# Synthesis of Symmetric and Dissymmetric Star-shaped Pentaarylcyclopentadienyl Ru(II) Complexes Containing Styryl-BODIPY Fragments

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We synthesised star-shaped ruthenium(II) complexes containing one or five styryl-BODIPY units arranged around a central trisindazolylrutheniumcyclopentadienyl fragment. A symmetric complex was obtained following a five-fold Suzuki-Miyaura reaction of the pentabrominated key precursor while desymmetrisation was next achieved *via* a modular synthetic approach based on sequential chemoselective Suzuki-Miyaura reactions on a key building block bearing one iodophenyl and four bromophenyl groups.

Keywords: Ruthenium, BODIPY, Desymmetrization

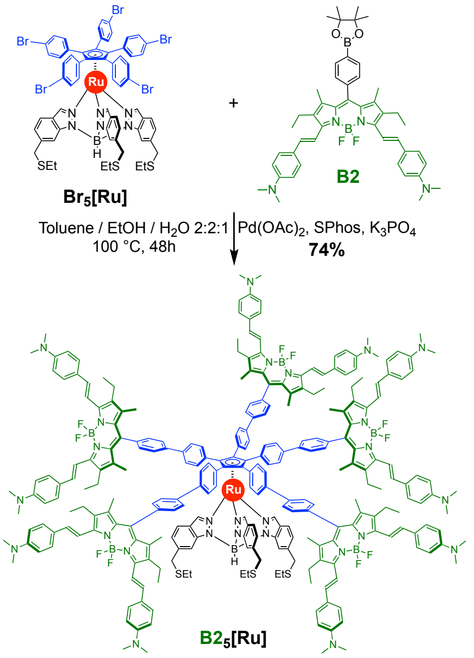
With the ultimate goal to create complex nanomachineries,[1] various types of molecular motors[2] or gears[3] have been designed but only a few are based on coordination complexes. With a large number of metals and a wide variety of ligands available, coordination chemistry is a very versatile and efficient tool to assemble mechanical subunits to prepare synthetic molecular machines.[4] In the last decade, we designed and synthesised a series of star-shaped molecular motors[5] and gears subunits[6] based on heteroleptic ruthenium(II) complexes containing a hydrotris(indazolyl)-borate ligand as anchoring platform and a functionalised pentaarylcyclopentadienyl ligand as rotating subunit. These compounds interestingly exhibited controlled clockwise or anticlockwise unidirectional rotation once anchored on metallic surfaces.[7]

As nanosized movable entities, molecular machines can be fuelled by various sources of energy such as light, chemicals or electrons. Chemical fuels generate waste while addressing electrons at the single-molecule level remains highly challenging, so light appears to be a particularly clean and easy to operate as well as highly efficient and non-invasive source of energy.[8] In our efforts to expand the set of mechanical tasks performed by our rotary molecular machines, it was envisioned to exploit light as a stimulus and integrate a photoactivable function in their design, allowing for instance the light-induced engagement or disengagement of cogwheels within a train of molecular gears. It is thus of prime importance to explore the possibility to incorporate various kinds and numbers of photoactive subunits in the backbone of our ruthenium(II)-based molecular motors and gears. This goal requires the development of synthetic strategies allowing to obtain not only symmetric structures but also desymmetrised complexes, which are more challenging to be prepared but also more promising in terms of properties as shown for obtaining high unidirectionality in previously reported molecular motors.[7]

In our effort to build up such photoactive systems, we report in this paper the synthesis of extended star-shaped molecules based on pentaarylcyclopentadienyl ruthenium(II) complexes functionalised with five peripheral photoactive BODIPY units. In a preliminary work, the photophysical properties of the rotor-like Ru(II) complexes were investigated, demonstrating that they are viable platforms for the creation of systems that can be photoactivated.[9] To this end, two strongly fluorescent BODIPYs were selected: **B1** as a standard fluorescent BODIPY fragment and **B2** as a derivative incorporating two photochemically isomerisable styryl groups on the pyrrole α-positions for photo-mechanical applications. The symmetric ruthenium(II) complex **B2$_5$[Ru]** was then synthesised as well as a desymmetrised ruthenium(II) complex with four BODIPYs and one styryl-BODIPY **B1$_4$B2$_1$[Ru]** (Scheme 1 and 2). The parent compound **B1$_5$[Ru]** has been previously synthesised[10] but the absence of photochemically isomerisable styryl groups drastically limits its potentialities in light-induced motions.

