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Directed synthesis of symmetric and dissymmetric molecular motors built around a ruthenium cyclopentadienyl tris(indazolyl)borate complex

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ABSTRACT

This article focuses on the synthesis of a family of rotary molecular motors based on a penta-substituted cyclopentadienyl tris(indazolyl)borate ruthenium(II) complex. In order to demonstrate a movement of rotation in this family of molecular motors, dissymmetric derivatives with one ferrocene missing have also been synthesized. The molecules have been prepared with ester and thioether-functionalized tris(indazolyl)borate ligands in view of studying them as single molecules on various surfaces by STM or AFM techniques.

1. Introduction

A current trend in the physical and biological sciences is the miniaturization of machinery from the macroscopic to the microscopic world.[1] To achieve this goal two complementary strategies have been developed, giving birth to nanosciences. The first one is the 'top-down' approach, which consists in the miniaturization of existing objects following micro-scale technologies. Micro-scale machines are the ultra-miniaturized versions of machines of our everyday life. However, this approach is reaching some physical limits due to the incompatibility of such technology with the 1–10 nm scale. The opposite approach, known as the 'bottom-up' strategy, starts from atoms and molecules and follows a monumentalization[2] strategy consisting in the association of different modular functional units through the formation of covalent bonds within only one molecule, which provides sufficient resources for the molecule to be a machine.[3-4] Among theses machines, molecular rotary motors represent a particular challenge for the control of a unidirectional movement.[5]

In our laboratory, we have designed[6] an electrically fuelled molecular rotary motor aimed at being studied as a single molecule by near-field microscopic techniques.[7] This family of molecular motors is based on a piano stool ruthenium complex (Fig. 1) with a tripodal hydrotris(indazolyl) borate ligand[8] functionalized to be anchored on a surface (i.e., a stator) and a substituted pentaphenylcyclopentadienyl (Cp) ligand[9] with five arms terminated by electroactive groups (i.e., a rotor). The functionalized tripodal ligands were designed to have three anchoring groups pointing in the opposite direction of the coordination site in order not to interfere sterically with it.[10] Each functional group is connected at the 6-position of indazole, which should be the optimal orientation for anchoring on a surface. The ester function has been found to strongly interact with oxide surfaces,[11] being spontaneously deprotected to the acid during the deposition process. In order to

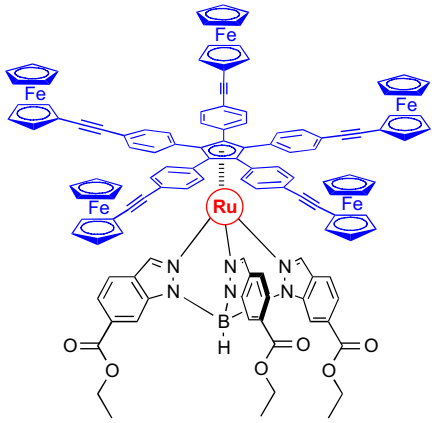

Figure 1. Molecular motor functionalized for oxide surface deposition.

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interact with a metallic surface, the thioether function was chosen to alleviate the problem encountered with oxidatively unstable thiols and is known to interact strongly with a gold surface.[12]

The motor is constituted of electron rich aromatic building blocks to obtain a structure with maximum rigidity and with a minimum of degrees of freedom. This rigidity is crucial in view of recovering most of the work produced by the rotation of the upper Cp ligand. The principle of this motor is to deposit the molecule between two electrodes of a nanojunction and to control the rotation by the flow of electrons.[13]

In this kind of system, a crucial problem lies in a practical way to evidence the rotation. Due to the high symmetry of the molecule, two images obtained after a 72° rotation are indistinguishable with a C_5-symmetric rotor such as a Cp carrying five identical substituents. However, this issue can be partly addressed by using compounds of lower symmetry or tagged compounds.[14] For that purpose, we designed a dissymmetrized rotor in which one ferrocene electroactive group is missing. Lowering the symmetry of the molecule should help to prove a movement and monitor the rotation, the missing ferrocene acting as a probe for the position of the rotor.

The initial design involves a motor deposited between two metallic nanoelectrodes on an insulating surface. To reach this goal, we have recently reported the synthesis of a molecular motor with ester-functionalized tris(indazolyl)borate stators[15] designed to be deposited on insulating oxide surfaces used in molecular scale Non-Contact Atomic Force Microscope (NC-AFM) experiments. However, preliminary experiments using Scanning Tunnelling Microscopy (STM) on a conducting surface should be easier to interpret and thus very useful to understand the behaviour of the molecule.[16] Moreover, for a molecule deposited near an atomic step of the surface, the STM tip and the surface could also act as the two electrodes of a nanojunction and an electro-induced rotation might be observed. Thus the synthesis of a stator functionalized for the deposition onto metallic surfaces used in STM experiments is also required.

In this paper, we report the synthesis of symmetric and dissymmetric molecular motors functionalized for metallic surface deposition. The dissymmetric analogue functionalized for oxide surfaces is also reported.

2. Results and discussion

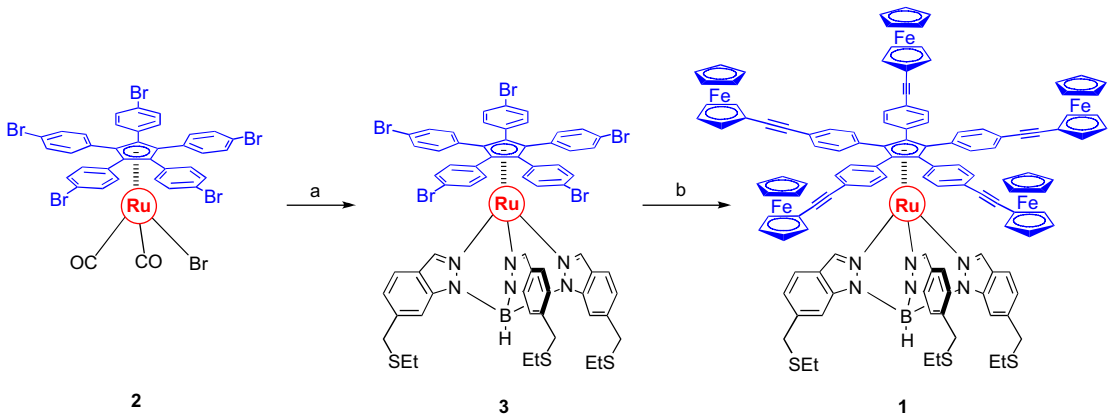
2.1. Symmetric motor for STM experiments

