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Supporting Information

Synthesis of molecular motors incorporating a *p*-phenylene-conjugated or a bicyclo[2,2,2]octane-insulated electroactive groups

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Abstract:

The insulating role of the bicyclo[2,2,2]octane fragment has been theoretically evaluated by comparing the electronic coupling parameter (V_{ab}) in 1,4-bis(ferrocenyl)benzene (**1**) and 1,4-bis(ferrocenyl)bicyclo[2,2,2] octane (**2**). The geometries were optimized by DFT and an Extended Huckel calculation was performed to evaluate V_{ab} by the dimer splitting method. The calculations showed a 12-fold decrease of the electronic coupling from 60 meV for **1** to 5 meV for **2**.

The second part describes the synthesis of two potential molecular motors with one incorporating the bicyclo[2,2,2]octane insulating fragment. These molecules are based on a ruthenium complex bearing a tripodal stator functionalized to be anchored onto surfaces. The ferrocenyl electroactive groups and the cyclopentadienyl (Cp) rotor are connected via a p-phenylene spacer (**5**) or via a spacer incorporating an insulating bicyclo[2,2,2]octane moiety (**6**).

Résumé:

Le rôle isolant du fragment bicyclo[2,2,2]octane a été évalué théoriquement en comparant le paramètre de couplage électronique (V_{ab}) dans le 1,4-bis(ferrocényl)benzène (**1**) et le 1,4-bis(ferrocényl)bicyclo[2,2,2]octane (**2**). Les géométries ont été optimisées par DFT et des calculs Huckel étendu ont été réalisés pour évaluer le V_{ab} par la méthode de l'éclatement du dimère. Les calculs ont montré une diminution d'un facteur 12 du couplage électronique de 60 meV pour **1** à 5 meV pour **2**.

La deuxième partie de l'article décrit la synthèse de deux moteurs moléculaires potentiels dont un incorporant le fragment isolant bicyclo[2,2,2]octane. Ces molécules sont constituées d'un complexe de ruthénium avec un stator tripodal fonctionnalisé pour s'accrocher à une surface. Les groupements électroactifs ferrocényles sont connectés au rotor cyclopentadiényle (Cp) via un espaceur *p*-phénylène (**5**) ou via

un espaceur incorporant un fragment isolant bicyclo[2,2,2]octane (**6**).

Introduction

In the field of nanosciences, a growing interest has appeared in the design and synthesis of molecular machines.[1] A molecular machine can be defined as a device that performs a controlled work under a specific stimulation. Among those, molecular motors present a real challenge in the control of motion at a molecular level. A molecular rotary motor[2] is a machine that consumes energy to perform a unidirectional 360° rotation in a repetitive way. Such motors already exist in Nature like, for example, ATP synthase.[3] However, among the large number of synthetic molecular rotors described,[4] only a few of them fulfill the conditions to become a potential motor. Indeed, in order to recover the work produced by the rotation of the motor, its structure should be as rigid as possible and with a minimum of degrees of freedom.
Recently, we have presented the concept of an electrically-fuelled single molecular rotary motor.[5] This concept is based on the transport of electrons between two electrodes by electroactive groups attached to a central rotatable core. The motor is based on a ruthenium complex with a piano stool geometry bearing two different ligands which would act as a rotor and a stator. The stator is a tripodal hydrotris(indazolyl)borate ligand functionalized by ester groups meant to interact strongly with the oxide surfaces commonly used in AFM experiments. The rotor is a cyclopentadienyl (Cp) ligand connected to five electroactive groups (EG) by linear and rigid arms. The final goal is to study a single molecule positioned between the two electrodes of a nanojunction. The electroactive group near the anode is supposed to be oxidized and then pushed back, by electrostatic repulsion, towards the cathode where it would be reduced (Figure 1, top). The rotation of the rotor would place another electroactive group near the anode and a new cycle would occur.

Figure 1.

In this case the rotation has to compete with the undesired intramolecular electron transfer between the electroactive groups (Figure 1, bottom). The rotation, a fifth of a turn in the case of a C_5-symmetric rotor, has to be as fast as possible to minimize the competing intramolecular electron transfer between two electroactive units otherwise the electrons could travel through the carbon skeleton without rotation of the whole rotor. We have already described the incorporation of a *trans*-platinum spacer in the arms to insulate the electroactive groups.[6, 7] However, experimental and

theoretical studies have shown that the *trans*-platinum complex was a moderate insulator which reduced the electronic coupling by a factor of 3 only, compared to a fully conjugated spacer. This could be due to the influence of the platinum d orbitals. A rigid and linear organic spacer with saturated carbons should act as a better insulator and might be more robust for a study by near field microscopy. The well known 1,4-disubstituted bicyclo[2,2,2]octane is a good candidate,[8] having a rigid saturated backbone to maintain the linearity and rigidity of the arms
In the first part of this paper, we present a theoretical study on bisferrocenyl model compounds[9] to evaluate the insulating character of the bicyclo[2,2,2]octane fragment. In a second part, we report the synthesis of two star-shaped molecules which can potentially act as molecular motors since they incorporate ester groups to anchor the molecules onto oxide surfaces. These motors bear ferrocene terminal electroactive groups linked to the central Cp by either a *p*-phenylene spacer in complex **5** or a spacer containing bicyclo[2,2,2]octane insulating fragments in complex **6**.

Results and Discussion

Investigation of the insulating role of the bicyclo[2,2,2]octane fragment

The influence of a bicyclo[2,2,2]octane fragment on the electronic communication between two metallic centres has been studied by comparing the electronic coupling parameter in bimetallic complexes with a conjugated *p*-phenylene bridging ligand (**1**) and a bicyclo[2,2,2]octane ligand (**2**) (Figure 2). In these two compounds the distance between the two iron atoms (8.26 Å and 8.22 Å for **1** and **2** respectively) is almost the same and enables to focus on the pure influence of the skeleton on the electronic communication.

Figure 2.

The geometry of **1** and **2** (Figure 3) has been optimized by DFT starting from a geometry built up from X-ray structures for the ferrocenyl moieties and an optimized molecular mechanics geometry for the bridging ligand. The calculations were performed using the GAMESS[10] software with a hybrid functional (B3LYP) and a 6-31G* basis set for all the atoms. A conformer with the starting syn geometry for the ferrocenyl moieties has been chosen to get a plane of symmetry between the two metallic centres in order to be able to use the dimer splitting method[11] to evaluate the electronic coupling parameter (V_{ab}). The optimized structures are presented in Figure 3. In both cases, the two Cp cycles covalently linked to the bridge are almost coplanar (torsion angle 0.6° and 0.8°

in **1** and **2** respectively). In the optimized geometry of **1** the phenyl group is not coplanar with the Cp rings (torsion angle of 10°) due to steric hindrance between the hydrogen atoms of the rings. Besides, the average Fe-C distances within the ferrocenes in the optimized structures (2.054 Å) are similar to the X-ray values (2.045 Å).

