

Synthesis and Reactivity of [Penta(4-halogenophenyl)cyclopentadienyl]-[hydrotris(indazolyl)borato]ruthenium(II) Complexes: Rotation-Induced Fosbury Flop in an Organometallic Molecular Turnstile

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Abstract: The preparation of ruthenium(II) complexes coordinated to a penta(4-halogeno)phenylcyclopentadienyl ligand and to the hydrotris(indazolyl)borate ligand are detailed. Our strategy involves first the coordination of the penta(4-bromo)phenylcyclopentadienyl ligand by reaction with the ruthenium–carbonyl cluster followed by the coordination of the tripodal ligand. The pentabrominated precursor was successfully converted to the penta-iodinated derivative by using the

Klapars–Buchwald methodology, applied for the first time on organometallic substrates. Cross-coupling reactions were performed on both pentabromo and penta-iodo complexes to introduce in a single step the five peripheric ferrocenyl fragments required to obtain a

Keywords: cross-coupling • density functional calculations • molecular turnstiles • ruthenium • sandwich complexes

potential molecular motor. The two ligands present in the ruthenium complexes undergo a correlated rotation that was established both experimentally by NMR experiments and an X-ray diffraction study, and theoretically by DFT calculations. The potential-energy curve obtained by DFT revealed the energy barrier of the gearing mechanism to be only 4.5 kcal mol^{−1}. These sterically highly constrained complexes can be regarded as organometallic molecular turnstiles.

Introduction

The control of rotation is at the heart of the bottom-up strategy to build molecular devices such as molecular machines and motors.^[1,2] In the constant quest for novel molecular components, multistep chemical synthesis is expected to play a major role because it allows chemists to prepare tailor-made compounds with predetermined shape and programmed movement or functions. This has stimulated the design and synthesis of a variety of compounds that resemble macroscopic machinery. We call such molecules “technomimetic”^[2] because they are designed to transpose macro-

scopic objects at the molecular level, including the motions these objects are able to undergo. Such systems that function in an analogous fashion to macroscopic mechanical systems have recently led to the synthesis and description of many molecular-scale systems as innovative as molecular gears,^[3] wheels,^[4] nanovehicles,^[5] wheelbarrows,^[6] and turnstiles.^[7] These are providing 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.

One of the earliest examples of a molecular gear was simultaneously reported by Mislow and Iwamura.^[8] The molecule consists of a bistriptycene linked by a methylene or an oxygen bridge to give an analogue of a three-toothed bevel gear. Simple carbon-derived rotors such as triptycene are limited by valency to three cog-teeth. To increase the number of cog-teeth available in the rotor and in the search for the synthesis of a molecular motor,^[9] we became interested in the possibility of utilising metallocenes, in particular half-sandwich complexes with the “piano stool” structure. They present interesting characteristics for our purpose: one can build complex molecules presenting only one significant degree of freedom in internal rotation, and it is possible to

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200800689>.

perform different chemistries on the upper and lower parts of the molecule, giving access to a wide range of compounds. Thus, we studied the synthesis of a family of ruthenium complexes containing two different ligands, a penta-phenyl-substituted cyclopentadienyl (Cp) and a hydrotris(indazolyl)borate (Tp^{4Bo}) ligand. This family of complexes is much less common than the well-studied family of (cyclopentadienyl)[hydrotris(pyrazolyl)borato]ruthenium [RuCpTp] complexes.^[10]

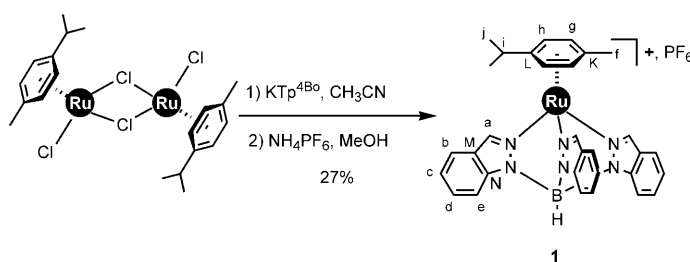
In this paper, we present the synthesis of [penta(4-halogenophenyl)cyclopentadienyl][hydrotris(indazolyl)borato]ruthenium half-sandwich complexes. As halogens, bromine and iodine were selected because of their potential in cross-coupling reactions that enable the introduction of functional building blocks. The brominated and iodinated derivatives were prepared and cross-coupling reactions achieved on both structures. The syntheses appeared to be relatively difficult and several strategies had to be explored. The combination of two bulky ligands (substituted Cp and Tp^{4Bo}) around the metallic core revealed very interesting behaviour: a lateral gearing effect that was established experimentally by NMR and X-ray experiments and theoretically by a DFT study of the molecular motions. From a technomimetic point of view, these complexes behave as organometallic molecular turnstiles with two correlated rotations, that is, the primary rotation of one ligand with respect to the other induces a secondary rotation.

Abstract in French: La préparation de complexes de ruthénium coordonné au ligand penta(4-halogéno)phényl cyclopentadiényle et au ligand hydrotris(indazolyle)borate sont détaillées. Notre stratégie implique tout d'abord la coordination du ligand penta(4-bromo)phénylcyclopentadiényle par réaction avec le cluster de ruthénium carbonyle suivie par la coordination du ligand tripode. Le précurseur pentabromé a ensuite été converti avec succès en dérivé pentaiodé en utilisant la méthodologie développée par Klapars et Buchwald qui a été utilisée pour la première fois sur des substrats organométalliques. Des réactions de couplages croisés ont ensuite été effectuées sur les dérivés pentabromés et pentaiodés afin d'introduire simultanément les cinq fragments ferrocényl périphériques requis pour obtenir un moteur moléculaire potentiel. Les deux ligands présents dans les complexes de ruthénium sont le siège d'une rotation secondaire corrélée qui a été mise en évidence expérimentalement par des expériences de RMN et une étude de diffraction des rayons X, et théoriquement par des calculs DFT. La courbe d'énergie potentielle obtenue par DFT permet d'accéder à la barrière de rotation de ce mécanisme d'engrenage qui n'est que de 4.5 kcal mol⁻¹. Ces complexes stériquement très contraints peuvent être considérés comme des tourniquets moléculaires organométalliques.

Results and Discussion

Synthesis of [penta(4-bromophenyl)cyclopentadienyl][hydrotris(indazolyl)borato]ruthenium complexes: Hydrotris(indazolyl)borate ligand (Tp^{4Bo}) is a versatile ligand belonging to the family of scorpionates developed by Trofimenko.^[10] It has been shown that Tp^{4Bo} binds in a facial tripodal mode and its geometry is particularly well suited to mimic macroscopic gears.^[3] Two routes have been described in the literature to synthesise half-sandwich RuCpTp and RuCp*Tp complexes. The most general one has been described by Tocher and co-workers^[11] and involves the coordination of the scorpionate ligand followed by the coordination of the cyclopentadienyl ligand. For this purpose, [Ru(η⁶-p-cymene)Tp^{4Bo}] hexafluorophosphate was synthesised by reaction of [Ru(p-cymene)Cl₂]₂ with KTp^{4Bo} in acetonitrile for 18 h at room temperature.