In the last decade, the continuous improvement of near-field microscopic techniques such as STM or AFM has led to the imaging and study of physico-chemical properties of various molecules.[17] These techniques allow the visualization and manipulation of only one molecule and therefore the electrical[18] and mechanical properties[19] of a single molecule deposited on a surface can be investigated. For this kind of studies, STM is often preferred to AFM due to its higher resolution and the possibility to simulate the images. However, conducting or semi-conducting surfaces are required for STM imaging. Recently, a tris(indazolyl)borate ligand functionalized by thioether groups has been described to anchor organometallic complexes onto metallic surfaces suitable for STM imaging.[10] We have subsequently designed a molecular motor suitable for metallic surface deposition (**1**) by incorporating this functionalized scorpionate ligand. The synthetic route (Scheme 1) is based on a modular strategy using a quintuple palladium catalyzed coupling reaction between the versatile pentabrominated ruthenium complex (**3**) and ethynylferrocene.

The ruthenium complex **3** was prepared by heating under microwave irradiation in a sealed tube bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (**2**)[10] with potassium hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate in a mixture of DMF and acetonitrile. After purification by column chromatography, **3** was obtained in a 24% yield. The coupling between an alkyne and an aryl bromide is in general achieved under Sonogashira conditions,[21] i.e., using catalytic CuI and $Pd(PPh_3)_4$. However, the five bromines in **3** are strongly deactivated towards the oxidative addition step on the palladium catalyst by the connection to a formal anionic entity (Cp). Nevertheless, Negishi coupling conditions[22] using a solution of [(ferrocenyl)ethynyl]zinc chloride and $Pd(PPh_3)_4$ in refluxing THF were successful. Compound **1** was isolated after purification by column chromatography in 42% yield corresponding to 84% by coupling reaction. ^{1}H NMR spectroscopy clearly showed an AA′BB′ pattern for the phenyl groups attached to the central Cp ring, the quadruplet and triplet system of the ethyl groups of the thioeter and an integration of 45 protons for the ferrocene moieties. The presence of the five ferrocene units was also confirmed by MALDI-TOF spectrometry.

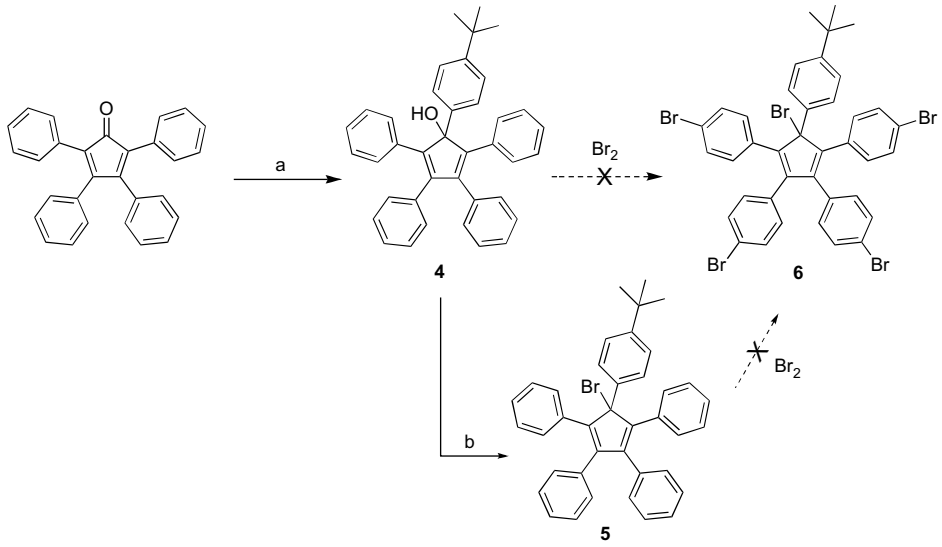
2.2. Dissymmetric Cp ligand synthesis

In order to monitor the rotation by near-field microscopy, a dissymmetric rotor with only four electroactive groups could be a promising candidate since the missing group could act as a probe. A rational synthesis of a dissymmetrized pentaphenylcyclopentadienyl ligand is thus needed. The coupling of 4 equiv of ethynylferrocene with 1-bromo-1,2,3,4,5-*p*-bromophenylcyclopentadiene gives access to the statistical mixture of penta-, tetra-, tri-, di- and mono-ferrocenyl compounds, which



2 3 1

Scheme 1. Reagents and conditions: (a) potassium hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate, microwave, DMF/CH_3CN, 120 °C, 10 min, 24%; (b) [(ferrocenyl)ethynyl]zinc chloride, $Pd(PPh_3)_4$, THF, reflux, 24 h, 42%.



Scheme 2. Reagents and conditions: (a) 4-*tert*-butylphenyllithium, Et_2O, 2 h, 81%; (b) HBr, AcOH, 95 °C, 2 h, 78%.