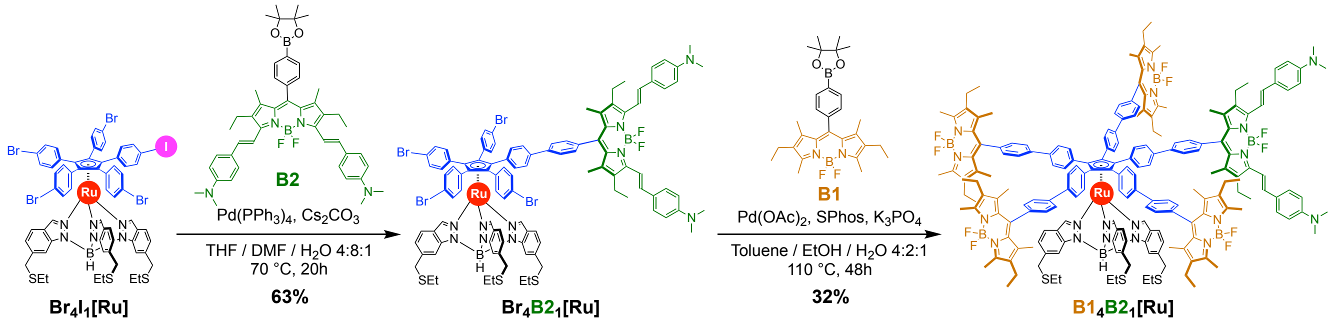
Our general strategy for the synthesis of the symmetric target compound **B2$_5$[Ru]** relies on the post-functionalisation of a ruthenium(II) complex as key intermediate, incorporating a thioether-functionalised hydrotris(indazolyl)borate tripod in combination with a penta(*p*-halogenophenyl)cyclopentadienyl ligand.[11] A variety of transition metal-catalysed cross-coupling reactions are tolerated, which leads in a divergent manner to a family of piano-stool ruthenium complexes with a five-fold substituted cyclopentadienyl ligand, exhibiting potential mechanical functions stimulated by light. However, when desymmetrised cyclopentadienyl units are desired, the synthetic strategy appeared to be much more chalenging than anticipated. In the course of our previous work towards desymmetrised complexes, we explored the chemoselective functionalization of penta(4-halogenophenyl)cyclopentadienyl ruthenium complex **Br$_4$I$_1$[Ru]** incorporating a single aryl iodide moiety. The discrimination of aryl iodides over bromides, although largely exploited in cross-couplings such as Sonogashira or Stille couplings, remains difficult in the case of Suzuki-Miyaura coupling, due to a change of rate-determining step in the catalytic cycle. In a previous paper,[6c] we reported the successful single Suzuki-Miyaura cross-coupling of complex **Br$_4$I$_1$[Ru]** using copper(I) thiophene-2-carboxylate (CuTC) as a stoichiometric additive in the presence of the mild Pd(PPh$_3$)$_4$ catalyst in THF. Unfortunately, these conditions are restricted to the use of boronic acids as coupling partners, since an interaction between the latter and CuTC is expected to occur prior to the actual coupling. Indeed, when these conditions were tested for the coupling of precursor **Br$_4$I$_1$[Ru]** with boronic ester **B2**, no conversion was observed. Since boronic acid function should be avoided in **B2** due to the presence of amino groups, we explored alternative reaction conditions that could favour a chemoselective functionalization of **Br$_4$I$_1$[Ru]** in the presence of a boronic ester.