Figure 3.

The experimental electronic communication in a dimetallic complex can be obtained by monitoring the intervalence transition in the Fe^{II}-Fe^{III} mixed-valence species generated at the half oxidation of the complex. The electronic coupling parameter can thus be determined experimentally from the parameters of the intervalence transition band by the Hush formula. However, the electronic coupling parameter can also be theoretically determined from the calculation of molecular orbitals by the dimer splitting method.[11] The diferrocenyl complex can be formally decomposed into a free ligand of the bis(cyclopentadiene) type and two iron atoms. The main interaction between the metals orbitals and the bridging ligand arises from the $3dx^2$-y^2 orbitals which can overlap with 2pz orbitals of π symmetry of the bridging ligand (Figure 4). This interaction between the orbitals of the ligand and the iron orbitals lifts the degeneracy of the molecular orbitals based on the $3dx^2$-y^2 iron orbitals. In the case of complexes bearing a symmetry element, such as here a plane of symmetry, the system is reduced to two levels. In the mixed-valence complex there is an electron hole in these two molecular orbitals (symmetrical and antisymmetrical). The energy difference between these two MOs corresponds to 2 V_{ab}.

Figure 4.

Since the DFT method tends to underestimate the energy gap between the different orbitals, in particular the HOMO-LUMO gap,[12] we have estimated V_{ab} from Extended Hückel orbitals. An extended Hückel calculation has been performed on the DFT-optimized geometry with the HyperChem Professional 6 program package,[13] using parameters optimized for iron. V_{ab} was determined from the energy difference between the significant symmetrical and antisymmetrical orbitals based on the $3dx^2$-y^2 orbitals of the iron atoms (Figure 5). Considering the Hückel parameter for the iron 3d orbital to be -11 eV, the electronic coupling parameter V_{ab} for complex **1** (with a phenyl spacer between the two ferrocenyl groups) is 60 meV, which corresponds to a moderately coupled system. This value is slightly higher than the published experimental electronic coupling parameter (43 meV) obtained by a spectroelectrochemical study.[14] The same calculations for compound **2** gave a V_{ab} value equal to 5 meV, i.e. it is a much less coupled system. In both cases the highest energy orbital is antisymmetrical and the lowest is symmetrical with respect to the plane of symmetry. Thus, for a given Fe-Fe distance, the insertion of bicyclo[2,2,2]octane linker compared to a conjugated phenyl linker results in a 12-fold decrease in the electronic coupling, which demonstrates the insulating role of the bicyclo[2,2,2]octane moiety. This result quantifies the insulating role of the bicyclo[2,2,2]octane fragment and confirms the photochemical studies available in the literature.[15] This property can be easily interpreted in terms of pure σ character of the saturated backbone of the bicyclo[2,2,2]octane.

Figure 5.

The V_{ab} value depends on the parameters used for the extended Hückel calculation, in particular the energy of the iron 3d orbitals. To validate our calculations, the energy of the 3d orbitals of the free iron was varied from -10.5 to -11.5 eV, which greatly influences the absolute V_{ab} value but does not alter the observed trend: the value for the bicyclo[2,2,2]octane compound is always much lower than for the phenyl containing compound (see Supplementary Information for details).

Thus, these calculations clearly show the insulating role of the rigid and linear bicyclo[2,2,2]octane spacer. Compared to a conjugated *p*-phenylene linker, the bicyclo[2,2,2]octane decreases the electronic coupling parameter by one order of magnitude, which is exactly what is required for our objective to minimize electronic communication between the electroactive groups of our target molecular motors.

Synthesis of the molecular motors

The synthesis of the motors was based on a modular strategy, the key step being the coupling between the pentabrominated ruthenium complex **3** and a selected arm (Scheme 1). The X-ray structure of complex **3** clearly showed the coordination of both ligands with the tripodal substituted tris(indazolyl)borate ligand (Tp^{4Bo}) binding in a facial tripodal mode (i.e. κ^3-N,N′,N″), in line with the ^{1}H-NMR data. The average ruthenium-nitrogen distance is 2.16 Å which is larger compared to the distance of 2.11 Å measured in the unsubstituted Cp analogous complex.[16] This can be due to the steric hindrance of the five phenyl substituents on the Cp ring. This steric hindrance is also reflected by the Cp-ruthenium distance which is 1.82 Å in **3** and 1.78 Å in the non-substituted Cp analogous complex. The complex has a piano stool structure with the phenyl substituents fitting in the vacant spaces of the tripodal ligand. It must also be noted that the ester groups are particularly well-oriented to bind simultaneously to a surface. Moreover, due to symmetry considerations, the superimposition of a tripodal ligand bearing a C_3 axis and a penta-substituted Cp of C_5 symmetry causes differentiation, in the solid state, of the five *p*-bromophenyl rings connected to the Cp. It is not possible to have a symmetrical structure, and as shown on the X-ray structure (Figure 6) there are three types of phenyl rings considering the dihedral angle between the plane of the phenyl ring and the plane of the cp ring. The two phenyl rings located above the indazole have to be tilted at 40° and 44° due to steric hindrance with the tripodal ligand. The phenyl group located in the gap between the indazoles is almost perpendicular (87°) whereas the two remaining phenyl rings are tilted of by an intermediate angle (63° and 68°).

Figure 6

The versatility of the palladium-catalysed C-C bond formation offers a great choice of coupling reactions. The linearity required in our design implies the use a sp^2-sp or sp^2-sp^2 coupling. Previously, we had coupled **3** with alkyne-terminated arms but the presence of triple bonds could be a drawback in view of the future deposition onto surfaces as shown by preliminary experiments. A Suzuki coupling reaction between an arylboronic acid and **3** could be a good alternative and should also increase the rigidity of the arm as biaryl compounds are known to be more rigid than alkynes.[17]

Scheme 1.