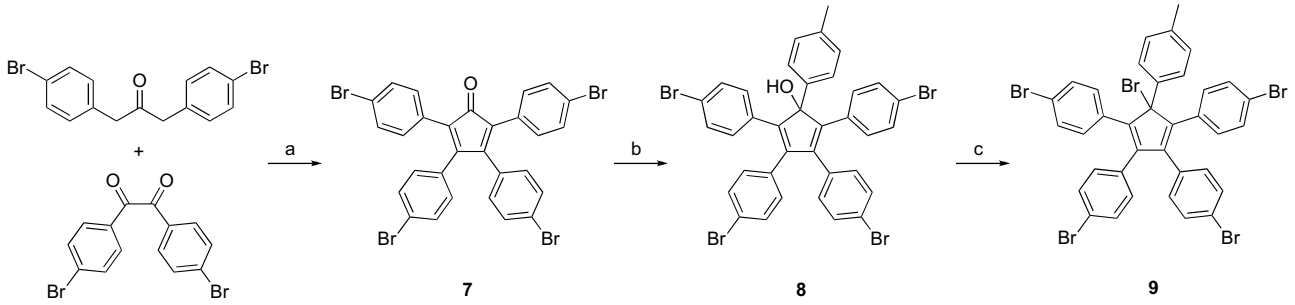
cannot be separated due to their similar polarities (only the penta-substituted product can be separated since its high symmetry decreases its polarity and brings a good differentiation with respect to the others). We therefore opted for a controlled synthesis of the tetra-ferrocenyl derivative. The key feature of our strategy is to block one position of the Cp ring during the synthesis, in order to differentiate it from the other four substituents.

In this objective, the first idea (Scheme 2) was a bromination of the pentaphenyl-cyclopentadienol (**4**) in which one phenyl group is *para*-substituted by a *tert*-butyl blocking group. Compound **4** was obtained by a nucleophilic addition of 4-*tert*-butylphenyllithium on the pentaphenyl cyclopentadienone in an 81% yield.[23] The selective bromination in the *para* positions of the pentaphenylcylopentadiene has been described with neat bromine at room temperature.[20] However, a selective bromination of **4** under these conditions could not be achieved and only a mixture of polybrominated products was observed. Supposing that the hydroxyl group could be responsible for these selectivity problems, it was substituted by a bromine using a mixture of hydrobromic acid and acetic acid to yield **5**.[24] Bromination attempts with neat bromine or in solution in CCl_4 with or without iron were unsuccessful. Compound **6** could not be obtained selectively in a good yield.

Nevertheless, this issue could be overcome following an alternative strategy by using a nucleophilic addition of a Grignard reagent on the tetrabrominated cyclopentadienone (**7**)[25] (Scheme 3). This modular strategy could allow the introduction of a large variety of substituents in a controlled manner. In our case, a methyl group was chosen as a convenient ^{1}H NMR probe.

The first step involves the condensation of 1,3-di(4-bromophenyl)propan-2-one[26] with 4,4′-dibromobenzil under basic conditions, yielding the tetrabrominated cyclopentadienone **7** in 68% yield after recrystallization. The *p*-tolyl substituent is then introduced by a nucleophilic addition of the Grignard reagent *p*-tolylmagnesium bromide.[27] The functionalized cyclopentadienol **8** is obtained after recrystallization in hexane in an 88% yield as a single regioisomer. In the pentaphenylcyclopentadiene family, it is known[28] that coordination is not possible via the classical cyclopentadienide generated under basic conditions because of the strong steric hindrance. The coordination of ruthenium to this type of ligand can only take place if there is a bromine atom on the Cp ring, following Manners' methodology,[29] which consists of the oxidative addition of the carbon–bromine bond on the ruthenium carbonyl cluster. For that purpose, the hydroxy group of **8** was replaced by a bromine atom. After reaction with HBr in acetic acid, the brominated Cp **9** was purified by column chromatography and was obtained in 62% yield as a mixture of three regioisomers (Fig. 2).

The three regioisomers of **9** are probably formed via an SN_1 mechanism since the SN_2 and SN_2' mechanisms would give rise only to one or two regioisomers, respectively. Their proportion can be quantified by ^{1}H NMR, using the methyl group of the tolyl substituent as a probe. In the aliphatic region three singlets are observed (Fig. 3, top), corresponding to the three regioisomers with a 1.4:1.7:1.9 ratio, which is close to the statistical 1:2:2 mixture. The formation of pentaarylcyclopentadienyl carbocations from the



Scheme 3. Reagents and conditions: (a) KOH, EtOH, reflux, 40 min, 68%; (b) 4-tolylmagnesium bromide, THF, 25 °C, 2 h, 88%; (c) HBr, AcOH, 95 °C, 2 h, 62%. Compound **9** was obtained as a mixture of three regioisomers.

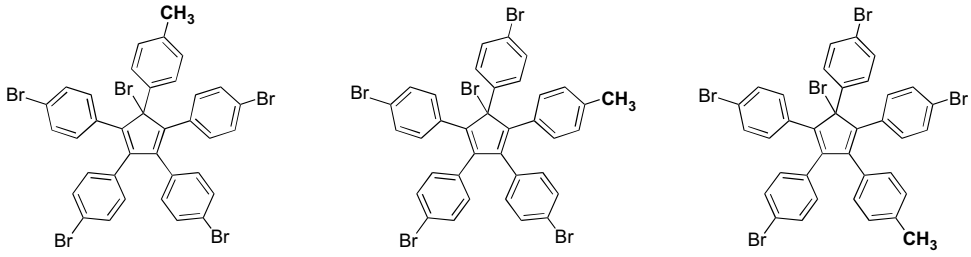


Figure 2. The three regioisomers formed simultaneously during the synthesis of the brominated cyclopentadiene **9**.