After treatment with an ammonium hexafluorophosphate solution and recrystallisation from methanol (with Et₂O as a non-solvent), (η⁶-p-cymene)[hydrotris(indazolyl)borato]ruthenium hexafluorophosphate was isolated as orange crystals in 27% yield (Scheme 1).

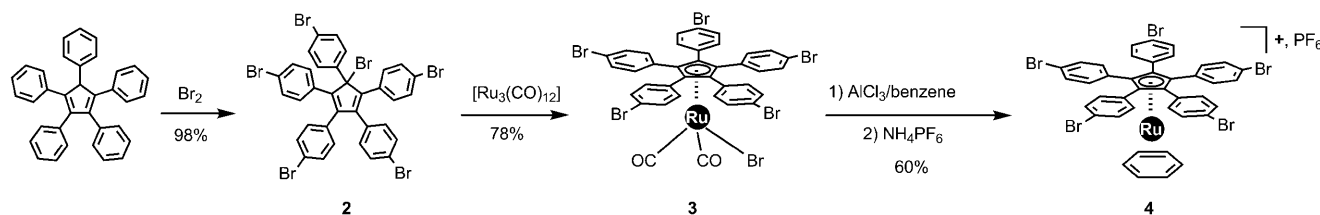


Scheme 1. Synthesis of (η⁶-p-cymene)[hydrotris(indazolyl)borato]ruthenium hexafluorophosphate.

Photochemical^[12] and thermal labilisation of the p-cymene ligand were attempted in acetonitrile in the presence of 1,2,3,4,5-penta(phenyl)cyclopentadiene without success under various conditions, including microwave heating.

We subsequently investigated another synthetic route involving the coordination of the Cp ligand in a first step. As proposed by Mann and co-workers,^[13] this strategy involves the use of the (acetonitrile)(η⁵-cyclopentadienyltris)ruthenium(II) complex in which the labile acetonitrile ligands can be easily substituted by a Tp ligand. A similar strategy was described by Singleton^[14] using as intermediate the chloro-(η⁵-cyclopentadienyl)(η⁴-cycloocta-1,5-dienyl)ruthenium(II) complex, a versatile precursor because cycloocta-1,5-diene is labile. However, both strategies failed with pentaphenylcyclopentadienyl ligands, possibly due to the strong steric hindrance in the neighbourhood of the coordination site.

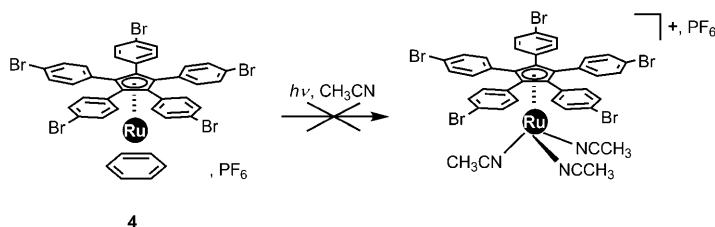
These difficulties led us to follow an alternative strategy that requires the synthesis of (η⁶-benzene)[η⁵-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl]ruthenium as a key intermediate. Bromination of the commercially available 1,2,3,4,5-penta(phenyl)cyclopentadiene was achieved by



Scheme 2. Synthesis of $(\eta^6\text{-benzene})[\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}]$ ruthenium hexafluorophosphate.

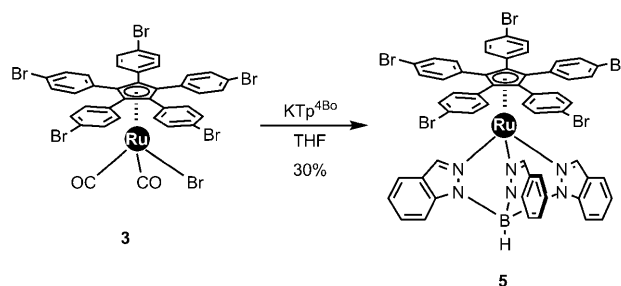
treatment with neat bromine at room temperature for 2 h, which produced regioselectively **2**, 1-bromo-1,2,3,4,5-penta(4-bromophenyl)cyclopentadiene (Scheme 2). Similarly to the oxidative addition of 1-bromo-1,2,3,4,5-pentaphenylcyclopentadiene on the ruthenium–dodecacarbonyl cluster,^[15] the reaction of **2** with $[\text{Ru}_3(\text{CO})_{12}]$ yielded complex **3**, the bromidodicarbonyl $[\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}]$ ruthenium complex, $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Br}(\text{CO})_2]$. Moreover, the IR spectrum of complex **3** displayed two characteristic vibration bands of the carbonyl ligands at 2003 and 2048 cm^{-1} comparable to the ones of $[\text{RuCpBr}(\text{CO})_2]$.^[15] The substitution of the carbonyl and bromine ligands was achieved in benzene at reflux in the presence of aluminium chloride, as shown by Pauson and McVey^[16] for the synthesis of bromidodicarbonyl $(\eta^5\text{-1,2,3,4,5-penta(phenyl)cyclopentadienyl})$ iron. The photolabilisation of the arene ligand and its substitution by a scorpionate was demonstrated by Mann and co-workers.^[17] After counterion exchange by treatment with an excess of ammonium hexafluorophosphate, $(\eta^6\text{-benzene})[\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}]$ ruthenium hexafluorophosphate (**4**) was obtained by crystallisation in 60% yield. ^1H NMR analysis showed a free rotation of the $\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}$ and $\eta^6\text{-benzene}$ ligands with only a singlet for the benzene ring.

Unfortunately, by following a standard procedure, irradiation of complex **4** in acetonitrile with a 400-W UV lamp did not allow us to obtain the target complex (Scheme 3). TLC analysis showed the formation of numerous side products, indicating a probable generation of bromine radicals during the experiment.



Scheme 3. Attempted photolabilisation of the benzene in acetonitrile.

In order to obtain complex **5**, as shown in Scheme 4, complex **4** and $\text{KTp}^{4\text{Bo}}$ were heated in THF at reflux under argon atmosphere for 24 h. After purification by silica-gel



Scheme 4. Synthesis of $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$.

column chromatography, **5** was obtained as a yellow solid in 30% yield.

Notably, two equivalents of $\text{KTp}^{4\text{Bo}}$ are needed to obtain such a yield. The use of only one equivalent produced **5** in a 16% isolated yield, whereas a larger excess did not increase the yield. Reaction time, temperature and solvent were varied, but none of these changes resulted in an improved yield. Nevertheless, it must be noted that the coordination of the tripodal ligand is the result of two steps and the presence of various ligands ($\text{Tp}^{4\text{Bo}}$, Cp, CO, Br) in the reaction mixture may allow numerous side reactions. The slightest ligand scrambling produces side products.

The piano-stool structure of the $[\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}][\text{hydrotris(indazol-1-yl)borato}]$ -ruthenium complex (**5**) was confirmed by ^1H NMR analysis. The three indazoles are chemically equivalent, resonating at the same frequency. Moreover, the signals for protons 1 and 4 are largely shifted downfield indicating a strong shielding effect of the phenyls of the $\eta^5\text{-1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl}$ ligand on the indazole of $\text{Tp}^{4\text{Bo}}$, as expected for such interpenetrated ligands.