Synthesis of the model complex (4)

The five bromines in **3** are strongly deactivated towards the oxidative addition step of the palladium catalyst by the connection to a formal anionic entity (Cp), as shown previously.[5] The Buchwald universal catalyst (2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine in presence of palladium acetate) was thus tested, as it was described to be a very efficient Suzuki coupling catalyst for deactivated substrates.[18] Since the bicyclo[2,2,2]octane containing fragment **14** requires 8 steps to be synthesized, the coupling reaction conditions were optimized with 4-*tert*-butylphenyl boronic acid[19]. Since a *tert*-butyl group is sterically and electronically very similar to a bicyclo[2,2,2]octane, the *tert*-butyl substituted phenylboronic acid should be a good model for the optimization of the reaction before using compound **14**. For the same reasons of similar steric and electronic properties, the resulting coupling product is also a good model to evaluate the oxidation potential of the ruthenium centre. Therefore, the ruthenium complex **3** was heated overnight in toluene with 20 equivalents of 4-*tert*-

butylphenyl boronic acid in the presence of palladium acetate (0.3 eq.) and the Buchwald phosphine (0.6 eq.). NMR showing that the reaction was not complete, another 20 equivalents of boronic acid and catalyst were added and the mixture was heated another night. After purification by column chromatography the product of quintuple coupling **4** was obtained in a 25 % yield (corresponding to 75% per coupling reaction). The product was characterized by mass spectrometry and ^{1}H-NMR with an integration of 45 for the protons of the *tert*-butyl groups and 3 for the H_a protons of the tripodal ligand.

Synthesis of the molecular motor with *p*-phenylene conjugated electroactive groups (5)

To study the electrochemical behaviour of closely connected ferrocenyl groups, a ruthenium complex with short *p*-phenylene spacers between the ruthenium core and the ferrocenyl electroactive groups has been designed. A quintuple Suzuki coupling reaction between the ruthenium precursor **3** and ferrocene boronic acid (Scheme 1) was undertaken and yielded the resulting ruthenium complex **5**, similarly to the procedure used to obtain **4**. The coupling was achieved by reacting **3** with two times 20 equivalents of ferrocene boronic acid with the Buchwald universal catalyst. After purification by column chromatography, the potential motor **5** was isolated in 32% yield (corresponding to 79% per coupling reaction). The presence of the ferrocenyl moieties was confirmed by MALDI-TOF spectrometry and ^{1}H-NMR which shows clearly an integration of 45 protons for the ferrocenyl protons and 20 for the AA’BB’ pattern of the phenyl protons.

Synthesis of the bicyclo[2,2,2]octane precursor (15)

The synthesis of the functionalized arm (**15**) (Scheme 3) was adapted from a procedure described by Zimmerman.[20] The bicyclo [2,2,2]octane ring was obtained via the key intermediate 1,4-bis(4-bromophenyl)bicyclo[2,2,2]octane (**13**) (Scheme 2). The double addition of acrylonitrile on 3-phenylpropan-2-one under basic conditions yielded, after recrystallisation, 3-acetyl-1,5-dicyano-3-phenyl-pentane (**7**).[21] Hydrolysis of the nitrile functions was performed under aqueous basic conditions to obtain the diacid **8** in 72% yield.[21] The formation of the cyclohexanone ring was achieved by heating **8** in acetic anhydride to form a cyclic anhydride intermediate which was further thermolyzed at 250°C to yield the functionalized cyclohexanone **9** after distillation. The ketolisation reaction[22] between the acetyl enolate moiety and the ketone of the cyclohexanone ring was used as a key step to build the bicyclo[2,2,2]octane ring. After purification by recrystallisation, **10** was obtained in a 73% yield. The remaining carbonyl group was reduced under modified Wolf-Kishner conditions.[23] **10** was first heated at reflux during 5 hours in hydrazine to form the hydrazone. Potassium hydroxide and diethylene glycol were then added and the mixture was heated at 220°C until the end of the gaseous evolution to give **11** after purification in a 62% yield. A Friedel-Craft alkylation of **11** on benzene in the presence of sulfuric acid yielded **12** after purification by column chromatography in a 33% yield.[24] Bromination of **12** in the para positions was achieved by heating **12** in carbon tetrachloride in the presence of bromine with a catalytic amount of iron powder.[20] After purification by column chromatography, **13** was obtained in 65% yield. Thus, after 8 steps, the bicyclo[2,2,2]octane containing building block **13** was obtained in gram scale with a 2.4% overall yield (corresponding to an average yield of 62% per step).

Scheme 2.

The symmetric bicyclo[2,2,2]octane fragment (**13**) with two *p*-bromophenyl substituents can be used to introduce stepwise the ferrocenyl moiety and a boronic ester for the coupling to the ruthenium core **3**. First the ferrocenes were introduced via a Suzuki coupling reaction between **13** and ferroceneboronic acid using the Buchwald universal catalyst (Scheme 2).[18] A statistical mixture of a symmetric (bis(ferrocenyl)) and dissymmetric (**14)** coupling product was obtained. After separation by column chromatography, the dissymmetric coupling product **14** was obtained in a 31% yield. Single crystals suitable for X-ray diffraction were grown by slow diffusion of methanol into a solution of **14** in dichloromethane. The X-ray structure (Figure 7) showed the almost perfect linearity of the 1,4 positions of the disubstituted 1,4-biyclo[2,2,2]octane with an angle of 179° between the two bonds connected to the biyclooctane fragment.

Figure 7

The remaining bromine can be easily converted to the corresponding boronic pinacol ester by using the Miyaura methodology.[25] **14** was heated in DMF with $PdCl_2$(dppf) and bis(pinacolato)diboron to give **15** after purification by column chromatography in a 66% yield (Scheme 3).

Synthesis of the molecular motor with bicyclo[2,2,2]octane-insulated electroactive groups (6)

The functionalized arm **15** was coupled via a palladium catalyzed coupling reaction with the pentabrominated ruthenium complex (**3**). As previously, the synthesis of the molecular motor **6** was achieved by a quintuple Suzuki coupling reaction between the boronic ester **15** and **3** using the Buchwald universal catalyst. After purification by column chromatography, **6** was obtained in a 29% yield corresponding to 78% per coupling. The complex was fully characterized by NMR and mass spectrometry. Again an integration of 45 protons for the signals of the ferrocene units was obtained and a broad singlet integrating for 60 protons of the bicyclo[2,2,2]octane moiety was observed in ^{1}H-NMR. The presence of the five arms was also confirmed by MALDI-TOF spectrometry.

Scheme 3.