The styryl-BODIPY **B2** was prepared from BODIPY **B1** *via* a double Knœvenagel condensation with *p*-dimethylaminobenzaldehyde in the presence of piperidine and acetic acid. The reaction was run in refluxing toluene and a Dean-Stark apparatus was used to trap water. The selective formation of *trans*-styryl moieties on both pyrrole α-positions was achieved with a 20% yield. This moderate yield is mostly related to purification issues. **B2** was characterised by mass spectrometry as well as $^1$H, $^{13}$C, $^{11}$B and $^{19}$F NMR spectroscopy. The $^{19}$F NMR spectrum of **B2** exhibits a quadruplet shifted to -139.1 ppm with a coupling constant $J$ ($^{11}$B-$^{19}$F) of 35.0 Hz. The *trans*-configuration of the *p*-dimethylaminostyryl fragments was unambiguously confirmed by $^1$H NMR spectroscopy, which revealed a 16.6 Hz coupling constant between vinylic protons. Next, styryl-BODIPY derivative **B2** was used as coupling partner in a Suzuki-Miyaura reaction with key intermediate **Br$_5$[Ru]** in the presence of Pd(OAc)$_2$/SPhos as catalytic system and K$_3$PO$_4$ as base, to afford the five-fold substituted target compound **B2$_5$[Ru]** in 74% yield (Scheme 1), corresponding to 94% yield per newly-formed C-C bond. The use of a biphasic solvent system combining toluene/ethanol/water (2:2:1) is the key to increase the reaction efficiency. Without this biphasic solvent system, only trace amounts of **B2$_5$[Ru]** were observed. **B2$_5$[Ru]** was characterised by mass spectrometry as well as $^1$H, $^{13}$C, $^{11}$B and $^{19}$F NMR spectroscopy. In the $^1$H NMR spectrum (Fig. S5), integration of the two AA'BB' systems corresponding to the 4,4'-biphenyl linkers and of the methyl and ethyl groups located on the pyrrole rings, as compared to protons belonging to the equivalent indazole rings shows that five styryl-BODIPY moieties have been grafted. In addition, the coupling constant of 16.4 Hz between the two sets of 10 vinyl protons confirms the *trans*-geometry of the styryl units. Finally, both the $^{11}$B and $^{19}$F NMR spectra (Fig. S7 and Fig. S8) exhibit a single signal located at 1.32 ppm and -139.1 ppm, respectively, in agreement with the chemical shifts observed for the BODIPY unit of precursor **B2**. This indicates that all styryl-BODIPYs are equivalent in this five-fold substituted ruthenium complex.



**Scheme 1.** Synthesis of the symmetric **B2$_5$[Ru]** starting from **Br$_5$[Ru]**.

To synthesise the desymmetrised complex **B1$_4$B2$_1$[Ru]** bearing different BODIPYs, the penta(*p*-halogenophenyl)cyclopentadienyl ruthenium(II) key building block, incorporating a single *p*-iodophenyl group (**Br$_4$I$_1$[Ru]**, Scheme 2) was prepared.[6] Thanks to the difference in reactivities of aryl iodides *vs* bromides in palladium-catalysed cross-couplings, this platform was expected to allow the sequential introduction of substituents



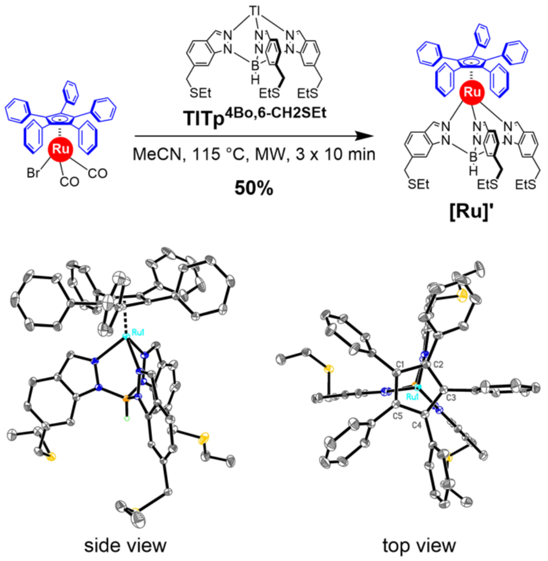
**Scheme 2.** Synthesis of the desymmetrised star-shaped Ru-based system **B1$_4$B2$_1$[Ru]** starting from key intermediate **Br$_4$I$_1$[Ru]**.

on the cyclopentadienyl ligand to yield desymmetrised ruthenium complexes in a controlled manner.