X-ray structure of 5: Crystals of $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ (**5**) suitable for X-ray diffraction were obtained from the slow diffusion of methanol in a benzene solution of the complex $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ cocrystallised with two benzene molecules. The X-ray structure of $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ confirmed the coordination of both ligands, as shown in Figure 1.^[18] As shown by Trofimenko,^[19] $\text{Tp}^{4\text{Bo}}$ binds in a facial tripodal mode (i.e., $\kappa^3\text{-N,N',N''}$). The complex has a piano-stool structure with the Cp substituents fitting in the vacant spaces of the tripodal ligand. The distance between the Cp ligand and the ruthenium atom is 1.79 Å

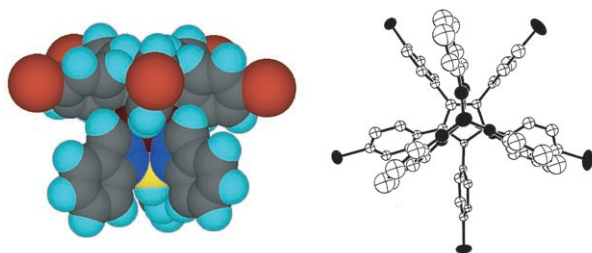


Figure 1. Crystal structure of **5**: space-filling (side view, left) and ORTEP (bottom view, right) representations.

and the average distance between the three coordinated nitrogen atoms and the ruthenium centre is 2.16 Å.

By analogy with ethane, as shown in Figure 2, two remarkable conformations can be defined: the eclipsed conformation, in which the dihedral angle between a CH bond of the η^5 -cyclopentadienyl ligand and one indazole of the scorpionate ligand is 0°, and the staggered conformation, in which this dihedral angle is 12°.

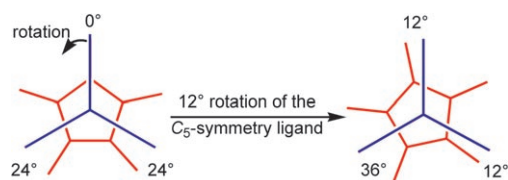


Figure 2. Eclipsed (left) and staggered (right) conformations of a complex bearing a C_3 and a C_5 symmetry ligand. Interconversion occurs upon a 12° rotation (represented counterclockwise on the figure). For symmetry reasons, the staggered conformation appears every 24°.

The $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ complex crystallises in a conformation close to the staggered one. For symmetry considerations, the superimposition of a tripodal ligand bearing a C_3 axis and a penta-substituted Cp of C_5 symmetry causes differentiation of the five 4-bromophenyl rings, considering the dihedral angle between the plane of the phenyl ring and the plane of the Cp ring. One is exactly perpendicular (90°), and the two groups that are not located above indazole are almost perpendicular (81°). Due to steric hindrance with the tripodal ligand, the remaining two phenyl rings have to be tilted at 35° and 36° to minimise steric interactions.

The comparison of the X-ray crystal structures of $[\text{RuCpTp}^{4\text{Bo}}]$ ^[20] and **5**^[18] reveals a small increase in bond lengths in the latter: +0.02 Å for the Ru–C bonds, and +0.02 Å for the Ru–N bonds. The Ru–C and Ru–N bond lengths are summarised in Table 1. This trend is reproduced by DFT calculations on both systems (+0.05 Å and +0.01 Å for the Ru–C and Ru–N bonds, respectively). This stretching of the metal–ligand bonds reflects the steric hindrance in **5** due to the interactions of the 4-bromophenyl substituents with the indazole rings of the tripodal ligand, but the magnitude of the effect is small.

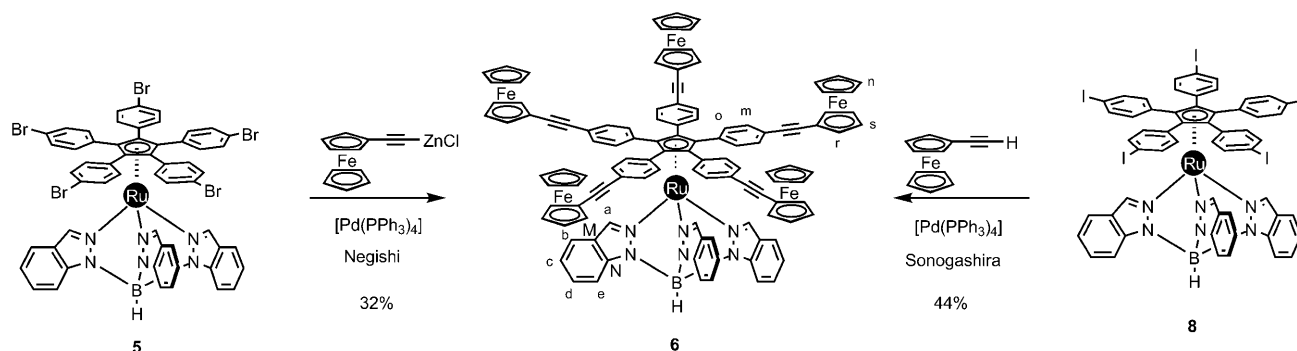
Table 1. Selected bond lengths in $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ and $[\text{RuCpTp}^{4\text{Bo}}]$.

	$[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}]$ (5)	$[\text{RuCpTp}^{4\text{Bo}}]$
Ru–N(1)	2.158(5)	2.142(7)
Ru–N(3)	2.159(4)	2.108(7)
Ru–N(5)	2.131(5)	2.098(7)
Ru–C(1)	2.192(5)	2.140(10)
Ru–C(2)	2.186(5)	2.155(13)
Ru–C(3)	2.186(5)	2.166(11)
Ru–C(4)	2.142(5)	2.143(13)
Ru–C(5)	2.207(5)	2.131(11)

Reactivity of the pentabrominated derivative $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$: Our research on electron-triggered molecular motors involves an active part based on a ruthenium–cyclopentadienyl (Cp) complex. In this design the Cp ligand is substituted by five linear and rigid arms, each terminated by an electroactive group. Ferrocene was selected as an electroactive group because it exhibits reversible oxidation in various solvents.^[21] The molecule is intended to be deposited between two electrodes of a nanojunction and should transform a current of electrons into a unidirectional rotation motion.^[9] The quintuple Sonogashira coupling reaction^[22] was attempted between $[\text{Ru}\{\eta^5\text{-Cp(4-BrPh)}_5\}\text{Tp}^{4\text{Bo}}]$ (**5**) and ethynylferrocene without success. Different alkynes and catalytic systems were tested, but even the use of very electron-rich and hindered phosphines such as tris(*tert*-butylphosphine) did not allow us to obtain the coupling product. This may be due to the high electron density of the bromide derivative, which is covalently linked to a formal anionic entity (Cp). The electron-rich character of the carbon–bromide bond precludes the oxidative addition on the palladium catalyst.

In accordance with the results obtained by Tobe et al.^[23] for the synthesis of differentially substituted hexaethynylbenzenes based on tandem Sonogashira and Negishi^[24] cross-coupling reactions, we tried to overcome the poor reactivity of the aryl bromide centres by using Negishi conditions. The specificity of this protocol lies in the use of a freshly prepared alkynyl zinc chloride solution instead of an alkynyl cuprate generated in situ. In contrast to the Sonogashira conditions, the five ferrocenyl groups were simultaneously covalently attached to the pentaphenyl Cp ligand by a quintuple coupling of ethynylferrocene with **5** with a 32 % yield, which corresponds to a yield of 80 % per coupling (Scheme 5). ¹H 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 integrating for 45 protons. The presence of the five ethynylferrocene units was also confirmed by mass spectrometry.