Electrochemistry

Cyclic voltammetry (Figure 8) of the molecular motors **5** and **6** showed two reversible oxidation waves corresponding to the successive oxidation of the irons and the ruthenium centres. The 5:1 ratio between these two waves is consistent with the ratio between the iron and ruthenium atoms in both molecules. In complexes **5** and **6,** the five iron centres are first reversibly oxidized simultaneously at a potential of 0.47 V/SCE and 0.42 V/SCE respectively (Table 1). In complex **6**, the iron oxidation potential is comparable to the one in the ferrocene-functionalized building block **14** (0.44 V/SCE), showing that the bicyclo[2,2,2]octane spacer enables a good spatial and electronic insulation of the electroactive groups. However, the oxidation potential in complex **5** is slightly higher compared to **6**. This is probably due to a spatial proximity and maybe some electronic interactions between the ferrocenyl groups. It must be noted this potential is similar to hexa(ferrocenylphenyl)benzene[26] (0.47 V/SCE) where the six ferrocenyls groups are connected via a *p*-phenylene spacer to a central benzene core.

Figure 8.

In complex **6**, the ruthenium is reversibly oxidized at a potential of 0.76 V/SCE, very close to the one in the model ruthenium complex **4** (0.77 V/SCE), showing the absence of influence of the ferrocenium centres on the oxidation of the ruthenium centre. On the other hand, in **5**, the oxidation potential of the ruthenium is shifted at 0.89 V/SCE by the combined electronic and strongly distance dependant electrostatic effects of the neighbouring ferrocenium fragments. This effect is also outlined by a larger difference in the oxidation potentials of the iron and the ruthenium centres in **5** (Δ=0.42 V) than in **6** (Δ=0.34 V). In summary the fact that the redox potentials of **6** (0.42 and 0.76) are very close to the potentials of the monometallics models (0.44 and 0.77) confirms experimentally that the bicyclo[2,2,2]octane is an efficient insulating spacer.

Table 1.

Conclusion

A theoretical approach combining a DFT geometry optimization and extended Hückel calculations on two bis-ferrocenyl model compounds allowed to estimate the electronic communication parameter V_{ab} between ferrocene units. A 12-fold attenuation of the V_{ab} was observed in the presence of a bicyclo[2,2,2]octane spacer compared to a conjugated *p*-phenylene spacer. This clearly shows the insulating role of the bicyclo[2,2,2]octane fragment.

On the basis of these results, we have synthesized two molecular motors incorporating ester anchoring groups on the tris(indazolyl)borate part (stator) to be anchored onto surfaces. In the first ruthenium complex, the ferrocenyl electroactive groups and the cyclopentadienyl (Cp) rotor are connected via a conjugated *p*-phenylene spacer. The second complex bears a bicyclo[2,2,2] octane insulating moiety in the rotor, and thus fulfills all the requirements for an electrically driven molecular motor. By comparison to the motor incorporating *trans*-bisacetylide platinum(II) insulating groups,[6] the insulation of the electroactive groups is more efficient and the absence of triple bonds in the backbone gives rise to a more rigid structure which should be more stable towards the deposition process. Work is now underway to anchor these molecules on an oxide surface in view of addressing them as single molecules with two metallic nanoelectrodes. The demonstration of a controlled rotary movement will then need further experimental developments by physical methods such as scanning probe microscopies or the analysis of the time dependence of the current in a two-electrode configuration.

Experimental Section

Computational details

Calculations were performed with the GAMESS[10] (General Atomic and Molecular Electronic Structure System) software. Complete geometry optimizations were carried out using the density functional theory method with the conventional Becke-3-Lee-Yang-Parr (B3LYP) exchange-correlation functional. 6-31G and 6-31G* basis set were used for all the atoms. The 6-31G* basis set gave an optimized geometry for the ferrocenyl moiety with a better correlation with X-ray data for the Fe-C distance. Also see the Supporting Information for the molecular modeling coordinates of **1** and **2**, the parameters used in the calculations for the atoms C, H and Fe, energy of the orbitals and V_{ab} of **1** and **2** as a function of the energy of the iron 3d orbitals.

Synthesis

All commercially available chemicals were of reagent grade and were used without further purification. Ferroceneboronic acid, acrylonitrile and phenylacetone were purchased from Aldrich. Bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II),[6] potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate[16] and 4-*tert*-butylphenyl boronic acid[19] was 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 on Bruker AM 250, Avance 300 or Avance 500 spectrometers and full assignments were achieved using COSY, ROESY, HMBC and HMQC methods. 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; q for quadruplet; m for multiplet. The numbering scheme is given in schemes 1 and 3 (*vide supra*).

UV-Visible-Near Infra-Red spectra were recorded on a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10-10. Cyclic voltammetry was performed with an AUTOLAB PGSTAT 100 potentiostat using a Pt disc (1mm diameter) as working electrode and a Pt counter electrode. The reference electrode used was the saturated calomel electrode (SCE).

h^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (3)

Bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (55 mg, 0.05 mmol, 1eq) and potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (62 mg, 0.1 mmol, 2eq) were heated in a sealed tube at 150 °C under microwave irradiation during 10 minutes 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 a yellow solid (15 mg, 19%). ^{1}H NMR: (250 MHz, CD_2Cl_2) δ 8.76 (s, 3H, H_d), 7.95 (s, 3H, H_a), 7.68 (d, 3H, J = 8.5 Hz, H_c), 7.45 (d, 3H, J = 8.5 Hz, H_b), 7.21 (s broad, 20H, H_{o-m}), 4.47 (q, 6H, J = 7.1 Hz, CH_2), 1.48 (t, 9H, J = 7.1 Hz, CH_3); ^{13}C NMR: (63 MHz, CD_2Cl_2) δ 166.81; 143.22; 140.77; 135.10; 131.82; 130.92; 129.30; 125.35; 122.24; 121.26; 119.86; 113.97; 88.05; 61.38; 14.31; MS: (APCI) 1522 $[M]^+$.

h^5-1,2,3,4,5-penta-(4-(4′-*tert*-butylphenyl) phenyl) cyclopentadienyl hydrotris [6-(ethoxy-carbonyl) indazol-1-yl] borate ruthenium(II*)* (4)