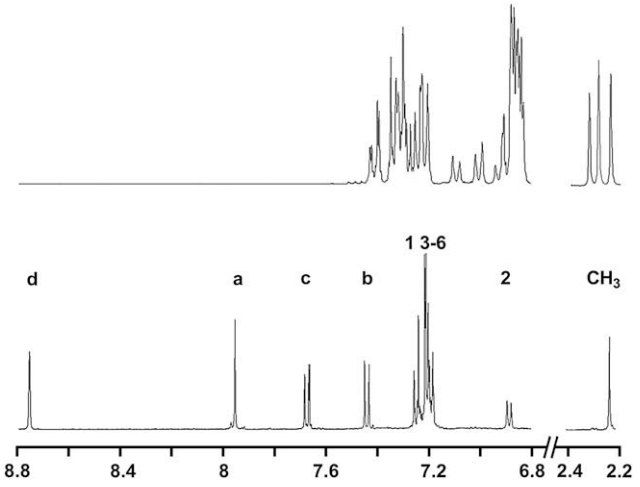
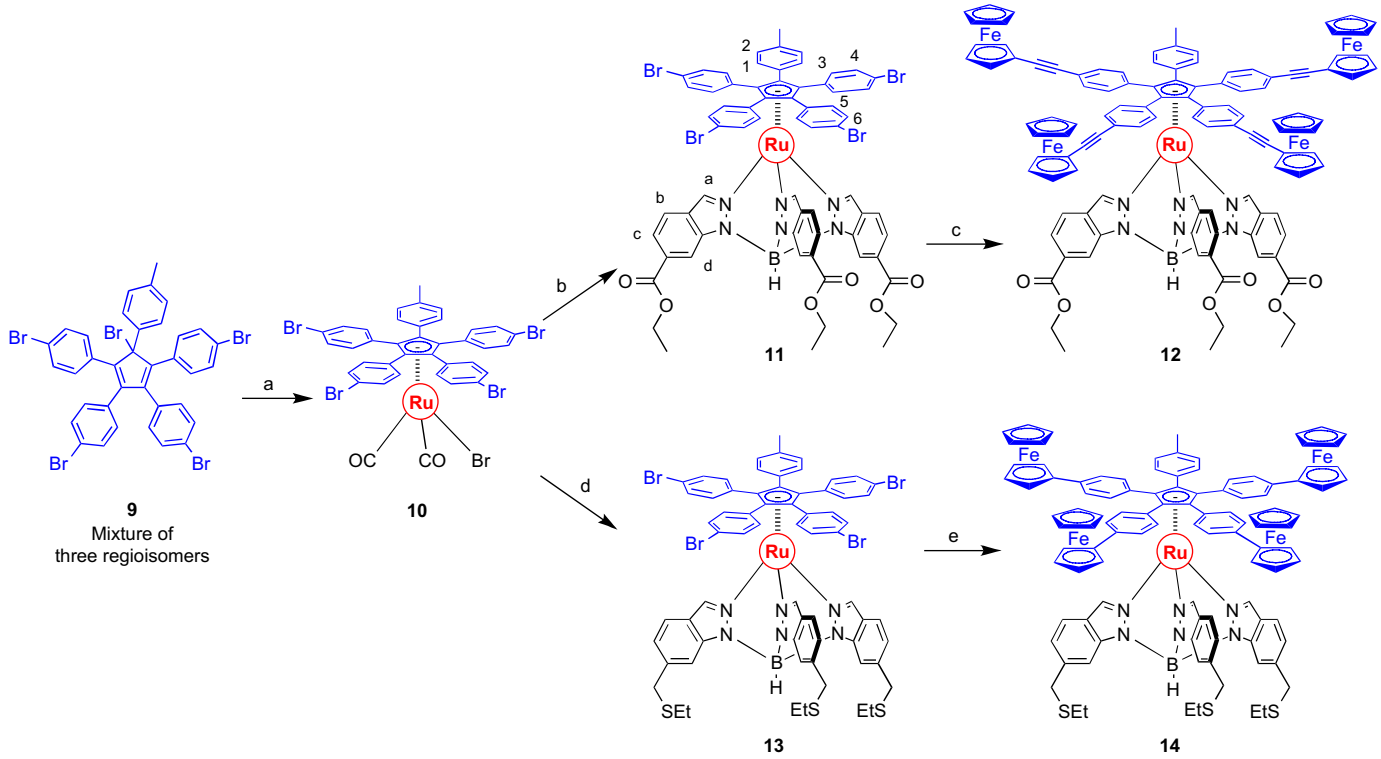


Figure 3. Top: ^{1}H NMR (CD_2Cl_2, 250 MHz) spectrum of ligand **9** with the three singlets corresponding to the three regioisomers in the 2–3 ppm region and the complex signals in the aromatic region. Bottom: ^{1}H NMR (CD_2Cl_2, 250 MHz) spectrum of ruthenium complex **12** with one singlet corresponding to the methyl group in the 2–3 ppm region.

corresponding alcohols under acidic conditions has been studied in detail.[30] It must be stated that the postulated Cp^{+} intermediate is antiaromatic. The presence of this mixture of regioisomers is not a problem since the next step, which consists in the aromatization of the Cp ring through its coordination, leads to the same compound for all three regioisomers.

2.3. Dissymmetric molecular motor for oxide surfaces

The dissymmetric Cp ligand **9** was subsequently coordinated to synthesize a molecular motor functionalized for oxide surface grafting and AFM studies. As shown in Scheme 4, coordination of the three regioisomers of ligand **9** with $Ru_3(CO)_{12}$ gave complex **10** with a 48% yield after purification by column chromatography. The two carbonyl groups and the bromide ligand can be substituted by the hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate tripodal ligand by heating under microwave irradiation in a sealed tube at 150° for 10 min. The ruthenium precursor of the molecular motor **11** was subsequently reacted using the Negishi cross-coupling conditions[22] with [(ferrocenyl)ethynyl]zinc chloride. The dissymmetrized molecule **12** was obtained in 49% yield, which corresponds to 84% yield per coupling reaction. The presence of the



Scheme 4. Reagents and conditions: (a) $Ru_3(CO)_{12}$, toluene, 2 h, reflux, 48%; (b) potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate, microwave, DMF/CH_3CN, 150 °C, 10 min, 30%; (c) [(ferrocenyl)ethynyl]zinc chloride, $Pd(PPh_3)_4$, THF, reflux, 24 h, 49%; (d) potassium hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate, microwave, DMF/CH_3CN, 120 °C, 10 min, 27%; (e) ferroceneboronic acid, $Pd(OAc)_2$, 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine, K_3PO_4, toluene, 100 °C, overnight, 52%.

ferrocenyl moieties was confirmed by ^{1}H NMR spectroscopy with an integration of 36 for the protons of the ferrocenyl groups and 3 for the protons of the tolyl group. Moreover, the ^{1}H NMR spectrum also clearly showed three AA′BB′ patterns for the phenyl protons of the rotor with a 2:2:1 ratio. MALDI-TOF spectrometry also confirmed the presence of the four ferrocene units.