Synthesis of [penta(4-iodophenyl)cyclopentadienyl][hydrotris(indazolyl)borato]ruthenium complexes by halogen-exchange reaction: Because the conversion to organozinc precursors is not quantitative and not compatible with all the organic functions or organometallic building blocks, we decided to substitute the bromine atoms for iodine centres to



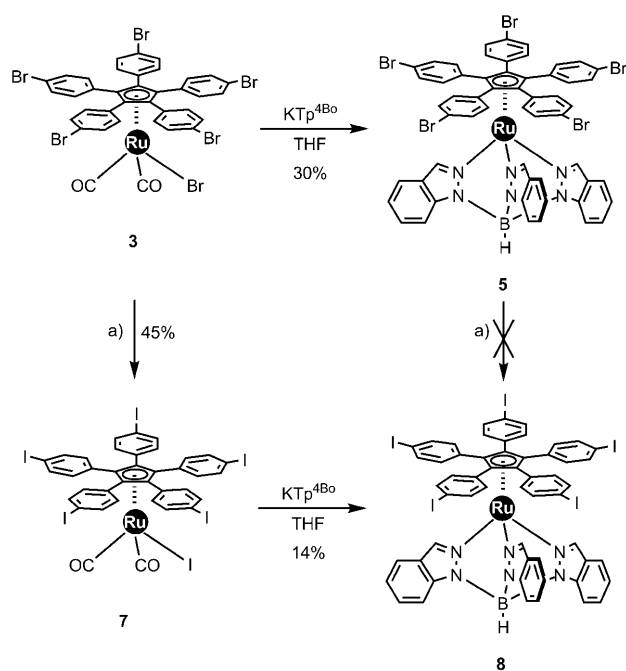
Scheme 5. Palladium-catalysed coupling strategy.

overcome the lack of reactivity of the polybrominated pentaphenylcyclopentadienyl moiety. A halogen-exchange reaction was investigated to activate the penta(4-bromo)phenylcyclopentadienyl ligand towards palladium-catalysed coupling reactions. The pentaiodinated analogue of complex **5** was envisaged because aryl iodides are more reactive in palladium-catalysed cross-coupling reactions. The most commonly used reaction to convert an aryl bromide into an aryl iodide consists of the preparation of the organolithium derivative in a first step followed by quenching with iodine. However, this reaction is not universal and, in particular, it is not suited for polybromide precursors because polyanionic species are difficult to generate and are often accompanied by solubility problems.

In 2002, Klapars and Buchwald described a very efficient copper-catalysed halogen-exchange reaction in aryl halides, consisting of an aromatic Finkelstein reaction.^[25] They showed it was possible to exchange a bromide with an iodide by treatment of the substrate with copper iodide, sodium iodide and a catalytic amount of *N,N'*-dimethyl-*trans*-cyclohexanediamine, with 93–99% yield for the conversion of monohalogen derivatives. The reaction seems to tolerate many organic functions and is efficient with various electrodonating or electrowithdrawing groups. Nevertheless, it must be noted that, to our knowledge, there are no examples of this halogen-exchange reaction on organometallic or coordination compounds.

This reaction was first tested on $[\text{Ru}(\eta^5\text{-Cp}(4\text{-BrPh})_3)\text{Tp}^{4\text{Bo}}]$ (**5**), but the result was not satisfactory because an analysis of the crude mixture by mass spectrometry showed partial conversion of the starting complex and production of all the possible products resulting from 1-to-5 halogen exchange. Performing the same reaction on the precursor complex **3** gave access to the pentaiodinated analogue **7** which, after coordination of ligand $\text{Tp}^{4\text{Bo}}$ as shown in Scheme 6, yielded $[\text{Ru}(\eta^5\text{-Cp}(4\text{-IPh})_3)\text{Tp}^{4\text{Bo}}]$ (**8**).

The periodination of complex $[\text{Ru}(\eta^5\text{-Cp}(4\text{-BrPh})_3)\text{Br}(\text{CO})_2]$ (**3**) was achieved at 110 °C in dioxane in the presence of sodium iodide (20 equiv), copper iodide (2.5 equiv) and *N,N'*-dimethyl-*trans*-cyclohexanediamine in catalytic amount (Scheme 6). After 24 h of heating, the desired compound **7** was obtained in a 45% isolated yield.



Scheme 6. Iodination reactions performed on the ruthenium complexes. a) 2.5 equiv CuI, 20 equiv NaI, 0.5 equiv (*rac*)-*trans*-*N,N'*-dimethyl-1,2-cyclohexanediamine, dioxane, Ar, 110 °C, 24 h.

This complex was characterised by ^1H - and ^{13}C NMR spectroscopy, mass spectrometry and infrared spectroscopy. The carbonyl vibrations ($\nu_{\text{C=O}}=2000$ and 2042 cm^{-1}) are similar to those of the brominated complex **3** ($\nu_{\text{C=O}}=2003$ and 2048 cm^{-1}).

Compound **7** was converted into the pentaiodinated **8** by reaction with $\text{KTp}^{4\text{Bo}}$ (2 equiv) in refluxing THF for 24 h. Compound **8** was isolated in 14% yield by column chromatography, and this compound was also fully characterised by ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. The comparison of the ^1H NMR spectra of the pentabrominated and the pentaiodinated complexes (**5** and **8**) showed a shift of the phenyl signals due to the effect of the iodine centres. Indeed, the protons located *ortho* to the halogen atom are shifted downfield by 0.20 ppm and the protons *meta* to the

halogen atom are shifted upfield by 0.17 ppm in the case of the iodine derivatives. Interestingly, these shifts are very close to the values given in the commonly used incremental tables, 0.21 and 0.13 ppm, respectively.

Reactivity of the pentaiodinated derivative $[\text{Ru}(\eta^5\text{-Cp}(4\text{-IPh})_5)\text{Tp}^{4\text{Bo}}]$: As shown in Scheme 5, the Sonogashira coupling conditions were very efficient with the pentaiodinated precursor (whereas the pentabrominated analogue gave no reaction) and allowed the direct connection of the five ethynylferrocene moieties onto complex **8**. This was accomplished in a single step, leading to complex **6** after a quintuple coupling reaction with a 44 % yield corresponding to an excellent 85 % per coupling. This is the best yield obtained to date for this family of molecules involving a quintuple coupling in the last synthetic step.

Electrochemistry: Cyclic voltammetry of complex **6** showed two reversible oxidation waves corresponding to the successive oxidation of the iron centres and the ruthenium centre. The 5:1 ratio between these two waves is consistent with the ratio between the iron and ruthenium atoms in the complex. In complex **6**, the five iron centres are first reversibly^[21] and simultaneously oxidised at a potential of 0.52 V/saturated calomel electrode (SCE) (Table 2), followed by the reversible oxidation of the ruthenium centre at 0.82 V/SCE, which is similar to the value obtained with **1**. The lower oxidation potential for the iron moiety in **6** versus ethynylferrocene (Ethynyl-Fc) is in line with the replacement of a hydrogen atom by an electron-rich aromatic substituent.