In a Schlenk tube, η^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl] borate ruthenium(II) (20 mg, 13.2 µmol, 1 eq.), 4-*tert*-butylphenylboronic acid (47 mg, 264 µmol, 20 eq), palladium acetate (1 mg, 4.5 µmol, 0.3 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexylphosphine (3 mg, 7.3 µmol, 0.6 eq.) and anhydrous K_3PO_4 (28 mg, 0.132 mmol, 10 eq.) were placed under argon. Freshly distilled toluene (1 ml) was added and the mixture was heated at 100°C overnight. After cooling down additional 4-*tert*-butylphenylboronic acid (47 mg, 264 µmol, 20 eq), palladium acetate (1 mg, 4.5 µmol, 0.3 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexyl phosphine (3 mg, 7.3 µmol, 0.5 eq.) and anhydrous K_3PO_4 (28 mg, 0.132 mmol, 10 eq.) 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 (SiO_2: CH_2Cl_2) to give **4** as a yellow solid (6 mg, 25%). ^{1}H-NMR (500 MHz, CD_2Cl_2) d: 8.80 (s, 3H, H_d), 7.65 (s, 3H, H_a), 7.65 (d, 3H, J = 8.5Hz, H_c), 7.55 (d, 10H, J = 8.5 Hz, H_1), 7.47 (d, 10H, J = 8.5 Hz, H_3), 7.40 (m, 13H, H_4 H_b), 7.35 (d, 10H, J = 8.5 Hz, H_2), 4.47 (q, 6H, J = 7.1Hz, OCH_2), 1.48 (t, 9H, J = 7.1 Hz, CH_3), 1.30 (s, 45H, CH_3 ^{t}Bu); ^{13}C NMR: (126 MHz, CD_2Cl_2) δ 166.97; 150.64; 143.18; 141.01; 139.76; 137.17; 134.20; 132.45; 128.82; 126.40; 125.78; 125.70; 125.49; 120.92; 119.81; 113.91; 88.97; 61.29; 34.46; 31.09; 14.33; UV/Vis (CH_2Cl_2) l_{max} / nm (e / mol^{-1}.L.cm^{-1}) 269 (97 000); 343 (26 000); 366 (22 000); MS: (FAB) 1787 $[M]^+$; High Resolution LSI Calculated $[M]^+$: 1787.7936 ($C_{115}H_{113}BN_6O_6Ru$) Found: 1787.7908 (100% $[M]^+$);CV (CH_2Cl_2, ^{n}Bu$_4$NPF$_6$,), $E_{\mathrm{Ru(II)-Ru(III)}}$ (V/SCE): +0.77 rev (Sweep rate: 100 mV.s^{-1}).

h^5-1,2,3,4,5-penta-(4-(ferrocenyl)phenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl] borate ruthenium(II*)* (5)

In a Schlenk tube, η^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl] borate ruthenium(II) (35 mg, 0.023 mmol, 1 eq.), ferroceneboronic acid (106 mg, 0.46 mmol, 20 eq.), palladium acetate (2.6 mg, 12 µmol, 0.5 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexylphosphine (9.5 mg, 23 µmol, 1 eq.) and anhydrous K_3PO_4 (49 mg, 0.23 mmol, 10 eq.) 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 (106 mg, 0.46 mmol, 20 eq.), palladium acetate (2.6 mg, 12 µmol, 0.5 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexylphosphine (9.5 mg, 23 µmol, 1 eq.) and anhydrous K_3PO_4 (49 mg, 0.23 mmol, 10 eq.) 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 (SiO_2: CH_2Cl_2) to give **5** as an orange solid (15 mg, 32%). ^1H NMR: (500 MHz, CD_2Cl_2) δ 8.80 (s, 3H, H_d), 8.25 (s, 3H, H_a), 7.64 (d, 3H, *J* = 8.5 Hz, H_c), 7.45 (d, 3H, *J* = 8.5 Hz, H_b), 7.35 (d, 10H, *J* = 8.5 Hz, H_1), 7.22 (d, 10H, *J* = 8.5 Hz, H_2), 4.55 (t, 10H, *J* = 1.8 Hz, H_3), 4.46 (q, 6H, *J* = 7.1 Hz, OCH_2), 4.25 (t, 10H, *J* = 1.8 Hz, H_4), 3.94 (s, 25H, Cp), 1.47 (t, 9H, *J* = 7.1 Hz, CH_3); ^{13}C NMR: (126 MHz, CD_2Cl_2) δ 166.95; 143.18; 140.55; 138.63; 133.49; 131.51; 128.75; 125.49; 124.83; 120.98; 119.72; 113.94; 88.55; 84.18; 69.87; 69.30; 66.42; 61.29; 14.32; UV/Vis (CH_2Cl_2) l_{max} / nm (*e* / $mol^{-1}.L.cm^{-1}$) 285 (99 000); 340 (54 000); 362 (49 000); MS: (MALDI-TOF) 2046 $[M]^+$; High Resolution LSI Calculated $[M]^+$: 2046.3040 ($C_{115}H_{93}BFe_5N_6O_6Ru$) Found: 2046.3023 (100% $[M]^+$); CV (CH_2Cl_2, $^nBu_4NPF_6$,), $E_{\mathrm{Fe(II)-Fe(III)}}$ (V/SCE): +0.47 rev, (5 e) ; $E_{\mathrm{Ru(II)-Ru(III)}}$ (V/SCE): 0.89 rev (1 e) (Sweep rate: 100 $mV.s^{-1}$).

h^5-1,2,3,4,5-penta[4-[4-ferrocenylphenyl)-4-phenyl-bicyclo[2,2,2]octane] phenyl] cyclopentadienyl hydrotris[6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (6)