2.4. Dissymmetric molecular motor for metallic surfaces

A dissymmetric motor specially designed for STM studies with a shorter rotor has been synthesized using a Suzuki coupling reaction[31] between ferroceneboronic acid and **13** (Scheme 4). Biaryl bonds being less flexible than alkynes, the rigidity of the arms should also be increased. Moreover, this design allows to avoid triple bonds, which have been shown to be very reactive on metallic surfaces.[32]

The ruthenium precursor **10** was reacted with the hydrotris[6-((ethylsulfanyl)methyl) indazol-1-yl]borate tripodal ligand by heating under microwave irradiation in a sealed tube at 120° to yield **13**. The Buchwald universal catalyst (2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine in the presence of palladium acetate), which has been reported to be a very efficient Suzuki coupling catalyst for deactivated substrates[33] was thus chosen for the quadruple coupling step. Therefore, the ruthenium complex **13** was reacted in toluene with two times 20 equiv of ferroceneboronic acid in the presence of palladium acetate (0.3 equiv) and the Buchwald phosphine (0.6 equiv). After purification by column chromatography, the product of quadruple coupling **14** was obtained in a 52% yield (corresponding to 85% per coupling reaction). The product was characterized by mass spectrometry and ^{1}H NMR with an integration of 45 for the protons of the ferrocenyl groups and 3 for the H_a protons of the tripodal ligand. Compound was also characterized by MALDI-TOF mass spectrometry.

3. Conclusion

In summary, we have synthesized a molecular motor functionalized for metallic surface deposition and STM imaging (compound **1**). In order to monitor the rotation, a versatile strategy to obtain a dissymmetrized cyclopentadienyl ligand has been developed. This ligand has been incorporated in the family of electron-fuelled molecular rotary motors by coordination to a ruthenium tris(indazolyl)borate complex to act as a dissymmetric rotor. Scanning probe microscopic studies are underway, on oxide surfaces for the ester-functionalized dissymetrized ruthenium complex (compound **12**) and metallic surfaces for the thioether-functionalized dissymetrized ruthenium complex (compound **14**) to prove the rotation of the molecule. We are hoping to use the rotor of lower symmetry for real-time imaging of the rotation.

4. Experimental section

4.1. General

All commercially available chemicals were of reagent grade and were used without further purification. 4,4′-Dibromobenzil and ethynylferrocene were purchased from Aldrich. Ruthenium carbonyl was purchased from Strem. Bromo η^5-1,2,3,4,5-penta-(4-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (**2**),[20] potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate,[10] hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate,[10] 1-(4-*tert*-butylphenyl)-2,3,4,5-tetraphenylcyclopentadien-1-ol (**4**),[23] 1-bromo-1-(4-*tert*-butylphenyl)-2,3,4,5-tetraphenyl cyclopentadiene (**5**)[24] and 1,3-di(4-bromophenyl)propan-2-one[26] were prepared according to the literature procedures. Toluene was dried and distilled over CaH_2, THF over sodium with benzophenone and diethylamine over KOH. 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 AM 250 spectrometer, Avance 300 and Avance 500, and full assignments were made using COSY, ROESY, HMBC and HMQC methods when necessary. Chemical shifts are defined with respect to TMS=0 ppm for ^{1}H 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; td for triplet of doublets; q for quadruplet; m for multiplet. The numbering scheme is given in Scheme 4 (molecule **11**, vide supra). UV–vis spectra were recorded on a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10-10.

4.2. Synthesis

*4.2.1. η^5-1,2,3,4,5-Penta-(4-(ferrocenylethynyl)phenyl) cyclopentadienyl hydrotris[6-((ethylsulfanyl) methyl)indazol-1-yl]borate ruthenium(II) (**1**)*

In a two-necked flask, a solution of η^5-1,2,3,4,5-penta-(4-bromophenyl)cyclopentadienyl hydrotris[6-((ethylsulfanyl) methyl)indazol-1-yl]borate ruthenium(II) (**3**) (50 mg, 0.032 mmol) and $Pd(PPh_3)_4$ (19 mg, 0.5 equiv) in 6 mL of freshly distilled THF was degassed. A freshly prepared solution of 0.2 M (ferrocenylethynyl)zinc chloride (0.65 mmol, 20 equiv) was then added. The mixture was heated under reflux for 24 h. Additional reactants were added (19 mg of $Pd(PPh_3)_4$ and 0.65 mmol of (ferrocenylethynyl)zinc chloride) and heating at reflux was maintained for another 24 h. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by flash column chromatography (SiO_2: cyclohexane/CH_2Cl_2 0–50%) to give **1** as an orange solid (30 mg, 42%). λ_{max} (ε) (CH_2Cl_2)/nm 265 (195,000), 305 (152,300), 358 (52,200), 437 (9300); ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 7.93 (s, 3H, H_a), 7.90 (s, 3H, H_d), 7.39 (d, 3H, J=8.7 Hz, H_b), 7.37 (d, 10H, J=8.5 Hz, H_o), 7.18 (d, 10H, J=8.5 Hz, H_m), 7.04 (dd, 3H, J=8.7, 1 Hz, H_c), 4.44 (t, 10H, J=1.8 Hz, subs Cp), 4.21 (t, 10H, J=1.8 Hz, subs Cp), 4.20 (s, 25H, Cp), 3.90 (s, 6H, CH_2S), 2.45 (q, 6H, J=7.4 Hz, CH_2CH_3), 1.28 (t, 9H, J=7.1 Hz, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 143.64, 140.39, 137.56, 133.56, 133.15, 130.19, 122.95, 122.17, 122.10, 120.03, 110.95, 89.34, 87.68, 85.26, 71.37, 69.93, 68.94, 64.95, 36.44, 25.23, 14.34; MS (MALDI-TOF) m/z 2172.1 ([M^+], 100%); High resolution LSI m/z 2173.3055 ([$M+H]^+$, 100%, calculated for $C_{125}H_{100}BFe_5N_6RuS_3$: 2173.3117).