Table 2. Oxidation potentials of iron and ruthenium in V vs SCE. All waves were reversible (CH_2Cl_2 , $n\text{Bu}_4\text{NPF}_6$ 0.1 M, Pt working and counter electrode).

	5	6	Ethynyl-Fc
$E_{1/2}(\text{ox}) \text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$	–	0.52	0.59
$E_{1/2}(\text{ox}) \text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$	0.80	0.82	–

The relative oxidation potentials are compatible with our objective, in the sense that the ruthenium centre will remain inert towards the redox cycles of the peripheral electroactive groups. Indeed, the cyclic voltammogram (see Supporting Information) shows that the two oxidation processes do not overlap, which means that oxidation of the ferrocene fragments will not affect the ruthenium centre.

Study of the rotation in solution—evidence for a lateral gearing effect: The rotation was studied both experimentally and theoretically on complex **5**. In this complex, an additional steric interference exists relative to the case of $[\text{RuCpTp}^{4\text{Bo}}]$ due to the interaction between the bromophenyl units and the indazolyl paddles, so that one could anticipate a slow or restricted rotation.

The dissymmetry of the complex was exploited to study the dynamics of the rotation in **5**. Because the tripodal ligand bears a C_3 axis and the penta-substituted Cp is of C_5

symmetry, chemical equivalence in the ^1H NMR spectrum is a proof of free rotation of one ligand with respect to the other one. For instance, in the ^1H NMR spectrum of **5**, the rotational freedom of the Cp ring was evidenced because the three indazolyl groups are equivalent, as shown in Figure 3. The 4-bromophenyl rings are also free to rotate, as evidenced by the chemical equivalence of the two *ortho* protons (H_o) and of the two *meta* protons (H_m).

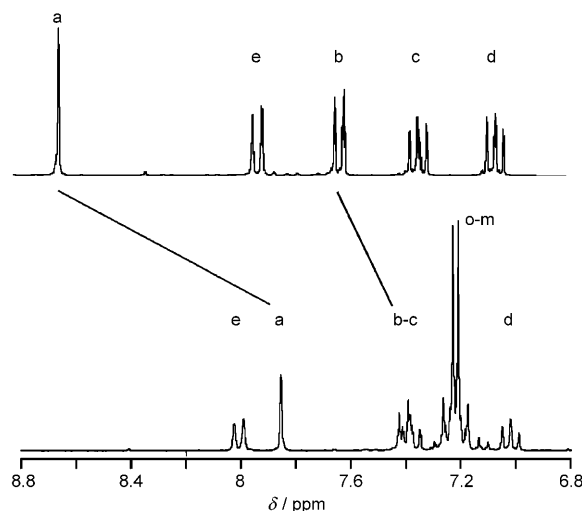


Figure 3. ^1H NMR (CD_2Cl_2 , 250 MHz) spectrum of **3** (bottom) compared to $[\text{RuCpTp}^{4\text{Bo}}]$ (top) at 25 °C.

These protons are referred to as an $\text{AA}'\text{BB}'$ spin system. In addition, there are striking differences between the spectrum of $[\text{Ru}(\eta^5\text{-Cp})\text{Tp}^{4\text{Bo}}]$, which we have also synthesised, and the spectrum of **5**. Protons a and b (see numbering scheme in Scheme 5) are significantly shielded from 8.62 to 7.86 ppm for protons a and from 7.60 to 7.39 ppm for protons b. This shielding is explained by the location of these protons in the shielding cones of the 4-bromophenyl rings, evidencing the two ligands fitting into each other in solution, just like in the solid state. Variable-temperature ^1H NMR spectroscopy from -90°C to 120°C did not show any significant differences in terms of equivalence of protons. Thus, the rotation barrier could not be measured by NMR analysis and must be low.

The apparent paradox of the free rotation evidenced by NMR analysis and the embedding of the aromatics highlighted by X-ray diffraction can only be explained by two correlated rotation processes. Because the two ligands are interpenetrated, the rotation of the Cp ring should only be possible if the 4-bromophenyl groups tip over to settle in the vacant spaces of the tripodal ligand. Figure 4 represents the rotation of the upper Cp ligand (action 1) inducing the secondary rotation of the 4-bromophenyl rings (action 2). DFT calculations were performed to support this hypothesis in order to elucidate the molecular motions that correspond to a lateral gearing effect.

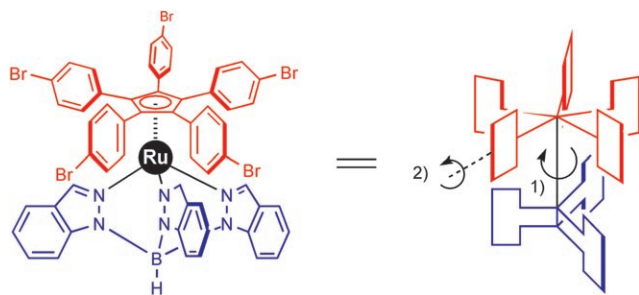


Figure 4. Representation of the secondary rotation: the rotation of the upper Cp ligand (action 1) results in the paddles tipping over (action 2).

DFT analysis: The symmetry of the two parts of the molecule suggests that the potential-energy curve should have a high periodicity. If we start from a conformation in which a 4-bromophenyl group (paddle) sits just above an indazol ring (leg), it is clear that a rotation by 24° ($1/15$ th of a turn) makes another coincidence happen (Figure 2). Hence, we predict that the potential-energy curve should present closely spaced extrema. To systematise the analysis, we define an eclipsed and a staggered conformation from the value of the smallest dihedral angle between a paddle and a leg, that is, 0° and 12° , respectively (see above). Simple steric considerations suggest that the staggered conformation should be an energy minimum, whereas the eclipsed one should be a transition state. The geometry close to the staggered one obtained for the X-ray crystal structure (Figure 1) is not exactly reproduced by DFT calculations. At this level, it is found that the most stable conformation is the eclipsed one (Figure 5a). The paddle that sits exactly above a leg is tilted with respect to the Cp ring plane by 31° only, that is, by much less than the others (53 to 85°). This privileged posi-

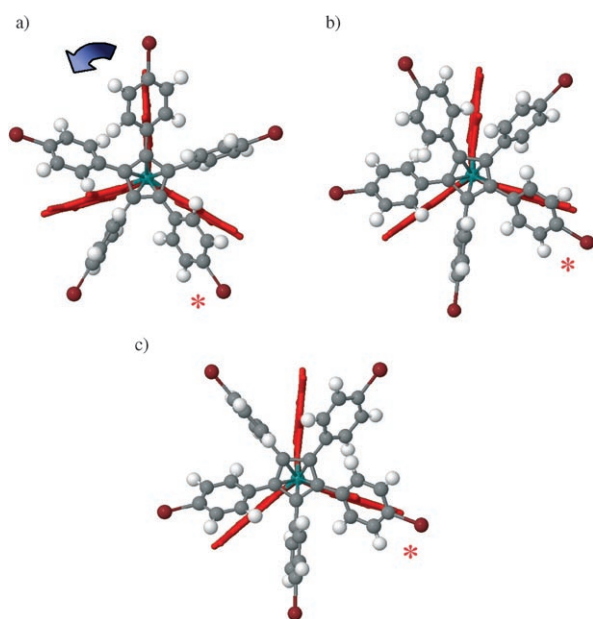


Figure 5. a) DFT minimum, b) transition state and c) DFT minimum similar to that in a) after $1/15$ th of a turn.

tion can be explained by the dispersion interaction, which favours weak CH/π attractive interactions^[26] between the leg and the paddle overhanging. Hybrid DFT functionals are able to describe this particular dispersion interaction, although it is underestimated with respect to the MP2 and CCSD(T) level of theories.