In a Schlenk tube, η^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl] borate ruthenium(II) (25 mg, 0.016 mmol, 1 eq.), 4-[(4-ferrocenylphenyl)bicyclo[2.2.2]octane]phenylboronic pinacol ester **15** (75 mg, 0.13 mmol, 8 eq.), palladium acetate (1.8 mg, 8 µmol, 0.5 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexylphosphine (6.8 mg, 16 µmol, 1 eq.) and anhydrous K_3PO_4 (35 mg, 0.16 mmol, 10 eq.) were placed under argon. Freshly distilled toluene (1.5 ml) and degassed water (100 µl) were added and the mixture was heated at 100°C overnight. After cooling down, additional 4-[(4-ferrocenylphenyl) bicyclo[2.2.2]octane] phenylboronic pinacol ester (75 mg, 0.13 mmol, 8 eq.), palladium acetate (1.8 mg, 8 µmol, 0.5 eq.), 2-(2′,6′-dimethoxy biphenyl)dicyclohexylphosphine (6.8 mg, 16 µmol, 1 eq.) and anhydrous K_3PO_4 (35 mg, 0.16 mmol, 10 eq.) 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 (SiO_2: CH_2Cl_2) to give **6** as an orange solid (16 mg, 29%). ^1H NMR: (500 MHz, CD_2Cl_2) δ 8.81 (s, 3H, H_d), 8.20 (s, 3H, H_a), 7.66 (d, 3H, *J* = 8.5 Hz, H_c), 7.57 (d, 10H, *J* = 8.4 Hz, H_1), 7.50 (d, 10H, *J* = 8.5 Hz, H_4), 7.44-7.37 (m, 33H, H_2 H_3 H_5 H_b), 7.28 (d, 10H, *J* = 8.5 Hz, H_6), 4.60 (t, 10H, *J* = 1.8 Hz, H_7), 4.48 (q, 6H, *J* = 7.1 Hz, OCH_2), 4.28 (t, 10H, *J* = 1.8 Hz, H_8), 4.03 (s, 25H, Cp), 1.98 (s, 60H, CH_2 bicyclo), 1.49 (t, 9H, *J* = 7.1 Hz, CH_3); ^{13}C NMR: (126 MHz, CD_2Cl_2) δ 166.97; 149.52; 147.68; 143.19; 141.03; 139.74; 137.31; 136.31; 134.22; 132.48; 128.84; 126.46; 126.07; 125.97; 125.72; 125.50; 120.94; 119.83; 113.91; 88.99; 85.70;

68.52; 68.76; 66.48; 61.30; 34.92; 34.83; 32.83; 32.77; 14.34; UV/Vis (CH_2Cl_2) l_{max} / nm (e / mol^{-1}.L.cm^{-1}) 277 (205 000); 342 (44 000); 368 (31 000); MS: (MALDI-TOF) 3348 $[M]^+$; HR MALDI-TOF Calculated $[M]^+$: 3348.096 ($C_{215}H_{193}BFe_5N_6O_6Ru$) Found: 3348.061 (100% $[M]^+$); CV (CH_2Cl_2, $^nBu_4NPF_6$,), $E_{\text{Fe(II)-Fe(III)}}$ (V/SCE): +0.42 rev, (5 e) ; $E_{\text{Ru(II)-Ru(III)}}$ (V/SCE): 0.76 rev (1 e) (Sweep rate: 100 mV.s^{-1}).

3-acetyl-1,5-dicyano-3-phenyl-pentane (7)
In a two-neck flask, acrylonitrile (33 ml, 0.5 mol, 2 eq.) was added dropwise under vigorous stirring to a solution of phenylacetone (33 ml, 0.25 mol, 1 eq.) and 'tritonB' (2.63 ml, 0.015 mol) in *tert*-butanol (64 ml) at a temperature kept between 20 and 25°C. After the end of the addition, the mixture was stirred for one additional hour. After filtration and washings with methanol, a white solid was obtained. Recrystallization in ethanol yielded **7** as a white solid (45.79 g, 76%). ^1H NMR (250 MHz, CD_2Cl_2) d: 7.44-7.37 (m, 3H, Ph), 7.18-7.14 (m, 2H, Ph), 2.43-2.23 (m, 4H, CH_2CN), 2.19-2.01 (m, 4H, CH_2), 1.94 (s, 3H, Me); MS: (DCI/NH_3) 258 $[M+NH_4]^+$.

3-acetyl-3-phenyl-1,5-pentanedicarboxylic acid (8)
In a round-bottom flask, **7** (45.79 g, 0.190 mol, 1 eq.) was heated at reflux overnight in water (210 ml) with KOH (21 g, 0.526 mol, 2.75 eq.). Activated charcoal was added and the mixture was filtered over celite. The filtrate was acidified with concentred hydrochloric acid to yield a white precipitate. The product was recrystallized in water to give **8** as a white solid (38.50 g, 72%). ^1H NMR: (250 MHz, acetone d^6) d: 7.47-7.40 (m, 2H, Ph), 7.36-7.28 (m, 3H, Ph), 2.36-2.28 (m, 4H, CH_2COOH), 2.11-2.03 (m, 2H, CH_2), 1.89 (s, 3H, Me); MS: (DCI/NH_3) 277 $[M-H]^-$.

4-acetyl-4-phenylcyclohexanone (9)
In a round-bottom flask, **8** (38.50 g, 0.138 mol, 1 eq.) and potassium acetate (0.38 g, 3.84 mmol, 2.8%) were heated at reflux in acetic anhydride (71 ml, 1.39 mol, 5 eq.) during 2 hours. The acetic acid formed was distilled under reduced pressure, and then the mixture was heated at 250°C to distill the cyclohexanone. After recrystallization in hexane **9** was obtained as a white solid (13.43 g, 45%). ^1H NMR: (250 MHz, CD_2Cl_2) d: 7.41-7.34 (m, 5H, Ph), 2.49-2.32 (m, 8H, CH_2), 1.97 (s, 3H, CH_3); MS: (DCI/NH_3) 234 $[M+NH_4]^+$, 251 $[M+N_2H_7]^+$.

1-hydroxy-4-phenylbicyclo[2.2.2]octan-3-one (10)
In a round bottom flask, **9** (10.63 g, 0.049 mol, 1 eq.) was added to a solution of potassium hydroxyde (11.8 g, 0.211 mol, 4.3 eq.) in absolute ethanol (52 ml). The mixture was stirred at room temperature overnight. Water was added (150 ml) and the precipitate was filtered and washed with water. After drying under vacuum **10** was obtained as a white solid was

obtained (7.77 g, 73%). ^{1}H NMR: (250 MHz, CD_2Cl_2) d: 7.36-7.16 (m, 5H, Ph), 2.56-2.55 (m, 2H, CH_2-CO), 2.27-1.85 (m, 8H, CH_2 bicyclo), 1.67 (s, 1H, OH); MS: (DCI/NH_3) 234 $[M+NH_4]^+$, 251 $[M+N_2H_7]^+$.

1-hydroxy-4-phenylbicyclo[2.2.2]octane (11)
In a round-bottom flask, **10** (7.77 g, 0.036 mol, 1 eq) was heated at reflux in hydrazine hydrate (45 ml) during 5 hours. After the mixture was cooled, potassium hydroxide (10.1 g, 0.18 mol) and diethyleneglycol (63 ml) were added. The apparatus was set up for distillation and the temperature was set at 160°C during 1 hour, then the temperature was raised to 220°C where it was maintained until the end of the nitrogen evolution. The reaction mixture was cooled down and poured into water (300 ml), extracted with ether, washed with hydrochloric acid (1M) and dried over magnesium sulfate. Crystallization from cyclohexane gave **11** as a white solid (4.57 g, 62%). ^{1}H NMR: (250 MHz, CD_2Cl_2) d: 7.33-7.26 (m, 5H, Ph), 2.00-1.94 (m, 6H, CH_2 bicyclo), 1.77-1.72 (m, 6H, CH_2 bicyclo), 1.43 (s, 1H, OH); MS: (FAB) 202 $[M]^+$.