As already explained, boronic acid function should be avoided in **B2** due to the presence of amino groups. Then, we explored alternative reaction conditions that could favour a chemoselective functionalization of **Br$_4$I$_1$[Ru]** in the presence of a boronic ester. We already knew that the conditions used for the coupling of **Br$_5$[Ru]** with **B1** or **B2** (*i.e.* Pd(OAc)$_2$, SPhos, $K_3PO_4$ in toluene/EtOH/H$_2$O at 100 °C) lead to very efficient coupling of aryl bromides and would thus be detrimental to a chemoselective coupling. We thus turned to conditions used previously in our group for the statistical monocoupling of **Br$_5$[Ru]** (*i.e.* PdCl$_2$(dppf), $Cs_2CO_3$ in DMF/H$_2$O at 100 °C),[12] employing a less activated catalyst such as Pd(PPh$_3$)$_4$ and lowering the temperature to 70 °C to favour the oxidative addition of the weaker C-I bond (Scheme 2).[6] This strategy proved to be successful, and the coupling of **Br$_4$I$_1$[Ru]** with **B2** took place with high chemoselectivity to give rise to **Br$_4$B2$_1$[Ru]** in 63% yield via a single Suzuki-Miyaura coupling. The four remaining *p*-bromophenylene groups were subsequently submitted to distinct Suzuki-Miyaura coupling conditions in the presence of an excess of BODIPY-derivative **B1**. Compared with the conditions for iodophenylene functionalisation, the Pd(OAc)$_2$/SPhos catalytic system was employed here in combination with $K_3PO_4$ as base at a higher temperature (110 °C).[13] Again, the use of a biphasic solvent system combining toluene/ethanol/water (4:2:1) appeared crucial. The desymmetrised target complex **B1$_4$B2$_1$[Ru]** was obtained in 32% yield, thus corresponding to 75% yield per single C-C coupling.

Both complexes were characterised by mass spectrometry as well as $^1$H, $^{13}$C, $^{11}$B and $^{19}$F NMR spectroscopy. Looking in detail at the $^1$H-NMR in the 7.9-8.2 ppm region, two signals corresponding to the indazol ring (Fig S13, protons a and b) are surrounded by small signals integrating for a few %. Since the MALDI-TOF MS spectrum showed one single peak, we believe this signals correspond to isomers with the alkene bond of the **B2** fragment in the Z configuration. Due to the loss of $C_5$ symmetry on the cyclopentadienyl ligand, the $^1$H and $^{13}$C NMR spectra are more complex (Fig. S13 and Fig. S14, respectively, for **B1$_4$B2$_1$[Ru]**) compared to the BODIPY-substituted symmetric counterpart **B2$_5$[Ru]**. In the $^1$H NMR spectrum of intermediate **Br$_4$B2$_1$[Ru]** (Fig. S9), integration of the methyl and ethyl groups located on the pyrrole rings, as compared to protons belonging to the equivalent indazole rings, clearly shows that a single styryl-BODIPY moiety has been coupled. The *trans*-configuration of the styryl groups is again confirmed by the 17.0 Hz coupling constant between the vinyl protons. In the case of the target complex **B1$_4$B2$_1$[Ru]**, the $^{19}$F NMR spectrum (Figure 2) exhibits two distinct signals located at -139.3 ppm and -145.7 ppm, respectively, with an integral ratio of 1 to 4. These chemical shifts are in full agreement with those observed for precursors **B2** (-139.1 ppm) and **B1** (-145.7 ppm), which shows that the ruthenium(II) complex incorporates a single styryl-BODIPY unit combined with four BODIPY moieties. This is also confirmed by the integral ratios in the $^1$H NMR spectrum and by mass spectrometry.

The model system **[Ru]'** incorporating a bare pentaphenylcyclopentadienyl ligand in combination with the thioether-functionalised hydrotris(indazolyl)borate tripod (Scheme 3), has been also synthesized to help in the assignment of the signals of $^1$H and $^{13}$C NMR spectra and to have an X-ray structure of the central part of our molecules.



**Scheme 3.** Synthesis of model compound **[Ru]'** (top), and side view (bottom left) and top view (bottom right) of the molecular structure of ruthenium complex **[Ru]'**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms (except for B–H), solvent molecule and disordered atoms are omitted for clarity. The centroid of the cyclopentadienyl ligand is distant from the ruthenium atom by 1.80 Å and the average distance between the three coordinated nitrogens and the ruthenium centre is 2.14 Å.

This compound was synthesised starting from the known bromido dicarbonyl η$^5$-1,2,3,4,5-pentaphenylcyclopentadienyl ruthenium(II)[12] *via* a ligand exchange process in the presence of thallium hydrotris(indazolyl)borate **TlTp$^{4Bo,6-CH2SEt}$** [11] in acetonitrile under microwave irradiation (Scheme 3, top). Complex **[Ru]'** was obtained in 50% yield and fully characterised by mass spectrometry, elemental analysis and NMR spectroscopy. Single crystals were also obtained by slow evaporation of a 1:2 methanol/CH$_2$Cl$_2$ solution of complex **[Ru]'**, thus allowing the resolution of its structure by X-ray diffraction (Scheme 3, bottom). The X-ray structure is similar to previous structures obtained for this family of Ru(II) complexes[5,6] bearing a pentaphenylcyclopentadienyl and a trisindazolylborate ligand with the later binding in a facial tripodal mode (i.e. κ$^3$-*N*,*N*',*N*''). The complex has a piano stool structure with the cp ligand fitting in the vacant spaces of the tripodal ligand.