The potential-energy curve obtained by DFT gave access to the energy barrier of the gearing mechanism. A transition state, corresponding to an intermediate during the rotation process, was found by DFT at $4.5 \text{ kcal mol}^{-1}$ above the minimum. It resembles the staggered geometry (Figure 5b), but one paddle (*) starts to interact with a leg, prefiguring the nearby minimum geometry (Figure 5c). The differences between the X-ray structure and the computed minimum and transition-state structures are subtle and also involve differences in orientation of the phenyl rings with respect to the Cp ring. Thus, we can conclude that the upper part remains strongly linked to the lower part during the rotation process, while being almost free to rotate.

Closer inspection of the structure strongly suggests that the rotation must involve some “gearing effect”, that is, a correlated motion of the upper part with respect to the lower part (Figure 4, motion 1), and of a paddle around the Cp–phenyl single bond (Figure 4, motion 2). This is reminiscent of the “Fosbury flop”.^[27]

Conclusion

The synthesis of the active part of molecular motors was achieved through cross-coupling reactions performed on a polyhalogenated ruthenium complex. The coupling reactions involving the polybrominated complex were either ineffective (Sonogashira) or successful (Negishi), however, the latter requires in a first step the conversion of a terminal alkyne into an organozinc intermediate, which restricts the scope of this reaction. To overcome this problem, the polybrominated complex was successfully converted into its polyiodinated analogue by using the Klapars–Buchwald methodology, which was applied, to the best of our knowledge, for the first time to an organometallic substrate. Under Sonogashira conditions, an excellent 85% yield per coupling was achieved with the pentaiodinated complex.

An X-ray diffraction study showed that the two ligands coordinated to ruthenium were strongly embedded, however, free rotation was evidenced both experimentally by NMR analysis and theoretically by DFT. This is reminiscent of macroscopic molecular turnstiles that undergo correlated rotation motions.

Work is now underway to anchor analogous complexes onto oxide surfaces for the observation of molecular motions on the unimolecular scale; however, the demonstration of a controlled rotary movement requires further experimental developments by scanning probe microscopy. Moreover, the lateral gearing effect may be exploited in nanomechanics to use the work produced during rotation of the molecule.

Experimental Section

Computational details: All calculations were performed with the Gaussian03 suite of programs,^[28] using the B3PW91^[29] hybrid functionals. Relativistic effective core potentials developed by the Stuttgart group and their associated basis sets were used for all atoms.^[30] Geometry optimisations were achieved in the gas phase without symmetry constraints. Calculations of vibrational frequencies were systematically done to characterise the nature of stationary points. The path of the chemical reaction was traced from the transition state to the products and reactants by using the intrinsic reaction coordinate method.^[31] Gibbs free energies were calculated by means of the harmonic frequencies, that is, by a straightforward application of the statistical thermodynamics equations given in standard textbooks.^[32]

Synthesis: All commercially available chemicals were of reagent grade and were used without further purification. Ethynylferrocene was purchased from Aldrich. Ruthenium carbonyl, $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ and 1,2,3,4,5-pentaphenylcyclopentadiene were purchased from Strem. Potassium hydrotris(indazol-1-yl)borate,^[19] [(ferrocenyl)ethynyl]zinc chloride^[9a] were prepared according to literature procedures. Toluene was dried over CaH_2 and THF over sodium with benzophenone. 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 by using Bruker AM250 or Avance500 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 were used to describe the signals: s for singlet; d for doublet; t for triplet; q for quadruplet; m for multiplet. The numbering schemes are given in Scheme 1 (for hydrotris(indazol-1-yl)borate and coordinated *p*-cymene) and Scheme 5 (for ferrocenes and pentaphenylcyclopentadienyl). UV/Vis-near infra-red spectra were recorded by using a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed by using a Nermag R10–10. Cyclic voltammetry was performed by using an AUTOLAB PGSTAT100 potentiostat using a Pt disc (1 mm diameter) as working electrode and a Pt counter electrode. The reference electrode used was the saturated calomel electrode (SCE).

(η^6 -*p*-Cymene)[hydrotris(indazol-1-yl)borato]ruthenium(II) hexafluorophosphate $[\text{Ru}(p\text{-cymene})\text{Tp}^{\text{ab}}]\text{PF}_6$ (1**):** $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (200 mg, 0.32 mmol, 1 equiv) was stirred in degassed acetonitrile (40 mL) for 20 min and potassium hydrotris(indazol-1-yl)borate (260 mg, 0.64 mmol, 2 equiv) was added. The mixture was stirred at RT in the dark overnight. Acetonitrile was then removed under reduced pressure and the reaction mixture was redissolved in methanol. A solution of ammonium hexafluorophosphate was then added (407 mg, 2.5 mmol, 8 equiv). The reaction mixture was filtered through a pad of neutral alumina. Compound **1** was obtained by recrystallisation from methanol/ Et_2O , affording the desired product (130 mg, 0.17 mmol, 27%). ^1H NMR ($[\text{D}_6]\text{acetone}$): δ = 9.11 (d, 4J = 0.8 Hz, 3H; H_a), 7.82 (dd, 3J = 8.7, 4J = 0.9 Hz, 3H; H_b), 7.74 (dd, 3J = 8.7, 4J = 0.9 Hz, 3H; H_c), 7.41 (dd, 3J = 7.25, 4J = 6.8 Hz, 3H; H_d), 7.16 (dt, 3J = 7.25, 4J = 6.8 Hz, 3H; H_e), 6.61 (d, 3J = 6.4 Hz, 2H; H_f), 6.38 (d, 3J = 6.4 Hz, 2H; H_g), 3.32 (m, 1H; H_i), 2.62 (s, 6H; H_j), 1.37 ppm (d, 3J = 6.9 Hz, 3H; H_k); ^{13}C NMR ($[\text{D}_6]\text{acetone}$): δ = 141.8 (C_M), 138.8 (C_A), 128.9 (C_C), 124.4 (C_N), 121.0 (C_D), 119.3 (C_E), 112.5 (C_B), 105.9 (C_K), 101.8 (C_L), 84.0 (C_H), 83.1 (C_G), 31.5 (C_I), 22.3 (C_J), 18.3 ppm (C_F); MS (MNBA-FAB): m/z (%): 599 (100) $[\text{M}-\text{PF}_6]^+$; HRMS (FAB): m/z calcd for $\text{C}_{31}\text{H}_{30}\text{BN}_6\text{Ru}$: 599.1668 $[\text{M}]^+$; found: 599.1686.

