111.1 μL, 0.79 mmol, 2 equiv), indazole (93.5 mg, 0.79 mmol, 1.5 equiv) and 4-(diazenyl(4-methoxyphenyl))indazole (**7**) (100 mg, 0.36 mmol, 1 equiv) in 3 mL of benzene was transferred via canula. The medium was stirred for 12 h at room temperature. The mixture was filtered under vacuum to remove the colourless ammonium salt. A solution of potassium *tert*-butoxide (44.4 mg, 0.36 mmol, 1 equiv) in 3 mL of THF/benzene (1/1) was added and the medium was stirred for 12 additional hours under argon at 60 °C. After evaporation of the solvents, the mixture of tripodal ligands was extracted with ether. The compounds were used without further purification. In a schlenk flask, cyclopentadienyl tris(acetonitrile) ruthenium(II) hexafluorophosphate (46 mg, 0.10 mmol, 1 equiv) was added under argon to the mixture of tripodal ligands (65 mg, 0.10 mmol, 1 equiv) in 3 mL of anhydrous acetonitrile. The medium was stirred under reflux for 12 h. After evaporation of the solvent, the crude material was purified by column chromatography ($SiO_2 \cdot CH_2Cl_2$/AcOEt 8/2). Compound **9** was obtained in 3% yield as a green solid. MS (ESI): 740.10 ($[M+H]^+$, 100%, calcd 740.2); ^1H NMR ($CDCl_3$) δ: 9.76 (1H, m, H_a); 7.72 (2H, m, $H_{a'}$); 7.61 (2H, m); 7.55 (3H, m); 7.52 (3H, m); 7.35 (5H, m, BPh); 7.13 (4H, m); 6.91 (3H, m); 4.07 (5H, m, Cp); 3.91 (3H, m, OCH_3) 162.8; 143.2; 139.7; 138.9; 138.7; 137.4; 137.1; 136.9; 136.2; 135.6; 134; 2122.7; 122.3; 119.3; 112.4; 111.0; 70.4; 36.4; 25.2; 54.7; UV λ_{max} (ε) (CH_2Cl_2)/nm: 261 (703), 272 (666), 295 (500), 384 (518).

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