1,4-diphenylbicyclo[2.2.2]octane (12)
To a stirred solution of **11** in a round bottom flask, (4.58 g, 0.23 mol, 1 eq.) in benzene (530 ml) concentred sulfuric acid (5.3 ml) was added under argon. The mixture was heated at reflux during 4 hours. After cooling the mixture was poured into water (500 ml) and extracted with dichloromethane. Purification by column chromatography (SiO_2: hexane/CH_2Cl_2 5%) afforded **12** as a white solid (2.0 g, 33%). ^{1}H NMR: (300 MHz, CD_2Cl_2) d: 7.41-7.37 (m, 4H, H_o), 7.34-7.29 (m, 4H, H_m), 7.21-7.16 (m, 2H, H_p), 1.98 (s, 12H, CH_2 bicyclo); ^{13}C NMR: (76 MHz, CD_2Cl_2) δ 150.08; 128.12; 125.59; 35.04; 32.84; MS: (DCI/NH_3) 262 $[M]^+$.

1,4-di-(4-bromophenyl)bicyclo[2.2.2]octane (13)
To a solution of 1,4-diphenylbicyclo[2.2.2]octane **12** (2.0 g, 7.6 mmol, 1 eq.) in a round bottom flask and iron powder (87 mg, 1.56 mmol, 0.2 eq.) in CCl_4 (100 ml) was added a solution of Br_2 (0.78 ml, 15.2 mol, 2 eq.) in CCl_4 (67 ml). The mixture was heated at reflux during 3 hours. After cooling, the mixture was poured into an aqueous 1% solution of $NaBH_4$ (250 ml). The product was extracted with dichloromethane and the organic phases washed with water and dried over $MgSO_4$. The product was purified by column chromatography (SiO_2: hexane/CH_2Cl_2 10%) to give **13** as a white solid (2.08 g, 65%). ^{1}H NMR: (300 MHz, CD_2Cl_2) d: 7.43 (d, 4H, J = 8.5Hz, H_{arom}), 7.25 (d, 4H, J = 8.5Hz, H_{arom}), 1.93 (s, 12H, CH_2 bicyclo); ^{13}C NMR: (76 MHz, CD_2Cl_2) δ 149.01; 131.09; 127.60; 119.32; 34.92; 32.62; MS: (DCI/NH_3) 420 $[M]^+$.

1-(4-bromophenyl)-4-(4-ferrocenylphenyl)bicyclo[2.2.2]octane (14)

In a Schlenk tube, 1,4-di-(4-bromophenyl)bicyclo[2.2.2]octane (230 mg, 0.54 mmol, 1 eq), ferroceneboronic acid (126 mg, 0.54 mmol, 1 eq), palladium acetate (1.2 mg, 5 μmol, 1%), 2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine (4.5 mg, 10 μmol, 2%) and anhydrous K_3PO_4 (232 mg, 1.1 mmol, 2 eq) were placed under argon. Freshly distilled toluene (4 ml) was 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 (SiO_2: Cyclohexane/CH_2Cl_2 0-10%) to give in the first fraction a white solid corresponding to unreacted **13** (70 mg), then in the second fraction the dissymmetric product **14** as an orange solid (90 mg, 31%) and finally the symmetric bis(ferrocenyl) product as an orange solid (45 mg, 13%). ^1H NMR: (300 MHz, CD_2Cl_2) δ 7.43 (m, 4H), 7.28 (m, 4H), 4.62 (t, 2H, *J* = 1.9 Hz, subs Cp), 4.29 (t, 2H, *J* = 1.9 Hz, subs Cp), 4.04 (s, 5H, Cp), 1.97 (s, 12H, CH_2 bicyclo); ^{13}C NMR: (76 MHz, CD_2Cl_2) δ 149.29; 147.52; 136.38; 131.06; 127.65; 125.99; 125.50; 119.25; 85.70; 69.54; 68.80; 66.50; 34.98; 34.79; 32.77; 32.69; MS: (DCI/NH_3) 526 $[M+H]^+$; High Resolution LSI Calculated $[M]^+$: 524.0802 ($C_{30}H_{29}BrFe$) Found: 524.0801 (100% $[M+H]^+$); CV (CH_2Cl_2, $^nBu_4NPF_6$,), $E_{\mathrm{Fe(II)-Fe(III)}}$ (*V*/SCE): +0.44 rev (Sweep rate: 100 mV.s^{-1}).

4-[(4-ferrocenylphenyl)bicyclo[2.2.2]octane]phenylboronic pinacol ester (15)

In a Schlenk tube, 1-(4-bromophenyl)-4-(4-ferrocenylphenyl)bicyclo[2.2.2]octane (90 mg, 0.17 mmol, 1 eq), bis(pinacolato) diboron (43 mg, 0.17 mmol, 1 eq), potassium acetate (50 mg, 0.51 mmol, 3 eq) and dry DMF (2 ml) were degassed under argon during 20 min. $PdCl_2$(dppf) was added and the mixture was heated at 80°C overnight. The crude reaction mixture was evaporated under vacuum and then purified by column chromatography (SiO_2: Cyclohexane/CH_2Cl_2 50%) to give **15** as an orange solid (65 mg, 66%). ^1H NMR: (300 MHz, CD_2Cl_2) δ 7.70 (d, 2H, *J* = 8.4 Hz), 7.42 (d, 2H, *J* = 8.6 Hz), 7.39 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.6 Hz), 4.62 (t, 2H, *J* = 1.9 Hz, subs Cp), 4.29 (t, 2H, *J* = 1.9 Hz, subs Cp), 4.04 (s, 5H, Cp), 1.98 (s, 12H, CH_2 bicyclo), 1.32 (s, 12H, CH_3); ^{13}C NMR: (76 MHz, CD_2Cl_2) δ 153.38; 147.66; 136.25; 134.52; 125.92; 125.45; 124.98; 85.74; 83.62; 69.50; 68.73; 66.44; 35.24; 34.79; 32.69; 32.65; 24.65; MS: (DCI/NH_3) 573 $[M+H]^+$, 590 $[M+NH_4]^+$, 607 $[M+N_2H_7]^+$; High Resolution LSI Calculated $[M]^+$: 572.2549 ($C_{36}H_{41}BFeO_2$) Found: 572.2534 (100% $[M]^+$).