*4.2.2. η^5-1,2,3,4,5-Penta-(4-bromophenyl)cyclopentadienyl hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate ruthenium(II) (**3**)*

Bromo η^5-1,2,3,4,5-penta-(4-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (55 mg, 0.05 mmol, 1 equiv) and potassium hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate (62 mg, 0.1 mmol, 2 equiv) were heated in a sealed tube at 100 °C under microwave irradiation for 10 min in 2 mL of acetonitrile. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2 40%) to give **3** as a yellow solid (20 mg, 24%). λ_{max} (ε) (CH_2Cl_2)/nm 295 (280,700), 312 (251,000), 397 (32,600); ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 7.92 (s, 3H, H_d), 7.83 (d, 3H, J=0.7 Hz, H_a), 7.39 (dd, 3H, J=8.3, 0.6 Hz, H_b), 7.27 (d, 10H, J=8.9 Hz, H_o), 7.23 (d, 10H, J=8.9 Hz, H_m), 7.08 (dd, 3H, J=8.3, 1.3 Hz, H_c), 3.93 (s, 3H, CH_2SEt), 2.50 (q, 6H, J=7.4 Hz, CH_2), 1.31 (t, 9H, J=7.4 Hz, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 143.63, 140.23, 137.78, 135.14, 132.13, 130.65, 122.31, 122.00, 121.87, 120.02, 110.92, 87.06, 36.42, 25.27, 14.33; MS (DCI/NH_3) m/z 1529.0 ([M^+], 100%);

High resolution LSI *m*/*z* 1528.8779 ([M+H]$^+$, 100%, calculated for $C_{65}H_{55}BBr_5N_6RuS_3$: 1528.8704).

4.2.3. Tetra(4-bromophenyl)cyclopentadienone (**7**)

A solution of potassium hydroxide (160 mg, 2.8 mmol, 1 equiv) in absolute ethanol (1.6 mL) was added to a refluxing solution of 4,4′-dibromobenzil (1.04 g, 2.8 mmol, 1 equiv) and 1,3 di(4-bromophenyl)propan-2-one (1.04 g, 2.8 mmol, 1 equiv) in absolute ethanol (4 mL). After 40 min at reflux, the mixture was cooled to 0 °C. The precipitate was filtered and washed with ethanol to give **7** as a purple solid (1.5 g, 68%). ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 7.34 (m, 8H), 7.09 (d, 4H, *J*=8.5 Hz), 6.80 (d, 4H, *J*=8.5 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ (ppm) 194.96, 135.47, 131.77, 131.57, 131.15, 130.77, 128.94, 123.89, 123.59, 122.45; MS (DCI/NH_3) *m*/*z* 701 [M+H]$^+$, 718 [M+NH_4]$^+$. Elemental analysis: calcd for $C_{29}H_{16}Br_4O$: C 49.7, H 2.3; found: C 49.4, H 2.2.

4.2.4. 1-(4-Tolyl)-2,3,4,5-tetra(4-bromophenyl) cyclopentadien-1-ol (**8**)

In a Schlenk tube under argon, a solution of *p*-tolylmagnesium bromide 1 M in THF (2 mL, 2 mmol, 2 equiv) was added dropwise at room temperature to a suspension of tetra(4-bromophenyl)cyclopentadienone (**7**) (700 mg, 1 mmol, 1 equiv) in 10 mL of THF. The solution was stirred 2 h at room temperature and the colour changed from purple to yellow. The solution was hydrolyzed by adding water and 1 M HCl. After washing with water, extraction with diethyl oxide and drying over magnesium sulfate, the solvent was evaporated. The crude product was recrystallized in hexane to afford **8** as a white solid (700 mg, 88%). ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 7.45 (d, 2H, *J*=8.1 Hz), 7.36 (d, 4H, *J*=8.5 Hz), 7.22 (d, 4H, *J*=8.6 Hz), 7.15 (d, 2H, *J*=8.1 Hz), 6.94 (d, 4H, *J*=8.6 Hz), 6.90 (d, 4H, *J*=8.5 Hz), 2.59 (s, 1H, OH), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 134.01, 133.30, 132.41, 132.28, 132.09, 131.91, 131.89, 131.66, 131.37, 131.13, 131.05, 130.22, 130.04, 129.23, 123.66, 21.74; MS (DCI/NH_3) *m*/*z* 793 [M+H]$^+$, 810 [M+NH_4]$^+$, 827 [M+N_2H_7]$^+$. Elemental analysis: calcd for $C_{36}H_{24}Br_4O$: C 54.3, H 3.0; found: C 54.6, H 3.1.

4.2.5. 1-Bromo-1-(4-tolyl)-2,3,4,5-tetra(4-bromophenyl) cyclopentadiene (mixture of isomers) (**9**)

1-(4-Tolyl)-2,3,4,5-tetra(4-bromophenyl)cyclopentadien-1-ol (**8**) (200 mg, 0.25 mmol, 1 equiv) was suspended in glacial acetic acid (4 mL). The solution was heated under argon to 60 °C and a solution of 48% HBr (0.4 mL) in glacial acetic acid (1.4 mL) was added dropwise. After addition, the solution was stirred at 95 °C for 2 h. After cooling down, water was added to precipitate the product, and it was filtered and washed with water. The crude product was purified by column chromatography (SiO_2: cyclohexane/CH_2Cl_2 0–10%) to give **9** as a yellow solid (135 mg, 62%) as mixture of isomers. λ_{max} (ε) (CH_2Cl_2)/nm 260 (33,100), 285 (36,100), 373 (3600); ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 7.4–6.8 (m, 20H), 2.32 (s, 0.84H, regioisomer 1CH_3), 2.29 (s, 1.14H, regioisomer 2CH_3), 2.24 (s, 1.02H, regioisomer 3CH_3); ^{13}C NMR (76 MHz, CD_2Cl_2) δ (ppm) 149.23, 148.26, 147.63, 147.38, 146.69, 142.57, 141.80, 141.35, 140.72, 140.19, 138.52, 138.02, 137.88, 134.55, 134.52, 133.31, 133.13, 133.03, 133.00, 132.90, 132.78, 132.66, 132.05, 131.98, 131.86, 131.74, 131.70, 131.66, 131.64, 131.41, 131.28, 131.22, 131.05, 130.93, 130.70, 130.19, 129.75, 129.47, 129.36, 129.30, 128.96, 128.59, 127.31, 122.32, 122.22, 122.03, 121.99, 121.92, 121.90, 121.82, 121.66, 21.08, 20.98, 20.85; MS (DCI/NH_3) *m*/*z* 856 [M]$^-$; HR-FABMS (*m*-NBA) *m*/*z* 849.7654 (M+H$^+$, calculated for $C_{36}H_{23}Br_5$: 849.7717).