1-Bromo-1,2,3,4,5-penta(4-bromophenyl)cyclopentadiene (2**):** Br_2 (2 mL, 45 mmol, 20 equiv) was slowly added to 1,2,3,4,5-pentaphenylcyclopentadiene (1 g, 2.2 mmol, 1 equiv) in a two-necked flask connected to a KOH solution to quench the acid vapors formed during the reaction. The solution was stirred for 2 h after the end of the bubbling. The reaction mixture was then diluted with dichloromethane (50 mL) and washed with potassium thiosulfate solution (1 M, 4×100 mL). After drying over MgSO_4 , the product was purified by flash column chromatography (silica gel: cyclohexane/dichloromethane 0–10%) to give **2** as a pale-yellow solid

(2 g, 2.1 mmol; 98%). ^1H NMR (CDCl_3): δ = 7.44–7.18 (m, 12H), 6.85–6.70 ppm (m, 8H); ^{13}C NMR (CDCl_3): δ = 147.7, 140.9, 134.0, 132.5, 132.1, 131.8, 131.7, 131.5, 131.4, 131.1, 129.1, 128.0, 122.5, 122.24, 122.15 ppm; MS (DCI/ NH_3): m/z (%): 914.6 (100) $[\text{M}+\text{H}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{35}\text{H}_{20}\text{Br}_6$: 913.6665 $[\text{M}]^+$; found: 913.6688; elemental analysis calcd (%) for $\text{C}_{35}\text{H}_{20}\text{Br}_6$: C 45.70, H 2.19; found: C 45.81, H 2.22.

Bromodiodicarbonyl(η^5 -[1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl]ruthenium(II) $[\text{Ru}(\eta^5\text{-Cp}(4\text{-BrPh})_5)\text{Br}(\text{CO})_2]$ (3**):** $[\text{Ru}_3(\text{CO})_{12}]$ (256 mg, 0.4 mmol, 1 equiv) and **2** (1.1 g, 1.2 mmol, 3 equiv) were heated under reflux for 2 h in freshly distilled toluene (20 mL). The solution turned rapidly from yellow to dark green and then to cherry red. The crude reaction mixture was evaporated under vacuum. A dichloromethane solution of the crude product was passed over a plug of silica to remove red polar side products. The product was adsorbed onto silica and then purified by flash column chromatography (silica gel: cyclohexane/dichloromethane 40%) to give **3** as a yellow solid (1.006 g, 0.934 mmol, 78%). ^1H NMR (CD_2Cl_2): δ = 7.29 (d, 3J = 8.7 Hz, 10H; H_m), 6.88 ppm (d, 3J = 8.7 Hz, 10H; H_o); ^{13}C NMR (CDCl_3): δ = 196.4, 134.5, 132.2, 128.6, 124.0, 106.0 ppm; IR: $\nu_{\text{C=O}}$ = 2003 (s) and 2048 cm^{-1} (s); MS (DCI/ NH_3): m/z : 1096 $[\text{M}+\text{NH}_4]^+$.

(η^6 -Benzene)(η^5 -1,2,3,4,5-penta(4-bromophenyl)cyclopentadienyl)ruthenium(II) hexafluorophosphate $[\text{Ru}(\eta^6\text{-benzene})(\eta^5\text{-Cp}(4\text{-BrPh})_5)]\text{PF}_6$ (4**):** A solution **3** (410 mg, 0.4 mmol) and aluminium chloride (67 mg) in freshly distilled benzene (15 mL) was purged with argon. The solution was stirred under reflux for 6 d. Benzene was evaporated and the reaction mixture was redissolved in dichloromethane (100 mL). A solution of NH_4PF_6 (700 mg) in acetonitrile (100 mL) was added to this solution. After 1 h stirring the solvents were removed under vacuum. The product was redissolved in dichloromethane and salts were filtered. The solution was evaporated under vacuum and redissolved in acetonitrile. Crystallisation of the compound was started by adding water and evaporating part of the acetonitrile. Allowing to cool to 0°C gave **4** as analytically pure yellow crystals (248 mg, 0.239 mmol, 60%). ^1H NMR (CDCl_3): δ = 7.36 (d, 3J = 8.2 Hz, 10H; H_m), 6.76 (d, 3J = 8.4 Hz, 10H; H_o), 6.47 ppm (s, 6H; H_a); ^{13}C NMR (CDCl_3): δ = 132.9, 132.2, 127.3, 124.2, 100.2, 91.7 ppm; MS (DCI/ NH_3): 1037 $[\text{M}+\text{NH}_4]^+$.

(η^5 -1,2,3,4,5-Penta(4-bromophenyl)cyclopentadienyl)[hydrotris(indazol-1-yl)borato]ruthenium(II) $[\text{Ru}(\eta^5\text{-Cp}(4\text{-BrPh})_5)\text{Tp}^{\text{ab}}]$ (5**):** Compound **4** (107 mg, 0.1 mmol, 1 equiv) and potassium hydrotris(indazol-1-yl)borate (80 mg, 0.2 mmol, 2 equiv) were heated under reflux for 24 h in freshly distilled THF (4 mL). The crude reaction mixture was evaporated under vacuum. The product was adsorbed onto silica and purified by column chromatography (silica gel: cyclohexane/dichloromethane 0–20%) to give compound **5**, which was recrystallised in dichloromethane/methanol to afford yellow crystals (39 mg, 0.030 mmol, 30%). ^1H NMR (CD_2Cl_2): δ = 8.04–7.98 (dd, 3J = 8.57, 4J = 0.84 Hz, 3H; H_c), 8.86 (d, 4J = 0.84 Hz, 3H; H_a), 7.44–7.34 (m, 6H; H_b , H_e), 7.27–7.17 (m, 20H; H_o , H_m), 7.06–6.98 ppm (ddd, 3J = 7.10, 3J = 6.90, 4J = 0.84 Hz, 3H; H_d); ^{13}C NMR (CDCl_3): δ = 143.6 (C_M), 140.4, 135.3, 132.3, 130.8, 126.8, 123.1 (C_N), 122.0, 120.7, 120.1, 111.6, 87.2 ppm; UV/Vis (CH_2Cl_2) λ_{max} (ϵ) = 295 (300/300), 311 (268/700), 396 nm (34/800); $E_{\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}}$ (V/SCE): +0.80 rev.; MS (DCI/ NH_3): m/z (%): 1305 (100) $[\text{M}+\text{H}]^+$; HRMS LSI: m/z calcd for $\text{C}_{56}\text{H}_{37}\text{BBr}_5\text{N}_6\text{Ru}$: 1300.8133 $[\text{M}+\text{H}]^+$; found: 1300.8177 $[\text{M}+\text{H}]^+$.

(Penta-{4-[(ferrocenyl)ethynyl]phenyl}cyclopentadienyl)[hydrotris(indazol-1-yl)borato]ruthenium $[\text{Ru}(\eta^5\text{-Cp}(\text{Ph-ethynyl-Fc})_5)\text{Tp}^{\text{ab}}]$ (6**)**

*From the pentabromide derivative (**5**) by means of a Negishi coupling:* In a three-necked flask, a solution of **5** (70 mg, 0.053 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (30 mg, 26 μmol , 0.5 equiv) in freshly distilled THF (10 mL) was degassed. A solution of [(ferrocenyl)ethynyl]zinc chloride (1 mmol, 4 equiv per bromide) was prepared as described in the literature^[9a] was then added. The mixture was heated under reflux for 24 h. Additional catalyst (30 mg) and reactants (1 mmol of [(ferrocenyl)ethynyl]zinc chloride) were added by using a syringe under argon and the mixture was kept under reflux for 24 h. The crude reaction mixture was evaporated under vacuum. The product was adsorbed onto silica and purified by flash column chromatography (silica gel: cyclohexane/ CH_2Cl_2 0–30%, R_f

(silica gel, cyclohexane/CH₂Cl₂ 30%)=0.12) to give **6** as an orange solid (33 mg, 0.017 mmol, 32 %).