X-ray crystallographic study

*Crystal Data for h^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (**3**)*

Yellow prismatic crystals suitable for X-ray analysis were obtained by dissolution of the compound in dichloromethane and slow liquid diffusion of methanol. $C_{67}H_{52}BBr_5N_6O_6Cl_4Ru$: M_r = 1690.40, Triclinic, space group P-1, a(Å) = 11.8455(7), b(Å) = 13.234(2), c(Å) = 25.192(2), a = 75.882(7), β = 84.952(6), γ = 63.888(7), V(Å^3) = 3438.4(5), Z = 2, ρ_{calc} = 1.6290(3) g.cm^{-3}, μ?MoK$_\alpha$?(mm^{-1}) = 3.343. Data were collected on a Nonius Kappa CCD diffractometer using MoK$_\alpha$ graphite monochromated radiation (λ = 0.71073 Å) at 298 K. 4510 reflections having I>2σ(I) were used for structure determination (6.02°<θ?<28.00°). For all computations the Bruker maXus software package was used. Final results: R(F) = 0.088, Rw(F) = 0.131, GoF = 1.011.

*Crystal Data for 1-(4-bromophenyl)-4-(4-ferrocenylphenyl)bicyclo[2.2.2]octane (**14**)*

Orange prismatic crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in a 1:1 pentane-methanol mixture. $C_{30}H_{29}BrFe$: M_r = 1050.56, Triclinic, space group P-1, a(Å) = 11.1034(6), b(Å) = 11.7933(4), c(Å) = 19.1249(14), a = 77.435(5), β = 79.063(7), γ = 71.404(5), V(Å^3) = 2297.0(2), Z = 4, ρ_{calc} = 1.5190(1) g.cm^{-3}, μ?MoK$_\alpha$?(mm^{-1}) = 2.412. Data were collected on a Nonius Kappa CCD diffractometer using MoK$_\alpha$ graphite monochromated radiation (λ = 0.71073 Å) at 200 K. 5144 reflections having I>3σ(I) were used for structure determination (0.00°<θ?<30.00°). For all computations the Bruker maXus software package was used. Final results : R(F) = 0.048, Rw(F) = 0.088, GoF = 0.749.

CCDC 630858 (**3**) and 631360 (**14**) contain the supplementarycrystallographic data for this paper. These data can be obtained free of charge from the CambridgeCrystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure 1. Desired behaviour (top): electron transport with the rotation of the rotor. Undesired behaviour (bottom): electron transport via intramolecular electron transfers without rotation.

Figure 2. Model dinuclear complexes used to study the electronic influence of the bicyclo[2,2,2]octane fragment.

Figure 3. DFT-optimized geometries of **1** (above) and **2** (below).

Figure 4. Overlap between the iron 3d orbitals and the $2p_z$ orbitals of the bridge.

Figure 5. Symmetrical and antisymmetrical molecular orbitals based on the dx^2-y^2 iron orbitals of complex **1** (left) and **2** (right) involved in the electronic coupling (with an orbital contour value of 0.05).

Figure 6 Thermal ellipsoid diagram (ORTEP) of **3**, top view (left) and side view (right). The ellipsoids are drawn at the 50% probability level, the molecules of co-crystallizing solvent (MeOH) and hydrogen atoms have been omitted for clarity.

Figure 7 Thermal ellipsoid diagram (ORTEP) of **14.** The ellipsoids are drawn at the 50% probability level and hydrogens have been omitted for clarity.

Figure 8. Cyclic voltammograms of **5** (dotted) and **6** (plain) (CH_2Cl_2, $^nBu_4NPF_6$, Pt working and counter electrode). All waves were reversible. The sweep rate was 100 $mV.s^{-1}$.

Scheme 1. Synthesis of the model complex **4** and the molecular motor **5**: (a) 4-*tert*-butylphenyl boronic acid, $Pd(OAc)_2$, 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine, K_3PO_4, toluene, 100°C, overnight, 25%; (b) ferrocene boronic acid, $Pd(OAc)_2$, 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine, K_3PO_4, toluene, 100°C, overnight, 32%

Scheme 2. Synthesis of the bicyclo[2,2,2]octane precursor **14**: (a) acrylonitrile, ‘triton B’, ^{t}BuOH, 20°C, 1 hour, 76%; (b) KOH, H_2O, reflux, overnight, 72%; (c) AcOK, Ac_2O, reflux, 2 hours, then distillation at 250°C, 45%; (d) KOH, EtOH, 20°C, overnight, 73%; (e) hydrazine, reflux, 5 hours, then KOH, diethylene glycol, 220°C, 62%; (f) conc H_2SO_4, benzene, reflux, 4 hours, 33%; (g) Br_2, Fe, CCl_4, reflux, 3 hours, 65%; (h) ferrocene boronic acid, $Pd(OAc)_2$, 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine, K_3PO_4, toluene, 100°C, overnight, 31%.

Scheme 3. Synthesis of the molecular motor **6**: (a) bis(pinacolato)diboron, $PdCl_2$(dppf), AcOK, DMF, 80°C, overnight, 66%; (b) **3**, $Pd(OAc)_2$, 2-(2′,6′-dimethoxybiphenyl) dicyclohexylphosphine, K_3PO_4, toluene (1% H_2O), 100°C, overnight, 29%.

Table 1. Oxidation potentials of iron and ruthenium in V/SCE (CH_2Cl_2, $^nBu_4NPF_6$ 0.1 M, Pt working and counter electrode).

	4	**5**	**6**	**14**
$E_{1/2}$(ox) Fe^{II}/Fe^{III}	-	0.47	0.42	0.44
$E_{1/2}$(ox) Ru^{II}/Ru^{III}	0.77	0.89	0.76	-

Table of Contents

The insulating role of 1,4-disubstituted bicyclo[2,2,2]octane has been examined in a theoretical study on bis-ferrocenyl model compounds. Two prototypes of electron-fuelled molecular motors have been synthesized, incorporating either conjugated or insulating spacers between the central core and the ferrocene terminal electroactive groups.

Keywords:

bicyclo[2,2,2]octane, half-sandwiched complexes, Molecular Motor, Mixed-valent compounds, Ruthenium