4.2.6. Bromo η^5-1-(4-tolyl)-2,3,4,5-tetra(4-bromophenyl) cyclopentadienyl dicarbonyl ruthenium(II) (**10**)

Ruthenium carbonyl (175 mg, 0.27 mmol, 1 equiv) and 1-bromo-1-(4-tolyl)-2,3,4,5-tetra(4-bromophenyl) cyclopentadiene (**9**) (700 mg, 0.82 mmol, 3 equiv) were heated under argon at reflux for 2 h in 15 mL of freshly distilled toluene. The solution was initially yellow turns rapidly to dark green and then to cherry red. The crude reaction mixture was evaporated under vacuum. The crude product was purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2 0–20%) to give **10** as a yellow solid (400 mg, 48%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 7.29 (m, 8H, H_3, H_5), 6.97 (d, 2H, *J*=8 Hz, H_1), 6.92 (m, 10H, H_2, H_4, H_6), 2.29 (s, 3H, CH_3); ^{13}C NMR (76 MHz, CD_2Cl_2) δ (ppm) 196.06, 139.33, 133.88, 133.86, 132.05, 131.44, 131.34, 128.99, 128.66, 128.20, 125.48, 123.24, 123.06, 107.24, 105.76, 104.86, 21.04; MS (DCI/NH_3) *m*/*z* 972 [M+NH_3−2CO]$^-$, 956 [M−2CO]$^-$; IR: $\nu_{C=O}$ 2007 (s) and 2048 (s) cm^{-1}.

4.2.7. η^5-1-(4-Tolyl)-2,3,4,5-tetra(4-bromophenyl)cyclopentadienyl hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate ruthenium(II) (**11**)

Bromo η^5-1-(4-tolyl)-2,3,4,5-tetra(4-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (**10**) (50 mg, 0.05 mmol, 1 equiv) and potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (61 mg, 0.1 mmol, 2 equiv) were heated in a sealed tube at 150 °C under microwave irradiation for 10 min in a mixture of 2 mL of acetonitrile and 1 mL of DMF. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by column chromatography (SiO_2, dichloromethane) to give **11** as a yellow solid (22 mg, 30%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.76 (s, 3H, H_d), 7.96 (s, 3H, H_a), 7.68 (d, 3H, *J*=8.5 Hz, H_c), 7.44 (d, 3H, *J*=8.5 Hz, H_b), 7.21 (br s, 18H, H_1, $H_{3\text{-}6}$), 6.89 (d, 2H, *J*=8.0 Hz, H_2), 4.47 (q, 6H, *J*=7.1 Hz, CH_2), 2.23 (s, 3H, $PhCH_3$), 1.48 (t, 9H, *J*=7.1 Hz, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 166.77, 143.07, 140.73, 137.98, 135.15, 135.07, 133.26, 132.26, 131.94, 130.73, 130.67, 129.02, 128.89, 128.31, 125.25, 121.99, 121.87, 121.05, 119.73, 113.85, 90.17, 88.05, 87.28, 61.29, 20.87, 14.24; MS (DCI/NH_3) *m*/*z* 1474 [M+NH_4]$^+$, 1457 [M+H]$^+$; MS (MALDI-TOF) *m*/*z* 1451.9678 ([M$^+$], 100%, calculated for $C_{66}H_{51}BBr_4N_6O_6Ru$: 1451.9740).

4.2.8. η^5-1-(4-Tolyl)-2,3,4,5-tetra(4-(ferrocenylethynyl) phenyl)cyclopentadienyl hydrotris[6-(ethoxy carbonyl)indazol-1-yl]borate ruthenium(II) (**12**)

In a two-necked flask was placed a solution of **11** (30 mg, 0.02 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.5 equiv) in 4 mL of freshly distilled THF. A freshly prepared solution of 0.2 M (ferrocenylethynyl)zinc chloride (0.40 mmol, 20 equiv) was then added. The mixture was heated under reflux for 24 h. Additional reactants were added (12 mg $Pd(PPh_3)_4$ and 0.40 mmol of (ferrocenylethynyl)zinc chloride) and heating at reflux was maintained for another 24 h. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by flash column chromatography (SiO_2: CH_2Cl_2) to give **12** as an orange solid (20 mg, 49%). λ_{max} (ε) (CH_2Cl_2)/nm 262 (97,000), 308 (85,500), 365 (42,600); ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.79 (s, 3H, H_d), 8.07 (s, 3H, H_a), 7.67 (d, 3H, *J*=8.5 Hz, H_c), 7.48 (d, 3H, *J*=8.5 Hz, H_b), 7.36 (m, 8H, H_3, H_5), 7.27 (d, 2H, *J*=8.2 Hz, H_1), 7.18 (m, 8H, H_4, H_6), 6.91 (d, 2H, *J*=8.2 Hz, H_2), 4.47 (q, 6H, *J*=7.1 Hz, CH_2), 4.44 (t, 8H, *J*=1.8 Hz, subs Cp), 4.21 (m, 8H, subs Cp), 4.20 (s, 10H, Cp), 4.19 (s, 10H, Cp), 2.25 (s, 3H, CH_3), 1.48 (t, 9H, *J*=7.1 Hz, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 166.86, 143.09, 140.87, 137.75, 133.56, 133.49, 133.39, 132.99, 132.82, 130.27, 130.22, 129.48, 128.88, 128.21, 125.36, 123.13, 123.03, 120.97, 119.75, 113.85, 89.82, 89.52, 89.46, 88.58, 88.29, 85.18, 71.38, 70.66, 69.93, 68.98, 64.87, 61.27, 22.71, 14.25; MS (MALDI/TOF) *m*/*z* 1972 [M]$^+$; HR-FAB$^+$–MS (*m*-NBA) *m*/*z* 1972.4070 (M$^+$, calculated for $C_{114}H_{87}BFe_4N_6O_6Ru$: 1972.3221).