The absorption spectra of **B1**, **B2**, **B2$_5$[Ru]** and **B1$_4$B2$_1$[Ru]** were recorded in CH$_2$Cl$_2$ at 298 K (Figure 4). The main absorption parameters are collected for each compound in the experimental section. Complexes **B2$_5$[Ru]** and **B1$_4$B2$_1$[Ru]** show an intense band in the UV region peaked around 270 nm like analogous ruthenium complexes[9] with similar molar absorption coefficients. In the visible region, the absorption spectra of **B2** and **B2$_5$[Ru]** are similar, with an absorption peak around 710 nm. Compared with **B1** which exhibit an absorption peak around 525 nm, and due to the effect of styryl fragments, the absorption spectra of **B2** and **B2$_5$[Ru]** are red-shifted. As expected, the extinction coefficient of **B2$_5$[Ru]** is almost five times higher than that of **B2**, in line with the presence of five styryl-BODIPY moieties in the complex. Finally, **B1$_4$B2$_1$[Ru]**, with four BODIPY and one styryl-BODIPY arms, exhibits both the absorption features at 526 nm (from **B1**) and 711 nm (from **B2**) with an intensity about four times larger than that of **B1** and almost equal to **B2** at their respective absorption wavelengths. This illustrates the additivity of the absorption features of the different chromophores in this compound.

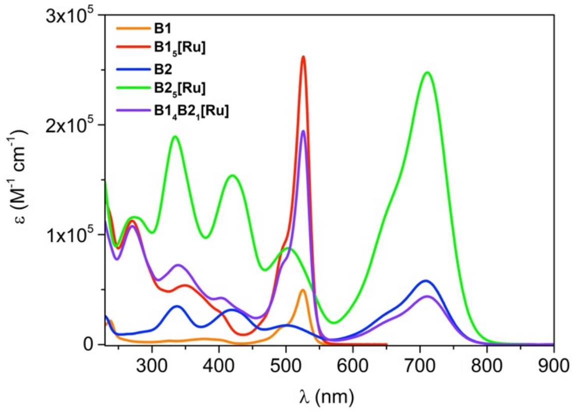


**Figure 1.** Absorption spectra of compounds **B1**, **B1$_5$[Ru]**, **B2**, **B2$_5$[Ru]** and **B1$_4$B2$_1$[Ru]** in $CH_2Cl_2$ at 298 K.

In conclusion, star-shaped ruthenium(II) complexes incorporating one (**B1$_4$B2$_1$[Ru]**), or five (**B2$_5$[Ru]**) photoisomerisable styryl-BODIPY units (**B2**) have been synthesised and characterised by $^1$H, $^{13}$C, $^{11}$B and $^{19}$F NMR spectroscopy, absorption and HR-mass spectrometry. The symmetric complex **B2$_5$[Ru]** was obtained following a five-fold Suzuki-Miyaura coupling with the corresponding BODIPY-substituted phenylboronic acid pinacol ester precursor **B2**. The dissymmetric **B1$_4$B2$_1$[Ru]** was obtained *via* two consecutive Suzuki-Miyaura chemoselective couplings under different conditions, starting from the preactivated key building block **Br$_4$I$_1$[Ru]**. The absorption spectra showed the additivity of the features of the different chromophores in the ruthenium(II) complexes containing five BODIPYs (**B1**), five styryl-BODIPYs (**B2**) and in the desymmetrised complex bearing four **B1** and one **B2** fragment. Work is now underway to investigate the photochemical and photophysical properties of these extended ruthenium complexes in more details, such as photoinduced electron and/or energy transfer processes. The *trans-cis* photoisomerisation of the styryl subunits will also be studied, with the goal to explore the potential of such ruthenium(II) complexes as mechanically-active components of photodeformable materials.

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Supporting Information is available with Full $^1$H, $^{13}$C, $^{19}$F and $^{11}$B NMR spectra of all new compounds and crystallographic data.on http://dx.doi.org/10.1246/cl.****.

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