From the pentaiodide derivative (**8**) by means of a Sonogashira coupling: In a Schlenk tube, **8** (24 mg, 0.016 mmol, 1 equiv), ethynylferrocene (33 mg, 0.16 mmol, 10 equiv), diisopropylamine (2 mL) and freshly distilled THF (166 μ L) were degassed under argon during 20 min. CuI (1 mg, 5 μ mol, 30 mol %) and [Pd(PPh₃)₄] (3.3 mg, 2.5 μ mol, 15 mol %) were added and the mixture was heated at 80 °C overnight. The same amounts of additional CuI, ethynylferrocene and Pd⁰ were added and the mixture was heated at 80 °C for another 24 h. Solvents were removed under reduced pressure and the crude material was subjected to column chromatography (silica gel, cyclohexane/CH₂Cl₂ 0–30 %) to give **6** as an orange solid (7.0 mg, 44 %).

¹H NMR (250 MHz, CDCl₃): δ =8.0 (d, ³J=8.4 Hz, 3H; H_c), 7.94 (s, 3H; H_a), 7.5–7.3 (d, 16H; H_m, H_b, H_c), 7.20–7.10 (d, ³J=8.0 Hz, 10H; H_o), 7.02 (t, ³J=7.5 Hz, 3H; H_d), 4.43 (t, ³J=2 Hz, 10H; H_i), 4.21 (s, 25H; H_n), 4.19 ppm (t, ³J=2 Hz, 10H; H_s); ¹³C NMR (66 MHz, CDCl₃): δ =143.4 (C_M), 140.2, 133.4, 133.2, 130.4, 126.4, 123.0 (C_N), 122.7, 122.4, 120.0, 111.7, 89.3, 87.5, 85.5, 71.4, 70.0, 68.8, 65.0 ppm; UV/Vis (CH₂Cl₂): λ_{max} (ϵ)=264 (225 000), 306 (169 200), 359 (58 000), 436 nm (10 400); CV(CH₂Cl₂, nBu₄NPF₆), $E_{\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}}$ (V/SCE): +0.52 rev, (5 e); $E_{\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}}$ (V/SCE): +0.82 rev (1 e); MS (MALDI-TOF): m/z (%): calcd for C₁₁₆H₈₁BN₆Fe₃Ru: 1950.2463 [M]⁺; found: 1950.3480 [M]⁺ (100); HRMS LSI calcd for C₁₁₆H₈₂BN₆Fe₃Ru 1951.2599 [M+H]⁺; found: 1951.2631 [M+H]⁺.

Dicarbonylido[η^5 -1,2,3,4,5-penta-(4-iodophenyl)cyclopentadienyl]ruthenium(II) [Ru(η^5 -Cp(4-IPh)₅)(CO)₂] (7**):** A Schlenk tube was charged with CuI (95 mg, 0.5 mmol, 2.5 equiv), **3** (200 mg, 0.2 mmol, 1 equiv) and NaI (600 mg, 4.0 mmol, 20 equiv). Under an argon atmosphere, racemic *trans*-N,N'-dimethyl-1,2-cyclohexanediamine (15 mg, 0.1 mmol, 0.5 equiv) and dioxane (3.0 mL) were added. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 24 h. The solvent was removed and the crude material was purified by column chromatography (silica gel: cyclohexane/dichloromethane (0–10 %)) to give 124 mg (0.09 mmol, 45 %) of **7** as an orange-brown solid. MS (DCI/NH₃): m/z : 1339 [M–2 CO + N₂H₇]⁺; ¹H NMR (CDCl₃): δ =7.49 (AA'BB' pattern, ³J=8.5 Hz, 10H; H_m), 6.71 ppm (AA'BB' pattern, ³J=8.5 Hz, 10H; H_o); ¹³C NMR (CD₂Cl₂): δ =196.1, 137.7, 134.3, 131.8, 128.8, 128.3, 123.6, 95.5 ppm; IR: $\nu_{\text{C=O}}$ =2000 (s), 2040 cm^{–1} (s).

[η^5 -1,2,3,4,5-Penta-(4-iodophenyl)cyclopentadienyl][hydrotris(indazol-1-yl)borato]ruthenium(II) [Ru(η^5 -Cp(4-IPh)₅)(Tp^{4Bo})] (8**)**

By halogen exchange (not isolated): A Schlenk tube was charged with CuI (18 mg, 0.075 mmol, 2.5 equiv), **5** (40 mg, 0.03 mmol, 1 equiv) and NaI (90 mg, 0.6 mmol, 20 equiv). Under an argon atmosphere, racemic *trans*-N,N'-dimethyl-1,2-cyclohexanediamine (4.8 mL, 0.03 mmol, 1 equiv) and dioxane (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 24 h. The solvent was removed and the crude material was purified by column chromatography (silica gel: cyclohexane/dichloromethane (0–10 %)) to give partially iodinated η^5 -1,2,3,4,5-penta-(4-halogenophenyl)-cyclopentadienyl complex.

By reaction of dicarbonylido[η^5 -(1,2,3,4,5-penta-(4-iodophenyl)cyclopentadienyl)] with Tp^{4Bo}: A mixture of **7** (144 mg; 0.12 mmol; 1 equiv) and potassium hydrotris(indazol-1-yl)borate (100 mg, 0.24 mmol, 2 equiv) was heated under reflux for 24 h in freshly distilled THF (8 mL). The crude reaction mixture was evaporated under vacuum. The product was adsorbed onto silica and then purified by flash column chromatography (silica gel: cyclohexane/dichloromethane 0–20 %) to give 24 mg (0.016 mmol, 14 %) of **8**. ¹H NMR (CDCl₃): δ =7.97 (d, ³J=8.5 Hz, 3H; H_c), 7.78 (s, 3H; H_a), 7.42–7.30 (m, 16H; H_m, H_b, H_c), 7.08–6.98 ppm (m, 13H; H_o, H_d); ¹³C NMR (CDCl₃): δ =142.8 (C_M), 139.4, 134.3, 132.1, 130.4, 126.2, 122.5 (C_N), 121.2, 120.1, 119.9, 111.1, 86.4 ppm; MS (DCI/NH₃): m/z (%): 1541 (100) [M+H]⁺; HRMS LSI: m/z calcd for C₃₆H₃₇BI₅N₆Ru: 1540.7440 [M+H]⁺; found: 1540.7497 [M+H]⁺.

Acknowledgements

This work was supported by the CNRS, the University Paul Sabatier (Toulouse) and the European Community. A.C. thanks the French Ministry of National Education and the Institut Universitaire de France for a PhD Fellowship. One of us (R.P.) thanks the Centre Informatique National de l'Enseignement Supérieur (CINES) for allocation of computational resources. Dr Isabelle M. Dixon is warmly acknowledged for her corrections and comments on this manuscript.

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Received: April 10, 2008
Published online: July 24, 2008