4.2.9. η^5-1-(4-Tolyl)-2,3,4,5-tetra(4-bromophenyl)cyclopentadienyl hydrotris[6-((ethylsulfanyl)methyl)indazol-1-yl]borate ruthenium(II) (**13**)

Bromo η^5-1-(4-tolyl)-2,3,4,5-tetra(4-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (**10**) (125 mg, 0.12 mmol, 1 equiv) and potassium hydrotris[6-((ethylsulfanyl)methyl)indazol-1-

yl]borate (154 mg, 0.24 mmol, 2 equiv) were heated in a sealed tube at 120 °C under microwave irradiation for 10 min in a mixture of 2 mL of acetonitrile and 1 mL of DMF. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane/dichloromethane 50:50) to give **13** as a yellow solid (50 mg, 27%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 7.88 (s, 3H, H_d), 7.81 (s, 3H, H_a), 7.33 (d, 3H, J=8.4 Hz, H_b), 7.27–7.16 (m, 18H, H_1, H_{3-6}), 7.03 (d, 3H, J=8.4 Hz, H_c), 6.87 (d, 2H, J=8.0 Hz, H_2), 3.90 (s, 6H, CH_2S), 2.46 (q, 6H, J=7.4 Hz, CH_2CH_3), 2.22 (s, 3H, $PhCH_3$), 1.27 (t, 9H, J=7.4 Hz, CH_2CH_3); ^{13}C NMR (76 MHz, CD_2Cl_2) δ (ppm) 143.71, 140.37, 137.74, 135.34, 135.26, 133.45, 132.77, 132.50, 130.65, 130.58, 129.44, 128.24, 122.30, 122.10, 121.82, 121.70, 120.05, 111.00, 89.25, 87.16, 86.50, 36.56, 30.25, 25.38, 20.94, 14.42; MS (FAB) m/z 1459 $[M+H]^+$; MS (MALDI-TOF) m/z 1457.9511 ($[M^+]$, 38%, calculated for $C_{66}H_{57}BBr_4N_6S_3Ru$: 1457.9677).

4.2.10. η^5-1-(4-Tolyl)-2,3,4,5-tetra(4-ferrocenylphenyl) cyclopentadienyl hydrotris[6-((ethylsulfanyl)methyl) indazol-1-yl]borate ruthenium(II) (**14**)

In a Schlenk tube, **12** (30 mg, 0.020 mmol, 1 equiv), ferroceneboronic acid (94 mg, 0.40 mmol, 20 equiv), palladium acetate (2.3 mg, 10 μmol, 0.5 equiv), 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine (8.5 mg, 20 μmol, 1 equiv) and anhydrous K_3PO_4 (43 mg, 0.20 mmol, 10 equiv) were placed under argon. Freshly distilled toluene (2 ml) was added and the mixture was heated at 100 °C overnight. After cooling down, additional ferroceneboronic acid (94 mg, 0.40 mmol, 20 equiv), palladium acetate (2.3 mg, 10 μmol, 0.5 equiv), 2-(2′,6′-dimethoxybiphenyl) dicyclohexyl phosphine (8.5 mg, 20 μmol, 1 equiv) and anhydrous K_3PO_4 (43 mg, 0.20 mmol, 10 equiv) were added and the mixture was heated at 100 °C overnight. The crude reaction mixture was evaporated under vacuum. The product was purified by column chromatography (Al_2O_3: cyclohexane/CH_2Cl_2 60:40) to give **14** as an orange solid (20 mg, 52%). λ_{max} (ε) (CH_2Cl_2)/nm 261 (163,200), 306 (127,500), 359 (42,600), 436 (7400); ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 8.07 (s, 3H, H_a), 7.81 (s, 3H, H_d), 7.34 (m, 11H, H_3, H_5, H_b), 7.31 (d, 2H, J=8.1 Hz, H_1), 7.18 (m, 8H, H_4, H_6), 6.99 (d, 3H, J=7.1 Hz, H_c), 6.90 (d, 2H, J=8.1 Hz, H_2), 4.56 (t, 4H, J=1.8 Hz, subs Cp), 4.54 (t, 4H, J=1.8 Hz, subs Cp), 4.25 (t, 4H, J=1.8 Hz, subs Cp), 4.24 (t, 4H, J=1.8 Hz, subs Cp), 3.93 (s, 20H, Cp), 3.90 (s, 6H, CH_2S), 2.48 (q, 6H, J=7.4 Hz, SCH_2), 2.21 (s, 3H, $PhCH_3$), 1.28 (t, 9H, J=7.4 Hz, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm) 143.71, 140.20, 138.29, 138.20, 137.29, 137.10, 133.63, 133.55, 132.13, 132.02, 130.95, 127.92, 124.74, 124.69, 122.22, 122.05, 120.02, 111.06, 89.69, 87.74, 86.52, 84.43, 84.35, 63.85, 69.82, 69.22, 69.19, 66.44, 66.42, 66.38, 66.36, 36.58, 25.37, 21.00, 14.43; MS (MALDI-TOF) m/z 1882.3 ($[M^+]$); High resolution LSI m/z 1883.3301 ($[M+H]^+$, 100%, calculated for $C_{106}H_{94}BFe_4N_6RuS_3$: 1883.3236).

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